



IRPTC

DATA PROFILES FOR CHEMICALS FOR THE EVALUATION OF THEIR HAZARDS TO THE ENVIRONMENT OF THE MEDITERRANEAN SEA

INTERNATIONAL REGISTER OF
POTENTIALLY TOXIC CHEMICALS (IRPTC)
1978

UNITED NATIONS ENVIRONMENT PROGRAMME
GENEVA, SWITZERLAND

IRPTC
Data Profile Series
Number One

DATA PROFILES FOR CHEMICALS
FOR THE EVALUATION
OF THEIR HAZARDS
TO THE ENVIRONMENT
OF THE
MEDITERRANEAN SEA

Volume I



INTERNATIONAL REGISTER OF POTENTIALLY TOXIC CHEMICALS
UNITED NATIONS ENVIRONMENT PROGRAMME
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RISCPT
Série de profils de données
Numéro un

PROFILS DE DONNEES POUR
L'EVALUATION DU DANGER
DES SUBSTANCES CHIMIQUES
POUR L'ENVIRONNEMENT DE
LA MEDITERRANEE

Volume I

REGISTRE INTERNATIONAL DES SUBSTANCES CHIMIQUES
POTENTIELLEMENT TOXIQUES
PROGRAMME DES NATIONS UNIES POUR L'ENVIRONNEMENT
GENEVE 1978

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Volume I

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PREFACE

Following its establishment in 1972 by the United Nations General Assembly, the United Nations Environment Programme (UNEP) selected the Mediterranean region as one of its "concentration areas", in which to fulfill its catalytic role by assisting the Mediterranean coastal states to secure measures for the adequate protection of the marine and coastal environment.

In collaboration with a number of United Nations Specialized Agencies, the UNEP convened the Intergovernmental Meeting on the Protection of the Mediterranean in Barcelona from 28 January to 4 February 1975. During that meeting, which was attended by 16 of the 18 Mediterranean coastal states, an Action Plan^{1/} was approved comprising three substantive components, i.e. legal (a framework Convention and related protocols), scientific (research, monitoring and assessment) and management (integrated planning). Its final objective was to assist governments in improving:

- (i) the information base on which environmentally sound national development policies could be formulated; and
- (ii) their ability to identify various options and to make rational choices and appropriate allocations of resources.

The legal framework of the Action Plan was adopted in the Final Act of the Conference of Plenipotentiaries of the Coastal States of the Mediterranean Region for the Protection of the Mediterranean Sea^{1/}, convened by UNEP in Barcelona from 2 to 16 February 1976. This Conference approved the texts of three legal instruments, namely:

- Convention for the Protection of the Mediterranean Sea against Pollution;
- Protocol for the Prevention of Pollution of the Mediterranean Sea by Dumping from Ships and Aircraft; and
- Protocol concerning Co-operation in Combating Pollution of the Mediterranean Sea by Oil and other Harmful Substances in Cases of Emergency.

Considering that the Convention was too broad to provide meaningful protection on its own, it was agreed that no state may be a contracting party to the Convention without also becoming a party to at least one of the protocols.

^{1/}Mediterranean Action Plan and the Final Act of the Conference of Plenipotentiaries of the Coastal States of the Mediterranean Region for the Protection of the Mediterranean Sea. UNEP 1978.

The Convention and protocols would enter into force following ratification by not fewer than six states. The Convention and the two protocols came into force on 12 February 1978 and at the end of 1978 had been ratified by eleven Mediterranean States and the European Economic Community.

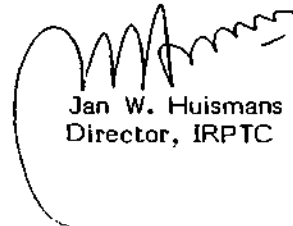
Efforts are under way to develop additional protocols. UNEP, in co-operation with the World Health Organisation (WHO), has sponsored a number of intergovernmental and expert consultations for the negotiation of a protocol for the protection of the Mediterranean Sea against pollution from land-based sources. A draft protocol will be reviewed by a meeting of governmental technical and legal experts in June 1979.

The present compendium of data profiles for chemicals for the evaluation of their hazards to the environment of the Mediterranean Sea is a first attempt by the International Register of Potentially Toxic Chemicals (IRPTC) to address this very difficult problem of presenting the necessary data for environmental hazard evaluation of chemicals to experts in the several disciplines of science concerned with environmental hygiene. While this document is addressed to the Mediterranean Action Plan for further development of its Draft Protocol for the Protection of the Mediterranean Sea Against Pollution from Land-Based Sources, it could be addressed equally well to any of the other international conventions which deal with the prevention of chemical pollution of the seas. The problem of marine pollution is not unique to one area of the world but is ubiquitous to all bodies of water, fresh and salt, which are bordered by human society. The evaluation of the data by experts of any geographic locale, thus, is likely to have an economic impact on all countries of the world, because the problems and their causes are identical for all. The accuracy of the evaluation becomes paramount to the effective use and control of society's chemicals which are essential for its well-being.

This accuracy becomes dependent on the availability of the appropriate data for a chemical substance to describe its behaviour in the environment. Without adequate information about this behaviour, unnecessary controls may be imposed on chemicals of benefit to society, while dangerous chemicals may be released to the environment until such time as they may have produced serious injury to man or his world.

Not all of the pollutants likely to be listed in the Draft Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources are identified as chemical substances and thus the problems are discussed in a narrative manner as a summary rather than presented as data profiles. Six summaries have been prepared by experts in their respective fields in this way, and are presented in Annex D, Consultants' Summaries. The chemical data profiles and these summaries are listed in Annex B of this report.

The profiles presented herein cannot be considered to be completely satisfactory for this task, as is explained in the text. However, it is hoped that this presentation will provide a basis for future action in the context of the Mediterranean Action Plan and other conventions assembled for similar purposes.



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PREFACE

Créé en 1972 par l'Assemblée générale des Nations Unies, le Programme des Nations Unies pour l'environnement (PNUE) a choisi la région méditerranéenne comme l'une des zones d'activité intense où il pourra jouer un rôle de catalyseur et aider les Etats côtiers de la Méditerranée à prendre des mesures pour protéger efficacement l'environnement marin et côtier.

En collaboration avec diverses institutions spécialisées des Nations Unies, le PNUE a organisé à Barcelone, du 28 janvier au 4 février 1975, une Réunion intergouvernementale sur la protection de la Méditerranée. Lors de cette réunion, à laquelle ont été représentés 16 des 18 Etats riverains de la Méditerranée, un Plan d'action^{1/} a été approuvé comprenant trois grands volets, à savoir, un volet juridique (Convention-cadre et protocoles annexes), un volet scientifique (recherche, contrôle et évaluation), et un volet gestionnaire (planification intégrée). L'objectif final était d'aider les gouvernements:

- i) à améliorer les informations sur lesquelles on puisse fonder des politiques nationales de développement qui soient rationnelles sur le plan de la protection de l'environnement;
- ii) à mieux déterminer les diverses options qui s'offrent à eux, effectuer des choix rationnels et procéder judicieusement aux affectations de ressources.

Le cadre juridique du Plan d'action a été adopté dans l'Acte Final de la Conférence de plénipotentiaires des Etats côtiers de la région méditerranéenne sur la protection de la mer Méditerranée^{1/}, organisée par le PNUE à Barcelone du 2 au 16 février 1976. La Conférence a adopté les trois instruments juridiques suivants:

- Convention pour la protection de la mer Méditerranée contre la pollution;
- Protocole relatif à la prévention de la pollution de la mer Méditerranée par les opérations d'immersion effectuées par les navires et aéronefs;
- Protocole relatif à la coopération en matière de lutte contre la pollution de la mer Méditerranée par les hydrocarbures et autres substances nuisibles en cas de situation critique.

^{1/} Plan d'action pour la Méditerranée et Acte final de la Conférence de plénipotentiaires des Etats côtiers de la région méditerranéenne sur la protection de la Méditerranée, PNUE 1978.

La Convention ayant un caractère trop général pour assurer une protection réelle par elle-même, il a été décidé qu'aucun Etat ne pourrait être Partie contractante à la Convention sans devenir également Partie à l'un au moins des protocoles.

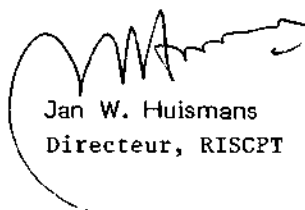
La Convention et les protocoles devaient entrer en vigueur après ratification par au moins six Etats. La Convention et ses deux protocoles sont entrés en vigueur le 12 février 1978 et, à la fin de 1978, ces textes avaient été ratifiés par onze Etats riverains de la Méditerranée et par la Communauté économique européenne.

On s'efforce maintenant de mettre au point de nouveaux protocoles. En coopération avec l'Organisation Mondiale de la Santé (OMS), le PNUÉ a parrainé diverses réunions intergouvernementales et consultations d'experts en vue de la négociation d'un protocole relatif à la protection de la mer Méditerranée contre la pollution d'origine tellurique. Un projet de protocole sera examiné lors d'une réunion d'experts techniques et juridiques des gouvernements en juin 1979.

Le présent recueil de profils de données relatives à des substances chimiques pour l'évaluation des dangers qu'elles présentent pour l'environnement de la Méditerranée constitue une première tentative visant à établir un Registre international de substances chimiques potentiellement toxiques (RISCPT). Ce registre devrait permettre de résoudre le très difficile problème qui consiste à soumettre à des experts des diverses disciplines scientifiques intéressant la salubrité de l'environnement les données nécessaires à une évaluation des dangers des substances chimiques pour l'environnement. Ce document devrait, dans le cadre du Plan d'action pour la Méditerranée, aboutir à l'élaboration d'un projet de protocole relatif à la protection de la mer Méditerranée contre la pollution d'origine tellurique, mais il intéresse aussi les autres conventions internationales concernant la prévention de la pollution chimique des mers. Le problème de la pollution marine ne se pose pas dans une seule région du monde, mais partout où il existe des étendues d'eau douce ou salée au bord desquelles sont installées des collectivités humaines. L'évaluation des données par des experts de quelque région que ce soit aura donc probablement un impact économique dans tous les pays du monde, parce que les problèmes et leurs causes sont les mêmes partout. L'exactitude de l'évaluation est indispensable à une utilisation et une réglementation efficaces des substances chimiques vitales pour le bien-être de la société. Cette exactitude suppose l'existence de données appropriées permettant de décrire le comportement d'une substance chimique dans l'environnement. Sans une bonne information à ce sujet, on risque de voir réglementer sans nécessité l'usage de substances chimiques utiles à la société, alors que par ailleurs des substances chimiques dangereuses seront rejetées dans l'environnement jusqu'au moment où leurs effets nocifs sur l'homme ou son environnement deviendront apparents.

Les polluants à inscrire dans le projet de protocole relatif à la protection de la mer Méditerranée contre la pollution d'origine tellurique ne sont pas tous identifiés comme des substances chimiques et les problèmes font donc l'objet de résumés descriptifs plutôt que de profils de données. Six résumés, établis par des experts des diverses disciplines sont présentés à l'annexe D "Résumés des consultants". Les profils de données concernant les substances chimiques ainsi que les résumés descriptifs sont énumérés à l'annexe B du présent rapport.

Comme expliqué dans le texte ci-après, les profils présentés ne peuvent pas être considérés comme absolument satisfaisants. Nous espérons néanmoins qu'ils pourront servir de base à une action future dans le contexte du Plan d'action pour la Méditerranée et des conventions analogues.



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1. INTRODUCTION

The Mediterranean Action Plan is a programme approved by countries of the region in reaction to a potential threat of pollution to the Mediterranean Sea. Increasing population density, industrial activity and traffic as well as intensified agriculture in areas close to the coast threaten the overall health of the Mediterranean Sea not only as a source of seafood and esthetic pleasure to inhabitants and tourists, but as a stable ecosystem, a necessary condition in itself.

Chemical pollutants are of major concern in the Mediterranean region, as in all areas of the world. About five million chemicals are known today; over 100,000 of these are in commercial use and approximately 1,000 new chemical substances are added to commerce each year. A number of these compounds can be expected to reach the estuaries, coastal areas and open water of the Mediterranean Sea from land-based sources.

As resources are limited, it will not be immediately possible to determine and control all substances with potential to pollute the Mediterranean. The most important substances must be identified and selected for regulatory efforts or further study and, therefore, pertinent criteria must be established.

Groups of experts have prepared lists of hazardous or potentially hazardous substances frequently referred to as "black" or "grey" lists. Conventions and governmental agencies classifying chemicals on such lists are found in Table I (de Reeder, 1977; Krul, 1976; UNEP, 1977).

Although the purpose of these lists is often the setting of priorities for further research rather than regulation, the philosophy is the same, i.e. listing of the substances likely to be potentially most hazardous.

For some of the substances on these lists a large amount of information exists, primarily due to the fact that their ability to produce noxious effects on man or the environment is well known. Such information has, for example, been developed for several mercury compounds and for some chlorinated biphenyls. For the majority of the mercury compounds or

Table 1
Conventions and Governments Classifying Chemicals
on
Black and Grey Lists
 (de Reeder, 1977;
 Krul, 1976; UNEP, 1977)

NAME	DATE	TITLE OR PURPOSE
Convention of Oslo	Feb.1972	Convention for the prevention of marine pollution by dumping from ships and aircraft
Convention of London	Dec.1972	Convention on the prevention of marine pollution by dumping of wastes and other water
Convention of Helsinki	March 1974	Convention on the protection of the marine environment of the Baltic Sea
European Convention	April 1974	Draft European Convention for the protection of international water courses against pollution
Rome criteria	Feb. and May 1974	Criteria and principles for discharges of matter or energy into coastal waters
Convention of Paris	June 1974	Convention for the prevention of marine pollution from landbased sources
Convention of Barcelona	Feb.1976	Convention for the protection of the Mediterranean Sea against pollution
European Communities Council Directive	May 1976	Convention concerning the protection of the Rhine against chemical pollution
International Commission for Protection of the Rhine against Pollution	1965	Commission for protection of the Rhine against pollution by general, specific, or incidental causes.

chlorinatedbiphenyls which are of commercial interest, however, there is very little available information. This is also the case for the majority of other substances in the environment.

In order to evaluate the environmental effects of substances for the purpose of classifying them for inclusion in (or exclusion from) the several lists, data indicating the presence of a substance in the Mediterranean Sea and its ability to produce a noxious effect must be found and presented. In the case that such data is not found to exist, further research is indicated.

The International Register of Potentially Toxic Chemicals (IRPTC) became operational as a programme activity centre of the United Nations Environment Programme (UNEP) in 1976 and has begun the development of a register of chemical substances which will include pertinent available data on the environmental behaviour and effect of both man-made and naturally occurring substances.

The register will include approximately 150 attributes (data fields) as presented in Annex A which will serve to identify a chemical substance, to describe its physical and chemical characteristics, to estimate its availability to the environment, to present biological effects on man and the environment which have been important for hazard evaluation, to identify methods of sampling and analysis for the substance, to identify the methods to be used in dealing with hazardous spills, to offer therapeutic measures for intoxication from the chemical and to present control regulations for the chemical.

Early in 1978 the Regional Seas Programme Activity Centre of UNEP requested that the IRPTC prepare data profiles for substances likely to be listed in the Draft Protocol for the Protection of the Mediterranean Sea Against Pollution from Land-Based Sources to be developed by a convention to be held in March, 1979. As a result, one of the tasks undertaken by the IRPTC in 1978 has been the development of data profiles for chemical hazard evaluation of selected substances likely to be found in the annexes cited above. These profiles, because of the limited availability of resources, do not contain information for all of the attributes planned

for the IRPTC register. However, care was taken to include Mediterranean Data. Therefore, the profiles prepared will be referred to in this report as Mediterranean Data Profiles.

2. APPROACH TAKEN

2.1 Development of Mediterranean Data Profiles

The first step in chemical data profile development is the determination of the attributes which are required for the hazard evaluation of a chemical, that is, of a substance which may be potentially damaging to man or to his environment.

The IRPTC has developed a list of attributes (Annex A) for its register, which either have been found to be used by agencies of the United Nations and international or national organizations for evaluating chemical hazards, or which have been selected by an international group of experts as being necessary for determining the potential hazard of a chemical to man and his environment.

Budgetary limitations and the short time available for developing the Mediterranean Data Profiles prevented the collection of data for all of the IRPTC attributes, nor are all of the problems associated with the selection of data addressed. The request received from the UNEP Regional Seas Programme Activity Centre was, however, augmented to finally include the following information or data files:

- total production or total consumption,
- production processes,
- use patterns,
- pathways leading to marine pollution,
- transformation in the marine environment,
- behaviour of a chemical substance in marine organisms,
- behaviour of the substance in man and other mammals,
- concentrations in water, sediments and biota,
- array of toxic effects on man and other mammals,

- toxic effects from special studies on mammals and other non-marine experimental systems,
- toxic or other effects on marine organisms and ecosystems,
- sampling and analysis,
- legislation for the protection of man and the marine environment, and narrative summaries for each of the substances for which data profiles were prepared.

It should be noted that these files do not include certain other attributes such as synonyms, fresh water and air data, descriptors, and chemical and physical properties, which were recommended for IRPTC to be necessary to evaluate environmental hazards (IRPTC, 1978).

The summaries, however, were an attempt not only to summarize the data from Mediterranean Data Profiles but also to provide additional data as was available, i.e., to add some of the missing information which would normally be included in the IRPTC Register.

2.2 Selection of Chemical Substances

The IRPTC was asked to prepare general descriptions of the main characteristics of each group of substances and to describe the "most important" individual substances within each group listed in the Annexes of the Draft Protocol for the Protection of the Mediterranean Sea Against Pollution from Land-Based Sources.

At the end of May 1978 an IRPTC working group met in Geneva to select those chemicals for which profiles should be developed. One of the working papers for this meeting was a list of several hundred chemicals. These chemicals were either listed in the Draft Protocol or included in at least one or more United Nations, international or national reports, monographs or criteria documents which had been prepared to evaluate the hazardous effects of chemicals. Although a large number of individual chemical substances were identified it was impossible to select either a "representative" or a "most important" individual substance for any group without additional information being made available.

The May working group recommended that in developing criteria for chemical selection, attention should be paid to the following:

- substances of major interest indicated by brackets in Annexes I and II of the draft protocol;
- substances present in the Mediterranean on a regional basis, i.e. not local pollution;
- substances which could be monitored by existing analytical methods;
- substances to which attention is already paid in the context of any of the seven approved pilot projects of the Coordinated Mediterranean Pollution Monitoring and Research Programme (MED POL).

Due to the fact that the selection Criteria required much of the same information which was eventually to be collected for the attributes of a substance, selection of a "representative" substance from a general group could not actually be made until considerable information for the attributes had been collected and scanned. This manner of selection also meant that the substances with the most research completed and published tended to be selected.

It became evident as literature was reviewed that the groups of the Annexes of the "Draft Protocol" were not homogeneous with respect to chemical or biological characteristics. It would have been desirable that these groups be comprised of generically similar substances with similar chemical or biological activity. Because they were not, it was difficult and usually impossible to select a "representative" chemical substance for a group. For example, the organohalogens include iodine, bromine, chlorine and fluorine atoms with alkyl and aryl molecular arrangements, some of which have marked differences in environmental activity by their spatial arrangement alone, i.e. identical chemical formula but the molecule has been twisted into different positions which cause different effects.

Another group includes twenty different elements and their compounds, each element of which has distinctly different chemical and biological characteristics and the elements' compounds increase the variant chemical and biological characteristics even more. In addition, because of the commercial interest in approximately 100,000 substances, many have not been adequately monitored for their occurrence or for their importance to the problem of pollution of the Mediterranean Sea.

Without adequate data, e.g., amounts produced and use characteristics, or the alternate information which would enable the estimation of the availability of a substance to the environment, it is difficult to determine the relative pollution potential of a substance.

2.3 Data Input

Data for the profiles, as may be available, is extracted from United Nations, international and national documents in which the chemical or biological information has been subjected to expert consultant review. Mammalian toxicity for many chemical substances can be found in these documents but very little marine data has been found to be the subject for review. Essentially, the substances subjected to review in this manner are chemicals which have already been known to be hazardous, e.g. there are several hundreds of review documents covering the mammalian toxicity of mercury and its compounds. Even the availability of a large number of documents, however, does not necessarily assure that the attributes of the data profiles will have the necessary data for evaluation.

When adequate data are not found in secondary literature sources, primary literature must be used. The majority of the marine data in the Mediterranean Data Profiles, for example, has been extracted from original papers. There are several advantages of using original literature such as the elimination of errors of transcription and interpretation, the availability of more accurate presentations and descriptions and the availability of additional supplementary data.

However, the advantage of using secondary information is that the data and the primary publications may have been evaluated by international committees of expert consultants to organizations such as the World Health Organization (WHO), the International Agency for Research on Cancer (IARC) or the Commission of the European Communities (CEC), or by national experts of the various national organizations who have the responsibility for making recommendations for the control of chemical hazards. The evaluated information in these documents should, therefore, be very reliable for any decisions that must be made for the safe use of a chemical.

The IRPTC has developed, within the constraints of the time available, input instructions for data extraction and input into the Mediterranean Data Profiles. The primary purpose of the instructions is to facilitate information handling so that the data is presented uniformly and is selected routinely without involvement of expert judgement.

All data are selected on the basis of criteria established before input rather than on the basis of expert evaluation during input. Data are entered in tabular form and in a cryptic manner with as much common nomenclature as could be found or developed during the period of data profile preparation.

The data in all attributes are referenced. When primary literature is quoted in a secondary source, the secondary source is cited as a guide for the reliability of the data. The primary reference is also cited in order to give the user the information needed to directly acquire the original for personal evaluation.

Whenever there are several published sources of information available for a particular subject area, a single reference is not used repeatedly, but different source documents are chosen to provide the user with several reference options should a more comprehensive review be desired.

Documents in any language can be used, but all data is translated into English, the language of the register.

When selecting data, the documents with the most complete description, i.e. those descriptions which contain all of the elements of a horizontal data line on a data input form, are given first priority. Literature selection begins with the most current literature and continues retrospectively until as many attributes as possible can be filled. The absence of data for a particular attribute implies that no relevant data were found in the literature reviewed. References are abbreviated within the profile and are complete in a bibliography which follows each profile.

The major difficulties encountered in data extraction have been the absence of standard methods of testing and of accepted definitions and uniform units for reporting scientific phenomena found in the literature. Chemicals are often referred to generically in the literature without defining the criteria for generic grouping, thus obfuscating the identity of the substance involved. This results in the elimination of much potentially useful information. For example "mercury" as reported in the literature often represents the metallic mercury, salts of mercury or any of the organomercury compounds. It is difficult or impossible to determine what actually was done or found with respect to the substance thus making the information extracted ambiguous.

2.4 Summary Preparation

Initially the IRPTC was requested to prepare general descriptions of the main characteristics of the chemical groups or categories included in the Draft Protocol. There were, however, problems in responding to this request and as a result most of the descriptions were prepared for those individual chemical substances for which data profiles had been developed. These descriptions of environmental effects, or summaries, have been expanded to include additional information about the groups of chemical substances, information which could not be supplied by the data profiles used for this study.

The summaries were developed, therefore, to complement the Mediterranean Data Profiles and to summarize the data presented and generally include for each substance the following categories: occurrence, environmental fate, monitoring and toxicity data.

The summaries are simple narrative statements of information collected rather than evaluations of that data. Evaluation was specifically omitted from the summaries and the data profiles at the request of the Regional Seas Programme Activity Centre in order that this evaluation could be undertaken by the expert representatives of the Mediterranean governments. This evaluation is to determine which chemical substances may require regulatory control by the member countries and what basis there is for requiring that control. These data profiles attempt to provide such information.

In most cases the primary limitation of the summaries as well as of the data profiles, was the inadequacy of data for a comprehensive profile for the chemicals selected. Mediterranean data is incomplete but is being continually augmented as research and monitoring results are published by the institutions of the countries bordering the Mediterranean Sea. Thus new data can be included in subsequent efforts to improve and expand the Mediterranean Data Profiles.

While attempts have been made to remove evaluative judgement from data selection, some evaluation of information continues to be involved. This is kept to a minimum by establishing well defined guidelines for the selection such as: the lowest dose found, as is done for the U.S. Registry of Toxic Effects of Chemical Substances (RTECS); the most recently published data by which the most recent technology may be included; or data reviewed by evaluation agencies of national and international organizations. This approach may often not include what might be considered the most authoritative publications since they may not meet the criteria for selection. However, the guidelines will certainly include publications which have used the authoritative publications for reference and, thus, these important publications will be found in their bibliographies. Therefore, using this process for selecting data, the data selected is not likely to be biased by faulty or controversial judgement because there is no qualitative judgement involved in the selection. Controversial data in the profile, however, may be identified by non-conformity with other collected data.

When such controversy does occur, the evaluators of the data should acquire the original publications from which the data was extracted and evaluate them. Additional information may be necessary to resolve some questions that are raised and additional consultations may be found necessary where the data becomes pivotal for regulatory or research initiatives.

3. FUTURE APPROACHES TO INFORMATION COLLECTION

3.1 Additional Attributes

In order that critical and objective evaluation of the potential hazard of a chemical pollutant to man and his environment can be accomplished, appropriate data must be made available. Essential elements of information for evaluation are: pertinent chemical and physical properties; effects in man and other living organisms and in the ecosystem; amounts produced; use patterns; distribution and transformation in the environment; and concentrations in air, water, food and soil. In addition, information on existing and proposed laws and regulations to control the use and disposal of a chemical and the means for sampling and analysis for determining compliance with regulatory direction is essential. Models of previously published regulations save a great deal of technical effort in establishing control mechanisms. Reliable methods for handling intoxication and for handling spills of the chemical are essential for those who have the responsibility for the safe use of chemicals within their respective countries.

In a recent study to determine what characteristics of a chemical are actually used by national and international agencies, including those of the United Nations, for the purpose of evaluating the potential harm of the substance to man and his environment, the IRPTC has developed a list of attributes for its register.

These attributes, when developed with appropriate data, not only describe this potential, but also permit the ranking according to the relative potential for the purpose of establishing priorities for research or regulatory control activities. Evaluative bodies or agencies would then have a tool with which they could determine the allocation of resources and the direction of effort for controlling pollution of land, air and sea by chemicals. This programme of attribute development would not preclude interim pollution control activity and could be included in any system of priority setting as it is developed.

3.2 Additional Chemicals

There are several mechanisms in use today for establishing priorities for regulatory or research activity for chemical substances. However, the processes involve an evaluation of the importance of a chemical either based on a limited number of pre-established selection criteria with little factual data, or based on consensus selection sometimes known as "Delphic" selection. Either process may be used for the beginning efforts to control hazards from chemicals, though neither is reliable for selecting any but the few most noxious substances nor are they useful in predicting chemical problems from chemicals whose noxious activity has not already produced serious environmental problems. The question that must be answered is how important chemicals, i.e., those chemicals which are likely to produce damage to man or his environment, can be identified and their relative importance for control activity be ranked, preferably before serious environmental damage occurs.

National and international efforts to achieve this goal have not produced satisfactory approaches as yet, though the search is a continuing effort. A successful approach requires that all detrimental effects that have been found for chemicals be listed with the substances known to produce them. All structurally similar substances could then be grouped generically and would then be suspect for producing the same effect. The problem to be faced is that of deciding what chemical substances are generically similar. Traditionally, generic groupings have been based entirely on chemical composition.

Such an attempt has been made within the various black and grey lists, e.g. organohalogenes, organotin compounds, organosilicones, etc. However, grouping generically in that manner may become quite inappropriate when one recognizes the variety of biological effects that can be found with the physical arrangement of stereoisomers of a molecule alone. Hexachlorocyclohexane for example has eight stereoisomers. Of these, the beta isomer is retained in the body fat of experimental animals for much longer periods of time than any other isomers (Fitzhugh et al., 1950). The cumulation of the beta isomer in fat was found to be responsible for human intoxication and fatalities. The insecticidal potency, another possible attribute, varies greatly with the stereo relationship of the molecule, the gamma isomer being 1000 times more toxic to insects than the alpha isomer and 10,000 times more than the delta. The other isomers have not been found to have insecticidal properties (Weger, 1971). Methyl n-butyl ketone, homologue of alkyl ketones, produces peripheral neuropathy in man and experimental animals while the other alkyl ketones have not been found to do so (Allen et al., 1975). Chemical isomers are well known to produce distinctively different biological effects. Alpha-naphthylamine is a very weak carcinogen or non-carcinogenic (IARC, 1974) substance while beta-naphthylamine is a relatively potent carcinogen for experimental animals (Conzelman, et al., 1972). Manipulating drug molecules to enhance a desired therapeutic effect or to reduce an undesired side-effect is a well recognized art practiced in the proprietary drug industry. The same principles must apply to chemicals released to the environment. Generic grouping of chemicals must involve a great number of characteristics other than chemical similarity before a group is formed for common measures of control or research. This variety of biological activity does exist for even the widely discussed group labelled as polychlorinated-biphenyls (PCB). Biodegradation varies greatly with the position of the chlorine atoms on the biphenyl molecule. Thus, the 2,3 and the 2,5 dichloro diphenyl molecules are biodegradable while the 1,3 and 1,2 dichloro diphenyl molecules are not. Very few of the substances that are known to exist in this generic grouping have been well studied. It is conceivable, therefore, that some of those chlorinated-biphenyl substances may not contribute to the problems known to be produced in the environment by PCB's.

Essentially, the problem of regulating the hazardous effects to man and his environment requires that chemical substances, or generic groups of substances that can be identified by common chemical, physical and biological characteristics, be examined and addressed individually. Thus, the objective should be the collection and collation of data on the effects of chemicals which have been demonstrated to be responsible for environmental damage. Then chemicals which have the same biological, chemical and physical characteristics are identified so that they can be evaluated for their potential to be placed in that generic group which would be expected to produce that damage. This objective cannot be completely accomplished for all substances in the near future because of the magnitude of the task, but certain of the more serious and obvious environmental problems can be addressed rather promptly in this manner.

Chemicals which are candidates for the IRPTC register will include commercial products such as industrial chemicals; agricultural chemicals, (pesticides used in agriculture and in public health); food additives and processing aids; drugs; cosmetics; dyes; paints; fuels, precursors, intermediates and chemical wastes from commercial production; and products formed by the reaction of the above substances in the environment.

Usually, chemicals are selected for priority attention after they have been found to be hazardous and often after considerable harm has been done to the environment and its inhabitants.

Several countries are now collecting chemicals that are in actual use within their borders. The EEC is planning to do the same. These inventories, when complete, should be a relatively accurate inventory of chemicals found in world commerce. Once these chemicals are in a register, information can be entered for classes of chemicals which may have an increased potential for producing environmental damage, e.g. biologically potent chemicals used as pesticides or drugs, environmentally available substances such as pesticides, fertilizers and detergents, and chemically active substances used for industrial production.

Selection of classes of chemicals by this means is likely to include chemicals which are of commercial interest, which have also been studied for their environmental impact, and which are expected to produce a serious environmental hazard.

3.3 Data Input Instructions

IRPTC data input instructions are being continuously augmented and revised as experience with data extraction and input is gained. The development of input instructions involves the identification of the manifold ways that scientific observations are reported in the published literature for any attribute. It also involves the description of the method for presenting the data in an unambiguous manner for ease of understanding, comparison and evaluation of the data by the user. The purpose of the instructions is to enable technically trained but not necessarily senior experienced personnel to extract and present data with a minimum of judgemental bias and a maximum of precision for user evaluation.

Instructions for data selection and presentation for the Mediterranean Data Profiles were developed and used, but many problems remain unresolved. Most of these do not interfere with use and evaluation of these profiles but might, in some instances, require user reference to original publications for resolution. Because IRPTC is in its early development stage, it was not able to address all of the problems of input in the six months available for the development of these profiles.

The work of input instruction development will continue for the attributes of the Mediterranean Data Profiles and for the balance of the IRPTC attributes, as well. Additional aspects of the input instructions which will enable the condensing of the information for less massive publications will also be addressed.

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I. INTRODUCTION

Le Plan d'Action pour la Méditerranée a été approuvé par les pays de la région pour faire face à toute menace de pollution de la mer Méditerranée. L'accroissement de la densité de la population, des activités industrielles et des transports et les méthodes agricoles intensives pratiquées au voisinage des côtes menacent la salubrité de la Méditerranée, qui n'est pas seulement pourvoyeuse de produits de la mer et source de plaisir esthétique pour les habitants des régions riveraines et les touristes, mais constitue aussi un écosystème stable et indispensable.

Comme dans toutes les mers du monde, les polluants chimiques constituent un grave danger pour le bassin méditerranéen. On connaît aujourd'hui quelque cinq millions de produits chimiques; sur ce nombre, plus de 100 000 entrent dans les échanges commerciaux et environ 1000 substances chimiques nouvelles viennent s'y ajouter chaque année. Un certain nombre de ces composés, partis de l'intérieur des terres, gagnent les estuaires, les zones côtières et les zones au large des côtes.

Comme les ressources sont limitées, on ne pourra pas dans l'immédiat recenser toutes les substances susceptibles de polluer la Méditerranée et en réglementer l'usage. Il faut donc recenser les substances les plus importantes en vue de leur réglementation ou d'un complément d'études, d'où la nécessité de mettre au point des critères appropriés.

Des groupes d'experts ont dressé des listes de substances dangereuses ou potentiellement dangereuses, appelées, selon le cas, listes "noires" ou listes "grises". Le tableau 1 (de Reeder, 1977; Krul, 1976; PNUF, 1977), énumère les conventions et les organismes d'Etat qui classent les produits chimiques sur de telles listes.

Bien que ces listes servent surtout à fixer des priorités en matière de recherche plutôt qu'à établir une réglementation, l'idée fondamentale est la même puisqu'il s'agit dans les deux cas de dresser la liste des substances potentiellement les plus dangereuses.

Il existe, pour certaines des substances figurant sur ces listes, une grande quantité d'informations, en raison surtout du fait que leurs effets nocifs sur l'homme ou le milieu sont bien connus. C'est ainsi que l'on a accumulé des renseignements sur plusieurs composés mercuriels et certains chlorodiphényles. Toutefois, pour la majorité des composés mercuriels ou des chlorodiphényles d'importance commerciale, les données disponibles sont très rares. Il en va de même de la majorité des autres substances présentes dans l'environnement.

Si l'on veut évaluer les effets des différentes substances sur l'environnement afin de les inclure (ou de les exclure) dans différentes listes, il faut trouver et présenter des données prouvant la présence de telle ou telle substance dans les eaux de la Méditerranée et démontrant qu'elle peut être nocive. En l'absence de telles données, il faut poursuivre les recherches.

Tableau 1

Conventions et gouvernements classant les produits chimiques
sur des listes noires et grises

(de Reeder, 1977;
Krul, 1976; PNUE, 1977)

DESIGNATION	DATE	TITRE OU OBJET
Convention d'Oslo	février 1972	Convention pour la prévention de la pollution marine par les opérations d'immersion effectuées par les navires et aéronefs
Convention de Londres	décembre 1972	Convention sur la prévention de la pollution des mers résultant de l'immersion de déchets et autres matières
Convention d'Helsinki	mars 1974	Convention pour la protection du milieu marin dans la zone de la mer Baltique
Convention européenne	avril 1974	Projet de convention européenne sur la protection des cours d'eau internationaux contre la pollution
Critères de Rome	février et mai 1974	Critères et principes applicables au rejet de matières ou d'énergie dans les eaux côtières
Convention de Paris	juin 1974	Convention pour la prévention de la pollution marine d'origine tellurique
Convention de Barcelone	février 1976	Convention pour la protection de la mer Méditerranée contre la pollution
Directive du Conseil des Communautés européennes	mai 1976	Convention relative à la protection du Rhin contre la pollution chimique
Commission internationale pour la protection du Rhin contre la pollution	1965	Convention pour la protection du Rhin contre la pollution par des causes générales, spécifiques ou accidentelles

Le Registre International des Substances Chimiques Potentiellement Toxiques (RISCPT), qui est devenu opérationnel en 1976 dans le cadre du Programme des Nations Unies pour l'Environnement (PNUE), comprendra une liste des substances chimiques, où l'on trouvera les données disponibles sur le comportement de l'environnement et sur les effets des substances fabriquées par l'homme ou existant à l'état naturel.

Le Registre comprendra environ 150 attributs ou séries de données (voir Annexe A) qui serviront à identifier la substance chimique, à en décrire les propriétés physiques et chimiques, à estimer les modalités de son passage dans le milieu, à indiquer ceux de ses effets biologiques sur l'homme et le milieu qui se sont révélés importants pour l'évaluation des risques, à définir les méthodes d'échantillonnage et d'analyse de la substance, à déterminer les méthodes à utiliser pour faire face aux déversements dangereux, à suggérer des mesures thérapeutiques en cas d'empoisonnement par le produit chimique et à proposer des mesures de réglementation.

Au début de 1978, le centre d'activité du PNUE pour les mers régionales a demandé au RISCPT de dresser des profils de données pour les substances susceptibles de figurer dans le projet de Protocole relatif à la protection de la mer Méditerranée contre la pollution d'origine tellurique, projet que doit établir une réunion prévue pour mars 1979. L'une des tâches du RISCPT en 1978 a donc consisté à mettre au point des profils de données pour l'évaluation des dangers chimiques de certaines substances susceptibles de figurer dans les annexes citées plus haut. Etant donné le peu de ressources dont on dispose, ces profils ne contiennent pas d'informations sur tous les attributs prévus pour le registre du RISCPT. Toutefois, on a eu soin d'y faire figurer des données pour la Méditerranée. C'est pourquoi, les profils établis seront désignés dans le présent rapport sous le nom de profils de données pour la Méditerranée.

2. METHODE ADOPTEE

2.1 Etablissement de profils de données pour la Méditerranée

L'établissement de profils de données pour les substances chimiques suppose en premier lieu que soient déterminés les attributs et caractéristiques des substances qui risquent d'être nocives pour l'homme ou son environnement.

Le RISCPT a établi une liste d'attributs (Annexe A) qui, ou bien sont utilisés par les institutions des Nations Unies et par diverses organisations internationales ou nationales, ou bien ont été jugés - par un groupe international d'experts - indispensables à l'évaluation critique des dangers potentiels des substances chimiques pour l'homme et son environnement.

L'insuffisance des crédits et le manque de temps n'ont pas permis de recueillir des données sur tous les attributs ni de résoudre tous les problèmes de sélection des données. Toutefois, les renseignements demandés par le Centre d'Activité du Programme pour les mers régionales, du PNUE, porteront en définitive sur les questions suivantes:

- production ou consommation totales,
- procédés de production,
- schémas d'utilisation,
- cheminements de la pollution marine,
- transformation dans le milieu marin,
- comportement d'une substance chimique dans les organismes marins,
- comportement de cette substance chez l'homme et d'autres mammifères,
- concentrations dans l'eau de mer, les sédiments et les biotes,
- ensemble des effets toxiques sur l'homme et les autres mammifères,
- effets toxiques établis par des études spéciales sur des mammifères et des systèmes expérimentaux non marins,
- effets toxiques ou autres sur les organismes marins et les écosystèmes,
- échantillonnage et analyse,
- législation relative à la protection de l'homme et du milieu marin, et exposés récapitulatifs sur chacune des substances pour lesquelles ont été préparés des profils de données.

On notera que cette liste laisse de côté certains autres attributs - synonymes, données concernant l'eau douce et l'air, descripteurs, propriétés chimiques et physiques, par exemple - que le RISCPT considère pourtant comme nécessaires à l'évaluation des risques pour l'environnement (RISCPT, 1978).

Les exposés récapitulatifs visaient non seulement à résumer les données tirées des profils établis pour la Méditerranée, mais aussi à fournir les données additionnelles disponibles, c'est-à-dire à compléter en partie les données qui devraient normalement figurer dans le Registre International des Substances Chimiques Potentiellement Toxiques.

2.2 Choix des substances chimiques

Le RISCPT a été invité à décrire d'une façon générale les principales caractéristiques de chaque groupe de substances ainsi que les substances "les plus importantes" au sein de chacun des groupes énumérés dans les annexes du Projet de Protocole relatif à la Protection de la Mer Méditerranée contre la Pollution d'origine tellurique.

A la fin du mois de mai 1978, un groupe de travail du RISCPT s'est réuni à Genève afin de choisir les substances pour lesquelles il convenait d'établir des profils. L'un des documents de travail préparés pour cette réunion contenait une liste de plusieurs centaines de produits chimiques. Les noms de ces substances figuraient soit dans le Projet de Protocole, soit dans un ou plusieurs rapports, monographies ou listes de critères établis par l'ONU, par des organismes internationaux ou des instituts nationaux afin d'évaluer les risques des substances chimiques. Bien qu'un grand nombre de substances chimiques aient été retenues, il a été impossible, faute de renseignements plus complets, de sélectionner dans aucun groupe une substance "représentative" ou "particulièrement importante".

Le groupe de travail réuni en mai a recommandé que, lors de l'élaboration de critères applicables au choix des substances chimiques, il soit tenu compte des substances suivantes:

- substances d'intérêt majeur indiquées entre parenthèses dans les annexes I et II du Projet de Protocole;
- substances présentes dans la Méditerranée à l'échelle régionale, et non simplement locale;
- substances dont la surveillance peut être assurée par les méthodes d'analyse existantes;
- substances déjà étudiées dans le cadre de l'un des sept projets pilotes approuvés au titre du Programme coordonné de Surveillance et de Recherche sur la Pollution dans la Méditerranée (MED POL).

Etant donné que l'établissement des critères de sélection exigeait à peu près les mêmes renseignements que ceux qui devaient être recueillis pour déterminer les attributs d'une substance, il n'a pas été possible, en attendant le rassemblement et l'examen d'une masse plus considérable de données sur les attributs de choisir une substance "représentative" au sein d'un groupe général. Cette méthode de sélection signifiait également que le choix allait se porter sur les substances ayant fait l'objet du plus grand nombre d'études et de publications.

L'examen de la documentation publiée a montré que les groupes de substances énumérés dans les annexes au projet de protocole n'étaient pas homogènes du point de vue de leurs caractéristiques chimiques et biologiques. Il aurait été souhaitable que ces groupes fussent composés de substances similaires présentant une activité chimique ou biologique analogue. Comme ce n'était pas le cas, il a été difficile et le plus souvent impossible de choisir dans un groupe une substance chimique "représentative". Par exemple, les organohalogénés comportent des atomes d'iode, de brome, de chlore et de fluor fixés sur différents squelettes alkylés ou arylés, dont certains exercent sur l'environnement des effets sensiblement différents par le seul fait de leur configuration; en d'autres termes, des corps de formules chimique identique peuvent avoir des effets environnementaux différents du fait des torsions qui modifient la géométrie de la molécule.

Un autre groupe comprend vingt éléments différents et leurs composés: or, chacun de ces éléments possède des caractéristiques chimiques et biologiques distinctes, et les composés accroissent encore davantage les variations des caractéristiques chimiques et biologiques. En outre, étant donné l'intérêt commercial que présentent environ 100 000 substances, beaucoup n'ont pas été soumises à une surveillance adéquate visant à déterminer leur présence dans la mer Méditerranée ou leur rôle dans la pollution.

En l'absence de données adéquates concernant, par exemple, les quantités produites et les caractéristiques d'utilisation, et en l'absence de renseignements permettant d'évaluer le passage d'une substance dans l'environnement, il est difficile de déterminer le potentiel polluant relatif de cette substance.

2.3 Saisie des données

Les données nécessaires à la constitution des profils, si elles existent, sont extraites de documents de l'ONU et de documents nationaux et internationaux dans lesquels des informations chimiques ou biologiques ont été analysées par des experts. On trouve dans ces documents des données relatives à la toxicité de nombreuses substances chimiques pour les mammifères mais on s'est aperçu que très peu de données relatives au milieu marin y étaient analysées. Les substances passées en revue sont essentiellement des produits chimiques dont on sait déjà qu'ils sont dangereux; ainsi, des centaines de documents traitent de la toxicité du Mercure et de ses dérivés pour les mammifères. Toutefois, même la profusion des documents ne garantit pas nécessairement que les profils de données contiendront les éléments nécessaires à l'évaluation.

Si les données adéquates ne figurent pas dans les sources de documentation secondaires, il faut recourir à la documentation primaire. La majorité des données des profils pour la Méditerranée relatives au milieu marin ont été tirées de documents originaux. L'utilisation de ces documents originaux présente plusieurs avantages, tels que l'élimination des erreurs de transcription et d'interprétation, l'existence d'exposés et de descriptions plus exacts, et la présence de données supplémentaires.

Toutefois, l'utilisation des documents secondaires a l'avantage suivant: les données et les publications primaires ont probablement été évaluées par des comités internationaux d'experts d'organisations telles que l'Organisation Mondiale de la Santé (OMS), le Centre International de Recherche sur le Cancer (CIRC) ou la Commission des Communautés Européennes (CCE), ou encore par des experts de différentes organisations nationales chargés de formuler des recommandations en vue de la protection de la population contre les dangers des produits chimiques. Les données d'évaluation figurant dans ces documents devraient donc constituer une base très faible pour toute décision relative à la sécurité d'emploi d'un produit chimique.

Le RISCPT a élaboré, dans le peu de temps dont il a disposé, des instructions sur l'extraction des données et leur introduction dans les profils de données sur la Méditerranée. Ces instructions visent essentiellement à faciliter la manipulation des informations, de telle sorte que celles-ci soient présentées de façon uniforme et soient choisies systématiquement sans l'intervention des experts.

Toutes les informations sont choisies selon des critères définis avant la saisie des données plutôt que sur la base d'une évaluation d'expert. Les données sont introduites sous forme de tableaux et de façon codée, en utilisant le plus possible la nomenclature courante relevée ou élaborée pendant la période de préparation des profils de données.

Les données relatives à tous les attributs et caractéristiques sont référencées. Lorsque la documentation primaire est citée dans une source secondaire, cette dernière est citée comme indication de la fiabilité des données. La référence primaire est également citée afin de donner à l'utilisateur les renseignements nécessaires pour se procurer directement l'original à des fins d'évaluation personnelle.

Lorsqu'il existe plusieurs sources publiées d'informations relatives à un domaine particulier, au lieu de répéter une seule et même référence, on cite différentes sources, afin d'offrir plusieurs possibilités de références à l'utilisateur qui désire se livrer à un examen plus complet.

On peut se servir de documents dans n'importe quelle langue, mais toutes les données sont traduites en anglais, langue du Registre.

Dans le choix des données, la priorité absolue est donnée aux documents comportant la description la plus complète, c'est-à-dire contenant tous les éléments d'une ligne horizontale de données sur un imprimé de saisie. Le choix de la documentation commence par les documents les plus actuels et continue en remontant dans le temps jusqu'à ce qu'on ait retrouvé le plus grand nombre possible d'attributs. L'absence de données pour une propriété particulière d'un produit signifie qu'aucune donnée pertinente n'a été relevée dans la documentation dépouillée. Les références figurent sous forme abrégée dans le profil et en toutes lettres dans la bibliographie qui suit chaque profil.

Les principales difficultés rencontrées en matière d'extraction des données ont été l'absence de méthodes d'épreuve normalisées et l'absence de définitions acceptées et d'unités uniformes pour rendre compte des phénomènes scientifiques décrits dans la documentation. Les substances chimiques sont souvent désignées dans les publications selon le groupe auquel elles appartiennent sans que l'on définisse les critères de groupement, ce qui masque l'identité de la substance étudiée. On aboutit ainsi à l'élimination de bon nombre de renseignements qui pourraient être utiles. Par exemple, le "mercure" mentionné dans la documentation correspond souvent au mercure métallique, aux sels de mercure ou à l'un quelconque des composés organo-mercurés. Il est alors difficile sinon impossible de déterminer ce qui a été effectivement fait ou observé, d'où l'ambiguïté des données extraites.

2.4 Préparation des résumés

A l'origine, le RISCPT était chargé de préparer des descriptions générales des principales caractéristiques des groupes ou catégories de produits chimiques figurant dans le projet de Protocole. Toutefois, des difficultés sont apparues dans l'exécution de cette mission, de sorte que la plupart des descriptions établies l'ont été pour les substances chimiques pour lesquelles des profils de données avaient été élaborés. Les descriptions ou résumés de leurs effets sur l'environnement ont été élargis et l'on a incorporé des informations supplémentaires sur les groupes de substances chimiques, informations qui ne pouvaient pas être fournies par les profils de données utilisés pour cette étude.

Les résumés ont donc été rédigés pour compléter les profils de données sur la Méditerranée, récapituler les données présentées et, d'une manière générale, indiquer pour chaque substance où on la rencontre, ce qu'elle devient dans l'environnement, comment on la surveille et quels sont ses effets toxiques.

Les résumés sont de simples exposés descriptifs des données recueillies et ne contiennent pas d'évaluation de ces données. En effet, toute évaluation a été expressément exclue à la demande du Centre d'activité du Programme pour les mers régionales, cette évaluation devant être entreprise par des experts représentant les gouvernements des pays riverains de la Méditerranée. L'évaluation devra déterminer pour quelles substances chimiques les pays membres devraient adopter des mesures de réglementation et sur quoi l'on pourrait fonder ces mesures. Les profils de données visent à fournir ce genre d'information.

Dans la plupart des cas, le principal défaut des résumés et des profils de données est que les données sont insuffisantes pour l'établissement d'un profil détaillé des produits chimiques retenus. Si les données relatives à la Méditerranée sont incomplètes, elles s'enrichissent sans cesse à mesure que les résultats des recherches et des travaux d'observation sont publiés par les centres spécialisés des pays riverains de la Méditerranée. Ces nouvelles données pourront servir à améliorer et développer les profils de données sur la Méditerranée.

Si l'on s'est attaché à éliminer toute évaluation dans le processus de sélection des données, une certaine évaluation des informations n'en subsiste pas moins. Elle est réduite à un minimum grâce à des directives précises concernant, par exemple, les points suivants: la plus faible dose constatée (U.S. Registry of Toxic Effects of Chemical Substances); les données les plus récemment publiées et la technologie la plus récente; ou les données étudiées par les services spécialisés des organisations nationales et internationales. Cette méthode laissera parfois de côté les publications faisant autorité mais qui ne satisfont pas aux critères de sélection. Toutefois, les directives retiendront certainement des publications qui se sont servies des études faisant autorité, lesquelles figureront dans leur bibliographie. Grâce à ce processus de sélection, les données retenues ne risquent pas d'être faussées par une appréciation erronée ou controversée puisqu'aucun jugement qualitatif n'intervient dans le choix. Toutefois, les données controversées figurant dans le profil pourront être décelées grâce à leur non-conformité aux autres données recueillies.

En cas de contestation, les évaluateurs de données se procureront les originaux et en évalueront les données. Des informations supplémentaires pourront être exigées pour résoudre certains problèmes et il pourra être nécessaire d'organiser des consultations supplémentaires lorsque les initiatives à prendre en matière de réglementation ou de recherche reposent fondamentalement sur ces données.

3. METHODES FUTURES DE COLLECTE DE L'INFORMATION

3.1 Attributs additionnels

Une évaluation critique et objective du risque auquel l'homme et son environnement peuvent être exposés du fait d'un polluant chimique suppose la connaissance de certaines données. Une bonne évaluation exige la connaissance des éléments d'information suivants: propriétés physiques et chimiques de la substance, ses effets sur l'homme, sur les autres organismes vivants et sur l'écosystème, les quantités produites, les modes d'utilisation, la distribution et la transformation de la substance dans l'environnement, les concentrations de la substance dans l'air, l'eau, les aliments et le sol. D'autre part, il est essentiel de connaître les lois et règlements existants et projetés concernant l'utilisation et l'élimination des substances chimiques, et les méthodes d'échantillonnage et d'analyse employées pour contrôler l'application des lois et règlements. En prenant pour modèle les règlements existants, on peut, quand on veut mettre en place un dispositif de réglementation, s'épargner bien des difficultés techniques. des méthodes fiables à appliquer en cas d'intoxication ou de rejet de substances chimiques sont absolument nécessaires à ceux qui, au niveau national, sont responsables de la sécurité d'emploi des substances chimiques.

Le RISCPT a récemment fait une étude pour déterminer sur quelles caractéristiques se fondent les institutions tant nationales qu'internationales, y compris l'ONU, pour évaluer le préjudice que les substances chimiques peuvent causer à l'homme et à son environnement, et il a, à cette occasion, établi une liste d'attributs à inscrire au Registre.

Assortis de données appropriées, ces attributs donnent une idée du potentiel de risque et permettent, selon son danger potentiel, d'assigner un rang de priorité à la substance concernée, soit à des fins de recherche, soit à des fins de réglementation. Les organismes ou institutions chargés de l'évaluation posséderont ainsi un outil de travail qui leur permettra de déterminer l'affectation des ressources et la direction des efforts visant à lutter contre la pollution des sols, de l'air et de la mer par les substances chimiques. Ce programme de définition des attributs des substances chimiques peut aller de pair avec une action immédiate de lutte contre la pollution et pourrait être intégré à tout programme de détermination des priorités à mesure qu'il est mis en œuvre.

3.2 Substances chimiques additionnelles

Plusieurs moyens sont actuellement utilisés pour fixer les priorités en matière de réglementation ou de recherche concernant les substances chimiques. Toutefois, le recours à ces moyens suppose une évaluation de l'importance de la substance chimique en cause, faite sur la base soit d'un nombre limité de critères de sélection préétablis, ne comportant guère de données concrètes, soit d'une sélection par consensus, parfois appelé "méthode de la pythie". On peut commencer par employer l'une ou l'autre méthode pour combattre les risques dus aux substances chimiques, mais l'une et l'autre ne permettent de sélectionner que quelques-unes des substances les plus nuisibles, et elles ne permettent pas de prévoir quels seront les problèmes chimiques que poseront les substances dont l'action nocive n'a pas encore causé de graves dommages à l'environnement. La question qui se pose est de savoir comment identifier les substances chimiques importantes - c'est-à-dire celles qui ont sans doute des effets nocifs sur l'homme ou son environnement - et quelle priorité il faut leur assigner dans les activités de réglementation, si possible avant qu'elles ne détériorent gravement l'environnement.

Les efforts qui ont été faits dans cette voie, tant sur le plan national que sur le plan international, n'ont pas encore permis de définir des méthodes satisfaisantes, mais ces efforts se poursuivent. Pour bien faire, il faudrait, au regard du nom des substances, dresser la liste de tous leurs effets adverses. On pourrait ensuite grouper par genre toutes les substances de structure similaire et postuler qu'elles produisent les mêmes effets. Le problème à résoudre est de savoir quelles sont ces substances chimiques similaires. Traditionnellement, leur classification est entièrement fondée sur la composition chimique.

On a tenté de grouper les substances des diverses listes noires et grises: organohalogénés, dérivés organiques de l'étain, silicones, etc. Mais la vanité de tels groupements apparaît lorsque l'on constate la diversité des effets biologiques selon l'arrangement physique des stéréo-isomères d'une seule molécule. Par exemple, l'héxachlorocyclohexane comporte huit stéréo-isomères. Parmi ceux-ci, l'isomère bêta reste dans la graisse des animaux d'expérience plus longtemps que tous les autres isomères (Fitzhugh et al., 1950). On a constaté que l'accumulation de l'isomère bêta dans la graisse est cause d'intoxications et de décès chez l'homme. L'action insecticide, autre attribut possible, varie beaucoup en fonction de la disposition spatiale des atomes dans la molécule; l'isomère gamma est en effet mille fois plus toxique pour les insectes que l'isomère alpha et 10000 fois plus toxique que l'isomère delta. On n'a pas observé de propriétés insecticides chez les autres isomères (Weger, 1971). Le n-butyl méthyl cétone, homologue des alkyl-cétones, provoque la neuropathie périphérique chez l'homme et les animaux d'expérience, alors que l'on n'a pas observé le même effet pour d'autres alkyl-cétones (Allen et al., 1975). On sait que les isomères chimiques produisent

des effets biologiques très différents. L'alpha-naphthylamine est ou bien faiblement cancérigène ou non cancérigène (CIRC, 1974), alors que la bêta-naphthylamine est un cancérigène relativement actif chez l'animal d'expérience (Conzelman et al., 1972). Manipuler les molécules de médicaments pour renforcer leur effet thérapeutique ou réduire des effets secondaires fâcheux est pratique courante dans l'industrie pharmaceutique. Ces remarques sont valables aussi pour les substances chimiques rejetées dans l'environnement. Dans le groupement des substances chimiques en fonction de leur similarité, à des fins de réglementation ou de recherche, il faudrait faire entrer en ligne de compte de nombreuses caractéristiques autres que la similitude chimique. L'activité biologique est très diverse même dans un groupe comme les diphenyles polychlorés (PCB). La biodégradation varie considérablement avec la position des atomes de chlore dans la molécule de biphenyle. Ainsi, les molécules de dichloro-2,3 et 2,5 diphenyle sont biodégradables, tandis qu'il n'en va pas de même des molécules de dichloro-1,3 et 1,2 diphenyle. Très peu de substances dont on sait qu'elles font partie de ce groupement ont été étudiées à fond. Aussi est-il concevable que certains diphenyles chlorés ne jouent aucun rôle dans la pollution de l'environnement par les PCB.

Si l'on veut enrayer les risques auxquels sont exposés l'homme et son environnement, il est indispensable d'examiner une à une les substances chimiques ou les groupements de substances et d'identifier leurs caractéristiques chimiques, physiques et biologiques communes. Il faut donc chercher à recueillir et à classer les données sur les effets des substances chimiques dont on sait, par démonstration, qu'elles sont nocives pour l'environnement. Ensuite, on identifiera les substances chimiques présentant les mêmes caractéristiques biologiques, chimiques et physiques pour voir si on peut les classer dans un même groupe qui est censé produire l'effet nocif en question. Vu l'ampleur de la tâche, il n'est pas question d'y parvenir dans un avenir proche pour toutes les substances, mais il est possible, en procédant ainsi, de s'attaquer assez rapidement à certains des problèmes les plus graves et les plus évidents que pose la protection de l'environnement.

Parmi les substances chimiques à inscrire au RISCPT figureront des produits commerciaux comme ceux qui sont utilisés dans l'industrie ou dans l'agriculture (pesticides employés en agriculture et en santé publique), les additifs alimentaires et les adjuvants de fabrication, les médicaments, les cosmétiques, les colorants, les peintures, les combustibles, les matières premières, les produits intermédiaires et les déchets chimiques de la production industrielle et commerciale, ainsi que les produits qui résultent de la réaction des substances susmentionnées dans l'environnement.

Habituellement, on ne décide d'étudier en priorité une substance chimique donnée qu'après que sa grave nocivité sur l'environnement et les êtres vivants a été démontrée.

Un certain nombre de pays ont entrepris de recueillir des données sur les substances chimiques utilisées sur leur territoire. La Communauté Européenne projette de faire de même. Quand cet inventaire sera achevé, on disposera d'un répertoire assez précis des substances chimiques que l'on trouve dans le commerce mondial. Une fois établi le registre de ces substances chimiques, on pourra y inscrire des données concernant les catégories de substances caractérisées par un plus fort potentiel de nocivité à l'égard de l'environnement, par exemple les substances chimiques biologiquement actives utilisées comme pesticides ou comme médicaments, des substances présentes dans l'environnement, comme les pesticides, les engrais et les détergents, et les substances chimiquement actives utilisées dans la production industrielle.

En opérant ainsi un choix entre les substances chimiques, on retiendra probablement des produits d'intérêt commercial, déjà étudiés pour leurs effets sur le milieu ambiant et susceptibles de nuire gravement à l'environnement.

3.3 Instructions pour la saisie des données

Au fur et à mesure qu'il acquiert de l'expérience en matière d'extraction et de saisie des données, le RISCPT révisé et développe constamment les instructions qu'il donne dans ce domaine. Pour établir de telles instructions il lui faut retrouver dans les publications (où elles paraissent sous des formes très diverses) les observations scientifiques concernant les différents attributs des produits chimiques. Il lui faut aussi décrire la méthode à utiliser pour présenter les données d'une manière claire permettant à l'utilisateur de comprendre, comparer et évaluer les données. L'objet des instructions est de permettre à des personnels techniquement formés, mais pas nécessairement nantis d'une longue expérience, d'extraire et de présenter les données avec un minimum de biais subjectif et un maximum de précision.

Les instructions relatives à la sélection et à la présentation des données en vue de la constitution de profils de données relatifs à la Méditerranée ont été mises au point et appliquées, mais de nombreux problèmes ne sont pas encore résolus. Le plus souvent, cela ne gêne pas l'utilisation et l'évaluation des profils mais, dans certains cas, l'utilisateur est obligé de consulter les publications originales. Parce qu'il n'en est encore qu'à ses débuts, le RISCPT n'a pas pu, dans les six mois dont il a disposé pour élaborer ces profils, s'attaquer à tous les problèmes de la saisie des données.

Le RISCPT continuera à travailler à la mise au point d'instructions concernant les attributs des profils de données relatifs à la Méditerranée mais aussi concernant les autres attributs auxquels il s'intéresse. Il s'efforcera également, en ce qui concerne les instructions de saisie des données, de condenser les renseignements afin de pouvoir les publier sous un plus petit volume.

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ANNEX A
IRPTC FILES/ATTRIBUTES

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OUTLINE
FOR IRPTC FILES/ATTRIBUTES

1. Identifiers for substances
IRPTC name and sequence number
Pointers (cross references)
Synonyms
Descriptors
2. Properties for predicting environmental fate/hazard potential
Melting point or range
Boiling point or range
Vapour pressure
Flash point
Flammable limits
Reactivity/stability
Density
Solubility (or miscibility) in water
Partition coefficient
Adsorption/desorption properties
3. Total production
Year
Area
Amount produced in tons
Trend
4. Production process(es)
Process(es)
Number of workers exposed
Intermediates, impurities and waste products
5. Use
Use
Geographic area
Substances added for a particular use
Trend
6. Pathways into the environment
Pathway
Quantity
Geographic area
7. Transport in the environment
Pathway
Quantity
Geographic area

8. Transformation
Process of transformation
Location of transformation
Environmental residence time
Environmental stability data
Transformation products
9. Behaviour in organisms
Description of organism
Route of exposure
Dose
Duration of exposure and clearance period
Retention
Clearance rate
Metabolites
10. Concentration
Description of sample
Geographic area
Date of sampling
Concentration
11. Effects on man
Array of toxic effects
 - Dose
 - Route of administration/exposure
 - Total exposure time; brief description of exposure
 - Description of organism/system
 - Description of effect
 - Observation in manSpecial studies
 - Description of organism
 - Route of administration
 - Dose
 - Total exposure time; brief description of exposure
 - Description of effect
12. Effects on the environment
Description of organism/system
Description of exposure concentration
Description of exposure/clearance time
Description of effect
13. Sampling and analysis
Sampling and preparation methods
Analytical methods

14. Spills
Date of spillage
Location
Quantity
Metereological conditions
Description of physical appearance
Cause
Effects on man
Emergency treatment
Evacuation measures
Effects on the environment
Measures taken to remove the chemical
15. Poisoning
16. Removal
Disposal and/or destruction method(s)
Recycling method(s)
17. Legal mechanisms
Country
Type of control mechanism
Description of control mechanism
Quantitative information
Date of entry or verification

File 1: Identifiers for Substances

Substances are interpreted here to include all mined, manufactured, processed, synthesised and naturally occurring inorganic and organic compounds. The list includes drugs, food additives, preservatives, ores, pesticides, dyes, detergents, lubricants, soaps, plastics, extracts from plant and animal sources, plants and animals which are toxic by contact or consumption, and industrial intermediates and waste products from production processes. Much of the information in the files thus refers to materials for which the exact composition is only imperfectly known. Even in the case of a supposedly "pure" substance there is usually some degree of uncertainty as to its exact composition and the impurities which may be present. This problem must be borne in mind in attempting to interpret the data presented since the toxic effects observed are in some cases due to the presence of a contaminant.

Substances excluded from the register are trade name products representing compounded or formulated proprietary mixtures available as commercial products. These exclusions have been made because of difficulties in assessing the contribution to the toxicity by each component of the mixture, and because the components of those formulations can be and are often changed by the producer by substitution of different chemicals with different toxic effect potential or by varying the concentrations and purity of the ingredients. Trade names are included when they represent a single active chemical entity. These substances may be impure commercial products of relatively constant composition. Radioactive labelled substances are not separately indexed, but are included with the entry for the non-labelled substance.

IRPTC name and sequence number

Used for sequence and identification purposes and as the official file name. The name is selected at the convenience of IRPTC from the CAS Ninth Index (non-inverted) with a purpose of grouping substances alphabetically in a proximate relationship. The IRPTC number is attached to the selected name and is used as a means of ordering the file alphabetically with the English alphabet. Letters from other alphabets are in an appropriate position with respect to this English alphabetic arrangement.

Pointers (cross-references)

This is a "relationship" field which provides pointers (cross-references) to related entries with the following relationships:

- individual substances contained as components where the primary substance is a mixture,

- impurities known to occur as contaminants in the primary substance,
- mixtures known to contain the primary substance as a component,
- substances known to contain the primary substance as an impurity,
- substances which are known to give rise to the primary substance as a metabolite,
- substances known to arise as a metabolite of the primary substance,
- related substances which do not differ in a toxicologically significant way, e.g. salts differing in the number of molecules of water of hydration.

The above pointers, other than the last one are associated with one or more citations to the primary or secondary literature indicating the source of the information establishing the relationship.

Synonyms

All synonyms in the IRPTC are used as cross references. Synonyms are input in the following categories:

- Chemical Abstracts preferred name and registry number for compounds and mixtures as applicable. Identified as CAS name and number.
- International Union of Pure and Applied Chemistry (IUPAC) Name(s). All available IUPAC Names are included.
- Common names as found in the literature. There is no limit to the number provided for.
- Trade names which describe a single chemical substance.
- Other names and numbers which help identify a chemical substance, e.g. United Nations Number.

Descriptors

- Molecular formula and molecular weight. The molecular formula represents the elemental composition of a chemical substance in terms of the number and kinds of atoms contained in its structure. The molecular formula is expressed in the Hill System. The molecular weight is calculated from the molecular formula.

- Wiswesser line notation (WLN). The WLN is a unique and unambiguous representation of a chemical structure in a single character string using a standardised arrangement of 40 symbols (numerics, alphabets, three special characters and blanks). Due to the variety of WLN dialects the IRPTC uses consistent publicly available sources, and extracts WLN's from these sources, i.e. the IRPTC does not generate its own dialect.

Rationale for the inclusion of this file

This file is necessary for the initial identification of a chemical substance. The IRPTC number and name are necessary to allow alphabetic arrangement of the file of chemical names. It allows construction of a unique name so that new data can be input under the correct file when only chemical structures or synonyms are given in the original literature. It is a useful method for identifying substances which are not covered by a Chemical Abstract Registry number. It also allows the identification and separation of chemical substances which appear to be identical except for their effect on biological systems. Further, different modifications of one chemical substance can be separated and given individual IRPTC numbers. This is necessary to provide the significant relationships as found in the literature. These relationships have a direct bearing on the hazard assessment of the substance.

Synonyms are essential to the identification of a chemical substance as the user often does not have the standard IRPTC name. The synonyms also facilitate the cross-reference from one data system to another. The Chemical Abstracts Service number is universally understood and allows conclusive recognition of a large number of chemical substances, and facilitates the merging, by computer, of data from other files such as CAS, NLM, EPA-TSCA, RTECS, etc. CAS connection tables can also be used to generate 3-dimensional structure by computer display.

The molecular formula and molecular weight are extremely useful for purposes of identification. They are also useful for computer sorting of substances and as a cross check on CAS number or name when matching data bases/banks to assure correctness of match. They are not difficult to obtain, for the most part, and they augment the value of the register considerably. Wiswesser Line Notations are included as they are becoming a valuable tool for predicting the potential toxicity of a chemical substance on the basis of structural similarities among chemicals.

File 2: Properties for predicting environmental fate/hazard potential

Melting point or range (including sublimation)

Data are listed in degrees Celsius, with conditions of measurement as near "normal" as possible, i.e. 101.3 kPa.

Boiling point or range

Data are listed in degrees Celsius, with conditions of measurement as near "normal" as possible, i.e. 101.3 kPa.

Vapour pressure

The equilibrium pressure of the saturated vapour above the liquid, measured in millimeters of mercury at 20°C. Data are listed in terms of kilopascal with conditions of measurement as near "normal" as possible, i.e. within the environmental temperature range of -20°C to 50°C. Data nearest 20°C are listed preferably.

Flash point

The temperature at which a liquid will give off sufficient flammable vapour for ignition to occur without an ignition source. Data are listed in degree celsius and the measuring device used is designated, i.e. open or closed cup.

Flammable limits

The range of gas or vapour concentrations which will burn or explode if any ignition source is present. Data are listed in mass or volume concentration, i.e. mass of a component divided by volume of system; or in volume or mass fraction, i.e. volume or mass of a component divided by volume or mass of a system.

Reactivity/stability

List conditions that could cause uncontrolled reactions are included, e.g. thermal instability, pH instability (hydrolysis products), photochemical reactivity, corrosion.

Density

The conditions of measurement are as near "normal" as possible, i.e. 101.3 kPa and within the range of -20°C to 50°C.

Solubility (or miscibility) in water.

Quantitative, precise data are included. Data nearest 20°C and 101.3 kPa are given priority. A qualitative statement is also included, e.g. slightly soluble, highly soluble. Data are quoted in mass concentration, i.e. mass of a component divided by volume of water; or in substance concentration, i.e. moles of substance of a solute divided by volume of water.

Partition coefficient

The measured or calculated ratio of the concentration of the chemical at equilibrium in n-octanol/water phase.

Adsorption/desorption properties

Adsorption to surfaces or leaching. In soil, sludge, sediments, etc. as described by Freundlich's equation or other reported means.

Rationale for the inclusion of this file

The melting point and boiling point identify the state of aggregation of a substance for a certain temperature in the environment. Risks occurring when chemicals are accidentally spilled can be estimated for their gravity, i.e. escaped gases are normally more difficult to control than spilled liquids and solids. Additionally, both indicate the temperature approaching which the storage of chemicals becomes hazardous, as a change in the state of aggregation may cause dangerous and uncontrollable evaporation or spillage into the environment.

Vapour pressure provides an indication of the relative tendency of a pure substance to volatilise and thus be distributed into various ecosystems. It is also important for hazard evaluation as it is related to the evaporation velocity of a liquid. Flash point and flammable limits are important as they indicate the danger of fire and explosion.

Reactivity and stability highlight the incompatibility of a chemical with common substances such as water, acids, alkalines, pipe line and container material if there is a possibility of corrosion, fire, explosion, or gas emission. They also indicate when toxic degradation products can be expected to be produced by sunlight or at certain temperatures. The degradation temperature substitutes the melting and boiling points for those substances that decompose before they change state of aggregation, e.g. chemically cross-linked high polymers which do not reach a liquid state without decomposition.

Density is useful for predicting the behaviour of insoluble chemicals in water, e.g. floating, sinking, suspended. Additionally, weight can be calculated on the basis of density, a factor which helps determine the adequacy of a container.

Solubility in water is an important characteristic of chemical substances since the degree of water solubility often determines the ultimate fate of the substance and its environmental significance, e.g. water soluble substances tend to be distributed more widely, to be less concentrated as a result, and to have a higher probability of being attacked by microorganisms.

The partition coefficient provides presumptive evidence of the likelihood of the chemical accumulating in a living system. This, in turn, may provide information about the chemical's distribution and persistence.

The tendency of a chemical to adsorb to soil surfaces has a profound effect on its transport, degradation, and bioavailability as adsorption reduces the concentration of a chemical in solution.

Although this information is for the most part published in handbooks, its inclusion, organised here along with the other IRPTC files facilitates the prediction of environmental fate and the assessment of potential hazard for users of the register, many of which may not have the above handbooks.

File 3: TOTAL PRODUCTION

Year

Data are entered for at least three years, where available; one figure is taken from more than 10 years back, and one is from a recent year. The data in this file are organised by year.

Area

To designate the area to which the data refers. World production estimates are entered first, followed by those for individual geographic areas.

Amount produced in tonnes

Production figures are listed; when they are not available, capacity figures are entered in their place and designated as such. Data are entered in metric tons. If different figures are found in the literature for identical areas and years, the different figures are listed.

Trend

A qualitative statement concerning production trend, prospective and retrospective is included as reported.

Rationale for the inclusion of this file

While the production quantities and capacities available are often relatively incomplete, it is believed that the user should be provided the figures and their source for his own estimation of the possible human exposure and environmental significance of each substance. Data on trend may suggest new hazards which are a result of an increasing production rate. Additionally, past production data are sometimes useful in epidemiological studies as some diseases, e.g. cancer, are delayed toxic effects.

File 4: PRODUCTION PROCESS(ES)

Process(es)

To include the name or a brief description of the processes found and an indication of whether each process is of major or minor importance (by geographic area) and whether the process is carried out in an open or closed system.

Number of workers exposed

To include the number of workers who are potentially exposed in the world, or by country, with a breakdown by production process if available.

Intermediates, impurities and waste products

To include any of the above which are found in the literature; when the information is available, each entry is designated as an intermediate, an impurity or a waste product. A pointer (cross reference) is given to the IRPTC number of each substance and when these substances are reported to be hazardous they are designated as such.

Rationale for the inclusion of this file

Information on production methods is included as it may make explicit the potential human or environmental impact of a substance. Such effects are local ones, arising directly from the substance or waste products of its manufacture; or distant ones resulting from contaminants or impurities introduced into the environment. This information is also useful in differentiating between chemical substances which would be considered identical apart from the fact that they cause different biological effects and are the result of different production processes.

File 5: USE

Use

To include as many reported uses as possible.

Geographic area

The geographic area to which the use refers, e.g. world, region, country. Uses are designated as major or minor for each particular geographic area.

Substances added for a particular use

To include the IRPTC names of any components added to the product for a particular use, e.g. stabilisers.

Trend

A qualitative statement concerning use trend (prospective and retrospective) as reported.

Rationale for the inclusion of this file

Inclusion of this information is felt to be essential in that it serves to define the population or environmental segment in which toxic effects might be anticipated to occur and the likelihood of environmental entry.

From the point of view of the epidemiological assessment of hazard where exposure to the substance in question is suspected of producing chronic effects, this information is critical to the identification of groups of persons who may be expected to be at high risk. Frequently such populations are to be found among the persons exposed in "minor use" situations where control of exposure is minimal or non-existent. The trend information is important in that it may direct attention to environmental segments in which toxic effects have not yet been noted but can be anticipated to occur in the future, as well as to the population(s) at risk.

File 6: PATHWAYS INTO THE ENVIRONMENT

Pathways

To include man made and natural pathways by which a chemical substance enters the environment, e.g.

- industrial and sewage effluents,
- land drainage,
- natural production by a chemical or biochemical reaction,
- leaching from solid waste, landfill, etc.,
- spills,
- deliberate application,
- geophysical modifications, and
- unintentional production.

Quantity

To include the quantity of a chemical substance that enters by the given pathway listed in metric units.

Geographic area

To include the geographic area to which the figures relate, e.g. world, region, country.

Rationale for the inclusion of this file

The attributes, in this file indicate the pathway of environmental entry of chemical compounds. They also show in which environmental compartments and geographic areas the compound in question can initially be expected to be found.

File 7: TRANSPORT IN THE ENVIRONMENT

Pathway

To include the natural pathways by which a chemical substance is transported within the environment, e.g.

- soil-air interphase exchange,
- water-air interphase exchange,
- evaporation,
- troposphere-stratosphere exchange,
- transport by rivers, oceans, ground water,
- adsorption,
- sedimentation,
- leaching.

Quantity

To include the reported quantity of a chemical substance that is transported via each pathway listed in metric units or percentage.

Geographic area

To include the area to which the figures relate, e.g. total world or a particular river basin.

Rationale for the inclusion of this file

The attributes in this file give an indication of the dispersion behaviour of chemical compounds. They enable the user to determine, in quantitative terms, in which environmental compartments, e.g. air, water, sediment, the chemical can be expected to be found.

File 8: TRANSFORMATION

This file includes any structural change of a chemical substance.

Process of transformation

The name or a brief description of the transformation process, e.g. hydrolysis, photooxydation, microbial methylation.

Location of transformation

A brief description of the location and the medium in which the transformation occurs, e.g. surface sea water, stratosphere, temperate pond, laboratory-brachish sediment, microorganisms in water purification system.

Environmental residence time ("half-life" of a substance at a location)

The percent disappearance of a substance from a location (environmental subcompartment as listed above) in a stated time in addition to transformation of a substance, e.g. "half-life" of a substance at a location.

Environmental stability data ("half-life" of a substance as far as chemical integrity is concerned)

Half-lives or similar rate data for chemical compounds obtained for different factors, e.g. half-life under conditions of hydrolysis at pH 9; half-life when exposed to sewage sludge, under controlled conditions. Include data calculated from physical and chemical parameters, e.g. evaporation rate, as well as those obtained from standardised laboratory model experiments, e.g. biodegradation in soil, water or sewage sludge.

Transformation products

The name and quantity in percentage or metric units of transformation products, as reported and the IRPTC name for any reported intermediates.

Rationale for the inclusion of this file

The chemical and biochemical transformation of a substance in different locations is included here for two reasons. Firstly, the rate of transformation (degradation) is one of the important factors in determining the concentration of a chemical substance, and secondly, transformation (structural change) of a chemical may result in a transformation product (metabolite) with undesirable properties, such as toxicity or persistence.

File 9: BEHAVIOUR IN ORGANISMS

This file includes man and other organisms as reported, e.g. mammals, fish, plants.

Description of organism

To include genus, species, common name, life stage, strain, as reported.

Route of exposure

The route of exposure e.g. direct uptake from water, diet, intubation, i.p. injection, inhalation, dermal, via roots.

Dose

Data are expressed either as concentration water (mg/l), air (mg/m³), or dose (mg/kg bw). The number of times the dose was given per day is also included.

Duration of exposure and clearance period

The duration of exposure and, when applicable, of clearance.

Retention

The percent retention in a given time period. To include total body, organ or tissue involved and whether data given are on dry weight, wet weight or fat basis.

Clearance rate

The percent clearance in the time period specified. To include tissue or organ involved and whether data given are on dry weight, wet weight or fat basis.

Metabolites

To include the IRPTC name of the reaction products, as reported, and the relative percentages of each.

Rationale for the inclusion of this file

The behaviour or pharmacokinetics of a chemical substance in an organism determines the availability of a chemical substance at the toxicity receptor site (target site). Metabolism usually aids excretion of the compound but can also result in reactive intermediates ultimately responsible for toxic action.

File 10: CONCENTRATIONS

Description of Sample

To include samples from the following media:

- human, e.g. concentrations in specific tissues of individuals exposed to differing environmental concentrations,
- air, e.g. cities, pristine environment, lower troposphere, stratosphere,
- water, e.g. ocean estuaries, fresh water, ground water, drinking water, waste water,
- soil and sediments, e.g. agricultural soil, pristine forest soil, sediment in sewage sludge, fallout areas, and unpolluted lakes,
- food, e.g. pesticide residue concentrations in plant and animal products. Included in this description would be the tissue from which the sample was taken, e.g. fat; in the case of mg/kg, wet weight or dry weight should be designated,
- non-human non-food biota, e.g. concentrations in different species at different trophic levels, and in organisms exposed to different environmental concentrations.

Geographic area

The area from which the sample was taken, as reported.

Date of sampling

The date of sampling as reported. Trends will be highlighted by a specific identifier.

Concentration

Data are entered in metric units.

Rationale for the inclusion of this file

While information on production and use may provide a basis for speculation on present or future environmental impacts, the actual effects which occur, or may be anticipated, as a consequence of the presence of a substance in the environment are determined by the concentrations which actually exist. Only where the actual concentrations have been determined can we do more than speculate on the probable effects. Some of this information is directly applicable to the human situation.

File 11: EFFECTS ON MAN

This file consists of two parts: an array of dose-effect relationships, and a section where the results of studies designed to produce a particular effect are given.

Array of toxic effects

This array is divided into two sections: 1) mg/kg bw/day, and 2) mg/m³/day. It includes effects ranging from acute lethal to those observed during long term exposure. The attributes in the array are as follows:

Dose

To include the amount of chemical substance administered or the amount of exposure in the air per day with the appropriate qualifying factors. The data are arranged in order of highest dose to lowest dose within the concentration categories and are given in mg/kg bw/day or mg/m³.

Total exposure time; brief description of exposure

The total exposure time in hours, days, years, etc. and any other relevant exposure information, as reported.

Route of administration/exposure

Entered as reported in the literature, e.g. oral (diet), inhalation.

Description of the organism/system

To include common name, strain, genus and species when commonly used, age and sex as reported.

Description of effect

The effect reported is described in as complete a way as the register allows. A toxic effects code such as that now being tested at the US National Institute of Occupational Safety and Health (NIOSH) will be used. The observation time is also given if it is longer than the duration of exposure.

Observation in man

These are added at the bottom of the array unless there is sufficient data on dose and exposure to warrant their being incorporated into the array. Both epidemiology and case report data are included.

Rationale for the inclusion of the array of toxic effects

This array indicates the order-of-magnitude toxicity in several species to the extent that the information is available. It gives the user an idea of the various effects which were reportedly caused by the substance as well as the dose at which the effect was reported to have been observed. It requires very well defined input and user instructions in order that it be used as it is designed to be used, i.e. to show the comparative toxicity of a large number of substances.

SPECIAL STUDIES

To include toxicology information from studies designed to produce a particular effect, e.g. behavioural effects, carcinogenicity, mutagenicity, potentiation/antagonism, reproductive effects, teratogenicity. Although the data elements are tailored slightly for each different study, they generally include the following:

Description of organism

To include genus, species, common name, age, sex, (number of generations for reproductive studies), life stage, as reported.

Route of administration

Listed as reported in the literature, e.g. dermal, oral (intubation).

Dose

To include the concentration of a substance administered in mg/kg bw or mg/m³.

Total exposure time; brief description of exposure

The total exposure time in hours, days, years, etc. and any other relevant exposure information, as reported.

Description of effect

The effect reported is described in as complete a way as the register allows. The observation time is given if it is longer than the duration of exposure. Statements such as the following are used to qualify the effect:

1. A comprehensive evaluation of the known studies designed to assess the possible effect of this substance in experimental systems has been carried out. The evaluation reached was as follows: (The evaluation, e.g. an IARC evaluation for carcinogenicity, is quoted and the reference is cited.)

2. This study, designed to evaluate the possible effects of the substance, resulted in a report of effects, but no comprehensive evaluation of this material was found in the literature reviewed.
3. This study, designed to evaluate the possible effects of this substance, was found in the literature reviewed. It did not result in a report of effects. No comprehensive evaluation of this information was found.
4. No study was found in the literature reviewed. This statement must be updated regularly. A statement concerning research in progress is given if it is provided by an evaluative body, e.g. International Agency for Research on Cancer.

Rationale for the inclusion of special studies

This information gives the user a brief idea of the extent of testing performed on the substance. It also provides him with any existing toxicologic evaluations which have been published. It provides a concise overview of data from the various screening studies which are becoming an increasingly important part of hierarchical schemes for the hazard assessment of substances.

File 12: EFFECTS ON THE ENVIRONMENT

This file consists of an array of dose-effect relationships on organisms and ecosystems and is divided into three sections ordered by 1) mg/kg bw, 2) mg/m³, and 3) mg/l.

Description of organism/system

To include genus, strain, common name, life stage, age, sex, as reported.

Description of exposure concentration

Data are listed in the appropriate metric units as reported.

Description of exposure/clearance time

Data are reported in hours, days, years, etc.

Description of effect

The effect reported is described in as complete a way as the register allows. If observation time was longer than time of exposure, the former is designated along with the effect. If the effect was reversed after a period of time, this information is also given as reported.

Rationale for the inclusion of this file

Effects of a chemical substance on various components of the environment should be considered seriously since man relies on animals, plants, water and air for his existence, health and psychological well-being. Direct toxic effect to animals and plants used for food are of particular importance but other effects which threaten the stability of ecosystems must also be considered.

File 13: SAMPLING AND ANALYSIS

This file includes sampling methods for air (particulate matter and gaseous), water, soil and sediment, animal and plant material. Whenever possible, documents with complete information on a particular sampling or analytical method are cited. Priority is given to those methods which have been approved by collaborative testing.

Sampling and preparation methods

The name and/or a brief description of each method.

Analytical method

This includes :

- Name and/or brief description of the method, and whether the method is qualitative or quantitative,
- Detection limit (minimum detectable amount) for the method,
- A general statement of the limitations/benefits of the method, i.e. interference, sophistication, method of choice, collaboratively tested in several laboratories. If the method is commonly used but inadequate, this is also stated.

Rationale for the inclusion of this file

Sampling and analysis form the basis for qualitative and quantitative identification which are of importance to the subsequent control of a substance in the environment.

File 14: SPILLS

Date of spillage

The day, month and year, entered as reported.

Location

The site and the extent (area) of the spill, briefly described.

Quantity

The amount of a substance spilled in metric units, as reported.

Metereological conditions

The metereological conditions at the time of the spill.

Description of physical appearance

A brief description of the physical appearance of the substance spilled.

Cause

The reported cause of the spill, e.g. defective equipment, human failure, as reported.

Effects on man

The number of people involved and a brief description of the effects reported. Where the individuals exposed are being followed for the purpose of evaluating possible chronic effects, an indication is provided of the source from which follow up information might be obtained. Cross references are also provided to entries in the toxicity files which provide additional information on long term human or environmental effects.

Emergency treatment

Immediate measures taken with a report of their success/failure, as well as any follow-up actions and their consequences.

Evacuation measures

Evacuation measures taken with a report of their success/failure.

Effects on the environment

To include a brief description of the acute or chronic effects on animals, plants, air, land, water, etc.

Measures taken to remove the chemical

Extinguishing or decontamination agents which have been used with a report of their success/failure as well as any follow-up actions taken and their reported consequences.

Rationale for the inclusion of this file

This data is useful for planning responses to future spills, in developing safety assessments for a material, and to facilitate minimisation of ecological damage. In addition this file will connect short-term exposure from spills with long-term effects and enable prediction of the total effect of a substance when spilled.

File 15: POISONING

This file includes references to evaluated information concerning diagnosis, prognosis and treatment of both acute and long term poisoning. Although this information is not available for the vast majority of substances, when it does exist in the form of publications recommended by state or national governments, international bodies or United Nations Organisations, it is cited here.

Rationale for the inclusion of this file

This file is preferentially designed to inform the user whether acute and chronic intoxication of man can be diagnosed from special symptoms and whether medical countermeasures are available. It should not contain detailed therapeutical measures; these can be obtained from the citation given.

File 16: REMOVAL

Disposal and/or destruction method(s)

To include the name or a brief identifying description of the method, e.g. incineration, landfill, chemical transformation, as well as a qualitative statement of its effectiveness, when reported.

Recycling method(s)

To include the name or a brief identifying description of the method as well as a qualitative statement of its effectiveness, when reported.

Rationale for the inclusion of this file

These data are useful in the identification of safe, adequate methods of removal. Without adequate removal, human and/or ecological harm will be aggravated.

File 17: LEGAL MECHANISMS

This file includes control of chemicals in:

- air
- water
- soil and sediments
- animals and plants
- food products
- consumer goods
- the occupational environment
- production
- packing
- transport and distribution
- removal

In the case that a legal mechanism could be placed in several sub-groups, a system of cross references is used. The material in these attributes is given as reported; translation or interpretation is avoided.

Country

The name of the country or political subdivision which produced the control mechanism. Local subdivisions within a county are not cited when their regulations replicate the countries national standard.

Type of control mechanism

The type of control mechanism, e.g. law, standard, proposed regulation, regulation, protocol, when supplied to the IRPTC.

Description of control mechanism

A brief description of the control mechanism, e.g. acceptable daily intake, allowable effluent level in water, paper and pulp industry control.

Quantitative information

Data are entered as reported. In the case that the units are other than metric, they are listed as found and the appropriate metric units are included in parenthesis.

Date of entry or verification

The date at which the latest verification of the status of the data was received by IRPTC.

Rationale for the inclusion of this file

Consideration of the legal instruments covered under this file will assist the user in:

- identifying gaps in his own control mechanisms,
- identifying legal standards which differ from his own, which he can use as a basis for evaluating his own national standard, and
- identifying those control mechanisms which have been effective in the past as well as those which have not.

Legal data found under this file are particularly valuable as the effects of substances are not limited to one nation, and therefore, standardisation of the various national controls is desirable.

Particularly for areas undergoing rapid industrialisation, it is important that information be available as quickly as possible suggesting that already industrialised areas consider a particular substance or process to be hazardous. Only if this information is available can intelligent decisions be made as to the desirability of undertaking particular activities.

ANNEX B

POLLUTANTS SELECTED FOR PRESENTATION

POLLUTANTS FROM ANNEX I OF DRAFT PROTOCOL	IRPTC SUMMARY	IRPTC INPUT DATA
1. Organohalogen compounds and substances which may form such compounds in the marine environment	Polychlorinated- biphenyls (PCB)	Aroclor 1254 Phenoclor DP6
2. Organophosphorus compounds and substances which may form such compounds in the marine environment	Malathion (MAL)	Malathion
3. Organotin compounds and substances which may form such compounds in the marine environment	Organotins (OSn)	Triphenyltin acetate Dibutyltin dichloride Diethyltin diiodide
4. Mercury and mercury compounds	Mercury (Hg)	Methylmercury Methylmercury chloride
5. Cadmium and cadmium compounds	Cadmium (Cd)	Cadmium chloride
6. Persistent mineral oils and persistent hydrocarbons of petroleum origin, in particular used lubricating oil	Petroleum hydrocarbon (PHC)	3,5 Dimethyl phenol Lubricants and cutting oils

POLLUTANTS FROM ANNEX 1 OF DRAFT PROTOCOL (Page 2)	IRPTC SUMMARY	IRPTC INPUT DATA
7. Persistent solid synthetic materials, in particular plastics, which may float, sink or remain in suspension and which may interfere with any legitimate use of the sea	<u>Consultant's Summary</u>	
8. Substances having proven which are potentially carcinogenic, teratogenic or mutagenic properties in or through the marine environment	Benzo(a)pyrene (BaP)	Benzo(a)pyrene
9. Radioactive wastes and other radioactive matter	<u>Consultant's Summary</u> "Radioactivity and the Mediterranean Sea"	

POLLUTANTS FROM ANNEX II OF DRAFT PROTOCOL	IRPTC SUMMARY	IRPTC INPUT DATA
1. Elements and their compounds	Zinc (Zn)	Zinc oxide
		Zinc chloride
		Zinc sulphate
	Chromium (Cr)	Sodium dichromate
		Calcium chromate
	Potassium dichromate	Potassium dichromate
	Lead (Pb)	Lead
	Selenium (Se)	Sodium selenate
	Arsenic (As)	Sodium arsenite
2. Biocides and their derivatives	Thallium (Tl)	Thallium
3. Organosilicon compounds and substances which may form such compounds in the marine environment	Carbamates (Car)	Carbaryl
4. Crude oils and hydrocarbons of petroleum origin and mixtures containing any of these	Organosilicon compounds (Osi)	Polydimethyl- siloxanes (PDMS) fluids and antifoams
5. Cyanides and fluorides	See category 6 of Annex I	
	Acrylonitrile (Cyanide) (AN)	Acrylonitrile
		Sodium fluoride
	Fluorides (F)	

POLLUTANTS FROM ANNEX II OF DRAFT PROTOCOL (Page 2)	IRPTC SUMMARY	IRPTC INPUT DATA
6. Non-biodegradable detergents and other surface-active substances	Alkylbenzene sulphonates (ABS)	ABS
7. Inorganic compounds of phosphorus and elemental phosphorus	Phosphorus and its Inorganic Compounds (P)	Yellow Phosphorus
8. Pathogenic micro-organisms	<u>Consultant's Summary</u> "Microbiological Pollution of Coastal Areas and Associated Public Health Hazards"	
9. Thermal pollution	<u>Consultant's Summary</u> "Effects of Thermal Water Discharges in the Marine Environment"	
10. Radioactive wastes and other radioactive matter	See category 9 of Annex I	
11. Substances which have a deleterious effect on the taste and/or smell of the products for human consumption derived from the aquatic environment	<u>Consultant's Summary</u>	
12. Substances which have an adverse effect on the Oxygen balance	<u>Consultant's Summary</u>	

ANNEX C

MEDITERRANEAN DATA PROFILES

Contents

Polychlorinated Biphenyls (C-PCB)
Organophosphorus Compounds (C-Mal)
Organotins (C-OSn)
Mercury (C-Hg)
Cadmium (C-Cd)
Petroleum Hydrocarbon (C-PHC)
Benzopyrene (C-BaP)
Zinc (C-Zn)
Chromium (C-Cr)
Lead (C-Pb)
Selenium (C-Se)
Arsenic (C-As)
Thallium (C-Tl)
Carbamate (C-Car)
Organosilicon Compounds (C-Osi)
Acrylonitrile (Cyanide) (C-AN)
Fluoride (C-F)
Alkylbenzene Sulphonate (ABS) (C-ABS)
Phosphorus and its Inorganic Compounds (C-P)

MEDITERRANEAN DATA PROFILE

POLYCHLORINATED BIPHENYLS

CONTENTS	Page
<u>Summary</u>	
PCB	C-PCB-4
<u>Total Production</u>	
PCB (generic)	C-PCB-15
<u>Total Consumption</u>	
Aroclor 1254	C-PCB-16
<u>Production Process(es)</u>	
PCB (generic)	C-PCB-17
<u>Use</u>	
PCB (generic)	C-PCB-18
<u>Pathways Leading to Marine Pollution</u>	
Aroclor 1254	C-PCB-19
Phenoclor DP5	C-PCB-20
<u>Biotic Transformation in the Marine Environment</u>	
Aroclor 1254	C-PCB-21
<u>Abiotic Transformation in the Marine Environment</u>	
Aroclor 1254	C-PCB-22
<u>Transformation in the Marine Environment</u>	
Phenoclor DP5	C-PCB-23

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<u>Behaviour of a Chemical Substance in</u> <u>Marine Organisms</u>	
Aroclor 1254	C-PCB-24
Phenoclor DP5	C-PCB-27
<u>Behaviour of the Substance in</u> <u>Man and Other Mammals</u>	
Aroclor 1254	C-PCB-28
Phenoclor DP6 ^a	C-PCB-30
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GENERAL SUMMARY - PCB

I. INTRODUCTION

Polychlorinated biphenyls (PCB) form a class of persistent chlorinated hydrocarbons and can accumulate both in the environment and in biological material. Their toxic and chemical properties are affected to a large extent by the degree of chlorination in the mixture, which is usually indicated by the commercial nomenclature for these compounds. In the Aroclor series, for example, a four digit code is used; biphenyls are generally indicated by 12 in the first two positions, while the last two digits represent the percentage by weight of chlorine in the mixture; thus, Aroclor 1254 (America) is a PCB mixture containing 54% chlorine. Other countries use similar terminology. Phenochlor DP6 (France) and Clophen A60 (W. Germany) both indicate biphenyls with an approximate mean content of 6 chlorine atoms per molecule (WHO-EHE, 1976).

It has been estimated that 1 million tonnes of PCB have been produced since 1930, and that about half of this amount has entered rivers and coastal waters as a result of industrial discharges. There is growing concern over the long-range effects of these compounds on the environment (NAS, 1977).

II. OCCURRENCE

A. Production

PCB are produced commercially by the progressive chlorination of biphenyl in the presence of a catalyst. Commercial PCB products are mixtures of isomers with different chlorine content, and impurities found include chlorinated dibenzofurans and chlorinated naphthalenes (WHO-EHE, 1976).

Since the first year of PCB production in 1930, the manufacture of these substances increased steadily until 1970, when US production totaled 33,000 tonnes (Nisbet and Sarofim, 1972). OECD (1973) reports US production in 1971 had dropped to 18,000 tonnes. Mediterranean countries producing PCB in 1971 included France (7,600 tonnes), Italy (1,500 tonnes) and Spain (about 1,500 tonnes).

B. Use

PCB are relatively non-flammable, have useful heat exchange and dielectric properties, and are now used primarily in the electrical industry in capacitors and transformers (EPA, 1976a).

PCB are also used in the formulation of lubricating and cutting oils, heat transfer and hydraulic systems, in pesticides, adhesives, plastics, inks, paints and sealants (WHO-EHE, 1976).

III. PCB IN THE ENVIRONMENT

A. Sources

1. Natural

PCB do not occur naturally in the environment, and so all levels in the atmosphere, soil and water can be attributed to man's activity.

2. Anthropogenic

The major source of environmental pollution with PCB, which eventually affects food chains, is the leakage and disposal of industrial fluids.

Widely dispersed small capacitors make collection of used PCB difficult, and leakage of PCB from dielectric, hydraulic and heat transfer systems also represent pathways for fluid PCB to enter the environment. Large dielectric systems allow economically feasible regeneration of the PCB when the equipment is scrapped (WHO-EHE, 1976).

Stirn et al. (1974) report a "large amount" of Phenoclor DP5 enters the Adriatic Sea in industrial effluents. A "considerable quantity" of Phenoclor DP5 is carried to the Mediterranean by aeolian transport (Elder et al., 1976).

Plastics, cutting oils, etc. are dispersive uses that ultimately release PCB to the environment. Release of PCB from landfills is considered to be a slow process due to their low volatility and low water solubility. Carnes et al. (1973) found little leaching from one site tested.

Olsson et al. (1973) found that PCB used in antifouling paint on ship bottoms can cause contamination of plankton, and provide a pathway for PCB to enter marine food chains. The same authors found that soot deposits on the ice of a lake near Stockholm contained 2.8ppm PCB on a dry weight basis. Aerial fallout into the coastal waters of California has been estimated at 1,800 kg/year (Young et al., 1976).

B. Transformation

1. Abiotic

PCB compounds are highly stable chemically, being

resistant to thermal degradation and hydrolysis. Herring et al. (1972) and Hutzinger et al. (1972) have found PCB susceptible to photolysis in laboratory studies.

In areas of high water temperature (e.g. Eastern Mediterranean) or high winds (e.g. Gulf of Lion), surface evaporation will increase, producing lower levels of Phenoclor DP5 in sea water (Elder and Villeneuve, 1977).

The solubility of PCB decreases with increasing chlorination (CEC, 1978b). A solubility range of 0.04-0.2ppm is reported by NAS (1977).

PCB in water is mainly adsorbed to particulate matter and is removed by sedimentation (Södergren, 1973). Concentrations of PCB in water may be several times greater than their solubility due to adsorption on suspended particles (Duke et al., 1970).

2. Biotic

Hydroxylation appears to be the primary mechanism for the metabolism of PCB (NRCC, 1978). Species differences in the ability to metabolise PCB have been noted by Jansson et al. (1975). The inability of wild guillemot to hydroxylate certain biphenyls (those with the 4 and 4' positions substituted with chlorine atoms) was contrasted by the seal. In further studies, the authors found that the major metabolic products in quail were para-hydroxy compounds formed by hydroxylation of the less substituted ring, while mice and rats produced mainly meta-hydroxy compounds, formed by hydroxylation of the most substituted ring. Metabolic products may be more toxic than the parent compounds (Sundström et al., 1975).

It is believed that the rate of metabolic attack decreases with increased chlorination (WHO-EHE, 1976). The more highly chlorinated PCB compounds may be metabolised by mechanisms other than hydroxylation, including isomerisation and dechlorination (NRCC, 1978).

Generally, PCB are highly resistant to biodegradation (EPA, 1976a).

C. Bioaccumulation

PCB are accumulated to a high degree by marine organisms. Direct uptake from the surrounding water seems to be more important than dietary uptake - on a lipid weight basis, the residue levels in different marine organisms are comparable, regardless of the organism's position in the food web. Organochlorines are lipid soluble, and the lipid fraction of aquatic animals seems to reach equilibrium with several residues in solution in the water. Marine mammals and birds, however, accumulate PCB to levels determined by their position in the food web, and the highest levels occur in specialised predator species. Fish-eating birds, for example, usually contain higher levels than species which feed on a wide range of organisms (CEC, 1978a).

PCB may be concentrated in the surface microlayers up to 10^4 times the levels in the ambient water, which is significant in relation to phytoplankton accumulation. Benthic organisms can accumulate PCB through ingestion of sedimentary particles or by absorption from direct contact with sediments and/or the surrounding water (NRCC, 1978).

Biomagnification coefficients for Aroclor 1254 in some marine organisms are as follows: pinfish (Lagodon rhomboides), 22,000 in 14-28 days; sheepshead minnow (Cyprinodon variegatus), 16,333 in 4 weeks (Hansen et al., 1971, 1973); oysters, 101,000-165,000; and shrimp, 26,000 (Hansen, 1976).

IV. MONITORING

A. Analysis

Most analysts use gas-liquid chromatography with an electron capture detector for determination of PCB. This method has a detection limit of 40ng and gives good separation of PCB from interferences (e.g. DDT and its metabolites), but large errors in accuracy may occur if the composition of the standard differs from that of the sample (NIOSH, 1977; WHO-EHE, 1976).

B. Amount in the Mediterranean

Elder and Villeneuve (1977) measured PCB concentrations at 37 stations in the Mediterranean including 9 stations where subsurface samples were taken. The PCB concentration didn't decrease with depth, and levels tend to increase from east to west. The range of concentrations was 0.0002-0.0086ug/l, with an average of 0.002ug/l. For comparison, Harvey et al. (1973) found PCB levels in the N. Atlantic to average 0.035ug/l.

Sediment concentrations of PCB varied greatly between open sea samples and coastal samples. Elder et al. (1976) reported that PCB were probably only present in the top 1.0mm of sediments. Concentrations from southern Mediterranean samples ranged from 0.8-9.0ug/kg dry weight. Coastal sediments at the 100m depth off Nice were exceptionally high, at 80-1,200ug/kg. Coastal sediments along the French/Italian coast from Sète to Genoa ranged from 0.8-30ug/kg dry weight (Duursma et al., 1974; Marchland et al., 1975).

PCB has contaminated sediments at depths of over 4,000m. The deeper sediments contained the more highly chlorinated PCB, which Elder et al. (1976) explained by assuming that the highly chlorinated hydrocarbons are more readily adsorbed to sedimenting particles and the less-chlorinated hydrocarbons are more easily decomposed.

Alzieu (1976) found concentrations of Phenoclor DP5 in the liver of the tuna, Thunnus thynnus, of 8.598mg/kg; the sardine, Sardinus pilchardus, contained 0.127mg/kg. These samples were both derived from the Mediterranean. In a study on the mussel, Mytilus edulis, de Lappe et al. (1972) found Phenoclor DP5 levels of 0.11mg/kg wet weight in samples from Port-de-Bouc, France. Mytilus from Marseilles contained 1.92mg/kg wet weight.

C. Amount Entering the Mediterranean

No information on the total amount of PCB entering the Mediterranean was found in the literature reviewed.

D. Regulations

In France, the use of PCB is restricted to closed systems, and only in well-defined applications; transformers and electrical equipment, condensers, heat transfer systems and hydraulic systems of mining installations (CEC, 1978b). No other regulations for Mediterranean countries were found in the literature searched.

Minimal risk concentrations for PCB in sea water range from 0.001-0.01ug/l, PCB depending on the degree of chlorination (NAS, 1972).

V. TOXICITY

A. Toxic or other Effects on Marine Organisms and Ecosystems

The acute toxicity of PCB is relatively low, and it is the long range chronic effects which are most important. The mixed nature of PCB make toxicity studies difficult to evaluate, due to the variable chlorine contents of the individual biphenyls. Impurities in crude PCB preparations also confuse interpretation of toxic properties (CEC, 1978a).

Generally, the toxicity of PCB compounds is inversely related to the percentage of chlorine in the PCB molecule. However, studies with the Japanese quail have indicated that toxicity is not simply a function of chlorine content (Hill et al., 1974).

Crustaceans are very sensitive to PCB exposure. Immature pink shrimps exposed to 0.94ppb of Aroclor 1254 responded with a mortality of 51% within 15 days (Stalling and Mayer, 1972).

Pinfish (Lagodon rhomboides) and spot (Leiostomus xanthurus) died when exposed to 5.0ppb of Aroclor 1254 for 14-45 days (Hansen et al, 1971). This was the lowest dose found to have caused fish mortality.

Very low PCB concentrations have been shown to inhibit the growth of different marine organisms. Inhibited growth of a marine diatom, Rhizosolenia setigera, was shown to occur at PCB concentrations as low as 0.1 ppb (Fisher and Wurster, 1973). It is generally assumed that PCB decreases the resistance of organisms to parasites and tumours. Marine bird populations seem to be more susceptible to highly chlorinated PCB than those containing lower percentages (CEC, 1978a).

The storage of organochlorine (e.g. PCB) residues in body fat provides a mechanism for avoidance of immediate toxic effects. Conditions of stress (e.g. starvation, reproduction, disease, etc.) which call upon fat reserves, hasten the mobilisation of these compounds, and may result in lethal effects (CEC, 1978a).

B. Toxic Effects on Man and Other Mammals

Though a limited number of PCB have been tested, it has been found that Kanechlor 500 and Aroclor 1254 are carcinogenic in mice, including benign and malignant liver-cell tumours following oral administration (IARC, 1973).

NIOSH (1978) reports that oral TDLo for rats was found to be 1220mg/kg bw/day in a 35 week continuous exposure (TDLo is the lowest dose reported to have elicited a toxic response). Liver effects were reported for a rat exposed for 2 years to oral doses of 5.0mg/kg bw/day (Ueda, 1976), and blood effects occurred at a 5.0mg/kg bw/day oral dose for 52 weeks in a rat (Allen et al., 1976).

Mink seem to be especially sensitive to PCB. Reproductive failure was noted in a 9 month study on a mink which ingested 0.2mg/kg bw/day of PCB (Ringer et al., 1972).

Human subjects have developed chloracne during 4 - 8 month exposure to airborne concentrations of PCB in the range of 5-7mg/m³ (Puccinelli, 1954). Finklea (1976) reports increased malignant melanoma and pancreatic cancer in human workers exposed to PCB.

The effect of PCB ingested by man in marine foods cannot be evaluated, even approximately, according to Bernhard (1978). The author points out, however, that the PCB body content in

fishes from certain parts of the Mediterranean is remarkably high, and that further investigations are necessary to determine possible health hazards. NAS (1977) also recommends evaluation of populations heavily exposed to PCB by the ingestion of contaminated foods.

Total Production

PCB (generic)		Chemical group: PCB		
year	area	amount	trend	citation (as reported in)
1971	OECD countries	48 400 tonnes	-	OECD, 1973, p.20
1971	France	7 600 "		
1971	Italy	1 500 "		
1971	Spain	1 500 "		
1973	France	21 330 000 pounds	-	EPA, 1976b, p.208
1973	Italy	5 550 000 "		

Total Consumption

Aroclor 1254

Chemical group: PCB

year	area	amount	trend	citation (as reported in)
1968	USA	4 445 tonnes	-	CRC, 1975, p.471
1969	USA	4 911 "		
1970	USA	6 210 "		
1971	USA	2 330 "		
1972	USA	1 747 "		
1973	USA	3 988 "		

Production Process(es)

PCB (generic)

Chemical group: PCB

process (major or minor by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
catalytic chlorination of biphenyl with anhydrous chlorine	-	-/chlorinated dibenzofurans and naphthalenes/-	NIOSH, 1977, p.22,23

Use

PCB (generic)		Chemical group: PCB		
use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
adhesives and plastics	France, 1971 (minor)	-	-	WHO, 1975, p.25
cutting oils	France, 1971 (minor)			
dielectric fluids	France, 1971 (major)			
heat exchangers				
hydraulic fluids	France, 1971 (minor)			
inks	France, 1971 (minor)			
paint and varnish	France, 1971 (minor)			
plastics	France, 1971 (minor)			

Pathways Leading to Marine Pollution

Aroclor 1254		Chemical Group: PCB	
Pathway	Quantity	Area	Citation
Aerial fallout	1 000 tons/year	USA 1972	Nisbet, I.C.T., 1976
Aerial fallout	1 800 kg/year	Californian coastal waters, 1973-74	Young, D.R. et al., 1976
Discharge of municipal waste water-major source (Total PCB)	19 000kg/1971 5 400kg/1974	Southern Californian Bight	Young, D.R. et al., 1976
Surface run off (Total PCB)	800kg	Los Angeles Basin	Young, D.R. et al., 1976
Industrial discharge (Total PCB)	250kg	San Pedro, San Diego	Young, D.R. et al., 1976

Pathways Leading to Marine Pollution

Phenochlor DP5		Chemical Group: PCB	
Pathway	Quantity	Area	Citation
Industrial effluent	"large amount"	Adriatic Sea	Stirn, J. et al., 1974
10 ⁴ tons produced by three Mediterranean countries - aeolian transport	"considerable quantity"	Mediterranean Sea	Elder, D.L. et al., 1976

Biotic Transformation in the Marine Environment

Aroclor 1254

Chemical Group: PCB

Process	Transformation		Products		Citation
	%	Time	Name	Quantity	
Mineralisation	26-50	22 days	-	-	Sayler, G.S. et al., 1977
dechlorination	60-90	60 days			
and co- metabolism					

Abiotic Transformation in the Marine Environment

Aroclor 1254

Chemical Group: PCB

Process	Location	Conditions			Products	Transformation		Citation		
		Temp. C.	pH	Chem. cata.		Light	Name		Quantity	%
Photolysis	Laboratory	14	9	-	16 RPR	Compound corresponding to addition of H2O to PCB mol. + polar carboxylic fraction.	-	-	48 hrs.	Hutzinger, O. et al., 1972.
Photolysis	Laboratory	30-33	-	-	Black light	Hydroxylated PCB mol. + a more polar carboxylic fraction	-	-	1 week	Hutzinger, O. et al., 1972.
Photolysis	Laboratory	-	-	-	Sun	Shift from higher to lower chlorinated biphenyls.	-	-	3 weeks	Herring, J.L. et al., 1972.

Transformation in the Marine Environment

Phenochlor DP5

Chemical group: PCB

Process	Medium	Parameters	Effect	Citation
Evaporation	Seawater	Increased temperature	In areas of higher water temperature (e.g. Eastern Mediterranean) or high winds, (e.g. Gulf of Lion) surface evaporation will increase producing lower levels in seawater	Elder, D.L. and Ville-neuve, J.P., 1977

Behaviour of a Chemical Substance in Marine Organisms

Aroclor 1254

Chemical Group: PCB

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn. Time mg/l	Tissue/ Organ	% Biomagnification Coefficient	%	Time	Name	Quantity		
Cyprinodon varie- gatus (Sheeps- head minnow)	-	-	Whole	-	16 333	-	-	-	-	Hansen, D.J. et al., 1973
Fishes	-	-	-	-	37 000	-	-	-	-	Hansen, D.J., 1976
Leiostomus xanth- urus (Spot)	-	-	-	14-28 days	37 000	50	28 days	-	-	Hansen, D.J. et al., 1971
Lagodon rhom- boides (Pin- fish)	-	-	-	14-28 days	22 000	-	-	-	-	Hansen, D.J. et al., 1971
Cerastoderma edule (Cockle)	-	-	Whole	14 days	150	0	21 days	Penta- + hexachlor- obiphenyls increased, di-, tri-, + tetrachlorobi- phenyls decreased	-	Langston, W.J., 1978b

Behaviour of a Chemical Substance in Marine Organisms

Aroclor 1254 (page 2)

Chemical Group: PCB

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn. mg/l	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
Macoma balthica (Tellin)	-	-	Whole	-	125	-	-	-	-	Langston, W.J., 1978b
Oysters	-	-	-	-	101 000 165 000	-	-	-	-	Hansen, D.J., 1976
Penaeus duorarum (Pink shrimp)	-	-	Ventral nerve	38	-	-	-	-	-	Nimmo, D.R. et al., 1975
Penaeus duorarum (Pink shrimp)	-	-	Hepato- pancreas	70	-	-	-	-	-	Nimmo, D.R. et al., 1975
Palaemonetes pugio (Grass shrimp)	-	-	Whole	-	11 000	10- 40	4 weeks	-	-	Nimmo, D.R. et al., 1974

Behaviour of a Chemical Substance in Marine Organisms

Aroclor 1254 (page 3)

Chemical Group: PCB

Organism	Route	Exposure Concn. mg/l	Time	Accumulation and Distribution			Loss		Metabolites		Citation
				Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
Penaeus duorarum (Pink shrimp)	-	-	-	Hepato- pancreas	-	2 500	-	-	-	-	Couch, J.A. and Nimmo, D.R., 1974
Shrimp	-	-	-	-	-	26 000	-	-	-	-	Hansen, D.J., 1976
Palaemonetes pugio (Grass shrimp)	-	-	-	Whole	-	8 065	5	24 days	-	-	Nimmo, D.R. et al., 1975

Behaviour of a Chemical Substance in Marine Organisms

Phenochlor DP5

Chemical Group: PCB

Organism	Route	Exposure Concn. Time	Accumulation and Distribution			Loss		Metabolites		Citation
			Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
Nereis diversi- color	Sed.	9.3mg/ kg dry wt. 70 days	-	-	9	88	65 days	-	-	Fowler, S.W. et al., 1978
Nereis diversi- color	W	0.00057 mg/l 14 days	-	-	800	-	-	-	-	Fowler, S.W. et al., 1978

Sed. - Sediment
W - Water

Behaviour of the Substance in Man and Other Mammals

Aroclor 1254

Chemical Group: PCB

description of organism	exposure		retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as re- ported in)
	route	concentration				
-	-	-	-	-	hydroxylated products	NRCC, 1978, p.32
cow (lactating)	oral (diet)	10-100mg/kg/bw	-	6-9%/7 days in milk, 2%/7 days in faeces and urine	-	Saschen- brecker et al., 1972 (NRCC, 1978, p.37)
rat (Wistar)	oral (diet)	2, 20 or 100 mg/kg diet	-	residue levels in adipose tissue remained relatively constant after 60 days	-	Grant et al., 1974 (NRCC, 1978, p.39)
rat (Sherman)	-	-	chronic exposure	magnification factor: 0.3 in faeces 0.001 in urine 0.006 in plasma 10 in fat	-	Curley et al., 1971 (NRCC, 1978, p.45)
rat (Wistar, male)	-	-	chronic exposure	magnification factor: 3-13 in adipose	-	Grant et al., 1972 (NRCC, 1978, p.45)

Behaviour of the Substance in Man and Other Mammals

Aroclor 1254 (page 2)

Chemical Group: PCB

description of organism	exposure		retention tissue/percent/time	clearance rate		metabolites name/amount/hazard	citation (as re- ported in)
	route	concentration		duration of exposure	percent/time		
rat (Wistar, male)	-	-	chronic exposure	magnification factor: 2.5 in fat	-	-	Leach, 1971 (NRCC, 1978, p.45)
rat (albino)	-	-	chronic exposure	magnification factor: max. 40-60 in all tissues	-	-	Monsanto Company, 1972 (NRCC, 1978, p.45)
dog (beagle)	-	-	chronic exposure	magnification factor: max. 7-8 in all tissues	-	-	Monsanto Company, 1972 (NRCC, 1978, p.45)

Behaviour of the Substance in Man and Other Mammals

Phenoclor DP6

Chemical Group: PCB

description of organism	route	concentration	exposure	duration of exposure	retention tissue/percent/time	clearance rate		metabolites name/amount/hazard	citation (as re- ported in)
						percent/time	name/amount/hazard		

Nothing found in the literature reviewed.

Concentrations in Water, Sediments and Biota

Aroclor 1254

Chemical Group: PCB

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Sediment 0-5 cm	Escambia Bay Florida, River outfall	GC	78.0/0.97 mg/kg dry wt.	1970/ 1972	Nimmo, D.R. et al., 1975
Water	Escambia Bay Florida	GC	0.0006 mg/L	1969 1971	Nimmo, D.R. et al., 1975
Fishmeal	Gulf of Maine USA	GLC	0.54 mg/kg wet wt.	1972	Zitko, V.O. et al., 1972
Mytilus californianus (mussel)	S. Californian Bight	EC-GC	0.52/0.14 mg/kg wet wt.	1971/ 1974	McDermott, D.J. et al., 1976
Morone saxatilis (Striped bass) -liver	Long Island USA	GC	1.08-10.0 mg/kg wet wt.	1972	Cahn, P.H. et al., 1977
Thunnus thynnus (Atlantic bluefin tuna)	Maine, USA	GC	1.35 mg/kg wet wt.	1972	Cahn, P.H. et al., 1977
Cetorhinus americanus (Basking shark) -liver	Maine, USA	GC	1.07 mg/kg wet wt.	1972	Zitko, V.O. et al., 1972
Silky shark	North Atlantic	GLC	5.8 mg/kg wet wt.	1971	Harvey, G.R. and Miklas, H.P., 1972

Concentrations in Water, Sediments and Biota

Aroclor 1254 (page 2)

Chemical Group: PCB

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Callinectes sapidus (Blue crab)	Escambia Bay Florida	GC	6.9 mg/kg wet wt.	1971	Nimmo, D.R. et al., 1975
Palaemonetes pugio (Grass shrimp)	Escambia Bay Florida	GC	0.42 mg/kg wet wt.	1971-72	Nimmo, D.R. et al., 1974
Zooplankton	North Atlantic	GLC	0.45 mg/kg wet wt.	1970	Harvey, G.R. and Miklas, H.P., 1972
Zooplankton	South Atlantic	GLC	0.0041 mg/ kg wet wt.	1971	Harvey, G.R. and Miklas, H.P., 1972

GC - Gas chromatography

GLC - Gas liquid chromatography

EC-GC - Electron capture gas chromatography

Concentrations in Water, Sediments and Biota

Phenochlor DP5

Chemical Group: PCB

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Seawater	N.W. Mediterranean	EC-GC	0.000013 mg/l	1974- 1975	Elder, D.L., 1975
Seawater	Mouth of the Rhone	EC-GC	0.000038 mg/l	1974	Elder, D.L., 1976
Seawater	N.W. Mediterranean	EC-GC	0.0000016 mg/l	1974	Marchand, M. and Duursma, E., 1975
Seawater	Aegean and Ionian Seas	EC-GC	0.0000002- 0.000002 mg/l	1975	Elder, D.L. and Villeneuve, J.P., 1977
Seawater	Western Basin	EC-GC	0.0000015 mg/l	1975	Elder, D.L. and Villeneuve, J.P., 1977
Seawater	Open Mediterranean	EC-GC	0.000002 mg/l	1974- 1975	Elder, D.L. et al., 1976
Ocean air	Cavalaire, France	EC-GC	0.3ng/m ³	1975	Elder, D.L. et al., 1976
Ocean air	African coast	EC-GC	0.2ng/m ³	1975	Elder, D.L. et al., 1976
Ocean air	Monaco	EC-GC	0.03ng/m ³ / 1.0ng/m	Feb 1976/ Oct 1975	Elder, D.L. et al., 1976
Sediment	Monaco	EC-GC	0.11 mg/kg dry wt.	-	Fowler, S.W. et al., 1978
Thunnus thynnus (Tuna) - liver	Mediterranean	GC	8.598 mg/kg	1973	Alzieu, C., 1976

Concentrations in Water, Sediments and Biota

Phenochlor DP5 (page 2)

Chemical Group: PCB

<u>Description of Sample</u>		<u>Analytical Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material</u>	<u>Origin</u>				
Sardinus pilchardus (Sardine)	Mediterranean	GC	0.127 mg/kg	1975	Alzieu, C., 1976
Sardinus pilchardus (Sardine)	Spain, Mediterranean Coast	EC-GC	0.03-6.9 mg/kg wet wt.	1970	Franco-Soler, J.M., 1973
Mytilus galloprovincialis (Mussel)	N.W. Mediterranean	EC-GC	5.0 mg/kg dry wt., 50-60 mg/kg lipid wt.	1973-74	Marchand, M. and Duursma, E., 1975
Mytilus galloprovincialis (Mussel)	N.W. Mediterranean	EC-GC	0.801-71686 mg/kg dry wt.	1973-74	Marchand, M. et al., 1976
Mytilus edulis (Mussel)	Port-de Bouc, France	GC	0.11 mg/kg wet wt.	1972	De Lappe, B.W. et al., 1972
Mytilus edulis (Mussel)	Marseilles, France	GC	1.92 mg/kg wet wt.	1972	De Lappe, B.W. et al., 1972
Mytilus edulis (Mussel)	Spain, Mediterranean Coast	EC-GC	0.4-1.8 mg/kg wet wt.	1970	Franco-Soler, J.M., 1973
Plankton	N.W. Mediterranean	EC-GC	0.15-0.7 mg/kg dry wt.	1973-74	Marchand, M. and Duursma, E., 1975

GC - Gas chromatography

GLC - Gas liquid chromatography

EC-GC - Electron capture gas chromatography

Array of Toxic Effects on Man and Other Mammals

Aroclor 1254

Chemical Group: PCB

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
3 000	single dose	oral	rat	ulceration of gastric and duodenal mucosa	Kimbrough, 1974 (DHEW, 1976, p.101)
1 295	-	oral	rat	LD50	NIOSH, 1978, p.20
1220	35 weeks, continuous	oral	rat	TDLo, neoplastic effects	NIOSH, 1978, p.20
500	4 days	oral (intub.)	rat (albino)	LD50	Tucker and Crab- tree, 1970, (NRCC, 1978, p.56)
150	14 weeks	oral (intub.)	rabbit	immuno- suppression	Koller and Thig- pen, 1973 (CRC, 1975, p.497)
25 (500ppm)	3 weeks	oral	rat (male)	growth de- pressed	Garthoff et al., 1975 (DHEW, 1976, p.84)

Array of Toxic Effects on Man and Other Mammals

Aroclor 1254 (page 2)

Chemical Group: PCB

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
14.3 (100mg/kg/ week)	14 weeks,	oral	rabbit	liver effects, uterus- atrophy	Koller and Zinkl, 1973, (DHEW 1976, p.108)
5	single dose	oral	rat (Wistar)	increased liver porphy- rin levels and -amino- levulinic acid synthet- ase	Grote et al., 1975 (NRCC, 1978 p.138)
5 (100mg/kg diet)	52 weeks	oral (diet)	rat	blood effects	Allen et al., 1976 (NRCC, 1978. p.108)
5.0 (100ppm)	2 years	oral (diet)	rat	liver effects	Ueda, 1976, p.27
0.5 (10ppm)	2 years	oral (diet)	rat	no effects found	
1	throughout gestation	oral	dog (beagle, female)	increase in fetal anomalies	NIOSH, 1977, p.98
0.83 (10ppm)	2 years	oral	dog (beagle, female)	liver damage	Ueda, 1976, p. 27
0.5 (10ppm)	24 months	oral (diet)	rat	3/24 liver tumours	NIOSH, 1977, p.117

Array of Toxic Effects on Man and Other Mammals

Aroclor 1254 (page 3)

Chemical Group: PCB

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
0.4 (20mg/kg diet)	135 days	oral (diet)	swine	increase in stomach lesions	Gilbertson and Fox, 1977 (NRCC, 1978, p.107)
0.2 (2mg/kg diet)	9 months	oral (diet)	mink (female)	reproductive failure	Ringer et al., 1972 (NRCC, 1978, p.136)
0.1 (2mg/kg diet)	246 days	oral (diet)	rat (Wistar, male)	liver effects (428 days)	Grant et al., 1974 (NRCC, 1978, p.105)
0.05 (0.5mg/kg diet)	9 months	oral (diet)	mink	increased secretion of thyroxine	Bryne et al., 1975 (NRCC, 1978, p.108)
0.025 (0.5mg/kg diet)	4 weeks	oral (diet)	rat	induction of hepatic enzymes	Litterst et al., 1972 (NRCC, 1978, p.80)
-	-	-	human (workers)	increase in malign- ant melan- oma and pancreatic cancer	Finklea, 1976 (NRCC, 1978, p.96)

Array of Toxic Effects on Man and Other Mammals

Aroclor 1254 (page 4)

Chemical Group: PCB

concentration in mg/m3 (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as report- ed in)
5-7	4-8 months	inhal.	human	chloracne	Puccinelli, 1954 (NIOSH, 1977, p.123)
1.5	31 weeks, (7hrs/day, 5 days/wk)	inhal.	rat	liver effects	Treon et al., 1956 (NIOSH, 1977, p.125)

Array of Toxic Effects on Man and Other Mammals

Phenoclor DP6

Chemical Group: PCB

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
100 (2g/kg diet)	26 days	oral	rat (diet)	liver and spleen effects, hepatic porphyria, death	Vos and Koeman, 1970 (WHO-EHE, 1976, p.50)
39.3 (118mg)	38 days (5x/week)	der- mal appl.	rabbit	dermal effects, liver and kidney damage	Vos and Beems, 1971 (NIOSH, 1977, p.71)

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Aroclor 1254

Chemical Group: PCB

BEHAVIOURAL EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
coturnix quail	oral (diet)	(200mg/kg diet)	7 days (daily)	depressed avoidance response	Kreitzer and Heinz, 1974 (NRCC, 1978, p.100)
coturnix quail	oral (diet)	(100mg/kg diet)	12 months (daily)	reduced aspects of biochemical adaptations to stress	Dieter, 1974 (NRCC, 1978, p.101)
pheasant chicks	trans-placental	-	(50mg/week for 17 weeks to mothers)	behavioural effects	Dahlgren and Linder, 1971 (NRCC, 1978, p.101)

These studies, designed to evaluate the possible effects of the substance on behaviour, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse (BALB/cj, male)	oral (diet)	60 (300ppm)	11 months (daily)	9/22 hepatomas, 22/22 adenofibrosis	Kimbrough and Linder, 1974 (IARC, 1973, p.276)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Aroclor 1254 (page 2)

Chemical Group: PCB

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse (BALB/cj, male)	oral (diet)	60 (300ppm)	6 months (daily)	1/24 hepatoma (11 months)	Kimbrough and Linder, 1974 (IARC, 1973, p.276)
rat	oral (diet)	0.5 (10ppm)	24 months (daily)	3/24 liver tumours	NIOSH, 1977, p.117

A comprehensive evaluation of the known studies designed to assess the possible carcinogenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"A limited number of PCB's have been tested. Kanechlor 500 and Aroclor 1254 are carcinogenic in mice inducing benign and malignant liver-cell tumours following oral administration, the only route tested. In rats, Kanechlor 500, 400 and 300 induced multiple hyperplastic liver nodules following oral administration." (IARC, 1973, p.281)

MUTAGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Osborne Mendel, male)	oral	150	5 days (daily)	no effects found (dominant lethal test)	Green et al., 1975a (DHEW, 1976, p.130)
rat (Osborne Mendel, male)	oral	150	5 days (daily)	inhibition of mitotic rate, no chromosomal aberrations found in bone marrow and spermatogonia	Green et al., 1975b (NRCC, 1978, p.98)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Aroclor 1254 (page 3)

Chemical Group: PCB

MUTAGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
ring dove	oral (diet)	(10mg/kg)	-	high frequency of chromosomal aberrations in embryos (2nd generation)	Peakall et al., 1972 (WHO, 1975, p.48)

description of system	reported results	citation (as reported in)
human lymphocytes cultures exposed to 100mg/kg Aroclor 1254	no chromosomal aberrations found	Hoopingarner et al., 1972 (WHO, 1973, p.48)

These studies, designed to evaluate the possible effects of the substance on gene mutation, chromosomal mutations, on DNA repair or recombination or on transformation, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
mouse	Mirex	changes in hepatic lysosomes	Abraham et al., 1974 (NRCC, 1978, p.118)

This study, designed to evaluate the possible effects which could result from the combination of this substance with one or more other substances, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Aroclor 1254 (page 4)

Chemical Group: PCB

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Sherman female)	oral (diet)	1 (20ppm)	2 generations (daily)	reduced litter size	Linder et al., 1974 (NIOSH, 1977, p.93)
swine (Hornel miniature)	oral	1	21 days before breeding, throughout gestation (daily)	resorptions	NIOSH, 1977, p.98
mink (female)	oral (diet)	0.2 (2mg/kg diet)	9 months (daily)	reproductive failure	Ringer et al., 1972 (NRCC, 1978, p.136)
mink	oral (diet)	0.06 (0.6mg/kg diet)	(daily)	reproductive failure reduced number of live young	Platonow and Karstad, 1973 (NRCC, 1978, p.86,87)

These studies, designed to evaluate the possible effects of the substance on reproduction, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Aroclor 1254 (page 5)

Chemical Group: PCB

TERATOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
dog (beagle, female)	oral	1	throughout gestation (daily)	increase in fetal anomalies	NIOSH, 1977, p. 98
mink	oral (diet)	0.06 (0.6mg/kg diet)	(daily)	dead fetus- es had marked physical deformities	Platonow and Karstad, 1973 (NRCC, 1978, p.87)

These studies, designed to evaluate the possible teratogenic effects of the substance, resulted in reports of the above effects but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Phenoclor DP6

Chemical Group: PCB

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

Nothing found in the literature reviewed.

MUTAGENICITY

Nothing found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

description of organisms	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as re- ported in)
rabbit	der- mal appl.	39.3 (118mg)	38 days (5x/week)	dilation and plugging of hair foll- icles, hyper- plasia and hyperkeratosis of epidermal epithelium, liver and kidney damage	Vos and Beems, 1971 (NIOSH, 1977, p.71)

This study, designed to evaluate the possible primary irritation effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Phenoclor DP6 (page 2)

Chemical Group: PCB

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or other Effects on Marine Organisms and Ecosystems

Aroclor 1254

Chemical Group: PCB

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Panaeid shrimp	Adult	0.09-0.32	48-96 hrs.	LC50	48-96 hrs.	Hansen, D.J., 1976
Gammarus faciatius (Scud)	Adult	2,400	96 hrs.	LC50	96 hrs.	Walker, C.R., 1976
Cyprinodon varie- gatus (Sheeps- minnow)	Adult female	0.001	4 weeks	Dec. survival of fry	4 weeks	Hansen, D.J., 1976
Marine invertebrate community	-	0.001-0.01	-	No. + variety of crabs, mol- luscs, arthro- pods and amphi- pods decreased; tunicates in- creased.	-	Hansen, D.J., 1974

Toxic or other Effects on Marine Organisms and Ecosystems

Aroclor 1254 (page 2)

Chemical Group: PCB

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Panaeus duorarum (Pink shrimp)	Adult	0.003-0.005	30 days	Cytoplasmic changes	30 days	Couch, J.A. + Nimmo, D.W.R., 1974.
Panaeus duorarum (Pink shrimp)	Adult	0.003-0.005	20-30 days	Increased in- cidence of a virus similar to Baculovirus	20-30 days	Couch, J.A. + Nimmo, D.W.R., 1974
Crassostrea virginica (Oyster)	Adult	0.005	24 weeks	Decreased growth	24 weeks	Nimmo, D.R. et al., 1975
Leiostomus xantheus (Spot)	Adult	0.005	2 weeks	Fatty changes in liver	2 weeks	Nimmo, D.R. et al., 1975
Lagodon rhomboides (Pinfish)	Adult	0.005	14-45 days	Fungal lesions on body	14-45 days	Hansen, D.J. et al., 1971

Toxic or other Effects on Marine Organisms and Ecosystems

Aroclor 1254 (page 3)

Chemical Group: PCB

System	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
Organism Ecosystem Non-living		mg/L				
Marine phyto-plankton	-	0.005	24 hrs.	10% reduction in rate of photosynthesis	24 hrs.	Moore, S.A. and Harris, R.C., 1972
Cyprinodon variegatus (Sheeps-head minnow)	Adult	0.01	4 weeks	Developed fin rot, 95% mortality	4 weeks	Hansen, D.J. et al., 1973
Palaemonetes pugio (Grass shrimp)	Adult	10.0	1.5 hr	Avoidance	1.5 hr	Hansen, D.J. et al., 1974

Toxic or other Effects on Marine Organisms and Ecosystems

Phenochlor DP5

Chemical Group: PCB

System	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
Organism						
Ecosystem						
Non-living						
mg/L						

Nothing found in the marine environment.

Analysis

PCB (generic)		Chemical group: PCB
analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
gas-liquid chromatography with electron capture detection (40ng)	large error in accuracy if the composition of the standard differs from that of sample/minimal interferences	NIOSH, 1977, p.196-200

Legislation for the Protection of Man
and the Marine Environment

Aroclor 1254

Chemical group: PCB

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
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Nothing found in the literature reviewed.

Legislation for the Protection of Man
and the Marine Environment

Phenoclor DP6

Chemical group: PCB

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
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Nothing found in the literature reviewed.

PCB

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MEDITERRANEAN DATA PROFILE

ORGANOPHOSPHORUS COMPOUNDS

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^a Nothing found in the literature reviewed

OUTLINE - GENERAL SUMMARY FOR MALATHION

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GENERAL SUMMARY FOR MALATHION

I. INTRODUCTION

Malathion, S-1, 2-bis (ethoxycarbonyl) ethyl-0,0-dimethyl phosphoro-dithioate (NAS, 1977), is an organophosphate insecticide synthesised primarily by the addition of dimethyl-dithiophosphoric acid to the diethyl-ester of maleic acid. It contains 36.35% carbon, 5.80% hydrogen, 9.38% phosphorus, 19.41% sulphur and 29.06% oxygen and has a molecular weight of 330.36. Malathion has a solubility of 145mg/l in distilled water and is miscible with many organic solvents (Bourquin, 1975).

Malathion, like many other organophosphate insecticides, is used widely to control crop pests, flies and mosquitoes, presumably because it is degradable. Even though malathion decomposes at high temperatures and with increasing alkalinity, it may be highly toxic to target and non-target organisms alike (Bookhout and Monroe, 1977).

Malathion acts as a nerve poison by blocking synaptic transmission in the cholinergic parts of the nervous system. The distribution of nerve impulse transfers is caused by excessive accumulation of the neurotransmitter acetylcholine (ACh). Malathion binds the active site of the acetylcholine esterase (AChe) and prevents breakdown of ACh (Coppage and Matthews, 1974).

II. OCCURRENCE

A. Production

The production of malathion involves a two-step process.

As a first step 0,0-dimethyl dithiophosphoric acid is produced as a result of the reaction of methanol with phosphorus pentasulphide. The acid then reacts with diethyl maleate or diethyl fumarate to produce malathion (NAS, 1977).

According to the CEC (1976) there are six plants that produce malathion within the EEC area. No information on the quantities produced in Europe was found in the literature reviewed.

In 1972 the total production in the USA was 14,000 tons (CEC, 1976).

B. Use

Malathion is an extensively used wide spectrum, organophosphorus insecticide. In 1972, agricultural, home and garden uses of malathion accounted for about two-thirds of the USA domestic use. The remaining one-third was used for industrial, commercial and governmental purposes. Malathion was one of the earliest organophosphorus compounds to be developed as an insecticide and is registered for use on more than 130 crops against a wide spectrum of insects and mites (NAS, 1977).

Malathion use in the USA during 1971 is estimated to have been approximately 1600 tons. This amount represented approximately 2% of the total insecticide use in the United States that year. It has been estimated that the use of malathion has increased since 1971 (NAS, 1977). In Italy the 1972 annual consumption was 484.6 tons (CEC, 1976).

III. MALATHION IN THE ENVIRONMENT

A. Sources

1. Natural

No evidence for the natural occurrence of this compound was found in the literature reviewed, possibly due to the fact that it appears to be anthropogenic in origin.

2. Anthropogenic

The application of malathion for the control of pests is clearly an important source of this chemical in the environment. In a single operation in 1971, the U.S. Air Force applied 15.3×10^4 l of technical grade malathion to 2,016,060 acres in counties along the coast of the Gulf of Mexico to control mosquitoes carrying Venezuelan Equine Encephalomyelitis virus (Bourquin, 1975).

B. Transformation

1. Abiotic

Malathion is soluble in water at approximately 145mg/liter at 25°C. The stability of malathion in solution is a function of pH. Its half-life at pH 9 is 12 days, whereas it is hydrolyzed instantaneously at pH 12 (NAS, 1977). At pH 8 the malathion half-life is 36 hours (Wolfe et al. 1975).

NAS (1977) has reported that between pH 5 and pH 7 no hydrolysis can be observed over a 12 day period.

Suteu et al. (1973) found the metabolites of hydrolysis of malathion to be non-toxic; the oxidation metabolite, malaoxon, was toxic but unstable.

Walker (1976) found that malathion dissipation was in direct proportion to both time and to increasing salinity. For example, after 7 days, 97% of the added malathion was degraded in 25 grams/liter 'salinity water', while only 53% was degraded in freshwater (i.e. zero grams per liter).

Malathion photolysis half-life is 990 hours in distilled water (pH 6), with wave lengths greater than 290nm. However, in a Suwanee River water sample which contained a large amount of coloured material, malathion was 50% degraded by sunlight in 16 hours (Wolfe et al., 1975).

2. Biotic

Malathion is rapidly degraded in vitro by salt-marsh bacteria to malathion-monocarboxylic acid, malathion-dicarboxylic acid and various phosphothionates as a result of carboxyesterase cleavage. In addition, some expected phosphatase activity produces desmethyl-malathion, phosphomono- and dithionates, 4-carbon dicarboxylic acids and the corresponding ethyl esters (Bourquin, 1975).

Walker (1976) isolated two cultures of bacteria capable of readily degrading malathion in the absence of additional energy sources, effecting respective losses of 78% and 58% during a 7 day period. Addition of peptone and glucose effected essentially 100% degradation of added insecticide during the 7 day incubation period.

Malathion also serves as a substrate for fungal degradation. Microbial degradation was found to be the chief mechanism of insecticide dissipation in Mississippi soils tested (Walker and Stojanovic, 1973).

It has been shown that the mammalian liver microsomal monooxygenase system converts malathion to malaaxon (O'Brien, 1957). Malathion is a phosphorodithioate insecticide and thus requires activation to the phosphate, if it is to become an active anticholinesterase agent (Metcalf and March, 1953). However, there is generally little accumulation of the toxic activation product in mammalian systems (Dahm et al., 1962).

C. Bioaccumulation

Malathion is rapidly absorbed from the digestive system after ingestion by mammals. Distribution is general; very low concentrations of malathion are found in many tissues. The concentrations in liver and bone are generally somewhat higher than those in other tissues (March et al., 1956).

IV. MONITORING

A. Analysis

Gas-liquid chromatography can detect 10.05-1.0ng of malathion with alkaliflame ionisation detector (NIOSH, 1976).

Thin-layer chromatography (both one and two dimensional) was used by Bourquin (1975) to separate extracts from biodegradation studies.

Infrared spectroscopy was used by Bourquin (1975) in conjunction with thin-layer chromatography.

B. Amount in the Mediterranean

No information concerning this topic was found in the literature reviewed.

C. Amount Entering the Mediterranean

No information concerning this topic was found in the literature reviewed.

D. Regulations

Turkey has set a maximum permissible level of 1.0ug/l for effluents. The Libyan Arab Republic has proposed a standard of 0.5mg/l for effluents discharged into urban sewage systems. Italy and Yugoslavia also have legislation regulating the discharge of organophosphates (WHO/UNEP, 1976).

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

Malathion acts as a nerve poison by blocking synaptic transmission in the cholinergic parts of the nervous system. The disruption of nerve impulse transfers is caused by excessive accumulation of the neurotransmitter acetylcholine (ACh). Malathion binds to the active site of the AChE and prevents breakdown of ACh. Coppage and Matthews (1974) state that AChE inhibitors probably cause death in higher vertebrates by blocking neurotransmission in the respiratory center of the brain or neuromuscular junctions of the respiratory apparatus, but this has not been confirmed for

fish. However, NAS (1977) reports that malathion requires activation to the phosphate, if it is to become an active anticholinesterase agent.

Coppage and Matthews (1974) reported a 96% acetylcholinesterase inhibition at a concentration of 0.2mg/l as measured after an exposure period of 24 hours in the sheeps head minnow, Cyrinodon variegatus. Furthermore, their study indicated that mean reductions in AChE activity of about 80% were critical in short term organophosphate poisoning of the fishes tested.

Earnest (1971) found a 96 hour LC50 of 0.08mg/l of malathion in the Korean shrimp, Palaemon macrodactylus. A 48 hour LC50 of 13.4 mg/l has been reported for the embryo of the mussel, Mytilus edulis (Liu and Lee, 1975).

Weis and Weis (1974, 1975, 1976) have found that 0.01mg/l of malathion for 14 days caused inhibited fin regeneration in the Killifish, Fundulus heteroclitus. The same species displayed 36% abnormal axis formation when the embryos were exposed to 0.1mg/l of malathion for 48 hours. The authors also found optic malformations in the fertilised eggs of the Atlantic silverside, Menidia menidia, at 0.01mg/l of malathion.

Malathion caused decreased pigmentation at a concentration of 0.01mg/l over a period of 10 days in the Killifish, Fundulus heteroclitus (Crawford and Guarino, 1975).

Malathion has also been shown to interfere with carbon fixation in phytoplankton, such that 1.0mg/l of malathion decreased ¹⁴C utilisation by 7% (Lowe, 1964). There is also documented evidence from the literature that arthropod pests develop resistance to malathion. Hence, increasing concentrations of malathion are needed to control pests, increasing the danger to non-target organisms (Bookhout and Monroe, 1977).

B. Toxic Effects in Man and Other Mammals

Studies with human volunteers indicate that the threshold of toxicity in man is 24mg/day (NAS, 1977). A daily dose of 24mg taken by 5 males for 56 days was followed by depression of plasma cholinesterase activity 2 weeks after the first administration.

Maximum depression amounting to about 23% of plasma cholinesterase activity occurred approximately 3 weeks after the cessation of administration. No clinically manifest side-effects were reported (FAO/WHO, 1963).

The cholinesterase of vertebrates may remain inhibited for several weeks after exposure due to irreversible inhibition by extremely small quantities of dealkylated oxygen-analog metabolites of thiophosphates (Coppage and Matthews, 1974).

Cumulative reduction of AChE by repetitive exposure has been demonstrated in some vertebrates; this may occur in fish subjected to similar repetitive exposure in the environment (Coppage and Matthews, 1974).

Malathion has been shown to cause skeletal malformations in birds, mammals and reptiles (Weis and Weis, 1976). In man, the LDLo, the lowest dose reported to cause a lethal effect, was found to be 50mg/kg bw/day (NIOSH, 1977). A 500mg/kg single dose taken by a 16 year old male resulted in cyanosis, incontinence, respiratory distress, miosis and hypotension (Mathewson and Hardy, 1970).

The toxicity of malathion is potentiated by several organophosphate compounds. A toxic effect has been reported in mice with chlorocyclizine phenobarbital (Welch and Coon, 1964). A low protein diet has been found to increase the lethal toxicity of malathion in the rat (Boyd and Tanikella, 1969).

Total Production

Malathion		Chemical Group: Organophosphorus compounds		
year	area	amount	trend	citation (as reported in)
1972	USA	14 000 tons	-	CEC, 1976, p. 6-22

Total Consumption

Malathion		Chemical Group: Organophosphorus Compounds		
year	area	amount	trend	citation (as reported in)
1972	Italy	484.6 tonnes	-	CEC, 1976, p. 6-33

Production Process(es)

Malathion

Chemical Group: Organophosphorus compounds

process (major or minor by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
addition of dimethyl- dithiophosphoric acid to diethylmaleate	-	-/trimethyldithio- phosphate, diethyl- maleate, toluene/ hydrogen sulfide, toluene, malathion, malathion impuri- ties, dimethyldi- thiophosphoric acid	CEC, 1976, p. 6-23, 28

Use

Malathion

Chemical Group: Organophosphorus compounds

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
insecticide	-	-	-	NAS, 1977, p. 620

Pathways Leading to Marine Pollution

Malathion		Chemical Group: Organophosphorus compounds	
Pathway	Quantity	Area	Citation
Deliberate application	-	-	Bookhout, C.G. and Monroe, R.J. 1977
Application for mosquito control	15.3x10 ⁴ L, single application 1971	Gulf of Mexico	Bourquin, A.W. 1975
Direct application as a pesticide reaching marine environment through run-off	-	-	Suteu, S. et al., 1973

Biotic Transformation in the Marine Environment

Malathion

Chemical Group: Organophosphorus
compounds

Process	Transformation		Products Name	Quantity	Citation
	%	Time			
Carboxyesterase cleavage	98-100	7 days	Malathion mono- carboxylic acid, malathion dicarboxylic acid	-	Walker, W.W. 1976
Phosphatase activity plus carboxyesterase cleavage	50 100	2 days 10 days	Desmethyl malathion phos- phomono- and dithionates, 4- carbon dicarb- oxylic acids, ethyl esters	-	Bourquin, A.W. 1975

Abiotic Transformation in the Marine Environment

Chemical Group: Organophosphorus compounds

Malathion

Process	Location	Conditions			Products	Transformation			Citation
		Temp. C.	pH	Chem. cata.		Light	Quantity	% Time	
Carboxyl ester hydrolysis	Laboratory	27	8	-	Malathion monoacid, 0,0-dimethyl phosphorodithioic acid, diethyl fumate. Acid proportions	-	50	36 hrs.	Wolfe, N.L. et al. 1975
Photolysis	Laboratory	-	6	-	-	290 nm	-	50 990 hrs.	Wolfe, N.L. et al. 1975
Hydrolysis	Laboratory	-	9	-	-	-	-	50 12 hrs.	Bookhout, C.G. + Costlow, J.D.Jr. 1976
Hydrolysis	-	-	-	-	Non-toxic metabolites	-	-	-	Suteu, S. et al. 1973
Oxidation	-	-	-	-	Malaoxon (toxic but unstable)	-	-	-	Suteu, S. et al. 1973

Behaviour of a Chemical Substance in Marine Organisms

Malathion

Chemical Group: Organophosphorus Compounds

Organism	Exposure				Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn.	Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity		
Lagodon rhom- boides (Pinfish)	Water	0.075 mg/L	24 hrs.	Whole	0.0	0	100	24 hr	Mala- thion monocar- boxylic acid, mala- thion dicar- boxylic acid	93% 7%		Cook, G.H. and Moore, J.C. 1976

Behaviour of the Substance in Man and Other Mammals

Malathion

Chemical Group: Organophosphorus compounds

description of organism	exposure		retention		clearance rate		metabolites		citation (as reported in)
	route	concentration	duration of exposure	tissue/percent/time	percent/time	name/amount/hazard	name/amount/hazard	name/amount/hazard	
mouse, rat, cow, human	oral	-	-	-	-	malaoxon/ the active form; hydrolyse-products/less toxic; malathion mono-and di-acids/ main metabolites	malaoxon/ the active form; hydrolyse-products/less toxic; malathion mono-and di-acids/ main metabolites	malaoxon/ the active form; hydrolyse-products/less toxic; malathion mono-and di-acids/ main metabolites	Heath, 1961 (FAO/WHO, 1963, p.90)
cow (lactating)	oral	1.3 mg/kg bw/ day	3 days	-	69%/4 days 77.2%/7 days	-	-	-	O'Brien et al. 1961 (FAO/WHO, 1967, p.172) , 148
human liver homogenate	-	-	-	-	-	desmethyl malathion, diethyl mercapto-succinate diethyl malate, carboxyesterase products	desmethyl malathion, diethyl mercapto-succinate diethyl malate, carboxyesterase products	desmethyl malathion, diethyl mercapto-succinate diethyl malate, carboxyesterase products	Matsumura and Ward 1966 (NIOSH, 1976, p.47)
cow	-	-	-	-	-	dimethyl phosphate	dimethyl phosphate	dimethyl phosphate	De Roeth et al. 1965 (NIOSH, 1976 p.168)

Behaviour of the Substance in Man and Other Mammals

Malathion (page 2)

Chemical Group: Organophosphorus compounds

description of organism	exposure		retention		clearance rate		metabolites		citation (as report- ed in)
	route	concentration	duration of exposure	tissue/percent/time	percent/time	name/amount/hazard	name/amount/hazard	name/amount/hazard	
mouse	-	-	-	-	-	phosphatase pro- ducts			Murphy, 1967 (NIOSH, 1976 p.168)
human	-	-	-	-	-	dimethyl phosphor- thioate, dimethyl phosphordithioate, dimethyl thiophos- phate			Thompson, 1974 (NIOSH, 1976 p.168)
human	-	-	-	-	-	dimethyl dithio- phosphate			Shafik and Enos, 1969 (NIOSH, 1976 p.168)
cow, rat, dog, mouse	-	-	-	-	-	desmethyl mala- thion			O'Brien, 1967 (NIOSH, 1976 p.168)
cow, rat, dog	-	-	-	-	-	malathion diacid			O'Brien, 1967 (NIOSH, 1976 p.168)

Concentrations in Water, Sediments and Biota

Malathion

Chemical Group: Organophosphorus
compounds

<u>Description of Sample</u>		<u>Analytical</u> <u>Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material</u>	<u>Origin</u>				

Nothing found in the marine environment

Array of Toxic Effects on Man and Other Mammals

Malathion

Chemical Group: Organophosphorus compounds

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
1401	-	oral	rat	LD50	NIOSH, 1978, p.24
857	-	oral	man	LDLo	NIOSH, 1978,p.24
700	single dose (gastric lavage was performed)	oral	human (31 year old woman)	cyanosis, sweating, salivation, miosis, fasciculations	Mathewson and Hardy, 1970 (NIOSH, 1976, p.32,171)
570	-	oral	guinea pig	LD50	Hagan, 1953 (NAS, 1977,p.623)
500	single dose (gastric lavage was performed)	oral	human (16 year old boy)	cyanosis, in- continence, respiratory distress, miosis, hypo- tension	Mathewson and Hardy, 1970 (NIOSH, 1976, p.33,172)
390-480 (90% pure)	-	oral	rat (male)	LD50	Frawley et al. 1957 (FAO/WHO, 1964,p.91)
380 (99% pure)	2 years	oral (diet)	rat (albino, male)	growth retar- dation, cho- linesterase inhibition in brain and erythrocytes	Clyne and Shaffer (NIOSH, 1976, p. 54)

Array of Toxic Effects on Man and Other Mammals

Malathion (page 2) Chemical Group: Organophosphorus compounds

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as repor- ted in)
250 (5000 ppm)	2 years	oral (diet)	dog	decreased food intake and growth	American Cyanamide Co, New York, 1955 (CEC, 1977 p. 59)
200	single dose	intra- venous	dog	severe signs, marked cholin- esterase in- hibition	Golz, 1955 (NIOSH, 1976,p.53)
125	3 generations	oral (diet)	rat	reduced fer- tility, survival and weight of offspring	American Cyanamid Co., 1967 (NIOSH, 1976, 124,125)
50	-	oral	human	LDLo	NIOSH, 1978, p.24
6	2 years (90% pure)	oral (diet)	rat (albino, male)	depressed cho- linesterase activity in brain, plasma and erythro- cytes	Clyne and Shaffer (NIOSH, 1976,p.54)
0.34 (24mg)	56 days	oral	human (volunteers)	decreased plasma cholin- esterase acti- vity	Moeller and Rider, 1962, (FAO /WHO, 1963, p.92)

Array of Toxic Effects on Man and Other Mammals

Malathion (page 3) Chemical Group: Organophosphorus compounds

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
5 (100 ppm)	6 weeks	oral (diet)	rat (male)	adrenal effects	Benes and Cerna, 1965 (CEC, 1977 p. 59)
0.23 (16mg)	47 days	oral	human (volunteers)	no signs or symptoms, reduced cholinesterase activity only after termination of study	Moeller and Rider, 1962 (NIOSH, 1976, p.171)
(90g)	16 weeks (5x/week)	dermal appl.	human (volunteers)	dermatitis	Hayes et al. 1960 (NIOSH, 1976, p.44)
(10% ethanol- solution)	2 days	dermal appl.	human (volunteers)	contact sensitisation	Milby and Epstein, 1964 (NIOSH, 1976,p.48)
(1% solution)	2 days	dermal appl.	human (occupational exposed)	3-5% positive reaction	Milby and Epstein, 1964 (NIOSH, 1976,p.48)

Array of Toxic Effects on Man and Other Mammals

Malathion (page 4) Chemical Group: Organophosphorus Compounds

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
(120 ml of a 50% spray)	single dose	oral	human (42 year old woman)	diarrhea, coma, bronchial hy- persecretion, miosis, fasci- culations, re- duced erythro- cyte cholin- esterase ac- tivity, ECG- changes	Goldin et al. 1964 (NIOSH, 1976, p.22, 170)
120 ml of a malathion preparation	single dose	oral	human (14 year old boy)	bronchial hy- persecretion, fasciculations areflexia, miosis, sweat- ing, blepha- roptosis	Amos and Hall, 1965 (NIOSH, 1976, p.26,171)
-	-	oral	human (45 year old woman)	cardiac and respiratory arrest, mio- sis, coma, areflexia, pulmonary edema, death	Harris et al. 1969 (NIOSH, 1976, p.28,171)
-	-	oral	human (264 people, who ingested malathion with suicidal intent)	vomiting, bronchorrhea, sweating, are- flexia, fasci- culations, hypotension, stupor, death	Nalin, 1973 (NIOSH, 1976, p.35,171)

Array of Toxic Effects on Man and Other Mammals

Malathion (page 5)

Chemical Group: Organophosphorus compounds

concentration in mg/m3 (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
123 (95% pure)	6 hours	inhal.	rabbit (New Zealand white)	decreased plasma and erythrocyte cholinesterase activity	Weeks et al. 1975 (NIOSH, 1976, p.59)
(60 ppm+, 90% pure)	2 days (6 hours/day)	inhal.	mouse, rat, guinea pig, rabbits	sneezing and nosebleed	Hazleton and Holland, 1953 (NIOSH, 1976, p.58)
(5 ppm+, 90% pure)	4 weeks (7 hours/day, 5 days/week)	inhal.	dog, rat, guinea pig	lacrimation, thickening and leukocytic infiltration of the intra-alveolar septa	Hazleton and Holland 1953 (NIOSH, 1976, p.58)
(5 ppm+, 90% pure)	6 weeks (7 hours/day 5 days/week)	inhal.	dog, rat	moderate inhibition of brain, plasma and erythrocyte cholinesterase activity	Hazleton and Holland, 1953 (NIOSH, 1976, p.58)

+ insufficient data for conversion.

Toxic Effects for Special Studies on Mammals and Other

Non-Marine Experimental Systems

Malathion

Chemical Group: Organophosphorus compounds

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed

CARCINOGENICITY

Nothing found in the literature reviewed

MUTAGENICITY

description of system	reported results	citation (as reported in)
Escherichia coli K-12/ gal Rs,8, a phenotypic gal- exposed to 0.2M malathion	no increase in forward mutation to 5-methyl tryptophan resistant colonies	Mohn, 1973 (NIOSH, 1976, p.72)
human hematopoietic cells exposed to 50 and 10ug/ml malathion	no increase in clear chromosomal lesions	Huang, 1973 (NIOSH, 1976, p.72)

These studies designed to evaluate the possible effects of a substance on gene mutation, chromosomal mutations, on DNA repair or recombination or on transformation, was found in the literature reviewed. They did not result in a report of any of these effects. No comprehensive evaluation of this information was found in the literature reviewed.

NEUROTOXICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
chicken	oral (diet)	2000 (10 000ppm)	15 weeks (daily)	100% mortality, only one showed muscle weakness, no microscopic evidence of nerve damage	Frawley et al. 1956 (NIOSH, 1976,p.71)

Toxic Effects for Special Studies on Mammals and Other

Non-Marine Experimental Systems

Malathion (page 2)

Chemical Group: Organophosphorus compounds

NEUROTOXICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
chicken	sub. cut	100	single dose	immediate muscle weakness of the legs	Durham et al. 1956 (NIOSH, 1976,p.70)

These studies, designed to evaluate the possible neurotoxic effects of the substance, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
mouse, rat, dog	ethyl-p-nitrophenyl thionobenzene-phosphate (EPN)	potentiates the cholinesterase inhibition	Frawley et al. 1957 (FAO/WHO, 1967, p.173)
rat (male)	fenitrothion	potentiation, when one half the LD50 doses were given	Benes and Cerna, 1966 (FAO/WHO, 1967, p.174)
rat	ethyl-p-nitrophenyl phenylthiophosphonate, Dipterex, Co-Ral	potentiating	Du Bois, 1961 (NIOSH, 1976, p.63)
-	Rommel, Delnav	potentiating	Murphy, 1969 (NIOSH,1976,p.63)
-	Baytex	potentiating	Murphy et al. 1959 (NIOSH,1976,p.63)

Toxic Effects for Special Studies on Mammals and Other

Non-Marine Experimental Systems

Malathion (page 3)

Chemical Group: Organophosphorus compounds

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
-	chlorphenvinfos	potentiating	CEC, 1977, p.85
-	phosalone	potentiating	CEC, 1977, p.86
-	dichlorvos	potentiating	CEC, 1977, p.86
rat (male)	tri-o-tolyl phosphate	potentiating, decreased the LD 50 value	Main and Braid,1962 (NIOSH,1976 p.63)
mouse (Swiss Webster)	chlorcyclizine, phenobarbital	decreased lethality	Welch and Coon,1964 (NIOSH, 1976, p.65)
rat (albino)	low protein diet	increased lethal toxicity (lower LD50 value)	Boyd and Tanikella, 1969 (NIOSH, 1976, p.69)

These studies designed to evaluate the possible effects which could result from the combination of this substance with one or more other substances, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

PRIMARY IRRITATION

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
human (volunteers)	dermal appl.	(10% ethanol solution)	2 days	contac sensitisation	Milby and Epstein, 1964 (NIOSH,1976 p.48)

Toxic Effects for Special Studies on Mammals and Other

Non-Marine Experimental Systems

Malathion (page 4)

Chemical Group: Organophosphorus compounds

PRIMARY IRRITATION

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
human (occupational exposed)	dermal appl.	(1% solution)	2 days	3-5% positive reaction	Milby and Epstein, 1964 (NIOSH, 1976 p.48)

These studies designed to evaluate the possible primary irritation effects of the substance, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

REPRODUCTIVE EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	oral (diet)	240	10 weeks (daily)	no effects on reproductive performance, reduced survival and weight gain of offspring	Kalow and Marton, 1961 (NIOSH, 1976 p.76)
rat	oral (diet)	125	3 generations (daily)	reduced fertility, survival and weight of offspring	American Cyanamid Co., 1967 (NIOSH, 1976 p.77)

These studies designed to evaluate the possible effects of the substance on reproduction, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects for Special Studies on Mammals and Other

Non-Marine Experimental Systems

Malathion (page 5)

Chemical Group: Organophosphorus compounds

TERATOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as re- ported in)
rat	intra- perit.	900	single dose	no teratogenic effects found	Kimbrough and Gaines, 1968 (NAS, 1977, p.625)

This study, designed to evaluate the possible teratogenic effects of this substance, was found in the literature reviewed. It did not result in a report of teratogenic effects. No comprehensive evaluation of this information was found in the literature reviewed.

Toxic or other Effects on Marine Organisms and Ecosystems

Chemical Group: Organophosphorus compounds

System	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
Organism Ecosystem Non-living		mg/L				
Morone saxatilis (Striped bass)	Adult	0.01	96 hrs.	LC50	96 hrs.	Korn, S. and Earnest, R. 1974
Palaemon macro- dactylus (Korean shrimp)	Adult	0.08	96 hrs.	LC50	96 hrs.	Earnest, R., 1971
Mytilus edulis (Mussel)	Embryo	13.4	48 hrs.	LC50	48 hrs.	Liu, D.H.W. and Lee, J.M. 1975
Fundulus hetero- clitus (Killi- fish)	Adult	0.01	14 days	Inhibition of fin regenera- tion	14 days	Weis, J.S. and Weis, P. 1975
Menidia menidia (Atlantic silver- side)	Fertil. eggs	0.01	-	Optic malfor- mations	-	Weis, J.S. and Weis, P. 1976

Toxic or other Effects on Marine Organisms and Ecosystems

Malathion (page 2)

Chemical Group: Organophosphorus compounds

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Fundulus hetero- clitus (Killi- fish)	Fertil. eggs	0.01	10 days	Decreased pig- mentation	10 days	Crawford, R.B. and Guarino, A.M., 1975
Callinectes sapidus (Blue crab)	Eggs	0.011	-	Increased time from hatch to 1st crab	-	Bookhout, C.G. and Monroe, R.J. 1977
Fundulus hetero- clitus (Killi- fish)	Embryo	0.1	48 hrs.	36% abnormal axis formation	48 hrs.	Weis, P. and Weis, J. S. 1974
Cyprinodon varie- gatus (Sheeps- head minnow)	Adult	0.2	24 hrs.	96% acetyl- cholinesterase inhibition	24 hrs.	Coppage, D.L. and Matthews, E. 1974

Toxic or other Effects on Marine Organisms and Ecosystems

Malathion (page 3)

Chemical Group: Organophosphorus compounds

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Phytoplankton	-	1.0	4 hrs.	Decreased C 14 utilisation	4 hrs.	Lowe, J.I. 1964
Mytilus edulis (Mussel)	Larvae	6.0	30 days	Decreased growth, decreased development to juveniles	30 days	Liu, D.H.W. and Lee, J.M. 1975
Enteromorpha intestinalis (Algae)	-	100.0	24 hrs.	Increased oxygen consumption	24 hrs.	Suteu, S. et al. 1973
Enteromorpha intestinalis (Algae)	-	1000	24 hrs.	Decreased respiration rate	-	Suteu, S. et al. 1973
Enteromorpha intestinalis (Algae)	-	10 000	24 hrs.	Inhibition of O ₂ consumption followed by death	-	Suteu, S. et al. 1973

Analysis

Malathion

Chemical Group: Organophosphorus compounds

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
gas-liquid chromatography (alkaliflame ionisation detector, 10.05-1.0ng)	expensive, sensitivity depending on careful adjustments, contamination possible, long cleanup procedure if interfering compounds present/ very sensitive, high specifi- city, not too time- consuming	NIOSH, 1976, p.134
thin-layer chromatography (two dimensional - qualitative)	-	Bourguin, 1975
infrared spectroscopy (with TLC)	-	Bourguin, 1975

Legislation for the Protection of Man
and the Marine Environment

Malathion

Chemical Group: Organophosphorus
compounds

general classification of control mechanism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in effluents	Italy	recommended limits for industrial and urban effluents discharged into waters	0.1mg/l into watercourses, 0.05mg/l into lakes, 0.2mg/l into the sea and sewers	WHO/UNEP, 1976, p.Italy-4
control of substances in effluents	Libyan Arab Republic	proposed stand- ards for efflu- ents discharged	0.1mg/l into surface water reservoirs for direct use in agriculture, 0.05mg/l into aquifers used for public water supply, 0.5mg/l into urban sewage systems	WHO/UNEP, 1976, p.Libyan Arab Republic-2
control of substances in effluents	Turkey	prohibition of discharges when the concentration exceeds the tolerance level	1.0ug/l for orano- phosphorus compounds	WHO/UNEP, 1976, p.Turkey-4
control of substances in effluents	Yugoslavia	maximum permissible concentrations of dangerous sub- stances discharg- ed into water used or intended for use as drinking- water, for produ- ction of food- stuffs, fish breeding, watering animals or public bathing	0.01mg/l	WHO/UNEP, 1976, p.Yugoslavia -2

Legislation for the Protection of Man
and the Marine Environment

Malathion (page 2)

Chemical Group: Organophosphorus
compounds

general classification of control mechanism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in water	Yugoslavia	maximum permissible concentrations of dangerous substances in interrepublic watercourses	0.05mg/l in class I and class II waters ^a 1.0mg/l in class III and class IV waters ^a	IDHL, 1978 (awaiting publication)

^a Class I: waters which, in their natural state, where necessary after disinfection, may be used for drinking purposes and in the food industry and, in the case of surface waters, for breeding Salmonidae. Class II: waters which, in their natural state, may be used for bathing and recreation, water sports, breeding of Cyprinidae, or which, after treatment, may be used for drinking purposes and in the food industry.

^b Class III: waters which may be used for irrigation and, after treatment, in industry other than the food industry. Class IV: waters which may be used for other purposes only after treatment.

Malathion

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GENERAL SUMMARY FOR ORGANOTINS

I. INTRODUCTION

Organotins are defined as compounds containing at least one carbon-tin bond. The tin occurs primarily in a +4 oxidation state, and the tetravalent structure may be expressed by the general formula $R_nSnX_{(4-n)}$, where R is an organic group, X is a anion, and n ranges in value from 1-4. Four series of compounds are known, categorized as R_1SnX_3 , R_2SnX_2 , R_3SnX and R_4Sn (respectively, mono-, di-, tri-, and tetraorganotins). In commercially important compounds, R is usually a butyl, octyl or phenyl group, and X is commonly chloride, fluoride, oxide, hydroxide, carboxylate or thiolate. The diorganotins and triorganotins are currently the most important categories produced commercially (CEC, 1976).

The trend toward increased consumption and the well documented toxicological effects of some organotins have combined to stimulate concern over possible contamination of marine ecosystems, including the Mediterranean Sea. The wide range of physical and chemical properties of the organotins and the lack of monitoring data presently available are problems in determining real or hypothetical hazards in the Mediterranean.

II. OCCURRENCE

A. Production

World production of organotins has increased steadily since the 1940s, reaching a level of 25000 tons in 1975 (NIOSH, 1976). This trend is expected to continue, as the use of PVC plastics containing diorganotin stabilisers seems to be increasing. About 70% of the total organotin market (17000 tons) was used for heat and light

stabilisation of PVC plastics. Organotin compounds used in biocides constitute most of the remaining consumption (CEC, 1976).

Production processes for organotin compounds include the Gignard process, the Wurtz method, and the aluminium technique (CEC, 1976).

B. Use

In addition to the major uses of organotins which are listed below, minor uses for various compounds include; solvents in flame resistant polyester, metal plating agents, gasoline additives, solder additives, anti-fogging agents, adhesion improvers for polychloroprene, wood preservatives, antiwear additives, curing agents, thermal or electrical coatings, water repellents, antioxidant or corrosion inhibitors, and film additives (NIOSH, 1976).

1. Monoorganotins

This group has found only limited use so far in the stabilisation of PVC films during manufacture (CEC, 1976) and as catalytic agents (NIOSH, 1976)

2. Diorganotins

The applications of the diorganotin compounds depend largely on their chemical properties. The plastics industry consumes the largest proportion of diorganotins for use as PVC stabilisers, the most important of which are dibutyltins and dioctyltins (NIOSH, 1976). Sulphur-containing compounds impart excellent heat stability to PVC, while non-sulphur containing compounds are used to provide resistance to light and weathering. Dioctyltin stabilisers have been used as additives for PVC

food packaging products. Other important commercial uses for diorganotins are as catalysts in the production of polyurethane foams, and as agents in the cold curing of silicone rubber. Smaller quantities are used for glass coating (dimethyltin chloride), as anthelmintics for poultry, and as stabilisers for lubricating oils, hydrogen peroxide, polyolefins and plastics (CEC, 1976).

3. Triorganotins

The triorganotin compounds are used mainly as biocides, their toxic properties largely dependant on the organic constituents. Textile preservation, wood protection, antifouling paints for ships, biocides in polymers, molluscicides, disinfectants, slimicides (for the paper industry), insecticides, general and agricultural fungicides, rodent repellents, and bactericides constitute the major uses for triorganotin derivatives (CEC, 1976).

4. Tetraorganotins

Tetraorganotin compounds are used as stabilisers for oils (corrosion inhibitors), catalysts for olefine polymerisation, and as intermediates in organotin synthesis (CEC, 1976).

III. ORGANOTINS IN THE ENVIRONMENT

A. Sources

Very little information on possible pathways to the marine environment through use of organotins was found in the literature reviewed. The increasing application of triorganotins in marine antifouling paints provides a direct pathway to the sea, but no figures were found for the amount of organotins

released in this manner. Seepage of organotins used as insecticides and fungicides into groundwaters, and direct application of tributyltin compounds to water to control snails in combating the tropical disease Bilharzia, are other possible sources of supply to the Mediterranean Sea. The application of triorganotins in disinfectants which are applied as waxes, polishes, sprays and in laundry washes may allow contamination of sewage effluents. Industrial discharges of triorganotins used as slimicides in the paper industry and for textile and lumber treatment may be further sources of contamination. No figures were presented in the literature reviewed for these applications, however.

No information on discharge of organotin compounds was found in the literature reviewed. However, all organotins manufactured on an industrial scale are "quite insoluble" in water (10-100 ppm) and generally low concentrations in waste waters can be further reduced by conventional active sludge treatment (CEC, 1976).

Adsorption to cellulose containing material, electrochemical methods and separation of organotin halides by addition of non-reactive, highly soluble salts are possible purification procedures, though it is unknown if they are actually practiced (CEC, 1976).

B. Transformation

1. Abiotic

The organotin compounds on which information is available appear to be somewhat persistent in the environment. Residual action was observed 8 months after tributyltin oxide and acetate were applied to water to control snails, and also 9 months after an application

of fentin acetate and chloride (CEC, 1976). Though the inorganic tin species formed by degradation of organotin compounds are considered to be non-toxic, very little is known about residence times under environmental conditions. Some organotin compounds may persist in water for up to a year. Exposure to light and air is thought to facilitate degradation of organotins (e.g. cyhexatin) used in agriculture (CEC, 1976).

2. Biotic

No information on biotic transformation of organotins was found in the literature reviewed.

C. Bioaccumulation

No studies on bioaccumulation of organotin compounds were found in the literature reviewed. However, bioaccumulation of tributyltin oxide and of fentin salts (triphenyltin salts) is considered "probable" in studies with aquatic systems (UNEP, 1977). Organotins are slightly soluble in water and readily soluble in fats, thus exhibiting characteristics of bioaccumulation (CEC, 1976).

IV. MONITORING

A. Analysis

Analytical methods for the determination of organotin compounds, and their respective detection limits, are as follows: gas chromatography with flame ionisation and flame photometry, 10 ng (Aue and Hill, 1972); electron-spin-resonance spectroscopy, 10 ug/l (Stegmann et al., 1977); spectrophotometric pyrocatechol violet method, 20 ng (Corbin, 1973).

B. Amount in the Mediterranean

No information on organotin concentrations in the Mediterranean was found in the literature reviewed.

C. Amount Entering the Mediterranean

No information on organotin concentrations in effluents entering the Mediterranean was found in the literature reviewed.

D. Regulations

No regulations on the production, use, or disposal of organotins were found in the literature searched. Italy sets a limit of 10 mg/l of tin, as Sn, for discharge into surface waters (IDHL, 1977). Criteria for occupational exposure to organotin compounds exist for several countries, but are of no concern to the marine environment.

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

The organotins show a wide range of toxic effects, depending on the number and type of organic side chains attached to the tin atom. The most toxic substances generally fall into the triorganotin category, these compounds showing high toxicity to marine invertebrates, fungi, and bacteria, as indicated by their use in antifouling paints (fentin and tributyltin salts).

Algae is also susceptible to the toxic effects of tributyltin oxide, showing reduced growth at concentrations of 0.25 ppm and total death at 0.5 ppm (CEC, 1976). Toxicity to marine fish is considered to be very high, though information is

limited. UNEP (1977) reports acute toxicity in fresh water studies with trout at concentrations of 28 ug/l of tributyltin oxide.

B. Toxic Effects on Man and Other Mammals

The toxic effects of certain organotins on man have been well documented, largely as a result of a large scale poisoning which occurred in France in 1954 due to use of "Stalidon", an oral medication containing diethyltin diiodide (DEDI). There were 210 cases of intoxication reported, and 98 deaths (NIOSH, 1976). Further studies with DEDI have established its toxicity in mammals. NIOSH (1978) reports an oral LDLo in rats of 100 mg/kg bw/day.

Studies with triphenyltin acetate (TPTA) establish its toxicity with mice, rats, rabbits and guinea pigs. Accidental contact with human subjects also indicates toxic effects of TPTA (NIOSH, 1976).

Dibutyltin dichloride (DBDC) has also shown high toxicity in laboratory studies on mice and rats. NIOSH (1978) reports an oral LD50 for DBDC in a rat of 150 mg/kg bw/day. A single oral dose of 50 mg/kg bw given to a rat caused bile duct, pancreas and liver damage (Barnes and Magee, 1958). A single intravenous dose of 1.0 mg/kg bw caused thymus effects in a rat (Seinen et al., 1977a).

A single dermal application of DBDC to human volunteers caused follicular inflammation and pustulation (Lyle, 1958).

Evidence of the toxic effects of organotins on humans has led to recommended standards for occupational exposure in the United States (NIOSH, 1976).

Total Production

Organotin compounds (generic)			Chemical Group: Organotin	
year	area	amount	trend	citation (as reported in)
1962	World	3 000 tons		NIOSH, 1976, p.24
1965	World	5 000 "		
1967	World	10 000 "		
1975	World	25 000 "	increasing	

Total Consumption

Organotin compounds (generic)			Chemical Group: Organotin	
year	area	amount (estimated)	trend	citation (as reported in)
1965	World	5 500 tonnes		CEC,1976,p.7-8
1967	World	8 500 "		
1969	World	14 000 "		
1971	World	17 000 "		
1973	World	22 500 "		
1975	World	25 000 "	increasing	

Production Process(es)

Organotin compounds (generic)		Chemical Group: Organotin	
process (major or minor by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
the Grignard process: $4RMgCl + SnCl_4 = R_4Sn + 4 MgCl_2$	-	magnesium chloride	CEC, 1976, p.7-10
the Wurtz method: $SnCl_4 + 4RCI + 8Na = R_4Sn + 8NaCl$	-	sodium chloride	CEC, 1976, p.7-10
the Aluminium-alkyl technique: $3SnCl_4 + 4R_3Al = 3R_4Sn + 4AlCl_3$	-	aluminium chloride	CEC, 1976, p.7-10

Use

Monoorganotin compounds

Chemical Group: Organotin

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
stabilisers	(minor)	-	-	NIOSH, 1976, Table XII-1
catalysts	"			
agents in flame retard- ent poly- esters	"			
curing agents	"			
thermal/ele- ctrical coatings	"			

Use

Diorganotin compounds

Chemical Group: Organotin

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
stabilisers for PVC	(major)	-	-	CEC, 1976, p.7-9,17
anthelmintics	(minor)			
glass sur- faces	"			
polyurethane catalysers	"			
silicone caoutchouc	"			
additives to lubricating oils	"			
biocides solvents, in flame resis- tent poly- esters,	(minor) "	-	-	NIOSH, 1976, Table XII-1
metal plating agents,	"			
solder addi- tives,	"			
adhesion im- provers for polychloro- prene,	"			
anti-wear addi- tives,	"			
curing agents,	"			
thermal or elec- trical coat- ing,	"			
antioxidants or corrosion in- hibitors	"			

Use

Triorganotin compounds

Chemical Group: Organotin

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
textile pre- servation	World (major)	-	-	CEC, 1976, p.7-11
wood preser- vation	"			
anti-fouling paints	"			
biocide in polymers	"			
molluscicide	"			
disinfectants	"			
slimicide for paper indus- try	"			
insecticides	"			
fungicides (plant pro- tection)	"			
catalysts stabilisers	World (minor)	-	-	NIOSH, 1976, Table XIII-1
solvents in flame resis- tant poly- esters,	"			
solder addi- tives,	"			
curing agents,	"			
thermal or ele- trical coat- ings,	"			
antioxidant or corrosion in- hibitors	"			
film additives	"			

Use

Tetraorganotin compounds		Chemical Group: Organotin		
use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
intermediates in organotin synthesis	World (major)	-	-	CEC, 1976, p.7-10
stabilisers for oil	World (minor)	-	-	CEC, 1976, p.7-9
catalysts for olefine poly- merisation	World (minor)			
biocides solvents, in flame resis- tant poly- esters,	World (minor) "	-	-	NIOSH, 1976, Table XII-1
metal plating agents,	"			
gasoline addi- tives,	"			
solder addi- tive,	"			
anti-fogging agent,	"			
adhesion im- provement for polychloro- prene	"			

Pathways Leading to Marine Pollution

Triphenyltin acetate

Chemical Group: Organotin

Pathway	Quantitiy	Area	Citation
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Nothing found in the marine environment.

Biotic Transformation in the Marine Environment

Triphenyltin acetate

Chemical Group: Organotin

Process	Transformation		Products		Citation
	%	Time	Name	Quantity	

Nothing found in the marine environment.

Abiotic Transformation in the Marine Environment

Triphenyltin acetate		Chemical Group: Organotin		
Process	Location	Conditions		Citation
		Temp C.	Products	
		pH	Name	
		Chem.	Quantity	
		Cata.	Transformation	
		Light	%	
			Time	

Nothing found in the marine environment.

Behaviour of a Chemical Substance in Marine Organisms

Triphenyltin acetate

Chemical Group: Organotin

Organism	Route	Exposure Concn. Time mg/l	Accumulation and Distribution		Loss		Metabolite		Citation
			Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity

Nothing found in the marine environment.

Behaviour of the Substance in Man and Other Mammals

Triphenyltin acetate (TPTA)

Chemical Group: Organotin

description of organism	exposure		retention tissue/percent/time	clearance rate percent/time		metabolites name/amount/hazard	citation (as reported in)
	route	concentration duration of exposure					

Nothing found in the literature reviewed.

Behaviour of the Substance in Man and Other Mammals

Dibutyltin dichloride (DBDC)

Chemical Group: Organotin

description of organism	exposure		retention tissue/percent/time	clearance rate		metabolites name/amount/hazard	citation (as reported in)
	route	concentration		duration of	percent/time		
				exposure			

Nothing found in the literature reviewed.

Behaviour of the Substance in Man and Other Mammals

Diethyltin diiodide (DEDI)

Chemical Group: Organotin

description of organism	exposure		retention tissue/percent/time	clearance rate		metabolites name/amount/hazard	citation (as reported in)
	route	concentration		duration of	percent/time		
				exposure			

Nothing found in the literature reviewed.

Concentrations in Water, Sediments and Biota

Triphenyltin acetate

Chemical Group: Organotin

<u>Description of Sample</u>		<u>Analytical Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material Sampled</u>	<u>Origin</u>				

Nothing found in the marine environment.

Array of Toxic Effects on Man and Other Mammals

Triphenyltin acetate (TPTA)

Chemical Group: Organotin

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
125,000	78 weeks (intermittant)	oral	mouse	TDLo, car- cinogenic effect	NIOSH,1978, p.23
136	-	oral	rat	LD50 (2-3 weeks)	Klimmer,1964 (NIOSH,1976, p.68)
125	-	oral	rat	LD50	NIOSH, 1978, p.23
81.3	-	oral	mouse	LD50	NIOSH, 1978, p.23
80	single dose	oral (intub.)	rat	general weak- ness, lack of mobility, hypothermia, coma, brain, lung, liver and kidney effects,death	Klimmer,1964 (NIOSH,1976, p.68)
30-50	-	oral	rabbit	LD50 (3 weeks)	Klimmer,1964 (NIOSH,1976, p.69)
21		oral	guinea pig	LD50 (3 weeks)	Klimmer,1964 (NIOSH,1976, p.69)
20	19 days	oral (diet)	rat (male) (Holtzman albino)	weight loss, testicular damage,blood clotting	Pate and Hays, 1968 (NIOSH,1976, p.70)

Array of Toxic Effects on Man and Other Mammals

Triphenyltin acetate (TPTA) (page 2)

Chemical Group: Organotin

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
20	4 days	oral (diet)	rat (female) (Holtzman)	ovary effects	Newton and Hays, 1968 (NIOSH, 1976, p.71)
10	-	oral	guinea pig	LDLo	NIOSH, 1978, p.23
2.5 (50 ppm in 0.05-0.2% tylose)	105 days	oral (intub.)	rat (Wistar)	listlessness, decreased weight gain, broncho-pneu- monia, liver kidney and spleen ef- fects, brain damage, death	Klimmer, 1964 (NIOSH, 1976, p.69)
2.5 (50 ppm)	90 days	oral (diet)	rat (Wistar)	increased brain weight, increased water content in spinal cord, decrea- sed pituitary gland and ovary weight	Verschuuren et al., 1966 (NIOSH, 1976, p.65)
1.25 (25 ppm)	"	"	"	decreased uterus weight	
0.5 (10 ppm)	"	"	"	decrease in leukocytes, possible CNS damage	
0.25 (5 ppm)	"	"	"	decreased thyroid weight	

Array of Toxic Effects on Man and Other Mammals

Triphenyltin acetate (TPTA) (page 3)

Chemical Group: Organotin

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
1 (20 ppm)	90 days	oral (diet)	guinea pig	increased liver and kidney weight, in- creased water content in brain and spinal cord, decreased uterus and testial weight	Verschuuren et al., 1966 (NIOSH, 1976, p.67)
0.5 (10 ppm)	"	"	"	increased pituitary gland weight	
0.25 (5 ppm)	"	"	"	decrease in lymphocytes and leuko- cytes, in- creased brain weight, death	
-	8 hours/day 2-10 days	-	human (weighing and bagging Brestan -20% TPTA)	irritation of skin and mucous mem- brane	Markicevic and Turko, 1967 (NIOSH, 1976, p.30)
-	single dose	dermal appl.	human (volunteers)	follicular inflammation and pustula- tion	Lyle, 1958 (NIOSH, 1976, p.26)
-	-	-	human (aerial spraying of Brestan 60- 60% TPTA)	dyspepsia, diarrhea, heartburn, dryness of mouth, visual disorders, liver damage	Horacek and Demcik, 1970 (NIOSH, 1976, p.30)

Array of Toxic Effects on Man and Other Mammals

Triphenyltin acetate (TPTA) (page 4)

Chemical Group: Organotin

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
-	-	dermal	human (spilled Brestan on hands and chest)	skin irrita- tion, dizi- ness, head- ache, epi- gastric pain, nausea, fati- gue, chronic hepatitis	Mijatovic, 1972 (NIOSH,1976, p.32)
concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
-	2 hours	inhal.	human (farmer spraying plants with a TPTA- solution)	general ma- laise, head- ache, uncon- sciousness	Guardascione and Di Bosco, 1967 (NIOSH,1976, p.29)
-	few minutes	inhal.	human (agriculture employee ex- posed to TPTA-powder)	facial flush- ing, vomit- ing, exces- sive saliva- tion, short- ness of breath, glu- cosurea	Guardascione and Di Bosco, 1967 (NIOSH,1976, p.29)
-	-	inhal.	human (farmer ex- posed to TPTA-dust)	headache, nausea, vomi- ting, epi- gastric pains	Guardascione and Di Bosco, 1967 (NIOSH,1976, p.30)

Array of Toxic Effects on Man and Other Mammals

Dibutyltin dichloride (DBDC)

Chemical Group: Organotin

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
180	-	intra- venous	mouse	LD50	NIOSH, 1978, p.23
150	-	oral	rat	LD50	NIOSH, 1978, p.23
50	3 days	oral (intub.)	rat	bile-duct and liver damage, death (15 months)	Barnes and Magee, 1958 (NIOSH,1976, p.53)
50	3 days	oral	mouse	liver damage	Barnes and Magee,1958 (NIOSH,1976, p.53)
50	single dose	oral (intub.)	rat	bile-duct, pancreas and liver damage	Barnes and Magee,1958 (NIOSH,1976, p.54)
20	single dose	oral (intub.)	rat (albino)	inflammatory bile-duct lesion (10 days)	Barnes and Stoner,1958 (NIOSH,1976, p.53)
16 (80 ppm)	90 days	oral (diet)	rat (weanlings)	growth reduc- tion, de- crease in hemoglobin	Gaunt et al., 1968 (NIOSH,1976, p.56)
10 (50ppm)	2 weeks	oral (diet)	rat (Wistar, weanlings)	thymus effects	Seinen et al., 1977a

Array of Toxic Effects on Man and Other Mammals

Dibutyltin dichloride (DBDC) (page 2)

Chemical Group: Organotin

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
5	single dose	intra- perit.	rat	central nerv- ous system damage;liver, kidney, and spleen effects; con- gestion of lungs; inter- stitial edema	Wakashin, 1975 (NIOSH,1976, p.65)
1	single dose	intra- perit.	mouse	liver, spleen and kidney effects	Yoshikawa and Ishii, 1961 (NIOSH,1976, p.45)
1	9 weeks, 3x/week	oral (intub.)	rat (Wistar, weanlings)	immuno- suppression	Seinen et al., 1977b
1	single dose	intra- venous	rat (Wistar, weanlings)	thymus effects	Seinen et al., 1977a
-	single dose	dermal appl.	human (volunteers)	follicular inflammation and pustula- tion	Lyle, 1958 (NIOSH,1976, p.26)
concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
1 470	1 hour	inhal.	rat	roughed fur, hypoactivity, ptosis, sali- vation (14 days)	Myers, 1976 (NIOSH,1976, p.49)

Array of Toxic Effects on Man and Other Mammals

Diethyltin diiodide (DEDI)

Chemical Group: Organotin

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
100	-	oral	rat	LDLo	NIOSH, 1978, p.23
26	-	intra- perit.	rat	LDLo	NIOSH, 1978, p.23
(total dose, 45-675 mg)	-	oral	human (3.5-31 years of age) (Stalinon medication)	headache, nausea, vom- iting, visual disorders, urinary blad- der disor- ders, brady- cardia, vertigo, convulsions, acute cere- bral, medul- lary and meningeal edema	Alajouanine et al., 1958 (NIOSH, 1976, p.26)
(total dose, 380-750 mg)				fatal dose	

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Triphenyltin acetate (TPTA)

Chemical Group: Organotin

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	oral	0.464	18 months (daily)	no increase in tumours	Innes et al., 1969 (NIOSH, 1976, p.88)
mouse	oral	125,000	78 weeks (intermittant)	TDLo (carcinogenic effects)	NIOSH, 1978, p.23

These studies, designed to evaluate the possible carcinogenic effects of the substance, resulted in a report in the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

MUTAGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse (male) (ICR/Ha Swiss 8-10 weeks old)	intra-perit.	12	single dose	no effect (modified dominant lethal assay)	Epstein et al., 1972 (NIOSH, 1976, p.90)
mouse (male) (ICR/Ha Swiss 8-10 weeks old)	oral (gavage)	6	5 days (daily)	no effect (modified dominant lethal assay)	Epstein et al., 1972 (NIOSH, 1976, p.90)

These studies, designed to evaluate the possible effects of a substance on gene mutation, chromosomal mutations, DNA repair or recombination or from transformation, was found in the literature reviewed. It did not result in a report of any of these effects. No comprehensive evaluation of this information was found.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Triphenyltin acetate (TPTA) (page 2) Chemical Group: Organotin

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (male) (Holtzman albino)	oral (diet)	20	19 days (daily)	testicular damage, sterility	Pate and Hays, 1968 (NIOSH, 1976, p.70)
rat (female) (Holtzman)	oral (diet)	20	4 days (daily)	ovary effects	Newton and Hays, 1968 (NIOSH, 1976, p.71)

These studies, designed to evaluate the possible effects of the substance on reproduction, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Dibutyltin dichloride (DBDC)

Chemical Group: Organotin

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

Nothing found in the literature reviewed.

MUTAGENICITY

Nothing found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Diethyltin diiodide (DEDI)

Chemical Group: Organotin

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

Nothing found in the literature reviewed.

MUTAGENICITY

Nothing found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Triphenyltin acetate		Chemical Group: Organotin				
System	Life stage	Concentration	Exposure time	Effect	Time of Observation	Citation
Organism Ecosystem Non-living		mg/l				

Nothing found in the marine environment.

Analysis

Organotin compounds (generic)

Chemical Group: Organotin

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
Gas chromatography with flame ionisation detector and flame photometry (10ng)	apparatus not commercially available in this form, must be assembled first/inexpensive selective procedure	Aue and Hill, 1972
Electron-spin-resonance spectroscopy (10ug/l)	interpretation of analytical results more complex/apparatus available in well-equipped laboratories, selective method rapid preparation	Stegmann et al., 1977
Pyrocatechol violet method (0.04-0.08ug of tin at a concentration of 0.004-0.01ppm in organic materials)	sampling rate limited by the decreased adsorption efficiency of charcoal at higher flowrates; pressure drops becomes excessive at higher flowrates; organic compounds in high concentrations in the environment sampled may displace organotins from the charcoal/ Suitable for determining many different organotins; readily accomplished	Corbin, 1973 (Niosh, 1976, p.149)

Legislation for the Protection of Man
and the Marine Environment

Organotin compounds (generic)

Chemical Group: Organotin

general classifica- tion of con- trol mechanism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in the water	Italy	regulation concerning acceptable limits for discharges into surface waters	10 mg/l tin as Sn	IDHL, 1977, p.630
control of substances in effluents	Libyan Arab Republic	proposed standards for effluents discharged	5mg/l of Sn into surface water reservoirs for direct use in agri- culture, and into aquifers used for public water supply	WHO/UNEP, 1976, p.Libyan Arab Republic-2
control of substances in effluents	Tunisia	proposed recommended values for dis- charges into surface waters and public sewers	0.0005mg/l as Sn into waters 0.1mg/l into public sewers	Kratel (unpublished)

Organotin

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MEDITERRANEAN DATA PROFILE

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I. INTRODUCTION

Mercury is widely recognised as one of the most toxic pollutants occurring in the environment. This distinction stems largely from the well-publicised poisonings in Japan from consumption of fish contaminated with methylmercury, followed by a similar outbreak in Iraq from consumption of seeds treated with a methylmercury fungicide. Subsequent concern has stimulated a large body of work dealing with mercury and its compounds. Especially significant was the discovery that inorganic mercury undergoes methylation by certain microorganisms, an important factor in understanding the toxicology and the cyclic behaviour of mercury in the environment. Unlike most other pollutants, mercury occurs naturally in a wide range of physical and chemical states, and has only become a pollutant as a result of man's activities. Mercury fulfills no known biological function in any type of organism, and its presence at even slightly elevated levels is poorly tolerated in most cases. Mercury and its compounds are subject to pronounced biomagnification, especially methylmercury in some species of fish. Recognition of these dangers has led to a world wide effort to curb the use of mercury and its compounds, especially the most toxic organomercurials (e.g. ethylmercury derivatives).

In its elemental state, mercury exists as a liquid metal, with a high vapour pressure of 1.2×10^{-3} mm (EPA, 1976). The volatility of mercury is considered to be an important property in relation to the degassing of the earth's crust. In addition to its elemental (Hg) state, mercury can occur as either a monovalent (Hg^+) or divalent (Hg^{++}) cation. The Hg^+ ion forms mercurous compounds, mostly salts, which are less soluble, and therefore less toxic, than the divalent compounds. Mercuric compounds formed with Hg^{++} include the organometallics, which possess a stable carbon-mercury bond as the result of mercury's very low affinity for oxygen (WHO-EHE, 1976).

The most important organomercurial compounds from a toxicological standpoint are the short chain alkylmercurials, in which the mercury is attached to a methyl or propyl group. These compounds, especially methylmercury, are of particular concern in this report due to their high toxicity and tendency to bioaccumulate in aquatic systems.

The solubility of elemental mercury vapour in air free water is approximately 20 ug/l at room temperature. In the presence of oxygen, however, the mercury is oxidised to form the divalent cation, and concentrations may reach 40 ug/l (WHO-EHE, 1976).

II OCCURRENCE

A. Production

Mercury is mined primarily as mercuric sulphide (cinnabar). The mined ore is crushed, ground and concentrated by flotation before being roasted to separate the mercury. Recovery rates are over 95% and the purity of the product is greater than 99% (OECD, 1974).

Stack losses during smelting of mercury should not exceed 2-3%, which represents about 300 tonnes per year, based on a world production figure of 10,000 tonnes in 1973. The dumping of solid wastes may result in high local levels of mercury in waterways (WHO-EHE, 1976).

World production of mercury in 1969 reached 10,236 tonnes, resulting from 2% annual increases since 1950 (WHO-EHE, 1976). Consumption on a world wide scale may now be decreasing, however, due to recognition of mercury's polluting potential.

CEC (1976) reports that in 1973, the world's largest mercury producing countries were Spain (2,194 tonnes) and Italy (1,127 tonnes). Other Mediterranean countries which produced mercury in 1973 were Yugoslavia (538 tonnes) and Turkey (226 tonnes).

B. Use

The uses of mercury are listed below in order of relative consumption by industrialised countries (WHO-EHE, 1976). Corresponding discharges to the environment are also given:

- chloralkali plants (25%), which lose mercury mainly to the atmosphere. Recent technology has allowed up to a 99% decrease in effluent losses of mercury (WHO-EHE, 1976);
- electrical equipment (20%), which may discharge considerable quantities of mercury due to breakage during use and by eventual disposal;
- paints (15%), using mercury as a biocidal additive, represent a completely non-recoverable application of mercury. A direct pathway to the ocean is available from anti-fouling paints used on ships;
- measurement and control systems (10%), using mercury in thermometers and gauges of all kinds, also represent a source of mercury discharge from breakage.
- agriculture (5%), using mercury as fungicidal seed coatings, represents a declining use of mercury due to its extreme toxicity. The many cases of mercury poisoning from consumption of treated seeds has led to restricted use of mercurial pesticides in nearly all Mediterranean countries;
- dental amalgams (3%), using small proportions of mercury with silver to form dental fillings.

- laboratories (2%), use mercury for a variety of applications. Discharges are difficult to ascertain;
- other uses (20%), include catalysis, medical, amalgamation, heat transfer media, in the paper-pulp industry, primers for military use and in boilers for driving turbines. Discharged mercury used as a catalyst in an acetaldehyde plant was responsible for the poisonings at Minamata Bay, Japan. Such discharges have been curtailed in most cases, and use in the paper pulp industry as slimicides has declined in favour of less persistent chemicals (IAEA, 1972).

Theoretically, it is estimated that 74% of mercury mined is reusable (WHO-EHE, 1976). Implementation of recently developed techniques could improve recovery significantly.

III MERCURY IN THE ENVIRONMENT

A. Sources

It is estimated that less than 20% of the mercury consumed in the USA is recovered (OECD, 1974). This figure may be optimistic according to an article by Korringa and Hagel (1974), which suggests that all mercury consumed is eventually discharged to the environment.

Studies on mercury levels found in Greenland ice fields indicate that man's activities have increased atmospheric concentrations of mercury considerably. One-third of present day "background" levels in rainwater has been attributed to man-made release (WHO-EHE, 1976).

The de-gassing of the earth's crust is thought to supply 25,000 - 150,000 tonnes of mercury per year to the atmosphere, with an additional natural input of 5,000 tonnes per year from rivers with a normal mercury content of less than 0.2 ug/l (WHO-EHE, 1976).

An estimate for man's contribution is roughly 20,000 tonnes per year, including substantial indirect release of mercury through the burning of fossil fuels. This is a considerable input in relation to the minimum figures for total natural release.

When viewing mercury discharges, it is more important to consider concentrations as a result of localised releases instead of total amounts discharged. Lakes, estuaries, bays and similar bodies of water may suffer dramatically from elevated mercury concentrations due to point discharges (WHO-EHE, 1976).

B. Transformation

The interconversion of mercury and its compounds in the environment can best be described as a cycle. On a global scale some of the mercury present in the atmosphere as an inorganic vapour is eventually delivered to the oceans through precipitation. Most of the mercury vapour is delivered from natural sources, through degassing of the earth's crust, volcanic discharges and evaporation from the oceans.

Though atmospheric levels of mercury have increased due to man's industrial activities, it is not believed that concentrations in the oceans will be altered substantially in the near future. This optimism is based on the natural occurrence of 70 million tonnes of mercury in a total ocean volume of $1.37 \times 10^9 \text{ km}^3$, and taking 50 ng/l as an average mercury concentration (WHO-EHE, 1976). The total input from man-made sources should be well distributed in all of the oceans as a result of circulation of surface waters.

However, a more local cycle as a result of man-made activity has been found to lead to high concentrations of mercury in several studies.

Contamination of fish is of particular concern, since the mercury present is often nearly 100% methylmercury, which is highly toxic.

The mechanism for accumulation of methylmercury is not completely understood. It is believed that methylmercury diffuses from sedimentary particles into the water, where it is rapidly accumulated by living organisms. This hypothesis is supported by the fact that no methylmercury is detected in filtered water (WHO-EHE, 1976).

Though uptake through the gills is considered a key process in many organisms, high concentrations in large carnivorous fish species suggests that methylmercury is also accumulated through the trophic levels. Tuna and swordfish, for example, are both long lived, highly active species with large appetites, allowing possible concentration through the food chain. It is well established that methylmercury concentrations show a positive correlation with the age (i.e. weight) of the fish. Their high activity necessitates a large volume of water pass through their gills each day, which may be a pathway for direct uptake of large amounts of mercury (WHO-EHE, 1976).

It is not known if the high mercury concentrations found in large predator species is related to the total mercury content of the oceans (70 million tonnes) or whether it is related to high localised concentrations which result from man's activities. High methylmercury concentrations in fish and shellfish subjected to point sources have definitely been confirmed, especially in fresh water systems and in areas like Minamata Bay in Japan.

Fowler et al. (1976) found a biomagnification coefficient of 10,000 in the euphasiid, Meganyctiphanes norvegica, after a 30 day exposure to 0.00025mg/l methylmercury.

Inorganic divalent mercury (Hg^{++}) may be formed from mercury vapor by oxidation in water or by enzymatic or chemical cleavage of carbon-mercury bonds in organomercurial compounds. This divalent cation is attached to suspended organic matter or is found in the sedimentary layers. In the anaerobic layer of the sediments, most of the mercury is believed to form insoluble HgS , which is oxidised very slowly. Residence times for these compounds have been estimated at 10-100 years in contaminated sediments (OECD, 1974). Mercury deposited on the uppermost sedimentary layer is methylated by microorganisms, forming methyl- and dimethylmercury. The methylmercury is readily absorbed by organisms, due to its ability to cross biological membranes. Dimethylmercury formation is favoured by alkaline conditions, and being unchanged and volatile, it is believed to diffuse from the aquatic environment to the atmosphere, where it is subject to removal by rainfall, completing the cycle.

There is some evidence that mercury enrichment occurs in surface layers of oil and surface films. Though the mechanism is poorly understood, it is believed that mercury is converted to a benzene soluble form which may be concentrated in a dispersed oil phase. Sorption from the atmosphere and extraction from the body of the sea are thought to be sources of this enrichment process, which may lead to uptake by microorganisms and eventual concentration in the food chain (FAO, 1977).

C. Bioaccumulation

Short chain alkylmercurials, especially methylmercury, have a strong tendency to bioaccumulate. Methylmercury is readily absorbed through biological membranes, is degraded into inorganic mercury much more slowly than other organomercurials, and is also excreted very slowly.

A whole tissue biomagnification factor of 600 was found for adult plaice, Pleuronectes platessa; the gill tissues showed a concentration factor of 5,516 (Pentreath, 1976).

IV MONITORING

A. Analysis

Bisogni and Lawrence (1974) report a benzene extraction and flameless atomic absorption technique for determining methylmercury. Gas-liquid chromatography or thin-layer chromatography are also used to separate and identify organomercurial compounds.

Colorimetric (dithizone) and neutron activation techniques are also common, the latter especially as a reference method. The lower limit for detection by these techniques is commonly in the range of 0.5-5.0 ng of mercury, though values as low as 0.1-0.3 ng of mercury may be detected (WHO-EHE, 1976).

B. Amount in the Mediterranean

Sea water usually contains about 0.1 ug/l of mercury, which is one-tenth of the concentration considered to represent a "distinct threat" to selected marine organisms (EPA, 1976). The Mediterranean Sea contains at least two regions with mercury concentrations well over this maximum safe limit of 1.0 ug/l of mercury. The Adriatic Sea at Ravenna yielded samples containing 0.42 - 2.0 ug/l and samples from the Liguro-Provencal region contained 2.9 - 3.6 ug/l. Lower values were reported for the Tyrrhenian Sea, with 0.04 - 0.2 ug/l of mercury (CEC, 1976). These seas border heavily industrialised areas, including regions in Italy where mercury is heavily mined. Point discharges from a chlor-alkali plant near Livorno, Italy, were found to raise mercury concentrations in sea water and biota to 0.2 ug/l. Values 10 km north or south of the outfall were less than 0.02 ug/l (UNEP, 1977a).

Robertson et al. (1972) report a mean mercury concentration of 0.965mg/kg dry weight for sediments from the Mediterranean.

In a study on 6 species of edible fish taken from Haifa and Acre Bays in Israel, Levitan et al. (1973) found mercury concentrations ranging from 0.408-2.04mg Hg/kg. Marchand (1977) studied mercury concentration in the mussel, Mytilus galloprovincialis, from various regions in the Mediterranean. His results from a low concentration of 0.024mg/kg dry weight from Corsica, to a high value of 0.182mg/kg dry weight in mussels from the N.E. Mediterranean

Cumont et al. (1972) found that fish caught in the Mediterranean contained higher levels of mercury than fish from the Atlantic. T. thynnus from the Mediterranean contained 2.35 times as much mercury as was found in Atlantic samples. Bernhard (1978) attributes the high levels to geochemical mercury anomalies which exist in the Mediterranean basin.

C. Amount Entering the Mediterranean

The data on mercury containing effluents entering the Mediterranean correspond well with the regional sea water concentrations mentioned above. It was estimated that the Adriatic Sea receives the highest proportion of the total mercury which enters the Mediterranean (42%). The Liguro-Provencal receives 25% of the mercury burden, while 8% enters the Tyrrhenian Sea. Higher than acceptable mercury concentrations are also expected to occur in the Aegean Sea, which receives 11% of total mercury, and in the Ionian Sea, receiving 8%. These five regions represent 84% of the total mercury entering the Mediterranean, which is estimated at 130 tons per year (UNEP, 1977b).

D. Regulations

Mediterranean countries which have legislation dealing with the discharge of mercury (generic) include Algeria, Egypt, France, Italy, Libyan Arab Republic, Spain, Tunisia, Turkey and Yugoslavia (WHO/UNEP, 1976; CEC, 1976; IDHL, 1978; Kratel, unpublished).

OECD (1974) has recommended the elimination of alkylmercury compounds from all uses that allow this material to reach the environment in any way. WHO/FAO (1974) has recommended that alkylmercury compounds should never be permitted for the treatment of seed to be exported for the production of food.

The EPA (1976) recommends a maximum daily consumption of 60 g/day (420 g/week) of fish contaminated with 0.5 mg/kg mercury. This corresponds to a daily intake of 0.03 mg of mercury.

V TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

The toxicity of mercury depends on its chemical speciation with alkylmercurial compounds being most toxic. The toxic properties of organomercuries are largely determined by the $R-Hg^+$ ion, and the physical properties are determined mainly by the associated anion (X^-).

Plankton growth is reduced to 50% by 1 ppb mercury, and all growth stops at 50ppb (NATO, 1976). Studies on algae established an LC_{50} range of 26-54 ppb of mercury (CEC, 1976). Other studies indicate that phytoplankton may be highly susceptible to organic mercury compounds (OECD, 1974).

A 96 hour LC50 for methylmercury has been found to occur at 0.15mg/l in the adult amphipod, Gammarus duebeni (Inman and Lockwood, 1977). GFCM (1978) reports 24 hour LC50s for the larva of Sepia officinalis at concentrations of 0.017-0.019mg/l, and for the shrimp, Panaeus kerathurus, at levels of 0.022mg/l.

The synergistic effect of mercury with other heavy metals (e.g. copper) causes much higher toxicity than expected on an additive basis. Conversely, selenium apparently reacts antagonistically with mercury - a ratio of 1:1 for selenium and mercury found in seals suggests a neutralising effect. A similar relationship is found in dolphins, marlin, tuna and porpoises, and may explain the apparently high tolerance of these organisms for mercury (CEC, 1976).

B. Toxicity in Man and Other Mammals

The mass poisonings at Minamata and Niigata in Japan stimulated intensive studies on the effects of methylmercury on man, and the toxicology has been well established. OECD (1974) reports central and peripheral nervous system damage, congenital disorders, and death as a result of exposure to methylmercury (oral and trans-placental) over a 5 year period at Minamata Bay, Japan. Mufti et al. (1976) have estimated that the doses in a mass poisoning in Iraq from the consumption of seeds contaminated with methylmercury averaged 0.08mg/kg bw/day over a 32 day period.

An oral LD50 for methylmercury chloride in the guinea pig has been reported to occur at 21mg/kg bw/day. The oral LDLo for humans, or the lowest dose reported to be lethal, for methylmercury chloride is 5.0mg/kg bw/day (NIOSH, 1978).

Mutagenic effects have been reported for methylmercury chloride (Fiskesjö, 1970), and reproductive effects have also been noted (Clegg, 1971). A dose of 2.0mg/kg bw of methylmercury chloride caused teratogenic effects in a rat (Nonaka, 1969).

Total Production

Mercury and mercury compounds (generic)

Chemical Group: Mercury

year	area	amount	trend	citation (as reported in)
1969	World	10 236 tonnes	-	CEC, 1976, p. 9-18
1973	World	9 784 "	-	
1969	Italy	1 680 "	-	
1973	Italy	1 127 "	-	
1969	Spain	2 222 "	-	
1973	Spain	2 194 "	-	
1969	Turkey	226 "	-	
1973	Turkey	226 "	-	
1969	Yugoslavia	494 "	-	
1973	Yugoslavia	538 "	-	

Production Process(es)

Organic mercury compounds

Chemical Group: Mercury

process (major or minor by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
Reaction of mercury or sodium amalgam with alkyl halides.	-	-	NATO, 1976, pp. M1-7

Use

Mercury and mercury compounds (generic)

Chemical Group: Mercury

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
agriculture	France, 1972 (minor)	-	-	CEC, 1976, p. 9-19
catalysis		-	-	
chloralkali	France, 1972 (major)	-	-	
control instruments	France, 1972 (major)	-	-	
dental appli- cations	France, 1972 (minor)	-	-	
electrical apparatus	France, 1972 (minor)	-	-	
laboratory use		-	-	
paints		-	-	
pharmaceu- ticals	France, 1972 (minor)	-	-	
pulp and paper		-	-	

Pathways Leading to Marine Pollution

Methylmercury		Chemical Group: Mercury	
Pathway	Quantity	Area	Citation
Methylation of inorganic mercury by sediment bacteria	-	San Francisco Bay	Olson, B.H. and Cooper, R.C., 1976
Natural production by photolysis of inorganic mercury	-	World	Jewett, K.L. et al., 1975
Conversion of metallic, inorganic and phenyl mercury compounds by hydro-spheric microflora	-	World	Kopfler, F.C., 1974
Synthesis from methyl-B ₁₂ compounds	-	World	Wood, J.M., 1974
Transmethylation in the presence of Sn ⁴⁺	-	-	Huey, C. et al., 1974

Biotic Transformation in the Marine Environment

Methylmercury

Chemical Group: Mercury

Process	Transformation		Products Name	Quantity	Citation
	%	Time			
Reduction	-	-	Inorganic mercury, methane	-	Wood, J. M., 1974
Methylation	-	-	Dimethyl mercury	-	Wood, J. M., 1974

Transformation in the Marine Environment

Methylmercury

Chemical group: Mercury

Process	Medium	Parameters	Effect	Citation
Photolysis	laboratory	light: 253.7uM	dimethyl mercury formation	Jewett, K.L. et al., 1975
Adsorption	1% suspension of sodic montmorillonite in seawater; 50 ug/l methyl mercury	20% salinity	2.41ug/g methyl mercury adsorbed	Frenet-Robin, M. and Boiteau, H.L., 1977
Adsorption	1% suspension of calcic montmorillonite in seawater; 50 ug/l methyl mercury	20% salinity	2.86ug/g methyl mercury adsorbed	Frenet-Robin, M. and Boiteau, H.L., 1977
Adsorption	1% suspension of calcic montmorillonite in seawater; 50 ug/l methyl mercury	10% salinity	3.04ug/g methyl mercury adsorbed	Frenet-Robin, M. and Boiteau, H.L., 1977
Adsorption	1% suspension of calcic montmorillonite in seawater; 10 ug/l methyl mercury	10% salinity	0.4ug/g methyl mercury adsorbed	Frenet-Robin, M. and Boiteau, H.L., 1977
Adsorption	1% suspension of kaolinite in seawater; 50 ug/l methyl mercury	20% salinity	0.71ug/g methyl mercury adsorbed	Frenet-Robin, M. and Boiteau, H.L., 1977

Behaviour of a Chemical Substance in Marine Organisms

Methylmercury

Chemical Group: Mercury

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn. Time mg/l	Tissue/	%	Biomagnification	%	Time	Name	Quantity	
Chrysophrys major (Red Sea bream)	-	-	M	-	80	-	-	-	-	Fujiki, M. et al., 1977
Pleuronectes platessa (Plaice)	-	-	E L A, gill A, whole	- - - -	500 2 000 5 516 600	- - - 50	- - - 275 days	- - - -	- - - -	Pentreath, R.J., 1976
Pleuronectes flesus (Flounder)	-	-	A, whole	-	-	50	640- 780 days	-	-	Järvenpää, T. et al., 1970
Esox lucius (Pike)	-	-	A, whole	-	-	50	640- 780 days	-	-	Järvenpää, T. et al., 1970
Anguilla vul- garis (Eel)	-	-	A, whole	-	-	50	910- 1030 days	-	-	Järvenpää, T. et al., 1970

Behaviour of a Chemical Substance in Marine Organisms

Methylmercury (page 2)

Chemical Group: Mercury

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn. mg/l	Tissue/	%	Biomagnification	%	Time	Name	Quantity	
Homarus americanus (Lobster)	-	-	Tail muscle	50	-	0	6 days	-	-	Guarino, A.M. et al., 1976
Homarus americanus (Lobster)	-	-	Hepato-pancreas	22.7	-	50	20.9 days	-	-	Guarino, A.M. et al., 1976
Mytilus galli-provincialis (Mussel)	inj. into foot muscle	-	-	-	-	50	1 000	-	-	Miettinen, J.K. et al., 1972
Mytilus galli-provincialis (Mussel)	SW	-	5 days	-	570	8	3 months	-	-	Fowler, S.W. et al., 1978
Lysmata seticaudata (Shrimp)	SW	-	5 days	M	68.8	2 270	529 days	-	-	Fowler, S.W. et al., 1978
Meganyctiphanes norvegica (Euphausiid)	SW	0.00025	30 days	-	10 000	3	3 days	-	-	Fowler, S.W. et al., 1976

Behaviour of a Chemical Substance in Marine Organisms

Methylmercury (page 3)

Chemical Group: Mercury

Organism	Exposure		Accumulation and Distribution			Loss %	Time	Metabolites		Citation
	Route	Concn. mg/l	Tissue/ %	Biomagnification	Name			Quantity		
Meganycitiph- anes norvegica (Euphausiid)	SW	0.0025	30 days	-	10 000	50	450	-	-	Fowler, S.W. et al., 1976a
Carcinus maenas inj. (shore crab) into HL	-	-	-	-	-	50	400+50 days	-	-	Miettinen, J.K. et al., 1972
Serranus scriba per os	-	-	-	-	-	50	267+27 days	-	-	Miettinen, J.K. et al., 1972
Tapes decuss- atus	inj. into foot muscle	-	-	-	-	50	481+40 days	-	-	Miettinen, J.K. et al., 1972

A - Adult
E - Egg
L - Larvae
SW - Seawater
M - Muscle
HL - Haemolymph

Behaviour of the Substance in Man and Other Mammals

Methylmercury chloride

Chemical Group: Mercury

description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)
rat	intra-venous	1 mg/kg bw	single dose	-	-	methylmercury-cystein, inorganic mercury and protein-bound mercury	Norseth and Clarkson, 1971, (WHO/FAO, 1972, p. 22)
human (volunteers)	oral	0.002 mg methyl-203 Hg	single dose	-	50%/76 ± 3 days	-	Miettinen et al., 1971 (WHO/FAO, 1972, p. 20)

Concentrations in Water, Sediments and Biota

Methylmercury		Chemical Group: Mercury			
Description of Sample	Analytical	Level(s)	Date(s)	Citation	
Material	Origin				
Sediment from salt marsh	Florida USA brackish	GC-EC	0.001 mg/kg dry wt.	1974-1976	Gardner, W.S. et al., 1978
Sediment	R.Mersey, UK	GC-EC	0.016 mg/kg dry wt.	1975-1976	Bartlett, P.D. et al., 1977
Sediment - intertidal	San Francisco Bay, USA	GC	1.9 mg/kg wet wt.	-	Olson, B.H. and Cooper, R.C., 1976
Trichura trichura (Cutless fish)	Florida, USA	GC-EC	3.8 mg/kg dry wt.	1974-1976	Gardner, W.S. et al., 1978
Clupea harengus (Baltic herring)	Baltic Sea, brackish	GLC	1.1-2.1 mg/kg wet wt.	1973-1975	Linko, R.R. and Terho, K., 1977
Esox lucius (Pike)	Baltic Sea, brackish	GLC	2.7 mg/kg wet wt.	1973-1975	Linko, R.R. and Terho, K., 1977
Mytilus galloprovincialis (Mussel)	Mediterranean	GC	0.23 mg/kg dry wt.	1974	Marchand, M., 1977
Littorina irrorata (Periwinkle)	Florida, USA brackish	GC-EC	0.61 mg/kg dry wt.	1974-1976	Gardner, W.S. et al., 1978
Homarus americanus (Lobster)	Atlantic	GC	0.11 mg/kg wet wt.	-	Guarino, A.M. et al., 1976

Concentrations in Water, Sediments and Biota

Methylmercury (page 2)

Chemical Group: Mercury

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Saltmarsh ecosystem-sediment	Georgia Coast USA	GC	None	-	Windom, H. et al., 1976
-spartina alterniflora	"	"	None	-	Windom, H. et al., 1976
-Littorina irrorata (Periwinkle)	"	"	0.61 mg/kg dry wt.	-	Windom, H. et al., 1976
-Uca sp. (Fiddler crab)	"	"	0.36 mg/kg dry wt.	-	Windom, H. et al., 1976
Yellowfin Tuna	Western Pacific and East Indian Ocean	GLC	0.25-0.30 mg/kg	1973	Hamada, M., et al., 1977
Yellowfin Tuna (Dark muscle)	Western Pacific and East Indian Ocean	GLC	0.04-0.46 mg/kg	-	Ueda, T., and Takeda, M., 1977
Plaice	Mediterranean	-	0.41 mg/kg	-	Cumont, G. et al., 1972
Bass	Mediterranean	-	0.44 mg/kg	-	Cumont, G. et al., 1972
Capelin	Mediterranean	-	0.70 mg/kg	-	Cumont, G. et al., 1972
Tursiops truncatus (Dolphin, adult - muscle)	Barcaggio, N. of Corsica	-	4.3 mg/kg wet wt.	1973	Viale, D., 1975

Concentrations in Water, Sediments and Biota

Methylmercury (page 3)

Chemical Group: Mercury

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Tursiops truncatus (Dolphin, juvenile - muscle)	Nr. Bastia, Corsica	-	0.7 mg/kg wet wt.	1973	Viale, D., 1975
Sphyræna sphyræna (Edible fish)	Haifa Bay, Israel	GC	0.434 mg Hg/kg	Dec 1971- June 1972	Levitan, S. et al., 1973
Sphyræna chrysotaenia (Edible fish)	Haifa Bay, Israel	GC	0.586 mg Hg/kg	Dec 1971- June 1972	Levitan, S. et al., 1973
Epinephelus guaza (Edible fish)	Haifa Bay, Israel	GC	0.51 mg Hg/kg	Dec 1971- June 1972	Levitan, S. et al., 1973
Sphyræna sphyræna (Edible fish)	Acre Bay, Israel	GC	1.67 mg Hg/kg	Dec 1971- June 1972	Levitan, S. et al., 1973
Sphyræna chrysotaenia (Edible fish)	Acre Bay, Israel	GC	0.408 mg Hg/kg	Dec 1971- June 1972	Levitan, S. et al., 1973
Epinephelus guaza (Edible fish)	Acre Bay, Israel	GC	2.04 mg Hg/kg	Dec 1971- June 1972	Levitan, S. et al., 1973
Mytilus galloprovincialis (Mussel)	N.E. Mediterranean	GC	0.182 mg/kg dry wt.	1974	Marchand, M., 1977
Mytilus galloprovincialis (Mussel)	St. Tropez, N.E. Mediterranean	GC	0.039 mg/kg dry wt.	1974	Marchand, M., 1977

Concentrations in Water, Sediments and Biota

Methylmercury (page 4)

Chemical Group: Mercury

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Mytilus gall- oprovincialis (Mussel)	Monaco, N.E. Mediterranean	GC	0.125 mg/ kg dry wt.	1974	Marchand, M., 1977
Mytilus gall- oprovincialis (Mussel)	Diana, Corsica	GC	0.024 mg/ kg dry wt.	1974	Marchand, M., 1977

GLC - Gas liquid chromatography

GC - Gas chromatography

EC - Electron capture detector

Array of Toxic Effects on Man and Other Mammals

Methylmercury ion

Chemical Group: Mercury

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
0.1 (2 mg/kg diet)	12 weeks	oral (diet)	rat	kidney effects	Fowler, 1972, (WHO/FAO, 1972, p. 23)
0.08	32 days (Iraq)	oral	human	death (epidemic)	Mufti et al. 1976, (WHO-EHE, 1976, p. 94)
0.005	daily (Sweden)	oral	human	no effect	Skerfving, 1974, (WHO-EHE, 1976, p. 96)
-	over 5 years (Minamata Bay, Japan)	oral, trans- placen- tal	human	central and peripheral nervous system damage, congenital disorders, death	OECD, 1974, p. 148

Array of Toxic Effects on Man and Other Mammals

Methylmercury chloride

Chemical Group: Mercury

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
58	-	oral	rat	LD50	IAEA, 1972, p.74
21	-	oral	guinea pig	LD50	NIOSH, 1978, p. 15
12.5 (10 mg Hg/kg)	7 days	oral	mouse	neurologi- cal signs	Suzuki, 1969, (IAEA, 1972, p. 75)
5		oral	human	LDLO	NIOSH, 1978, p. 15
5 2.5	6-17th day of gestation "	oral "	mouse "	reduced litter size all pups died with retarded cerebellar development (14 days post- partum)	Clegg, 1971, (WHO/FAO, 1972, p.24)
0.4 (0.3 mg Hg/kg)	140 days	oral (diet)	monkey (<u>Macaca</u> <u>mulatta</u> and <u>Macacus</u> <u>irus</u>)	neurologi- cal symp- toms	WHO/FAO, 1972, p.24
0.1 (0.1 mg Hg/kg)	140 days	oral	monkey (<u>Macaca</u> <u>mulatta</u> and <u>Macacus</u> <u>irus</u>)	weight de- pression	WHO/FAO, 1972, p.24

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Methylmercury chloride

Chemical Group: Mercury

BEHAVIORAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

Nothing found in the literature reviewed.

MUTAGENICITY

description of system	reported results	citation (as reported in)
human leucocytes	c-mitotic effects	Fiskesjö, 1970 (CRC, 1974, p. 170)

A comprehensive evaluation of the known studies designed to assess the possible mutagenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"It is obvious that mercury compounds have various effects on the genetic material. Apparently all compounds are active as c-mitotic agents, although the effectiveness is considerably higher for organic mercury compounds like alkyl and phenyl compounds than for inorganic ones. At least alkyl and phenyl mercury compounds also cause chromosome breakage and, to a minor extent, point mutations." (CEC, 1974, p. 181)

NEUROTOXICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	oral	12.5 (10 mg Hg/kg)	7 days	neurological signs	Suzuki, 1969 (IAEA, 1972, p.75)
monkey (<u>Macaca</u> <u>mulatta</u> and <u>Macacus</u> <u>irus</u>)	oral (diet)	0.4 (0.3 mg Hg/kg)	140 days	neurological symptoms	WHO/FAO, 1972, p.24

These studies, designed to evaluate the possible neurotoxic effects of the substance, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Methylmercury chloride (page 2)

Chemical Group: Mercury

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	oral	5	6 - 17th day of gestation (daily)	reduced litter size	Clegg, 1971 (WHO/FAO, 1972, p. 24)
"	"	2,5	"	all pups died with retarded cerebellar development (14 days post- partum)	

This study, designed to evaluate the possible effects of the substance on reproduction, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

TERATOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	trans- placental	2	1st 20 days of gestation (daily)	foetal brain damage	Nonaka, 1969, (IAEA, 1972, p. 76)

This study, designed to evaluate the possible teratogenic effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic or other Effects on Marine Organisms and Ecosystems

Methylmercury

Chemical Group: Mercury

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Gammarus duebeni (Amphipod)	Adult	0.15	96 hrs.	LC50	96 hrs.	Inman, C.B.E. and Lockwood, A.P.M., 1977
Gammarus duebeni (Amphipod)	Adult	0.03	96 hrs.	Dec. in haemo- lymph Na ⁺ , disruption of ionic regula- tory system	96 hrs.	Inman, C.B.E. and Lockwood, A.P.M. 1977
Mytilus edulis (Mussel)	Adult	0.4-2.4	24 hrs.	Dec. in feed- ing rate	24 hrs.	Dorn, P., 1976
Scorpaena porcus (Scorpion fish)	Adult	5.0	2 hrs.	Inhib. of gly- cin incorpora- tion in in- testine	2 hrs.	Pérès, G. et al., 1977

Toxic or other Effects on Marine Organisms and Ecosystems

Methylmercury (page 2)

Chemical Group: Mercury

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Balanus nubilis (Barnacle)	Adult	25.0	3 hrs.	Dec. Na + transport across muscle fibre membran- es, mitochond- rial changes.	3 hrs.	Hift, H. and Schultz, R., 1976.
Loligo peali (Squid)	Adult	87.0	15 min.	Blocks axonal action poten- tials	15 min.	Shrivastav, B.B. et al., 1976.
Fundulus hetero- clitus (Killi- fish)	Adult	100.0	5 hrs.	Dec. Na + up- take by gills	5 hrs.	Renfro, J.L. et al., 1974.
Pseudopleuronect- es americanus (Winter flounder)	Adult	1mg/kg per day intra- musc.	13 days	No effect on osmoregulation	14 days	Schmidt-Nielsen, B. et al., 1977.

Toxic or other Effects on Marine Organisms and Ecosystems

Methylmercury (page 3)

Chemical Group: Mercury

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Sepia officinalis	Larva	0.017- 0.019	24 hr	LC50	24 hr	GFCM, 1978
Penaeus kerathurus (Shrimp)	Post larva	0.022	24 hr	LC50	24 hr	GFCM, 1978
Scorpaena porcus	Adult	5.0	30 mins	Decreased intestinal incorporation of "glycolle 14"	30 mins	Pérès, G. et al., 1976
Tisbe dilatata (Crustacean)	Adult	0.005	4-40 days	Decreased no. of nauplii hatched; increases age at which females deposit eggs	4-40 days	Renzonei, A., 1976

Analysis

Methylmercury

Chemical group: Mercury

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
benzene-extraction and flameless atomic absorption	-/-	Bisogni and Lawrence, 1974 (NAS, 1977, p.278)

Legislation for the Protection of Man and the

Marine Environment

Methylmercury compounds (generic)

Chemical Group: Mercury

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in the environment	OECD Countries	OECD recom- mends the elimination of alkylmer- cury com- pounds from all uses that allow this material to reach the en- vironment in any way.	-	OECD, 1974, p. 191
control of substances in food	WHO/FAO	provisional tolerable weekly in- take recom- mendation	5 ug/kg bw of total mercury of which no more than 3.3 ug/kg bw should be methyl- mercury compounds	WHO/FAO, 1972, p. 28
control of substances used for plants	WHO/FAO	WHO/FAO re- commendation that alkyl- mercury com- pounds should never be per- mitted for the treat- ment of seed to be export- ed for pro- duction of food.	-	WHO/FAO, 1974, p. 23

Legislation for the Protection of Man and the
Marine Environment

Methylmercury compounds (generic)
(page 2)

Chemical Group: Mercury

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances used for plants	Algeria	authorisation and regulation concerning the use of mercury compounds for certain plant protection purposes	-	WHO/UNEP, 1976, p. Algeria-3
control of substances in waste- waters	Egypt	standard for mercury in industrial waste- water discharged into drainage canals	-	WHO/UNEP, 1976, p. Egypt-3
control of substances in industry	France	prohibition of mercury containing biocides in pulp and paper industries the mercury content in the soda lye may not exceed 1,5 mg/kg in these industries	-	CEC, 1976 p. 13-16
control of substances in water	France	the amount of mercury in the residual water may not exceed 2 g per ton produced chlorine in all new installations (after Feb. 28, 1974)		CEC, 1976 p. 13-16

Legislation for the Protection of Man and the

Marine Environment

Methylmercury compounds (generic)
(page 3)

Chemical Group: Mercury

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in the water	Italy	regulation concerning acceptable limits of mercury for discharges into surface water and public sewers	0.005 mg/l of Hg in ionic solu- tion, in the form of com- plexes, and in suspen- sion	IDHL, 1977, p. 630
control of substances in production and use	Italy	mercury fungicides may be produced and used solely for seed dressing		CEC, 1976 p. 13-23
control of substances in effluents	Libyan Arab Republic	proposed standards for effluents discharged	0.005 mg/l of Hg into surface water reservoirs for direct use in agriculture, and into aquifers used for public water supply, the sea and urban sewage systems	WHO/UNEP, 1976, p. Libyan Arab Rep- ublic-2

Legislation for the Protection of Man and the

Marine Environment

Methylmercury compounds (generic)
(page 4)

Chemical Group: Mercury

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in effluents	Spain	regulation concerning discharges from submarine outfalls	0.05 mg/l of Hg in not more than 50% of samples 0.10 mg/l of Hg in not more than 10% of samples	IDHL, 1978, p.193
control of substances in effluents	Tunisia	proposed recommended values for discharges into surface waters and public sewers	0.01 mg/l as Hg (Atomic absorption spectrophoto- metry)	Kratel (unpublished)
control of substances in effluents	Turkey	prohibition of discharges when the concentration exceeds the tolerance level	0.004 mg/l as Hg ions	Turkish law of 1 October 1971
control of substances in water	Yugoslavia	maximum permissible concentrations of dangerous substances in interrepublic watercourses	0.001 mg/l of Hg	IDHL, 1978, (awaiting publication)

Mercury

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I. INTRODUCTION

Cadmium (Cd) is a soft metal, closely related to zinc, and will be found wherever Zn occurs in nature. Cd is found in low concentrations in nearly all naturally occurring materials, though it apparently fulfills no biological function. Background levels of Cd are exceeded in some areas due to man's activities, and Cd can move between air, water and soil with relative ease. Once in water, much of the Cd will find its way into sediments, where benthic communities may be affected. Due to its long biologic half-life, Cd acts as a cumulative poison, i.e. its concentration in the body increases with age. The primary concern arising from environmental exposure of animals and man centres on effects from low-level chronic exposure. Cd is suspected of playing a role in several human diseases, including Itai-Itai disease; it is uncertain if the metal also contributes to the etiology of hypertension, carcinogenesis, mutagenesis or teratogenesis in humans.

II. OCCURRENCE

A. Production

The major commercial supply of Cd is as a by-product in the production of Zn from sphalerite (ZnS), with smaller quantities supplied by the copper and lead smelting industries. Approximately 70% of the total world production of Cd has occurred within the last 20 years, and this increasing trend is expected to continue in industrialised countries (CEC, 1977).

IARC (1976) reports an estimated world production of Cd in 1973 of 17,000 tonnes; CEC (1977) reports an estimated consumption for that year of 17,813 tonnes.

74% of world Cd production is supplied by Canada, Japan, the U.S., the U.S.S.R. and Zaire. Mediterranean countries with appreciable production are France, Italy, Spain, and Yugoslavia (IARC, 1976).

B. Uses

The major uses of Cd are for electroplating (45%); pigments used in paints, inks, plastics, etc. (21%); plastic stabilisers used mostly for PVC (15%); for alloys (7.5%); for nickel-cadmium batteries (3%) and for miscellaneous uses (8.5%), including electrical contact production, curing of rubber, in fungicides, and in solid state systems. These percentages of total use are based on U.S. consumption patterns (CEC, 1976).

Consumption figures for the Mediterranean area in 1973 were available for only two countries; France consumed 1,150 tonnes, while Italy used 430 tonnes (CEC, 1977).

An important problem related to the environment is the dispersive use of Cd - less than 10% of total production is probably recycled (CEC, 1977). The burning of oils, tyres, plastics and other solid wastes will release Cd to the atmosphere, and eventually these discharges may reach the marine environment. Improved recovery technology may develop with increased demand for Cd; presently, recycling of nickel-cadmium batteries seems a possibility with the highest chance of success.

III. CADMIUM IN THE ENVIRONMENT

A. Sources

Processes involved in the extraction, refinement and production of iron, steel, cadmium, zinc, lead and copper are major sources of

Cd pollution. Most of this Cd is released to the atmosphere, and the incineration of metal refuse, old tyres, PVC plastics, waste and fossil fuel combustion also contributes to the atmospheric Cd load. Water pollution results mainly from mining and beneficiation, hydrometallurgy, and electroplating, which may discharge effluents containing 100-500 ppm Cd, as well as other heavy metals, cyanides and metal surface cleaning agents (CEC, 1977).

Applications of sewage sludge and other Cd containing fertilisers (e.g. phosphate) may raise soil concentrations considerably and make Cd available for uptake by plants. Shafer (1977) reports that municipal waste discharge into S. California coastal waters contains 55.4/45.0 metric tons of Cd per year.

Other sources of Cd to the environment include tobacco combustion (about 1.4 mg per cigarette Cd), corrosion of galvanised metals, and wear of automobile tyres, which can contain 20-90 ppm Cd (CEC, 1977).

B. Transformations

1. Abiotic

Cd released to the atmosphere is rapidly oxidised, forming CdO, which is eventually removed from the air through precipitation or direct fallout. The rate of removal depends on atmospheric conditions. In soil, Cd is considered to be relatively immobile, but persistence in this phase is largely dependent on chemical form and characteristics of the soil. At low pH values, for example, Cd compounds are more soluble than in basic conditions. CdO (oxide), CdCO₃ (carbonate), Cd(OH)₂ (hydroxide) and CdS (sulfide) are relatively insoluble compounds which may form in soils.

The fluoride, chloride, bromide, iodide, nitrate and sulphate of Cd are relatively soluble, as are a wide range of Cd complexes, such as cyanides and amines. Alkyl-cadmium compounds are extremely unstable, reacting rapidly with water (CEC, 1977).

Leaching of Cd from soils into ground waters, and eventually into rivers and the ocean, contributes to municipal and industrial sources of water pollution by Cd. The fate of Cd in water depends on other constituents present. Adsorption to particulate matter in the water, chelation, and precipitation are the major reactions Cd undergoes in sea water. Sedimentation processes keep Cd concentrations in sea water quite low (about 0.1 ug/l).

Increased desorption (i.e. increased Cd in water) was found when the salinity was increased in a Rhine estuary sediment (de Groot et al., 1976).

2. Biotic

Under favourable soil conditions, Cd can be oxidised quite rapidly by microorganisms (EPA/ORNL, 1978). No further information on biotic transformation of Cd was found in the literature reviewed.

C. Bioaccumulation

Cd is accumulated to a high degree by a wide variety of marine organisms, including some plants. Concentration factors vary a great deal, with molluscs displaying the highest rates of accumulation, up to 2,260,000 times the levels found in the water (EPA/ORNL, 1978). High values in oysters could not be

statistically correlated with Cd concentrations in the surrounding water - possible ingestion of particulate Cd and effects of salinity may affect uptake. Due to sedimentation of Cd near estuaries, benthic concentrations in coastal regions may reach dangerous levels.

Jackim et al. (1977) found a biomagnification coefficient of 1,800 in the soft tissue of the mussel, Mytilus edulis, after a 14 day exposure to 0.005 ppm. The same organism displayed a concentration factor of 165 after a 5 day exposure to 0.70 ppm (George and Coombs, 1977). The shrimp, Crangon crangon, concentrated Cd 2,400 times in a 40 day exposure to 0.005 ppm (Dethlefsen, 1977).

Uptake of Cd is believed to occur both through the gills and through the food chain. However, there is little evidence for magnification through the trophic levels. Levels in predatory fish are not substantially higher than those in fish lower in the food chain. The liver and especially the kidneys in fish are the primary organs where Cd is concentrated.

IV. MONITORING

A. Analysis

Flameless atomic absorption spectrometry, with a detection limit of 1.0 ng, is a sensitive, inexpensive technique for measuring Cd (Blood and Grant, 1975). Koizumi and Yasuda (1976) report a detection limit of 0.1 pg for Zeeman atomic absorption spectrometry.

B. Amount in the Mediterranean

Cd concentrations in some sea water samples from the

Mediterranean are as follows: Alexandria, 0.001 mg/l; Suez 0.0019 mg/l (Ibragim and Patin, 1976); Adriatic coast, 0.000031 mg/l; La Spezia, Italy, 0.000079 mg/l (Nürnberg et al., 1976); Ras Beirut, Lebanon, 0.02 mg/l (Shiber and Shatila, 1978).

Sediments are the ultimate sink for Cd in the sea. Some Mediterranean sediment concentrations are: 0.18 mg/kg in sediments from Nice, France (Vernet et al., 1977); Ligurian Sea samples contained 1.7 mg/kg dry weight (Renfro and Oregioni, 1974); and Haifa Bay sediments contained 0.7 mg/kg dry weight of Cd (Roth and Hornung, 1977).

Majori et al. (1978) found Cd concentrations in the anchovy, Engraulis encrasicolus, of 0.34 mg/kg wet weight. A crustacean, Squilla mantis, contained 0.65-0.54 mg/kg wet weight of Cd. These samples were taken from the N. Adriatic. Mytilus galloprovincialis, a mussel, contained 1.9 mg/kg dry weight in samples from the N.W. Mediterranean (Fowler and Oregioni, 1976). Marine algae from Haifa Bay, Israel, contained 2.1 mg/kg dry weight of Cd (Roth and Hornung, 1977).

C. Amount Entering the Mediterranean

No information on total Cd reaching the Mediterranean was found in the literature reviewed. Worldwide inputs by man into coastal waters are estimated at 3540 tons per year (CEC, 1976).

D. Regulations

France, Italy, Tunisia, Turkey, and Yugoslavia are among the Mediterranean countries with legislation for the control of Cd (CEC, 1976; Kratel, unpublished; IDHL, 1978; WHO/UNEP, 1976). WHO/FAO (1972) has proposed a provisional maximum tolerable weekly intake of 400-500 ug Cd per individual.

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

The concentrations of Cd required to produce toxic effects in a wide range of marine organisms are generally much higher than would normally occur in sea water. However, sublethal effects have been noted in the literature at Cd concentrations which may occur in the Mediterranean. Daphnia magna showed a 50% reduction in reproduction at 0.7 ug/l of Cd (EPA, 1976).

Eisler and Hennekey (1977) have established the 96 hour LC50 for Cd in the softshell clam, Mya arenaria (2.5 mg/l) and for the mummichog, Fundulus heteroclitus (22.0 mg/l). A 24 hour delay in formation of brood pouches and decreased fecundity were found in the shrimp, Mysidopsis bahia, in a 23 day (life cycle) exposure to 0.0064 mg/l of Cd (Nimmo et al., 1978). A 20% decrease in photosynthesis was found for a natural phytoplankton community exposed to 0.01 mg/l of Cd (Ibragim and Patin, 1976).

B. Toxic Effects on Man and Other Mammals

Cd acts as a cumulative poison in man, i.e. body burden increases with age. The excretion of absorbed Cd is very slow, and it has a biological half-life in humans of 16-33 years. Food is the primary pathway for Cd uptake by man in normal situations, though heavy smoking may increase intake significantly. The kidneys and the liver together contain about half of the total Cd body burden (CEC, 1976).

Concern about possible effects on the general population exposed to low levels of Cd over long periods of time has been raised by the steadily increasing consumption of Cd, its release into the environment, and partly because of the outbreak of Itai-Itai disease in Japan, which has been attributed to high Cd levels in rice.

Nearly 100 deaths were caused by consumption of rice contaminated with Cd levels ten times greater than average concentrations in Japanese rice (CRC, 1976). Irrigation water polluted with Cd containing effluents from a zinc mining operation allowed uptake by the rice plants.

CEC (1977) reports an oral LD50 in the rat of 88 mg/kg bw/day. The oral LD50 for the guinea pig occurred at 63 mg/kg bw/day. Adrenal gland effects, anemia, testicular and ovarian necrosis and reduced hemoglobin levels have been reported in laboratory studies on the effect of Cd (NIOSH, 1978). IARC (1973, 1976) lists several studies indicating the carcinogenic potential of Cd. Shattering of chromosomes and multiple chromatid aberrations were found in a cultured hamster ovary cells exposed to 0.224 ppm CdCl₂ (Deaven and Campbell, 1976). Numerous studies have implicated Cd in reproductive effects and teratogenicity (NIOSH, 1976).

Total Production

Cadmium (generic)		Chemical Group: Cadmium		
year	area	amount	trend	citation (as reported in)
1950-1959	World	74 999 tonnes	-	CEC, 1977,
1960-1969	World	124 207 "	increasing	p.20
1970	World	16 500 tonnes	-	IARC, 1976,
1973	World	17 000 "		p.44
1950-1959	France	1 401 tonnes	-	CEC, 1977,
1960-1969	France	3 933 "		p.21
1970	France	528 "		
1971	France	579 "		
1972	France	572 "		
1973	France	606 "		
1950-1959	Italy	131 "		
1960-1969	Italy	697 "		
1970	Italy	426 "		
1971	Italy	350 "		
1972	Italy	416 "		
1973	Italy	397 "		
1950-1959	Spain	72 "		
1959-1960	Spain	556 "		
1950-1959	Yugoslavia	84 "		
1960-1969	Yugoslavia	718 "		

Total Consumption

Cadmium (generic)		Chemical group: Cadmium		
year	area	amount	trend	citation (as reported in)
1969	France	1 190 tonnes	-	CEC, 1977, p.22
1970	France	1 028 "		
1971	France	969 "		
1972	France	1 000 "		
1973	France	1 150 "		
1969	Italy	350 "		
1970	Italy	370 "		
1971	Italy	320 "		
1972	Italy	350 "		
1973	Italy	430 "		

Production Processes

Cadmium chloride

Chemical Group: Cadmium

process (major or minor by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
Reaction of cadmium metal with hydrochloric acid	-	-	IARC,1976, p.45

Use

Cadmium chloride		Chemical Group: Cadmium		
use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
pesticide	-	-	-	IARC, 1976, p.46
photographic materials				
phosphors				
non-pasture turf fungicides				
dyeing				
calico-printing of textiles				
thermoionic emission coatings for electronic vacuum tubes				
lubricant ingredient				
special mirrors				

Pathways Leading to Marine Pollution

Cadmium		Chemical Group: Cadmium	
Pathway	Quantity	Area	Citation
River outfall	1.2 x 10 ⁵ kg/yr	Gulf of St. Lawrence, Canada	Bewers, J.M. and Yeats, P.A., 1977
Storm runoff	1 metric ton/yr	Southern California Bight	Young, D.R. et al., 1977
Cooling waters	0.3 metric tons/yr	" (from 8 local generating stations)	Young, D.R. et al., 1977
Municipal waste dischargers (1974/1976)	55.4/45.0 metric tons/yr	Southern California coastal waters	Schafer, H.A., 1977
Rainfall	230 tons/yr	North Sea	Joint Group of Experts on the Scientific Aspects of Marine Pollution, 1976
Incineration of plastics, pigments and rubber goods	-	Ras Beirut, Lebanon	Shiber, J.G. and Shatila, T.A., 1978
Sewage from Beirut River	-	Ras Beirut, Lebanon	Shiber, J.G. and Shatila, T.A., 1978
Land drainage after pesticide spraying	-	Ras Beirut, Lebanon	Shiber, J.G. and Shatila, T.A., 1978

Transformation in the Marine Environment

Cadmium

Chemical group: Cadmium

Process	Medium	Parameters	Effect	Citation
Adsorption	clay suspensions	increased pH	decreased concentration of soluble Cd^{2+} ions	Farrah, H. and Pickering, W.F., 1977
Oxidation	reduced estuarine sediment, lab.	increased diss. O_2 , decreased pH, increased redox potential	increased soluble Cd present as hydrated divalent cations, soluble Cl^- and SO_4	Khalid, R.A. et al., 1978
Desorption	suspended solids mixed with sea water	increased salinity, increased pH, increased dilution ratio	Cd^{2+} ions released into water, undergo reactions producing:	Rohatgi, N. and Chen, K.Y., 1975
1) Soluble complex formation	suspended solids mixed with sea water	increased Cl^- ions	$CdOH^+$, $CdCl_2$, $CdCl^+$ and	
2) Adsorption onto hydrous oxides of Fe and Mn	suspended solids mixed with sea water	-	decreased free Cd^{2+} ions	

Transformation in the Marine Environment

Cadmium (page 2)

Chemical group: Cadmium

Process	Medium	Parameters	Effect	Citation
Desorption	Rhine estuary sediment	increased salinity	increased desorption - increased Cd in water	de Groot, A.J. et al., 1976
Leaching with acetic acid	Mediterranean sediment	decreased pH	100% desorption suggests all Cd in readily exchangeable form	Duursma, E.K., 1976
Oxidation	sediment	decreased pH	release of Cd into water. As oxidation proceeds CdCO ₃ becomes controlling solid	Lu, J.C.S. and Chen, K.Y., 1977
Chelation with NTA	Seawater in the laboratory	pH 8.0	50% remains as free Cd ²⁺ ions, the remainder is chelated forming CdNTA	Raspor, B. et al., 1977
Leaching with 1M acetic acid	Mediterranean sediment in the laboratory	pH decreases	100% Cd is desorbed from the sediment	Duursma, E.K., 1976

Behaviour of a Chemical Substance in Marine Organisms

Cadmium

Chemical Group: Cadmium

Organism	Exposure		Accumulation and Distribution				Loss	Metabolites		Citation
	Route	Concn. Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
Pleuronectes platessa (Plaice)	W	0.002 ppm	59 days	liver	-	115	-	-	-	Pentreath, R.J., 1977.
Anguilla (Eel)	W	0.13 mg/l	60 days	kidneys	20.1	123	-	-	-	Noel-Lambot, F. and Bouquegneau, J.M., 1977.
Mytilus edulis (Mussel)	W	0.005 ppm	14 days	soft tissue	-	1 800	-	-	-	Jackim, E. et al., 1977.
Mytilus edulis (Mussel)	W	0.70 ppm	5 days	"	-	165	-	-	-	George, S.G. and Coombs, T.L., 1977
Penaeus duorarum (Pink shrimp)	W	1.25 ppm	96 hrs.	exo- skele- ton	-	6.7	36	7 days	-	Nimmo, D.W.R. et al., 1977.

Behaviour of a Chemical Substance in Marine Organisms

Cadmium (page 2)

Chemical Group: Cadmium

Organism	Exposure			Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn.	Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
<i>Carcinus maenas</i> (Green crab)	W	-	6 days	whole body	-	7.4	-	-	-	-	Wright, D.A., 1977
<i>Penaeus duorarum</i> (Pink shrimp)	W	0.075 ppm	30 days	muscle	-	48	-	-	-	-	Nimmo, D.W.R. et al., 1977
<i>Crangon crangon</i> (Shrimp)	W	-	20 days	whole	-	260	0	7 days	-	-	Dethlefsen, V., 1977
<i>Homarus ameri- canus</i> (Lobster)	W	0.006 ppm	30 days	gills	-	566	-	-	-	-	Thurberg, F.P. et al., 1977
<i>Crangon crangon</i> (Shrimp)	W	0.005 ppm	40 days	whole	-	2,400	-	-	-	-	Dethlefsen, V., 1977
<i>Mytilus gallopr- ovincialis</i> (Mussel)	W	0.05 mg/l	4 days	soft tissue	-	53.2	67.7	27 days	-	-	Majori, L. and Petronio, F., 1973a
<i>Mytilus gallopr- ovincialis</i> (Mussel)	W	0.05 mg/l	4 days	-	-	54	63	26 days	-	-	Majori, L. and Petronio, F., 1973b

Behaviour of a Chemical Substance in Marine Organisms

Cadmium (page 3)

Chemical Group: Cadmium

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn.	Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity
Mya arenaria (Clam)	W	0.0275 mg/l	-	-	-	200	-	-	-	Majori, L. and Petronio, F., 1973 b
Meganyctiphanes norvegica (Euphausiid)	W+ F	5.5 uCi/l	15 days	whole	100	235	-	-	-	Benayoun, G. et al., 1974
Meganyctiphanes norvegica (Euphausiid)	W	5.5 uCi/l	15 days	whole	100	185	-	-	-	Benayoun, G. et al., 1974
Meganyctiphanes norvegica (Euphausiid)	W+ F	5.5 uCi/l	29 days	-	-	-	92	96 days	-	Benayoun, G. et al., 1974
Mytilus edulis (Mussel)	W	0.03- 0.05 mg/l	20 days	-	-	220	20	40 days	-	Calapaj, G. G., 1974

Behaviour of a Chemical Substance in Marine Organisms

Cadmium (page 4)

Chemical Group: Cadmium

Organism	Exposure		Accumulation and Distribution				Loss	Metabolites		Citation
	Route	Concn.	Time	Tissue/ Organ	%	Biomagnification Coefficient		%	Time	
Porphyra	W	0.02 ppm	24 hrs.	whole	-	1 933	-	-	-	Maeda, M. and Fujiyama, T., 1977
Fucus vesicu- losus	W	0.00081 mg/l	-	whole	-	13 000	-	-	-	Melhuus, A. et al., 1978

W - Water
F - Food

Behavior of the Substance in Man and Other Mammals

Cadmium chloride

Chemical Group: Cadmium

description of organism	route	exposure		duration of exposure	retention		clearance rate percent/time	metabolites		citation
		concentration			tissue/percent/time			name/amount/hazard	(as reported in)	
mouse (CBA)	intra- venous, sub cut.	-	-	-	-	-	-	cadmium-thionein causing greater kidney-damage, lethal at lower doses	Nordberg et al., 1975 (NIOSH, 1976 p.34)	
mouse	intra- perit.	17 uCi	single dose		-		50%/at least 100 days (10%/20 days)	-	Cotzias et al., 1961 (CRC, 1976, p.48)	
monkey (Saimiri scireus)	oral intub.	1.7, 0.17	single dose		whole body/2.7%/ 4 weeks whole body/2.45%/ 4.5 months		-	-	Nordberg et al., 1971 (CRC, 1976, p.48)	

Concentrations in Water, Sediments and Biota

Cadmium		Chemical Group: Cadmium			
Description of Sample Material	Origin	Analytical Method	Level(s)	Date(s)	Citation
Water	Sor fjorden, west coast of Norway	AAS	0.0022 mg/l	1972/ 1975	Melhuus, A et al., 1978
Seawater	Mediterranean (5m)	ASV	0.0028 mg/l	1975	Benon, P. et al., 1978
Water	Baltic	AAS	0.12 mg/l	1975	Kremling, K. and Petersen, H., 1978
Sediment (top 4 cm)	Dump site, Long Island Sound, USA	-	less than 1.0 mg/kg dry wt.	1971	Greig, R.A. et al., 1977
Sediment and coal ash (top 1 cm)	Baltic Sea	AAS	1.87 mg/kg dry wt.	1971	Erlenkeuser, H. et al., 1974
Sediment	Palos Verdes Peninsula, USA	AAS	80 mg/kg dry wt.	1975	Hershelman, G.P. et al., 1977
Crassostrea virginica (Commercial oyster)	Mississippi Estuary, USA	AAS	0.94/0.16 mg/kg wet wt.	1973/ 1975	Harvey, E.J. and Knight, L.A. Jr., 1978
Engraulis encrasicolus (Anchovy)	Northern Adriatic Sea	-	0.34 mg/ kg wet wt.	1974- 1975	Majori, L. et al., 1978
Squilla mantis (Crustacean)	"	-	0.65/0.54 mg/kg wet wt.	winter 1974-75/ 1975-76	Majori, L. et al., 1978

Concentrations in Water, and Sediments and Biota

Cadmium (page 2)

Chemical Group: Cadmium

<u>Description of Sample</u>		<u>Analytical</u> <u>Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material</u>	<u>Origin</u>				
Cancer irroratus (Shore crab) -flesh	Long Island Sound, USA	AAS	1.0 mg/kg wet wt.	1971- 1972	Greig, R.A. et al., 1977
Pitar morruana (Widgeon clam) -soft parts	Rhode Island USA	AAS	3.33 mg/ kg dry wt.	1973	Eisler, R. et al., 1978
Ascophyllum nodosum	Sor fjorden, west coast of Norway	AAS	15 mg/kg dry wt.	1974	Melhuus, A. et al., 1978
Seawater	Ras Beirut, Lebanon	AAS	0.02mg/l	1977	Shiber, J.G. and Shatila, T.A., 1978
Seawater	Haifa Bay, Israel	AAS	0.0007mg/l	1974	Roth, I. and Hornung, H., 1977
Seawater	Alexandria	AAS	0.001mg/l	-	Ibragim, A.M. and Patin, S.A., 1976
Seawater	Suez	AAS	0.0019mg/l	-	Ibragim, A.M. and Patin, S.A., 1976

Concentrations in Water, and Sediments and Biota

Cadmium (page 3)

Chemical Group: Cadmium

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Seawater (5-50m)	North west Mediterranean	ASV	0.00022 mg/l	1974	Fukai, R. and Huynh-Ngoc, L., 1976
Seawater (500m)	North west Mediterranean	ASV	0.00006-0.0003mg/l	1974	Fukai, R. and Huynh-Ngoc, L., 1976
Seawater	Jade Bay	DPASV	0.000021 mg/l	1975	Nurnberg, H.W. et al., 1976
Seawater	Adriatic Coast	DPASV	0.000031 mg/l	1975	Nurnberg, H.W. et al., 1976
Seawater	La Spezia, Italy	DPASV	0.000079 mg/l	1975	Nurnberg, H.W. et al., 1976
Sediment	Nice, France	-	0.18mg/kg	1976-77	Vernet, J.P. et al., 1977
Sediment	Ligurian Sea	AAS	1.7mg/kg dry wt.	1973	Renfro, W.C. and Oregioni, B., 1974
Sediment	Haifa Bay, Israel	AAS	0.7mg/kg dry wt.	1974	Roth, I. and Hornung, H., 1977
Sargus annularis - liver	Aegean Sea	RS	0.3mg/kg dry wt.	1973-74	Grimanis, A.P. et al., 1978
Gobius niger (Goby) - liver	Keratsini Bay, Aegean	RS	0.91mg/kg dry wt.	1973-74	Grimanis, A.P. et al., 1978

Concentrations in Water, and Sediments and Biota

Cadmium (page 4)

Chemical Group: Cadmium

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Commercial fish	Haifa Bay, Israel	AAS	0.33mg/kg dry wt.	1974	Roth, I. and Hornung, H., 1977
Delphinus delphis (Common dolphin) - muscle	Corsica	AAS	0.11mg/kg wet wt.	1973	Viale, D., 1975
Mullus barbatus (Mullet) - muscle	Marseilles, France	-	0.59mg/kg	1977	GFCM, 1978
Parapenaeus longirostris	Saronikos Gulf	NAA	0.05mg/kg wet wt.	1976	GFCM, 1978
Mullus surmuletus (Mullet) - muscle	Ankara, Turkey	-	0.135mg/kg wet wt.	1977	GFCM, 1978
Patella coerula (Mussel)	Ras Beirut, Lebanon	AAS	2.5mg/kg dry wt.	1977	Shiber, J.G. and Shatila, T.A., 1978
Mytilus galloprovincialis (Mussel)	North west Mediterranean	AAS	1.9mg/kg dry wt.	1974	Fowler, S.W. and Oregioni, B., 1976
Mytilus galloprovincialis (Mussel)	La Spezia, Italy	AAS	6.8mg/kg dry wt.	1975	Capelli, R et al., 1978
Mytilus galloprovincialis (Mussel)	Sicily	AAS	0.28mg/kg dry wt.	1976	Castagna, A. and Sarro, F., 1977

Concentrations in Water, and Sediments and Biota

Cadmium (page 5)

Chemical Group: Cadmium

<u>Description of Sample</u>		<u>Analytical Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material</u>	<u>Origin</u>				
Sepia officinalis (Squid)	La Spezia, Italy	-	0.5mg/kg	1974	Ciusa, W. et al., 1974
Tapes decussatus (Shellfish) - blood	Izmir Bay, Turkey	AAS	12.63mg/kg dry wt.	1976	Geldiay, R. and Uysal, H., 1976
Marine algae	Haifa Bay, Israel	AAS	2.1mg/kg dry wt.	1974	Roth, I. and Hornung, H., 1977
Microplankton	Hyeres, North west Mediterranean	AAS	2.8mg/kg dry wt.	1974	Fowler, S.W. et al., 1976
Acartia clausi (Zooplankton)	Upper Saronikos Gulf	NAA	0.52mg/kg dry wt.	1974	Zafiropoulos, D. and Grimanis, A.P., 1977
Dunlayella (Algae)	Ligurian Coast	DPASV	0.15mg/kg	1975	Nurnberg, H.W., et al., 1976
Blue algae	Ligurian Coast	DPASV	2.2mg/kg	1975	Nurnberg, H.W., et al., 1976

AAS - Atomic absorption spectroscopy
 ASV - Anodic stripping voltametry
 DPASV - Differential pulse stripping voltametry
 RS - Radiochemical separation
 NAA - Neutron activation analysis

Array of Toxic Effects on Man and Other Mammals

Cadmium chloride

Chemical Group: Cadmium

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
88	-	oral	rat	LD ₅₀	CEC, 1977, p.72
63	-	oral	guinea pig	LD ₅₀	CEC, 1977, p.72
33 (300 ppm)	70 days	oral (water)	rabbit	immuno- suppression	Koller, 1973 (CEC, 1977, p.112)
16 (300 ppm Cd)	54 weeks	oral (diet)	rabbit	anemia, proteinurea, glycosurea, appetite- and weight loss	Nomiyama et al., 1975 (NIOSH, 1976, p.37)
9	single dose	sub cut.	rabbit	testicular- cell destruction (5-21 days), hyperanemia, kidney, spleen and liver effects	Cameron and Foster, 1963 (IARC, 1976, p.58)
6.25 (50 ppm)	3 months	oral (water)	rat (34 days old)	reduced hemoglobin level	Decker et al., 1958 (NIOSH, 1976, p.26)
4.1 (2.5 mg Cd/ kg)	single dose	sub cut.	rat	ganglionic lesions	Gabbiani, 1966 (CRC, 1976, p.128)

Array of Toxic Effects on Man and Other Mammals

Cadmium chloride (page 2)

Chemical Group: Cadmium

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
3.7 (0.02 mmol/ kg)	single dose	sub cut.	rat (female)	ovarian necrosis	Parizek et al., 1968 (NIOSH, 1976, p.29)
2.0	7 days (1.0 mg/kg 2 x/day)	sub cut.	rat	pancreas effect	Merali and Singhal, 1975 (CEC, 1977, p.81)
1.4 (0.85 mg Cd/ kg)	single dose	sub cut.	rat (male)	testicular necrosis	Mason et al., 1964 (NIOSH, 1976, p.28)
1.0	45 days	intra- perit.	rat	adrenal gland effect	Singhal et al., 1976 (NIOSH, 1976, p.28)
0.94 (7.5 ug/g water)	1 year	oral (water)	rat (female)	kidney effect	Piscator and Larsson, 1972 (CRC, 1976, p.111)
0.82 (10 ppm Cd)	3 weeks	oral (diet)	rat	bone lesions	Yoshiki et al., 1975 (CEC, 1977, p.108)
0.75 (15 ppm)	6 months	oral (diet)	rat (3 weeks old)	bleached incisor teeth, anemia	Fitzhugh and Meiller, 1941 (NIOSH, 1976, p.26)

Array of Toxic Effects on Man and Other Mammals

Cadmium chloride (page 3)

Chemical Group: Cadmium

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
0.63 (5 ug/g water)	1 year	oral (water)	rat (Long Evans)	hypertension renal, arterial and arteriolar lesions	Kanisawa and Schroeder, 1969 (CRC, 1976, p.117)
0.25	11 weeks (5 x/week)	sub cut.	rabbit	renal lesions	Axelsson et al., 1968 (IARC, 1973, p.89)
0.2 (1 ug Cd/g water)	335 days	oral (water)	rat	liver effect	Sporn et al., 1970 (CRC, 1976, p.123)

Array of Toxic Effects on Man and Other Mammals

Cadmium chloride (page 4)

Chemical Group: Cadmium

concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation) (time)	citation (as reported in)
522 (320 mg Cd/ m ³)	30 minutes	inhal.	dog	LD ₉₀	Harrison et al., 1947 (CRC, 1976, p.93)
522 (0.32 mg Cd/l)	30 minutes	inhal.	dog	LC ₅₀	Harrison et al., 1947 (IARC, 1976, p.58)
420	30 minutes	inhal.	dog	LC ₉₀	NIOSH, 1978, p.6
10	2 hours	inhal.	rat	biochemical damage of the lungs	Hayes et al., 1976 (CEC, 1977, p.75)
8	30 minutes	inhal.	dog	LC ₉₀	CEC, 1977, p.75
0.2	66 days	inhal.	rat	reduced body weight, increased lung weight, emphysema, effects on alveolar macrophages, death	Baumert et al., 1976 (CEC, 1977, p.86)
0.2	7 days	inhal.	rat	increased lung weight, effects on alveolar macrophages	Baumert et al., 1976 (CEC, 1977, p.86)
0.05	7 days	inhal.	rat	effects on alveolar macrophages	Baumert et al., 1976 (CEC, 1977, p.86)

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Cadmium chloride

Chemical Group: Cadmium

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse (Charles Rivers)	sub cut.	5.5	single dose	interstitial-cell tumours (14 months)	Gunn et al., 1963 (IARC, 1976, p.55)
rat (Wistar)	sub cut.	3.7	single dose	interstitial-cell tumours (11 months) local fibro-sarcomas	Lucis et al., 1972 (IARC, 1976, p.56)
rat (Wistar)	sub cut.	0.85 (0.17 mg)	4 x	injection site sarcomas (12-16 months)	Gunn et al., 1967 (IARC, 1972, p.85)

A comprehensive evaluation of the known studies designed to assess the possible carcinogenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"Single or repeated subcutaneous injections of several inorganic cadmium compounds (cadmium chloride, sulphate, sulphide and oxide) result in the development of local sarcomas in rats. Local tumours were also produced in rats by intramuscular injection of cadmium powder and cadmium sulphide." (IARC, 1976, p. 64)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Cadmium chloride (page 2)

Chemical Group: Cadmium

MUTAGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse (male)	inter-perit.	7	-	no effect (modified dominant lethal assay)	Epstein et al., 1972 (NIOSH, 1976, p.32)

description of system	reported results	citation (as reported in)
cultured hamster ovary cells (0.224 ppm CdCl ₂)	multiple chromatid aberrations, shattering of chromosomes	Deaven and Campbell, 1976 (EPA/ORNL, 1978, p.152)
Drosophila melanogaster larvae (62 mg/l substrate)	no effect on chromosome breakage, induction of recessive lethals or chromosome repair mechanism	CRC, 1976, p.133

These studies, designed to evaluate the possible effects of this substance on gene mutation, chromosomal mutations, on DNA repair or recombination or on transformation, resulted in a report of the above effects, but no comprehensive evaluation of this information was found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Cadmium chloride (page 3)

Chemical Group: Cadmium

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
rat	Zn (II) Se (IV)	protective against injury in testes	Mason and Young, 1967 (NIOSH, 1976, p.29)
rat	ZnCl ₂ Zn(CH ₃ COO) ₂	lethality of injected CdCl ₂ reduced	Parizek et al., 1969a (NIOSH, 1976, p.35)
-	dietary zinc and copper	protective	NIOSH, 1976, p.36
rat	estrogen	reduced testicular damage	Gunn et al., 1965 (NIOSH, 1976, p.36)
mouse	cystein and other thiols	reduced testicular damage	Gunn et al., 1968 (NIOSH, 1976, p.36)
-	sodium selenite	blocking the uptake of cadmium into tissues	Parizek et al., 1969b (NIOSH, 1976, p.36)
hamster	sodium selenite	protective against teratogenic effects	Holmberg and Ferm, 1969 (NIOSH, 1976, p.36)

These studies, designed to evaluate the possible effects which could result from the combination of this substance with one or more other substances, resulted in reports of the above effects, but no comprehensive evaluation of this information was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Cadmium chloride (page 4)

Chemical Group: Cadmium

PRIMARY IRRITATION

Nothing found in the literature reviewed

REPRODUCTIVE EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	sub cut.	4	13th-19th day of gestation (daily)	embryo-lethality	Chernoff, 1972 (CEC, 1977, p.118)
rat (female)	sub cut.	3.7 (0.02 mmole/kg)	single dose	ovary hemorrhages and necrosis	Parizek et al., 1968 (NIOSH, 1976, p.29)
rat (male)	sub cut.	1.4 (0.85 mg Cd/kg)	single dose	testicular necrosis	Mason et al., 1964 (NIOSH, 1976, p.28)
mouse (CBA)	sub cut.	0.4	6 months (5 x/week)	testicular changes	Nordberg, 1975 (CEC, 1977, p.117)
mouse	sub cut.	0.33	7th day of gestation	embryo-lethality	Ishizu et al., 1973 (CEC, 1977, p.118)

These studies, designed to evaluate the possible effects of the substance on reproduction, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Cadmium chloride (page 5)

Chemical Group: Cadmium

TERATOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	oral	20	6th-19th day of gestation (daily)	teratogenic effects	Scharpf et al., 1972 (IARC, 1976, p.61)
rat (CD)	sub cut.	4	4x, starting at the 13th-16th day of gestation (daily)	micrognathia, cleft palate, club foot, small lungs	Chernoff, 1973, (NIOSH, 1976, p.30)
rat (Wistar)	intra-perit.	2.9	single dose on the 9th-11th day of gestation	anomalies of eyes and hydrocephaly and other malformations	Barr, 1973 (NIOSH, 1976, p.30)
mouse	sub cut.	0.33	7th day of gestation	exencephaly, opened eyes and other malformations	Ishizu et al., 1973 (NIOSH, 1976, p.30)

A comprehensive evaluation of the known studies designed to assess the possible teratogenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"There is reason for concern about teratogenic and carcinogenic effects. Experimental evidence of teratogenic effects of cadmium was developed in rodents given high doses of cadmium compounds." (NIOSH, 1976, p. 50)

Toxic or other Effects on Marine Organisms and Ecosystems

Cadmium		Chemical Group: Cadmium					
System	Organism	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
	Ecosystem						
	Non-living						
mg/L							
	<i>Mya arenaria</i> (Softshell clam)	Adult	2.5	96 hrs.	LC50	96 hrs.	Eisler, R. and Hennekey, R.J., 1977
	<i>Paragrapsus gaimardii</i> (Estuarine crab)	Adult	28.0	96 hrs.	LC50	96 hrs.	Sullivan, J.K., 1977
	<i>Fundulus heteroclitus</i> (Mummichog fish)	Adult	22.0	96 hrs.	LC50	96 hrs.	Eisler, R. and Hennekey, R.J., 1977
	<i>Morone saxatilis</i> (Striped bass)	Juvenile	0.0025	30 days	25% dec. gill tissue oxygen consumption.	30 days	Dawson, M.A., et al., 1977

Toxic or other Effects on Marine Organisms and Ecosystems

Cadmium (page 2)

Chemical Group: Cadmium

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Mysidopsis bahia (Opossum shrimp)	24 hrs. juvenile through life cycle to adult	0.0064	23 day (life cycle)	24 hr delay in formation of brood pouches. Dec. fecundity.	13 days	Nimmo, D.R. et al., 1978.
Pseudopleuronectes americanus (Winter flounder)	Adult	0.01	60 days	Inc. biosyn- thesis of an- hydrase and leucine amino- peptidase	60 days	Gould, E., 1977
Mysidopsis bahia (Opossum shrimp)	24 hrs. juvenile through life cycle to adult	0.0106	23 day (life cycle)	72 hr delay in release of brood.	20 days	Nimmo, D.R. et al., 1978.

Toxic or other Effects on Marine Organisms and Ecosystems

Cadmium (page 3)

Chemical Group: Cadmium

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Skeletonema costatum (Diatom)	-	0.025	2 days	Inc. division rate.	2 days	Berland, B.R. et al., 1977
Palaemonetes vulgaris (Grass shrimp)	-	0.075	10 days	Melanisation and necrosis of branchial lamellae. Infection by Fusarium sp.	10 days	Nimmo, D.W.R. et al., 1977
Carcinus maenas (Green crab)	-	0.5	48 hrs.	Inc. blood-serum osmolality	48 hrs.	Calabrese, A. et al., 1977
Nassarius obsoletus (Mud snail)	Adult	0.5	72 hrs.	Inc. oxygen consumption	72 hrs.	Calabrese, A. et al., 1977

Toxic or other Effects on Marine Organisms and Ecosystems

Cadmium (page 4)

Chemical Group: Cadmium

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Fundulus hetero- clitus (Mummichog fish)	embryo stage 14	10.0	-	32% malforma- tions	-	Weis, J.S. and Weis, P., 1977
Homarus americanus (Lobster)	egg	10.0	3 weeks	Rel. activity of mitochon- drial NAD-and NADP- malic enzymes and cytosol NADP- malic enzymes reduced.	3 weeks	Mounib, M.S. and Eisan, J.S., 1977
Tautoglabrus adspersus (Cunner)	Adult	24.0	96 hrs.	Depressed liver trans- aminase activ- ity. Dec. li- gand sensitiv- ity.	96 hrs.	Calabrese, A. et al., 1977

Toxic or other Effects on Marine Organisms and Ecosystems

Cadmium (page 5)

Chemical Group: Cadmium

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Nannoplankton	-	25.0	-	33% inhibition of photosynthesis.	-	Mills, A.L. and Colwell, R.R., 1977
Natural phytoplankton community	-	0.01	Short term	20% decrease in photosynthesis	-	Ibragim, A.M. and Patin, S.A., 1976
Skeletonema costatum (Diatom)	-	0.025-0.1	7 days	Initial stimulation followed by inhibition of growth	7 days	Berland, B.R. et al., 1977
Heterothrix sp. (Unicellular algae)	-	0.25 (Minimum)	17 days	Growth inhibition	17 days	Berland, B.R. et al., 1976
Penaeus kerathurus (Shrimp)	Nauplia	0.77	24 hrs.	LC50	24 hrs.	GFCM, 1978
Sparus aurata	Larva	2.8	24 hrs.	LC50	24 hrs.	GFCM, 1978

Toxic or other Effects on Marine Organisms and Ecosystems

Cadmium (page 6)

Chemical Group: Cadmium

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Sepia officinalis (Squid)	Larva	6-8	24 hrs.	LC50	24 hrs.	GFCM, 1978
Heterothrix sp. (Unicellular algae)	-	1.0 (Minimum)	17 days	Mortality	17 days	Berland, B.R. et al. 1976
Liza aurata	Juvenile	18	96 hrs.	45% mortality	96 hrs.	GFCM, 1978
Cylindrotheca closterium (Unicellular algae)	-	0.05 (Minimum)	17 days	Mortality	17 days	Berland, B.R. et al., 1976
Asterionella japonica (Diatom)	-	0.001 (Threshold)	-	Growth inhibition	-	Pesando, D. and Aubert, M., 1975
Cylindrotheca closterium (Unicellular algae)	-	0.005 (Minimum)	17 days	Growth inhibition	17 days	Berland, B.R. et al., 1976

Analysis

Cadmium ion		Chemical Group: Cadmium
analytical method(s) (detection limits)	limitations/benefits	citation (as reported in)
Flameless atomic absorption spectrometry (1ng)	precision in preparation affects results, reproductibility may be difficult/inexpensive, higher sensitivity than Flame - AAS	Blood and Grant, 1975
Zeeman atomic absorption spectrometry (0.1pg)	more sophisticated apparatus, not always available in laboratories/ high sensitivity, no chemical preparation of sample necessary, very fast, selective apparatus can be assembled using standard equipment	Koizumi and Yasuda, 1976

Legislation for the Protection of Man
and the Marine Environment

Cadmium (generic)

Chemical group: Cadmium

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in food	FAO/WHO	proposed provisional maximum tolerable weekly intake	400-500 ug per individual	WHO/FAO, 1972, p.57
control of substances in effluent	France	emission norm for surface treating industries	3 mg/l	CEC, 1976, p.13-16
control of substances in effluent	Italy	emission norm for discharge into surface waters and public sewers	0.02 mg/l as Cd	CEC, 1976, p.13-22
control of substances in water	Italy	regulation con- cerning acceptable limits for dis- charges into sur- face water and public sewers	0.02mg/l	IDHL, 1977, p.630
control of substances in effluents	Spain	regulation con- cerning discharges from submarine outfalls	0.5mg/l in not more than 50% of samples 1.0mg/l in not more than 10% of samples	IDHL, 1978, p.193
control of substances in effluents	Tunisia	proposed recomm- ended values for discharges into surface waters and public sewers	0.1mg/l as Cd (1. spectro- photometry with dithizone emission spectrography 2. atomic absorption spectro- photometry)	Kratel (unpublished)

Legislation for the Protection of Man
and the Marine Environment

Cadmium (generic) (page 2)

Chemical group: Cadmium

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in effluents	Turkey	pollution of dis- charges when the concentration exceeds the tolerance level	0.01mg/l as cadmium ion	WHO/UNEP, 1976, p.Turkey-4
control of substances in effluents	Yugoslavia	maximum permissible concentrations of dangerous sub- stances discharged into water used or intended for use as drinking water, for produc- tion of foodstuffs, fish breeding, watering of animals or public bathing	0.01mg/l 0.005mg/l for water used for breeding of <u>Salmonidae</u>	WHO/UNEP, 1976, p.Yugo- slavia-2
control of substances in water	Yugoslavia	maximum permissible concentrations of dangerous sub- stances in inter- republic water- courses	0.005mg/l in in class I and II waters ^a 0.01mg/l in class III and class IV waters ^b	IDHL, 1978 (awaiting publication)

^a Class I: waters which, in their natural state, where necessary after disinfection, may be used for drinking purposes and in the food industry and, in the case of surface waters, for breeding Salmonidae. Class II: waters which, in their natural state, may be used for bathing and recreation, water sports, breeding of Cyprinidae, or which, after treatment, may be used for drinking purposes and in the food industry.

^b Class III: waters which may be used for irrigation and, after treatment, in industry other than the food industry. Class IV: waters which may be used for other purposes only after treatment.

Cadmium

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MEDITERRANEAN DATA PROFILE

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^a Nothing found in the literature reviewed

OUTLINE - GENERAL SUMMARY FOR PETROLEUM HYDROCARBON

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I. INTRODUCTION

Land-based discharge is the largest source of oil pollution in the Mediterranean Sea. Though it is difficult to identify or quantify the various components making up the general class termed "petroleum hydrocarbons" (PHC), oils derived from land based sources will be treated as lubricating oils in this summary whenever the data permits. Most of these discharged lubricating oils have been used in automotive or industrial applications before finding their way to the ocean via river run off or direct discharge from coastal regions. The lubricating oils represent a very diverse group of petroleum products, in terms of standards and formulations, depending on use. They are mixtures of straight and branched chain paraffinics, naphthenics, aromatic and polycyclic aromatic hydrocarbons, where the number of carbon atoms per molecule is C_{17} (FIRL, 1976). In addition to the hydrocarbon content, most lubricating oils consist of up to 30% of their volume as additives, which may affect their persistence and toxicity in the marine environment.

Estimates of 0.5 to 1 million tonnes of oil entering the Mediterranean per year make it the most polluted sea in the world for which data is available (LeLourd, 1977). The closed nature of the Mediterranean basin is such that oil discharged here has little chance of escaping; accumulation will occur until it is degraded. Ecologically sensitive coastal regions will suffer the most from land based discharges, an important economic consideration in view of the high biologic productivity of these areas, as well as aesthetic factors which draw over 70 million tourists to the Mediterranean every year.

II. OCCURRENCE

A. Production

The literature reviewed revealed a paucity of monitoring data for lubricating oil production in Mediterranean countries. Figures were available for only two countries: the total supply of lubricating oils in 1975 for France was 1268×10^3 tonnes; for Italy, 815×10^3 tonnes (CEC, 1976). The significance of these figures is difficult to ascertain in terms of eventual pathways to the Mediterranean.

Oil production (generic) by Mediterranean countries in 1975 (with amounts assumed to be given in barrels per day) were as follows: Algeria, 935,000; Egypt, 225,000; France, 20,000; Israel, 185,000; Italy, 20,000; Libya, 1,400,000; Morocco, 700; Spain, 38,000; Syria, 175,000; Tunisia, 95,000; Turkey, 60,000; and Yugoslavia, 70,000 (UNEP, 1977).

Lubricating oils are produced by a process of atmospheric distillation of crude oil, followed by vacuum distillation (CEC, 1976).

B. Use

Lubricating oils can be divided into three major areas of use :

1. automotive lubricants, including crankcase oils and transmission, axle, bearing and chassis lubricants;

2. industrial lubricants are used in machine and engine oils, steam engine (cylinder) oils, textile machinery oils, steam turbine oils, refrigerating machine oils, gear oils and industrial greases;
3. oils in non-lubricating applications find many uses; for example, in paint and putty oils, cutting, transformer, heat transfer and rust preventative oils, etc. (FIRL, 1976).

CEC (1976) reports that the consumption of lubricating oils in 1975 by France was 1,268,000 tonnes; Italy consumed 815,000 tonnes.

III. OIL IN THE ENVIRONMENT

A. Sources

I. Natural

Though world-wide inputs of oil from natural seeps are very difficult to estimate, it is generally believed that about 0.6×10^6 tonnes per year are derived from this source, or 10% of total oil input (UNEP, 1977).

2. Anthropogenic

Lubricating oils are refined from crude oil through a distillation process, which may result in losses of up to 2% of the total processed. Using up to 11.78 barrels of raw water for each barrel of crude oil processed, refineries producing lube oils also discharge the highest concentration of oils in waste waters. A refinery in Sweden reports oil concentration in waste waters to range from

1-29 mg/l, but this is probably an exceptionally low figure (CEC, 1976). Goals for oil levels after treatment by an oily-water gravity separator are set at 150 mg/l, based primarily on the economics of waste water treatment (CEC, 1976). Other abatement methods include chemical precipitation, activated sludge treatment, flotation, filtration, adsorption, etc. Phenols, sulfides, metals, suspended solids, BOD, and COD are also contained in refinery effluents.

An estimated 26% of the world-wide oil input to the marine environment is carried by rivers. Industries located on inland waterways may discharge waste waters containing 20-5000 mg/l of oil, depending on the industry, production methods, and inplant control measures (CEC, 1976). The total waste water flow is a necessary criteria for determining a plant's impact due to effluents produced, as well as external control measures used. The PHC content may stem largely from lubricating oils, which are purposely wasted after use due to the content of metal fines, dust and grease, and due to the breakdown of the oil itself or its additives. Non-coastal municipal wastes will also enter the receiving waters and eventually reach the Mediterranean.

It has been estimated that per capita contribution of PHC to municipal sewage is 8 grams per day in coastal areas (NAS, 1975). Half of this amount is due to a wide variety of industrial wastes that are discharged into the sewer systems, while the other half results from municipal wastewaters (including gas stations, garages, commercial operations, etc.).

The concentrated populations in coastal regions of the Mediterranean, as well as the large number of tourists that visit the area every year, make municipal discharges of oils an important source of pollution. 10% of the total oil input into the world's oceans is derived from coastal industry (other than refineries) and municipal discharge (UNEP, 1977).

The considerable quantities of PHC deposited in urban areas through the operation of automobiles, oil heating systems, fallout, etc., are eventually washed into storm drains by rainfall and will enter the waterways. Oil pollution from this source is thought to account for 5% of the total world input or 0.3×10^6 million tonnes per year (UNEP, 1977). This estimate is based on a percentage of industrial and municipal wastes, and assumes that 75% of oil and grease runoff from urban areas is PHC (NAS, 1975).

PHC entering the atmosphere through combustion of fossil fuels (e.g. gasoline, fuel oils) adds another 0.6×10^6 tonnes per year, or 10% of the oil entering the world's oceans (UNEP, 1977).

Accidental spills, blowouts and leakage that occur in offshore drilling processes account for 0.08×10^6 tonnes per year, or 1% of the world total (UNEP, 1977). Increased production of oil in the Mediterranean may lead to significant increases of offshore drilling losses.

Bilge discharges, terminal operations, dry docking and accidents which occur during transportation of oil by sea account for losses of $2,133 \times 10^6$ tonnes per year of oil, or 35% of total discharges (UNEP,

1977). Though this is the largest single source of oil entering the marine environment, transportation discharges will not be elaborated on in this summary.

B. Transformation

1. Abiotic

Crude oils and refined petroleum products show a great deal of variation in chemical composition, which is important in determining their fate in the marine environment. The number of carbon atoms per molecule in the different fractions which constitute a petroleum product is especially important with regard to physical and chemical transformations in the ocean. Environmental factors also play a large role in determining the fate of oils at sea. Since accidental spills account for only 3-4% of the total addition of oil to the ocean each year, the effects of spreading via slicks will be omitted here. A great deal of attention has been focused on the effects of accidental spills recently, and most of the literature deals with the fate of petroleum in this form. The fate of oil entering the Mediterranean through chronic discharge will be emphasized whenever the data permits.

Transfer of oil from the ocean to the atmosphere can occur through evaporation or by direct exchange through wave produced spray or bubbles. Direct exchange is considered to be only temporary, since most of the oil re-enters the ocean after being transferred a short distance in the air.

There is some evidence for surface enrichment by PHC, which may be solubilized by naturally occurring surfactants that are concentrated in the sea surface microlayer (e.g. alcohol, fatty acids). This does not seem to be a universal process in open ocean waters, but some hydrocarbons may be made available to the atmosphere by this process, as well as by the well known slicks which form following a spill. Light hydrocarbons are most easily volatilisised (C_{15}), and molecules of over C_{25} will be affected very little by evaporation.

Solution is a process which competes with evaporation for the light hydrocarbons, though it is not as effective. Polar products of oxidation are also considerably more water soluble than the original PHC, and will enter the water column readily. The effects of solution are completely different than evaporation - oil entering the water column is available for uptake by marine organisms, while evaporated oil is considered lost to the aquatic environment. Equally important, sea water extracts of solubles from several oils have shown significant toxicity to some marine organisms (FAO, 1977).

Due to the low solubility of most petroleum products, emulsification is an important mode of dispersion in water. Oil-in-water emulsions consisting of particles ranging from 5 μ m to several millimeters have been found up to 250 km from their source (NAS, 1975). These particles are generated by stresses at the sea surface (e.g. waves, agitation), and eventually are dissolved in the water column, are adsorbed on particulate matter to be deposited in sediments, or are biodegraded.

Less important toxicologically, water-in-oil emulsions are believed to be a source of beach tar and pelagic tar lumps.

Photochemical oxidation of hydrocarbons is dependent on their chemical composition, as well as temperature and sunlight. Sulphur compounds are likely to inhibit oxidation, while some metals act as catalysts. Products of "auto-oxidation" are more soluble than the original compounds, and become dispersed in the water column.

Sedimentation occurs when the specific gravity of the oil exceeds that of sea water (1.025). The evaporation and dissolution of lighter hydrocarbons may lead to the formation of dense particles which sink; such particles have been recovered in the top several hundred metres (NAS, 1975). Formation and agglutination of dispersed particles on suspended sediments may be particularly important near estuaries. The availability of dense particulate matter to serve as nuclei may be important in sedimentation of oil spread on the surface. Oils incorporated into sediments may remain unchanged and toxic for long periods, due to low rates of bacterial degradation. This persistence may lead to long term effects on benthic communities or to the demise of sensitive species (EPA, 1976).

2. Biotic

Microbial degradation of PHC in marine systems is dependent on a broad range of environmental factors, which influence both the state of the oil and the populations of micro-organisms.

Growth and metabolism of microbial populations depend on such varied parameters as temperature, oxygen availability, sunlight, nutrient concentrations, pH, salinity, etc. Factors determining whether oils will be attacked include availability of alternative carbon sources, whether there is sufficient hydrocarbon substrate for a colony to develop on, and the presence of microbial predators. The state the oil is in (e.g. emulsified, in solution, etc.) depends on its chemical composition as well as environmental factors.

Biodegradation is a complex, multi-variable system, making exact predictions on rates of decomposition impossible. It is believed that biological oxidation rates in deep ocean water and sediments are very slow, due to low temperatures, oxygen deficiencies, lack of light and sparse populations of fungi and yeast. Complete degradation of petroleum by micro-organisms yields CO_2 , water, sulphates and nitrates as major products, though many biological reactions do not go to completion. Intermediate products include acids, aliphatic alcohols and equivalent aromatic derivatives which may be disruptive in marine ecosystems, though concentrations of these substances in the field as a result of petroleum degradation have not been measured. Fluctuation in microbial populations due to the presence of PHC may be due to competitive exclusion, pathogenicity or production of toxins by microorganisms which digest oil. Little is known of these interactions in marine systems.

C. Bioaccumulation

Several probable pathways for hydrocarbons to enter the marine foodweb have been suggested. One is through ingestion of particles with adsorbed PHC. A second pathway is direct uptake of dissolved or dispersed petroleum through the gills, which is considered most important for pelagic organisms. A third means would be passage into the gut of fish that gulp or drink contaminated water (FAO, 1977). Some information indicates the possibility of hydrocarbons being stored in vacuoles of certain bacterial strains. Since some marine animals feed on bacteria, this may be a route into the food web (NAS, 1975).

Once in the organism, oil may be stored, metabolised, or excreted. Lipid storage of hydrocarbons occurs in many marine organisms, leading to concentration factors of 2000 - 3000 in oysters after 49 days of exposure to a fuel oil. Even after being returned to "clean" water, the concentration factor remained 3000 after four weeks (CEC, 1976).

Aromatic fractions of hydrocarbons are apparently eliminated much more slowly than the aliphatic or alkane constituents. The liver (or liver-like organ in invertebrates) is the site of hydrocarbon metabolism. The metabolism of fish and some marine invertebrates appears to resemble mammalian, which allows degradation of considerable amounts of aromatic and paraffinic hydrocarbons. Plankton and some benthic invertebrates appear to be unable to metabolize appreciable amounts of either paraffinic or aromatic hydrocarbons. In fact, oil particles may be excreted unchanged by some organisms

(e.g. copepods). The fecal pellets of these organisms are denser than sea water, thus providing a pathway to the water column, where ingestion by other organisms may occur, and eventually to sediments, where benthic communities can be affected. Discharge of metabolic products by vertebrates occurs primarily from the gall bladder and kidney (NAS, 1975).

There is no evidence for food web magnification of PHC in the marine ecosystem. The ability of different species to accumulate hydrocarbons from the water appears to be more important than their position in the food web (NAS, 1975).

IV. MONITORING

A. Analysis

Petroleum hydrocarbons present many problems in terms of composition, concentrations and occurrence in marine environments. Techniques must be available to distinguish between petroleum hydrocarbons and those derived from biogenic sources. In addition to the hydrocarbon content, oils generally contain small concentrations of metals, and many lubricating oils contain potentially dangerous additives (e.g. siloxane antifoaming fluids). A large array of sampling and analytical techniques have been developed to cope with these problems, including: fluorescence analysis, with a detection limit of 10 mg/l (Czernbor, 1975); gas chromatography and mass spectroscopy, which can detect 1.0 mg/l of mineral oils (Miget, 1974).

B. Amount in the Mediterranean

The average concentration of oils in the surface layer of the open ocean appears to be less than 10 ug/l, though the PHC fraction of this estimate is unclear (NAS, 1975).

Marine larvae are intolerant of concentrations as low as 100 ug/l, and sub-lethal effects, on feeding behaviour for example, are felt at concentrations as low as 10 - 100 ug/l (EPA, 1976). Samples taken from the Mediterranean contain much higher levels of PHC, especially in regions of heavy industry.

The Adriatic yielded surface samples with an average concentration of 4000 ug/l. The Liguro-Provençal samples averaged 560 ug/l and the Aegean Sea contained 1700 ug/l at the surface. In most areas, the concentrations decreased substantially with depth, though this was not true for the Aegean (UNEP, 1977). Other areas in the Mediterranean show lower levels, but nearly all regions reported on contained higher than average sea water concentrations of PHC. In addition to dissolved and dispersed oil which is available for biologic uptake, petroleum pollution occurs in the form of beach tar and pelagic tar balls, which reach high concentrations especially in the Eastern Mediterranean due to surface currents. Concentrations of oil in sediments in ecologically sensitive littoral systems is of special concern, but no data was found in the literature searched for these areas.

C. Amounts entering the Mediterranean

The lack of coherent monitoring data for the Mediterranean area makes it practically impossible to give a direct estimate on the amount of oil entering the sea. However, based on a worldwide input of 4 million tonnes per annum (mta) it has been estimated that 0.5 - 1 million tonnes per year of oil are entering the

Mediterranean (LeLourd, 1977). This estimate may be based on an optimistic assumption of only 4 million tonnes per year entering the world's oceans - other sources estimate that up to 11 million tonnes per year may be discharged (FAO, 1977). In effect, the Mediterranean is considered to be the most oil-polluted sea in the world for which data are available. The largest source of this pollution is land-based discharges, which contribute 45% of the total input. Marine transportation accounts for an additional 35%, atmospheric rainout adds 10%, and natural seepage is thought to contribute another 10% (UNEP, 1977). An estimated 115,000 tonnes per year are reported to be entering the Mediterranean from industrial discharges in the coastal zone (UNEP, 1977). Regional effects of oil pollution may be particularly important in terms of oxygen supply to the Mediterranean - the northern Adriatic, The Aegean, and the Liguro-Provencale basin are the "lungs of the Mediterranean" (Ritchie-Calder, 1972). These areas are currently being subjected to high levels of oil pollution, due to heavy industrialisation, which may affect the ecology of the whole Mediterranean Sea.

D. Regulations

There is a great deal of legislation in Mediterranean countries dealing with the discharge of oils into waterways. Cyprus, Egypt, France, Greece, Italy, Libyan Arab Republic, Spain, Tunisia, Turkey and Yugoslavia all have regulations dealing with the discharge of oil (WHO/UNEP, 1976; IDHL, 1978; Kratel, unpublished).

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

Toxicity of oil to marine ecosystems depends on the composition of the petroleum, the concentration available for biotic uptake, and of course the type of organism exposed. Attention must be paid to population dynamics over a span of time, not only reactions of individuals. Altered reproduction, behaviour, metabolism, growth and histology are some of the sub-lethal effects which may alter the population structure of a species.

Diversity may decrease seriously altering the stability of the polluted ecosystem. Evaluations of the impact of oil on marine environments must also consider the tolerance of an organism at its most vulnerable life stage, usually the larval or juvenile period. In addition to direct biological toxicity, the presence of oil may cause oxygen depletion in the water due to demands by chemical and biological oxidation reactions. The complex interaction of these factors make evaluations of oil pollution difficult on an ecological scale, but considerable work has been done with individual organisms, both in the laboratory and in marine systems. It is difficult to summarise these experiments due to the variability in toxic properties for different oils tested. Generally a numerical limit for petroleum concentration can be determined by applying a safety factor of 0.01 to the lowest continuous flow 96 hour LC_{50} for several important and sensitive resident species (EPA, 1976).

A study specific for lubricating oils concluded that fish can produce mutagenic metabolites from polycyclic aromatic hydrocarbons contained in used crankcase oils, which are released to the environment in considerable quantities. The authors believe that such substances may represent a considerable mutagenic threat (Payne et al., 1978).

Tainting of commercial fish and shellfish is of serious economic concern in the Mediterranean. Concentrations as low as 1 - 10 ug/l have been reported to cause tainting in oysters (EPA, 1976)

Adverse aesthetic effects due to beach tar are another aspect of oil pollution that may eventually have serious economic repercussions on the Mediterranean area, which attracts over 70 million tourists each year (Tangi, 1977).

B. Toxic Effects on Man and Other Mammals

Polynuclear aromatic hydrocarbons (PAH), some of which are known to be carcinogenic to man (e.g. 3, 4, benzopyrene), occur in crude oils, and especially in refined oils. These compounds can be stored unchanged in the body fat of some marine organisms, especially in molluscan shellfish. Localised inputs of oil from sewage and refineries are thought to contribute significantly to background levels of PAH. Consumption of contaminated tissues by man may be a serious health hazard, especially in heavily industrialised regions. It is not known if compounds which cause carcinomas in marine tissues (i.e. metabolised carcinogens) represent a hazard to man.

There is a large body of work dealing with the occupational hazards of lubricating oils. Machine operators exposed to cutting oils for long periods (e.g. 20 to 30 years) have been known to develop carcinoma of the hands, forearms and scrotum (Mastromatteo, 1965). Inhalation of oil mists are believed to cause pulmonary cancer (Huguenin et al., 1950).

Payne et al. (1978) found that used crankcase oil induced mutagenicity when activated by rat or trout liver extracts.

Total Production

Lubricants and cutting oils

Chemical Group: Petroleum hydrocarbons

year	area	amount	trend	citation (as reported in)
1974	USA	70 694 000 barrels	-	FIRL, 1976,p.75

<u>Total Production</u>				
Oil (generic)		Chemical Group: Petroleum hydrocarbons		
year	area	amount	trend	citation (as reported in)
1971	World	2 478 400 000 tons	-	NAS, 1975, p.2
1975	World	2 700 000 000 tonnes		Le Lourd, 1977,p.319
1971	Algeria	35 900 000 tons	-	NAS, 1975, p.2
1971	France	1 900 000 "		
1971	Libya	132 900 000 "		
1971	Turkey	3 500 000 "		
1975	Algeria	935 000 b/d*	-	UNEP, 1977, p.102
1975	Egypt	225 000 "		
1975	France	20 000 "		
1975	Israel	185 000 "		
1975	Italy-Sicily	20 000 "		
1975	Libya	1400 000 "		
1975	Morocco	700 "		
1975	Spain	38 000 "		
1975	Syria	175 000 "		
1975	Tunisia	95 000 "		
1975	Turkey	60 000 "		
1975	Yugoslavia	70 000 "		

* assumed to be barrels/day

Total Consumption

Lubricants and cutting oils			Chemical Group: Petroleum hydrocarbons	
year	area	amount	trend	citation (as reported in)
1975	France	1 268 000 tonnes	-	CEC, 1976, p.12-38
1975	Italy	815 000 "		

Total Consumption

Oil (generic)		Chemical Group: Petroleum hydrocarbons		
year	area	amount	trend	citation (as reported in)
1971	France	103 000 000 tons	-	NAS, 1975, p. 3
1975	France	116 400 000 "	-	CEC, 1976, p.12-11
1971	Italy	92 000 000 "	-	NAS, 1975, p. 3
1975	Italy	92 000 000 "	-	CEC, 1976, p.11-12
1971	Spain	27 000 000 "	-	NAS, 1975, p. 3

Production Process(es)

Lubricants and cutting oils		Chemical Group: Petroleum hydrocarbons	
product	process (major or minor by geographic area)	composition/intermediates	citation (as reported in)
lubricating oils	atmospheric distillation, vacuum distillation	-/-	CEC, 1976, p.2-18
lubricating oils	distillation range: 302-815°C	mixture of straight and branched chain paraffinics (64-78%), naphthenics (13-31%) and aromatic and polycyclic aromatic hydrocarbons (0-11%), (17°C and above), additives up 30% volume/-	FIRL, 1976, p.52,57
automotive grade lubricating oils and other oils for high temperature applications	solvent extraction of lubricating oils, to remove naphthenic, aromatic and olefinic components	essentially paraffinic/-	FIRL, 1976, p.52
quenching oil used quenching oil	-	0.6-0.8 ppm benzo-a-pyrene/-	Desoille et al., 1973
	-	20 ppm benzo-a-pyrene/-	
oil mist	-	-/-	-

Use

Lubricants and cutting oils		Chemical Group: Petroleum hydrocarbons		
use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
<u>Automotive lubricants:</u> crankcase oils, transmission and axle lubricants, bearing and chassis lubricants	-	-	-	FIRL, 1976, p.73
<u>Industrial lubricants:</u> machine and engine oils, steam turbine oil, steam engine oils, textile-mach- inery oils, refrigerating machine oils, gear oils, industrial greases	-	-	-	FIRL, 1976, p.74

Use

Lubricants and cutting oils (page 2) Chemical Group: Petroleum hydrocarbons

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
<u>Oils in non-</u> <u>lubricating</u> <u>applications:</u> apron dressings brick oils, cable oils, coal spray oils flotation oils, form oils and compounds, fruit and vegetable preservatives, heat-transfer oils, ink oils, belt dressings, defoamers, polishing oils, paint and putty oils, paper-proces- sing oils, petroleum sulfonates, quenching oils, tempering oils, rub-roll oils, rust-preventive oils and com- pounds, spray oils, tanners' pro- ducts, textile-pro- cessing oils, transformer oils, cutting oils	-	-	-	Bland and Davidson, 1967 (FIRL, 1976, p.74)

Wastes

Lubricants and cutting oils

Chemical Group: Petroleum hydrocarbons

area/year	discharge amounts	sources (major/minor)	composition	citation (as reported in)
USA/year	1115 gallons	automotive lubricating oils (major), industrial and aviation lubricating oils (major), other industrial oils (minor), US government lubricating oils (minor)	-	CEC, 1976, p.12-39

Wastes

Mineral oil (generic)		Chemical Group: Petroleum hydrocarbons		
area/year	discharge amounts	sources (major/minor)	composition	citation (as reported in)
Mediterranean/ year	120 000 tonnes	industry (major)	-	Helmer, 1977, p.314

Wastes

Oil (generic)		Chemical Group: Petroleum hydrocarbons		
area/year	discharge amounts	sources (major/minor)	composition	citation (as reported in)
World/1975	4 000 000 tonnes 1 300 000 "	total land based discharge (major)	-	Le Lourd, 1977, p.319
World/year	6 113 000 t. 2 700 000 "	total land based discharge (major)	-	UNEP, 1977, p. 99
EEC/1976	1 800 000- tons 2 800 000	total	-	CEC, 1976, p.12-12
	1 000 000- " 1 200 000	industrial and urban discharge (major)		
	500 000- " 1 600 000	production, transportation, other sources (major)		
	100 000- " 300 000	refinery discharge		

Pathways Leading to Marine Pollution

3,5 Dimethyl Phenol Chemical Group: Petroleum hydrocarbons

Pathway	Quantity	Area	Citation
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Nothing found in the marine environment.

Biotic Transformation in the Marine Environment

3,5 Dimethyl Phenol

Chemical Group: Petroleum hydrocarbons

Process	Transformation		Products		Citation
	%	Time	Name	Quantity	

Nothing found in the marine environment.

Abiotic Transformation in the Marine Environment

3,5 Dimethyl Phenol

Chemical Group: Petroleum hydrocarbons

Process	Location	Conditions			Products		Transformation		Citation
		Temp	C.	pH	Chem	Light	Name	Quantity	Time
Exposure to air.	Water soluble fraction of a No. 2 fuel oil, laboratory.	-	-	-	-	-	Decreased DMP	-	10 120 hours
									Lee, W.Y. et al., 1978

Chemical Group: Petroleum hydrocarbons

3,5 Dimethyl Phenol

[illegible]

Nothing found in the marine environment.

Lubricants and cutting oils

description of organism	route	concentration	exposure	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard (as reported in)	citation
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Nothing found in the literature reviewed.

Concentrations in Water, Sediments and Biota

3,5 Dimethyl Phenol

Chemical Group: Petroleum hydrocarbons

<u>Description of Sample</u>		<u>Analytical Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material Sampled</u>	<u>Origin</u>				

Nothing found in the marine environment.

Array of Toxic Effects on Man and Other Mammals

Lubricants and cutting oils			Chemical Group: Petroleum hydrocarbons		
dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
540	single dose, motor oil (mult- grade SAE 10W- 20W-30)	aspira- tion	rat (male, albino Wistar)	1/5 deaths within 24 hours	Gerarde, 1963 (FIRL, 1976 p.79)
540	single dose, motor oil (high detergent additive)	aspira- tion	rat (male, albino Wistar)	1/5 death within 24 hours	Gerarde, 1963 (FIRL, 1976 p.79)
640	single dose, crankase oil (without additives)	aspira- tion	rat (male, albino Wistar)	0/5 death within 24 hours	Gerarde, 1963 (FIRL, 1976 p.80)
540	single dose, motor oil (multigrade)	aspira- tion	rat (male, albino Wistar)	0/5 death within 24 hours	Gerarde, 1963 (FIRL, 1976 p.80)
-	21 years, cutting fluids	-	human (machine operators)	squomas cell car- cinoma of hands, forearms and scro- tum	Mastromatteo, 1965
-	cutting oils	-	human (mainly tool-setters and machine operators)	scrotal cancer, skin tu- mours, bronchial tumours	Brown et al., 1975
-	mineral oils, and products based on miner- al oils such as metal working fluids	-	human	oil acne	Kinnear et al., 1954

Array of Toxic Effects on Man and Other Mammals

Lubricants and cutting oils (page 2) Chemical Group: Petroleum hydrocarbons

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
-	shale oil	-	human (workers in British mule spinning industry)	skin and scrotal cancer	Henry, 1946-1947
-	cutting oil	-	human (cutting metals)	skin cancer	Cruickshank and Gourevitsh, 1952
-	30 years, cutting oil	-	human (bar automatic machine workers)	epitheli- oma, most- ly of the scrotum	Thony et al., 1975

Array of Toxic Effects on Man and Mammals

Lubricants and cutting oils (page 3) Chemical Group: Petroleum hydrocarbons

concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
63-132	100-365 days, mists of automobile lubricating oil and smoke-screening oil	inhal.	monkey	increased incidence of infectious pneumonia, hyperplastic gastritis, death	Lushbaugh et al., 1950
-	2-3 years, used cutting oil mist	inhal.	human (man who had centrifuged used cutting oil for 23 years)	multifocal alveolar cell carcinoma of the lung, death	Despierres et al., 1965
-	oil mist	inhal.	human (metal working machine workers)	pulmonary cancer	Huguenin et al., 1950

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Lubricants and cutting oils

Chemical Group: Petroleum hydrocarbons

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	dermal appl.	-	cutting oils based on sulfurised mineral oils	carcinogenic	Gilman et al., 1955
mouse	dermal	-	unused and used cutting oil	papillomas - higher incidence with used oil	Dargent et al., 1967
mouse	dermal	-	unused and used cutting and quenching oils	skin tumours - higher incidence with used oil	Desoille et al., 1973
rat, guinea pig	dermal	-	unused and used cutting and quenching oils	no effect found	Desoille et al., 1973
mouse	dermal	-	commercial jute batching oil	malignant skin tumours	Roe et al., 1967
mouse	dermal appl.	-	long term, cutting oil	low incidence of skin tumours	Hueper et al., 1960
rat	oral (2 ml)		14 months (daily), highly refined diesel engine lubricating oil	2/40 foci of colonic mucosal hyperplasia, 1/40 colonic adenocarcinoma	Lushbaugh et al., 1948/1949

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Lubricants and cutting oils (page 2) Chemical Group: Petroleum hydrocarbons

CARCINOGENICITY

description of organism	route	concentration in mg/m ³ (conc. cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	inhal.	63-132	100-365 days, mists of automobile lubricating oil and smoke-screening oil	no increase in tumours	Lushbaugh et al., 1950
rat, guinea pig	inhal.	-	2 years (4 days/week, 6 hours/day), mists of cutting oil	multifocal adenomatosis in the lungs	Hueper et al., 1960

These studies, designed to evaluate the possible carcinogenic effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

MUTAGENICITY

description of system	reported results	citation
salmonella typhimurium strain TA 98	used crankcase oil induced His + revertant colonies, when activated by rat or trout liver extracts	Payne et al., 1978

This study, designed to evaluate the possible effects of the substance on gene mutation, chromosomal mutations, DNA repair or recombination or from transformation, resulted in a report of the above effect, but no comprehensive evaluation of this material was found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Lubricants and cutting oils (page 3) Chemical Group: Petroleum hydrocarbons

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
human (especially persons with fair hair)	UV-radiation	potentiates the tendency to develop skin cancer	Emmett, 1975

This study designed to evaluate the possible effects which could result from the combination of this substance with UV-radiation resulted in a report of potentiation but no comprehensive evaluation of this material was found in the literature reviewed.

PRIMARY IRRITATION

description of organism	route	dose in mg (dose cited)	total exposure time; brief description	effect (observation time)	citation (as re- ported in)
mouse	dermal	-	unused and used cutting oil	skin ulceration, hyperkeratosis and papillomas -higher incidence with used oil	Dargent et al., 1967

This study, designed to evaluate the possible primary irritation effects of the substance, resulted in a report of primary irritation effects, but no comprehensive evaluation of this material was found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

3,5 Dimethyl Phenol

Chemical Group: Petroleum hydrocarbons

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Agmenellum quadruplicatum (Coccolid blue-green alga)	-	10 mg on agar pad	3-7 days	100% mortality	3-7 days	Winter, K. et al., 1976

Analysis

Mineral oil (16C and above)

Chemical Group: Petroleum hydrocarbons

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
Fluorescence Analysis (10 mg/l)	bleaches may interfere/automatic procedure, very rapid for routing survey of waste waters, inexpensive, generally available	Czembor, 1975
Gas-Chromatography and Mass Spectroscopy (1.0 mg/l)	sampler works only for long-chain hydrocarbons with more than 16 carbon atoms, suitable only for surface films/inexpensive rapid method	Miget, 1974
Infrared Spectroscopy	inexpensive, rapid	Brown et al., 1974

Legislation for the Protection of Man and the
Marine Environment

Lubricants and cutting oils

Chemical Group: Petroleum hydrocarbons

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in water	Cyprus	the District Officer is empowered to prohibit or impose restric- tions and conditions upon dumping of any fluid lubrication oil into the sea within a specified distance from low- water mark, or from any pier, wharf, quay or jetty	-	WHO/UNEP, 1976, p. Cyprus-1

Legislation for the Protection of Man and the

Marine Environment

Mineral oil (generic)

Chemical Group: Petroleum hydrocarbons

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in water	Italy	regulation concerning acceptable limits for discharges into surface waters	5 mg/l	IDHL, 1977, p. 630
		and into public sewers	10 mg/l	

Legislation for the Protection of Man and the
Marine Environment

Oil (generic)		Chemical Group: Petroleum hydrocarbons		
general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in waste- waters discharged for surface irrigation	Egypt	standards for waste-water from public sewers and local wastes use of waste- waters from private sewers for surface irrigation needs a permit from the competent health authority	the amount of oil grease and resins must not exceed 20 mg/l if discharged onto sandy soil and 0,5 mg/l onto clay or muddy soil	WHO/UNEP, 1976, p. Egypt-3
control of substances in harbour and territorial waters	Egypt	regulations concerning oil discharges from ships and obligations for port refineries	-	WHO/UNEP, 1976, p. Egypt-1
control of substances in wastes	Egypt	regulation for wastes discharged from industrial establishments, garages, etc. traps must be constructed to isolate undesir- able substances such as oils, etc.	-	WHO/UNEP, 1976, p. Egypt-2

Legislation for the Protection of Man and the
Marine Environment

Oil (generic) (page 2)

Chemical Group: Petroleum hydrocarbons

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in waste- water	Egypt	standards for waste-waters from industrial and commercial establishments discharged into public sewers	the amount of oil, grease and resins must not exceed 100 mg/l	WHO/UNEP, 1976, p. Egypt-3
control of substances in waste- water	Egypt	standards for industrial waste-water discharged into the Nile and its delta and into drainage canals	the amount of oil and grease must not exceed 10 mg/l	WHO/UNEP, 1976, p. Egypt-3
control of substances in drinking- water supplies	France	installation of pipe-lines or tanks for hydro- carbons or chemicals may be prohibited or regulated within the protection zone around catchment points for water intended for use as drinking-water	-	WHO/UNEP, 1976, p. France-6
control of substances in waste- waters	France	regulations on refineries' effluents	5 ppm hydro- carbons (hexane extraction) 20 ppm hydro- carbons (infrared method)	CEC, 1976, p. 13-17

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Oil (generic) (page 3)

Chemical Group: Petroleum hydrocarbons

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in water	France	prohibition or restriction of discharge of certain oils and lubricants into surface waters and groundwater		IDHL, 1977, p.961
control of substances in water	Greece	regulations concerning oils and other criteria for sewage or indus- trial wastes discharged into surface water and seawater	-	WHO/UNEP, 1976, p. Greece-1
control of substances in water supplies in the Athens area	Greece	prohibition of direct or indirect dis- charge of oil into the waters concerned through- out the sector up- stream of treat- ment plants	-	WHO/UNEP, 1976, p. Greece-6
control of substances in effluents	Libyan Arab Republic	proposed stand- ards for efflu- ents discharged	2mg/l into surface water reservoirs for direct use in agriculture, and into aquifers used for public water supply 2.5mg/l into the sea 10mg/l into urban sewage systems	WHO/UNEP, 1976, p.Libian Arab Republic-2

Legislation for the Protection of Man and the

Marine Environment

Oil (generic) (page 4)

Chemical Group: Petroleum hydrocarbons

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in effluents	Spain	regulation concerning discharges from submarine outfalls	1.0mg/l in not more than 50% of samples 2.0mg/l in not more than 10% of samples	IDHL, 1978, p.193
control of substances in effluents	Tunisia	proposed recommended values for discharges into surface waters and public sewers	1-2mg/l into waters 100mg/l into public sewers when mechanic- al oil removal is used, 20mg/l into public sewers when demulsification- oil removal is used	Kratel (unpublished)
control of substances in effluents	Turkey	prohibition of discharges when the concen- tration exceeds the tolerance level	0.003mg/l for crude oil 10mg/l for normal grade petrol 30mg/l for super grade petrol 50mg/l for diesel and fuel oil	Turkish law of 1 October 1971

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Oil (generic) (page 5)

Chemical Group: Petroleum hydrocarbons

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in effluents	Yugoslavia	maximum permissible concentrations of dangerous substances discharged into waters used or intended for use as drinking water for production of foodstuffs, fish breeding, water- ing of animals or public bath- ing	0.1mg/l for petroleum and its derivatives before desulfu- rization 0.3mg/l for desulfurized petroleum and its derivatives 0.05mg/l for petroleum and its derivatives in solution and emulsion	WHO/UNEP, 1976, p.Yugoslavia- 2
control of substances in water	Yugoslavia	maximum permissible concentrations of dangerous substances in interrepublic watercourses	0.1mg/l of kerosene in class I and class II waters ^a 0.05mg/l of sulfur-contain- ing and other naphthas in class I and class II waters ^a 0.3mg/l of sul- fur-containing and other naphthas in class III and class IV waters ^b	IDHL, 1978 (awaiting publication)

^a Class I: waters which, in their natural state, where necessary after disinfection, may be used for drinking purposes and in the food industry and, in the case of surface waters, for breeding Salmonidae. Class II: waters which, in their natural state, may be used for bathing and recreation, water sports, breeding of Cyprinidae, or which, after treatment, may be used for drinking purposes and in the food industry.

^b Class III: waters which may be used for irrigation and, after treatment, in industry other than the food industry. Class IV: waters which may be used for other purposes only after treatment.

Petroleum hydrocarbon

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MEDITERRANEAN DATA PROFILE

BENZOPYRENE

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^aNothing found in the literature reviewed.

OUTLINE- GENERAL SUMMARY FOR BENZO(a)PYRENE

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GENERAL SUMMARY FOR BENZO(a)PYRENE

I. INTRODUCTION

Benzo(a)pyrene (BaP) is believed to be an indicator for an entire group of carcinogenic polycyclic aromatic hydrocarbons (PAH). It is the most stable compound from this group, and is among the most carcinogenic substances found in the environment. Levels of benzo(a)pyrene in the marine environment vary considerably, and fairly high levels are often found. Marine organisms are of interest as natural agents for the removal of BaP from sea water, as secondary sources of BaP, and as possible routes for the carcinogen to reach man (Zobova et al., 1976).

Polycyclic organic matter is released primarily to the atmosphere through the use of coal and petroleum products, burning of refuse, and the production of coke. Since PAH are mostly of low solubility and low vapour pressure, the major mode of transport in the environment is as particulate matter. PAH are widely distributed in the environment, though high local levels are correlated with heavy industrialisation and urbanisation (EPA, 1976).

II. OCCURRENCE

A. Production

Benzo(a)pyrene is not produced commercially, but occurs mainly as a pyrolysis product formed during the combustion of fossil fuels and most other natural products.

B. Use

Benzo(a)pyrene has no commercial applications. No information on this subject was found in literature reviewed.

III. BENZO(a)PYRENE IN THE ENVIRONMENT

A. Sources

1. Natural

Benzo(a)pyrene is most often used as a measure of the occurrence of other PAH compounds. The compounds may be natural products of animal and plant metabolisms, and there is evidence that bacteria can synthesise PAH. Erhardt (1972) found that Platymonas sp. synthesised 1.15 ug/l of B(a)P in 4 months in a culture medium. Erosion of exposed fossil fuel deposits and natural combustion processes (e.g. forest fires) are also thought to release PAH to the environment (EPA, 1976).

2. Anthropogenic

A major contributor to BaP levels in the atmosphere is the conventional gasoline powered automobile, as well as all other internal combustion engines. The introduction of emission control devices has reportedly reduced BaP emissions 85% from the pre-1965 levels. Fuel : air ratios are important in estimating BaP emissions from vehicles (NAS, 1972).

Stationary sources contributing to BaP in the atmosphere include heat and power generation, refuse burning and industrial emissions. Hangebrauk et al. (1967) considered the most important source of BaP derived from the burning of gas, oil, coal and wood is from the inefficient combustion of coal in home furnaces. The efficiency of combustion is more important than the type of fuel used, as reflected by local PAH concentrations which are associated with local fuel practices.

BaP emissions from hand stoked residential furnaces are estimated at 1700-3300mg/10⁶ BTU, while coal fired steam power plants release only 0.02-0.4mg/10⁶ BTU produced (NAS, 1972).

The great diversity of solid wastes that are disposed of by enclosed incineration and open burning has lead to uncertainties as to their actual contributions to atmospheric concentrations of PAH. The largest single contributor is believed to be coal refuse bank burning, a common occurrence in mining areas (NAS, 1972).

The estimated 0.5-1 million tonnes of oil which enters the Mediterranean each year make it one of the most oil-polluted seas in the world (LeLourd, 1977). Crude oil PAH are estimated to be on the order of 1% of total crude, and used petroleum products contain even larger amounts of the high boiling PAH compounds. Unused motor oil contains 26ug/kg BaP, compared to 5,800ug/kg BaP in spent crankcase oil (Sullivan, 1974).

Tobacco smoking is a major source of indoor PAH pollution. Depending on ventilation and smoking activities, the indoor pollution by cigarette smoke can be significant (NAS, 1972).

The significance of localised inputs of PAH into the atmosphere is apparent; levels in urban areas are generally about 10-100 times greater than in remote areas (EPA, 1976).

B. Transformation

1. Abiotic

Polycyclic aromatic compounds, including BaP, are highly reactive. There is evidence that they are degraded in air by photooxidation, by reaction with atmospheric oxidants, and by reaction with sulphur oxides. The availability of oxygen and light, as well as ambient temperature, will affect the rate of degradation considerably, as evidenced by dramatic reduction in the rates of photooxidation during winter months (EPA, 1976).

In water, photooxygenation by singlet oxygen is considered to be the dominant chemical process for degradation of PAH. These compounds are of low solubility and exist in water mainly as finely dispersed particles or adsorbed on a variety of particulates (e.g. minerals, organic matter). Adsorption of BaP on particulates and sediment clays is believed to be responsible for the extremely high concentrations found in samples from some river bottoms. Oxidation reactions give quinones as the major primary products, though endoperoxides, diols and dimers are also formed (EPA, 1976).

Zobova et al. (1976) found that 97% of BaP present in aerated sea water is transformed after three days, though no mechanism is described.

Suess (1972) reports that the degradation rates of BaP will be higher near the surface, due to more light, oxygen and higher temperatures. BaP in bottom deposits are expected to degrade very slowly, if at all, due to the lack of light and oxygen.

2. Biotic

Soil microorganisms, especially those adapted to high levels of BaP, are able to metabolise large amounts of the compound in relatively short time spans. Shabad (1968) found that various strains of bacteria isolated from highly contaminated soil could metabolise 75-86% of BaP in 5 days, while those from low benzo(a)pyrene areas could metabolise only 48-59% in the same time period.

Aquatic bacteria appear to be less efficient in metabolising PAH compounds than soil microorganisms. Bacteria in power plant and coke oven wastewater metabolised less than 15% of the BaP present (Poglazova et al., 1972).

ZoBell (1971) reports, however, that PAH degrading microorganisms commonly occur in polluted water as well as soil. A mixed culture of aerobic bacteria reduced the BaP content of dead plankton from 127ug/kg to only 4.0ug/kg in 15 days (97% transformation). The major oxidation product in marine systems was found to be cis-9,10-dihydroxy-9,10-dihydrobenzo(a)pyrene (Gibson, 1975).

The annelid worm, Tubifex was observed to accumulate BaP from water in amounts as high as 52ug/kg dry weight, but some was apparently metabolised by the worms. Other invertebrate species have been shown to metabolise PAH, but it is difficult to determine whether the compound was oxidised by the invertebrate or by the microorganisms occurring in the gut or growing on the integument (ZoBell, 1971).

Studies on rats, mice, hamsters and rabbits have indicated that PAH will only induce cancer when metabolically activated (NAS, 1972).

C. Bioaccumulation

The ability of marine organisms to accumulate low levels of BaP in seawater has been demonstrated in several studies.

Lee et al. (1972) found that three species of fish rapidly accumulated BaP through their gills. Metabolism occurred in the liver, and the BaP and its products were transferred to the bile. The water soluble metabolites were excreted mainly in the urine, and the gall bladder was the major storage site for BaP and its metabolites. An accumulation coefficient of 2,100 was found for the mudsucker, Gillichthys mirabilis, in a 25 hour exposure to 0.001mg/l BaP.

Neff et al. (1970) studied bioaccumulation of BaP in the clam, Rangia cuneata. A whole tissue concentration factor of 240 was found for a 24 hour exposure to 0.0305mg/l BaP. Nearly 75% of the BaP was found in the viscera, which includes the digestive system, gonads and heart. When returned to "clean" water, the clams released 71% of the BaP in 10 days.

The amount of BaP in seafood is appreciably higher than amounts in non-marine food, probably as the result of petroleum contamination (Sullivan, 1974). Due to BaP intake from other sources (e.g. tobacco, air, water), it is impossible to estimate the contribution of seafood to the total human intake of BaP (Suess, 1972).

IV. MONITORING

A. Analysis

Analytical methods for measuring BaP include: liquid and gas chromatography plus mass spectroscopy, with a 1ppb detection limit (May et al., 1975); gas-chromatography, which can detect

BaP in the ppb range (Junk et al., 1974); and high pressure liquid chromatography, with a detection limit of 10ng (Dong and Locke, 1976).

B. Amount in the Mediterranean

No information on the concentrations of BaP in open ocean or coastal waters of the Mediterranean was found in the literature reviewed. Sea water concentrations of 1.6ug/l of BaP were reported by Niaussat and Auger (1970) for samples from Clipperton Lagoon, and 5.5ug/l BaP was measured in Osaka Bay, Japan (Kawakami and Nishimura, 1976).

Sediment concentrations for the Mediterranean are as follows: sand and mud samples from the Bay of Naples, 2-120m deep, had BaP concentrations of 0.0238mg/kg dry weight (Bourcart and Mallet, 1965); sediments from the Adriatic had 0.03mg/kg dry weight (Piccinetti, 1968); and sediment samples from Villefranche contained 1.75mg/kg dry weight (Lalou, 1965).

Plankton from the French Mediterranean coast contained up to 0.005mg/kg dry weight of BaP (Suess, 1970). Mallet (1967) reports marine algae contained 0.06mg/kg of BaP. Crab from the Adriatic, Portunus sp., contained BaP concentrations of 0.857mg/kg dry weight (Scaccini and Scaccini-Cicatelli, 1969). Striped mullet, Mullus barbatus, from the N. Adriatic contained 0.0051mg/kg lipid weight of BaP (Giaccio, 1971).

C. Amount Entering the Mediterranean

No information of the amount of benzo(a)pyrene entering the Mediterranean was found in the literature searched.

Sullivan (1974) estimates that 10-20 tonnes of BaP are entering the world's oceans per year.

D. Regulations

Yugoslavia sets a maximum permissible concentration of total carcinogenic PAH in waters for public use of 0.0002mg/l (IDHL, 1978). No other information on this subject was found in the literature reviewed.

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

Benzo(a)pyrene has been shown to be toxic at very low levels to a variety of marine organisms. Lee et al. (1972) report that the marine copepod, Calanus helgolandicus, was killed by BaP at concentrations of 4.0ppb. A marine dinoflagellate, Gyrodinium sp., showed increased cell division periods and an increased mitotic index at BaP levels of 0.005mg/l (Ishio et al., 1977). Sea urchin eggs underwent abnormal cleavage and development in a three hour exposure to 5.0mg/l of BaP (de Lima-Zanghi, 1968).

Boney (1974) found that an application of 1.0mg/l of BaP to the meristematic region of a marine algae, Porphyra tenera, caused a 40% increase in growth over controls, in terms of cell production. In Porphyra, this results in tumour-like proliferations in the marginal areas of the frond.

B. Toxic Effects on Man and Other Mammals

Little is known about the toxicity of PAH compounds aside from information that many are carcinogenic in laboratory mammals and in humans. Some have also been shown to be mutagenic and/or teratogenic.

A single oral dose of 0.48mg/kg bw of BaP caused stomach tumours in a mouse (Peirce, 1961). An LD50 for rats was found to occur at 50mg/kg bw/day of BaP given in subcutaneous doses (NIOSH, 1978). IARC (1973) reports that a single, subcutaneous dose of 2.5mg/kg bw caused local sarcomas in a mouse, and that BaP produced tumours in all of the nine species for which data has been reported, following oral, dermal and intratracheal administrations. BaP has both a local and a systemic carcinogenic effect.

Human workers exposed to 0.002mg/m³ of BaP for more than 20 years in the workroom atmosphere showed increased lung cancer, skin cancer, leukemia, stomach and bladder cancer, and in some cases, death (Bridbord and French, 1978).

Total Production

Benzo(a)pyrene

Chemical group: Benzopyrene

year	area	amount	trend	citation (as reported in)
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Nothing found in the literature reviewed.

Production Process(es)

Benzo(a)pyrene		Chemical group: Benzopyrene	
process (major or minor- by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)

Nothing found in the literature reviewed.

Use

Benzo(a)pyrene

Chemical group: Benzopyrene

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
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Nothing found in the literature reviewed

Pathways Leading to Marine Pollution

Benzo(a)pyrene		Chemical Group: Benzopyrene	
Pathway	Quantity	Area	Citation
Terrestrial drainage	-	World	Zobell, C.E., 1971
Aerial transport	-	World	Zobell, C.E., 1971
Oil spills	-	World	Zobell, C.E., 1971
Marine operations	10-20 metric tonnes/annum	World	Sullivan, J.B., 1974
Natural synthesis by anaerobic bacteria	-	-	Erhardt, J.P., 1972
Human sewerage	-	Coastal regions	Corner, E.D.S., 1975
Platymonas sp.	1.15ug/l in 4 months	Culture medium	Erhardt, J.P., 1972
Coccolithus sp.	0.97ug/l in 4 months	Culture medium	Niaussat, P. and Ottenwalder, J., 1969
Anaerobic bacteria and plankton	8mg/kg in 15 days	Culture	Mallet, L. et al., 1967

Biotic Transformation in the Marine Environment

Benzo(a)pyrene		Chemical Group: Benzopyrene			
Process	Transformation		Products		Citation
	%	Time	Name	Quantity	
Oxidation	-	-	Cis-9,10-dihydroxy-9,10-dihydrobenzo(a)pyrene	Major	Gibson, D.T., 1975
			and Cis-7,8-dihydroxy-7,8-dihydrobenzo(a)pyrene	Minor	
-	97%	15 days	-	-	Zobell, C.E., 1971

Abiotic Transformation in the Marine Environment

Benzo(a)pyrene		Chemical Group: Benzopyrene							
Process	Location	Conditions			Products	Transformation		Citation	
		Temp. C	pH	Chem. cata.		Light	Quantity		%
Photolysis	Laboratory-aerated sea water	27	7-10	-	0.31 mW/cm	-	-	-	Suess, M.J., 1972
Photodegradation in presence of H_2O_2	-	-	-	-	-	Benzo(a)-pyrene excited to triplet state	-	-	Scaccini, A. and Scaccini-Ciccatelli, M., 1969.
-	Laboratory, aerated sea water	-	-	-	-	-	97%	3 days	Zobova, N.A. et al., 1976

Behaviour of a Chemical Substance in Marine Organisms

Benzo(a)pyrene

Chemical Group: Benzopyrene

Organism	Exposure			Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn.	Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
Odontogadus merlangus (Whiting)	W	0.001 mg/L	60 days	Whole	-	0.27	-	-	-	-	Zobova, N.A. et al., 1976
Gillichthys mirabilis (Mudsucker)	W	0.001 mg/L	25 hrs.	Whole	-	2 100	-	-	7,8-dihydro-7,8dihydroxybenzpyrene	-	Lee, R.F. et al., 1972
Mytilus gallo-provincialis (Black Sea mussel)	W	0.001 mg/L	123 days	Whole	-	56	-	-	-	-	Zobova, N.A. et al., 1976
Rangia cuneata (Clam)	W	0.0305 mg/L	24 hrs.	Viscera	65%	190	99%	30 days	-	-	Neff, J. M. and Anderson, J.W., 1975
Rangia cuneata (Clam)	W	0.0305 mg/L	24 hrs.	Whole	-	240	71%	10 days	-	-	Neff, J. M. et al., 1970

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Behaviour of a Chemical Substance in Marine Organisms

Benzo(a)pyrene (page 2)

Chemical Group: Benzopyrene

Organism	Exposure		Accumulation and Distribution				Loss		Metabolites		Citation
	Route	Concn. Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity		
Callinectes sapidus (Blue crab)	W	0.0025 mg/L 48 hrs.	Hepa- topanc- reas and gills	Major pro- portion	-	50%	6 days	Hydroxyben- zopyrene and polar meta- bolites	-	Lee, R.F. et al., 1976	
Calanus plumchrus (Marine plankton)	W	0.00125 mg/L 3 days	Whole	-	-	99%	17 days	³ H-hydroxy- benzopyrene and polar metabolites	-	Lee, R.F., 1975	

W - Water

Behaviour of the Substance in Man and Other Mammals

Benzo(a)pyrene		Chemical Group: Benzopyrene					
description of organism	route	exposure		retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard (as reported in)	citation
		concentration	duration of exposure				
mouse embryo cells	-	-	-	-	-	1,2-dihydroxy-1,2-dihydrobenzo(a)pyrene; 9,10-dihydroxy-9,10-dihydrobenzo(a)pyrene; 6-hydroxybenzo(a)pyrene; 3-hydroxybenzo(a)pyrene; 1,6-dihydroxybenzo(a)pyrene; 3,6-dihydroxybenzo(a)pyrene; benzo(a)pyrene-1,6-dione; benzo(a)pyrene-3,6-dione/none carcinogenic	Sims, 1970 (NAS, 1972, p.135)
-	-	-	-	-	-	Benzo(a)pyrene-7,8-diol-9,8-epoxide/ mutagenic, carcinogenic	Lehr et al., 1978, p.232
mouse (female, CD1, Charles River, 7-9 weeks old)	-	-	-	-	-	11-hydroxybenzo(a)pyrene/carcinogenic benzo(a)pyrene-7,8-dihydrodiol/carcinogenic	Slaga et al., 1978, p.374

Concentrations in Water, Sediments and Biota

Benzo(a)pyrene		Chemical Group: Benzopyrene			
Description of sample		Analytical Method	Level(s)	Date(s)	Citation
Material sampled	Origin				
Seawater	Osaka Bay, Japan	FS	0.0055 mg/L	1974	Kawakami, Y. and Nishimura H., 1976
Seawater	Clipperton Lagoon	-	1.6 mg/L	-	Niaussat, P. and Auger, C., 1970
Sediment 2-5cm	Osaka Bay, Japan, gas-works outlet.	FS	89.0 mg/kg dry wt.	1974	Kawakami, Y. and Nishimura H., 1976
Sediment (sand and mud)	Bay of Naples, Italy	-	3.0 mg/kg dry wt.	1964	Bourcart, J. and Mallet, L., 1965
Sand	Greenland	-	0.005 mg/kg dry wt.	-	Suess, M.J. 1972 quotes Mallet, L. et al., 1963
Sediment	Brittany coast, France	-	1.71 mg/kg dry wt.	-	Mallet, L., 1967
Engraulis encrasicolus (Anchovy)	San Diego Bay, U.S.A.	TLS	1.0/mg/kg dry wt.	-	Lee, R.F. et al., 1972
Mullus barbatus (Striped mullet)	N. Adriatic	FS	0.0051 mg/kg lipid wt.	-	Giaccio, M., 1971

Concentrations in Water, Sediments and Biota

Benzo(a)pyrene (page 2)

Chemical Group: Benzopyrene

Description of sample		Analytical Method	Level(s)	Date(s)	Citation
Material sampled	Origin				
Sediment	Maltese Coast	GC	0.12-1.9mg/kg dry wt.	1975	Sammut, M. and Nickless, G., 1978
Sediment (0.08-0.13m)	French Mediterranean Coast	GC	5.0mg/kg dry wt.	-	Suess, M. J., 1970
Sediment (75m)	Cerbere, W. Mediterranean	-	0.2mg/kg	-	Mallet, L., 1965
Sediment (black mud, 16m)	Villefranche, Alpes	-	1.5mg/kg	-	Bourcart, J. et al., 1961
Sediment (black mud)	Villefranche	FS	1.5mg/kg	-	Lalou, C., 1963
Sediment (sand)	Var, S.E. France	FS	0.034mg/kg dry wt.	-	Lalou, C., 1963
Sediment (mud)	Rhone	FS	0.906mg/kg dry wt.	-	Lalou, C., 1963
Sediment	Antibes	FS	0.18mg/kg dry wt.	-	Lalou, C., 1965
Sediment	Villefranche	FS	1.75mg/kg dry wt.	-	Lalou, C., 1965
Sediment	Adriatic	C	0.03mg/kg dry wt.	1965-66	Piccinetti, C., 1968

Concentrations in Water, Sediments and Biota

Benzo(a)pyrene (page 3)

Chemical Group: Benzopyrene

Description of sample		Analytical Method	Level(s)	Date(s)	Citation
Material sampled	Origin				
Sediment	Toulon	FS	0.006mg/kg dry wt.	-	Greffard, J. and Meury, J., 1967
Sediment (black mud)	Bay of Villefranche	FS	1.5mg/kg	-	Perdriau, J., 1964
Sardine	Bay of Naples, Italy	-	0.0654mg/kg	-	Bourcart, J. and Mallet, L., 1965
Raja miraletus (muscle)	Adriatic	C	0.1846mg/kg dry wt.	-	Piccinetti, C., 1968
Mytilus edulis (Mussel)	Eguillette, near Toulon	FS	0.022mg/kg dry wt.	-	Greffard, J. and Meury, J., 1967
Mussel (soft parts)	Bay of Naples, Italy	-	0.130-0.54 mg/kg dry wt.	-	Suess, M.J., 1970
Ostrea edulis (Oyster, soft tissue)	Adriatic	C	0.334mg/kg dry wt.	-	Piccinetti, C., 1968
Portunus sp (Crab)	Adriatic	-	0.857mg/kg dry wt.	1965-66	Scaccini, A. and Scaccini-Cicatelli, M., 1969
Holothuroidea (Echinoderm, muscle)	Antibes	FS	0.039mg/kg dry wt.	-	Lalou, C., 1965

Concentrations in Water, Sediments and Biota

Benzo(a)pyrene (page 4)

Chemical Group: Benzopyrene

Description of sample		Analytical Method	Level(s)	Date(s)	Citation
Material sampled	Origin				
Holothuroidea (Echinoderm, viscera)	Villefranche	-	1.029mg/kg dry wt.	-	Lalou, C., 1965
Plankton	Capri, Bay of Naples	-	0.0238mg/kg	1964	Bourcart, J. and Mallet, L., 1965
Plankton	Italy	-	0.006-0.021 mg/kg dry wt.	-	Suess, M.J., 1970
Plankton	French Mediter-ranean Coast	-	Up to 0.005 mg/kg dry wt.	-	Suess, M.J., 1970
Algae	Italy	-	0.002mg/kg dry wt.	-	Suess, M.J., 1970
Sediment (mud, sand, shell) 15-45m	Highly industri-alised area, Bay of Naples, Italy	-	1-3mg/kg dry wt.	-	Suess, M.J., 1970
Mytilus edulis (Mussel)	S. California	-	0.0082mg/kg wet wt.	-	Dunn, B.P. and Young, D.R., 1976
Portunus sp. (Crab)	Adriatic	-	0.857 mg/kg dry wt.	1965-66	Scaccini, A. and Scaccini-Cicatelli, 1969.

Concentrations in Water, Sediments and Biota

Benzo(a)pyrene (page 5)

Chemical Group: Benzopyrene

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material sampled	Origin				
Mytilus edulis (Mussel)	Oregon estuary, USA	FS	0.03 mg/kg dry wt.	1976	Mix, M.C. et al., 1977
Marine algae	N. Coast France	-	0.06 mg/kg dry wt.	1964	Mallet, L., 1967

Abbreviations:

FS - Fluorescent spectrophotometry

TLS - Thin layer spectrophotometry

C - Colorimetry

GC - Gas Chromatography

Array of Toxic Effects on Man and Other Mammals

Benzo(a)pyrene

Chemical group: Benzopyrene

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
4563	52 weeks	oral	rat	TDL ₀ , neo- plastic effects	NIOSH, 1978, p.5
1000	during gestation	oral	rat	TDLo, terato- genic effects	NIOSH, 1978, p.5
500 (100mg)	single dose	oral	rat (Sprague Dawley, 50 days old, female)	mammary tumours	Huggins and Yang, 1962 (IARC, 1973, p.103)
80 (2mg)	11th-15th day of gestation	sub cut., intra- perit.	mouse (ICR/Ha)	lung ademomas and skin car- cinomas in offspring	Bulay and Wattenberg, 1970 (IARC, 1973, p.113)
50	-	sub cut.	rat	LD ₅₀	NIOSH, 1978, p.5
50 (1.25mg)	single dose	injec- tion	mouse	pathological changes in lung tissue (60 days)	Draganov, 1966 (EPA, 1976, p.55)
4.8 (2x2mg/week)	6 months	oral (int- ub.)	hamster	stomach- papillomas and carcinomas	Dontenwill and Mohr, 1962 (IARC, 1973, p.104)
0.48 (0.012mg)	single dose	oral (int- ub.)	mouse	stomach tumours	Peirce, 1961 (IARC, 1973, p.102)
(1% solution in benzene)	4 months (120x)	dermal appl.	human (26 patients)	verrucae	Cottini and Mazzone, 1939 (IARC, 1973, p.114)

Array of Toxic Effects on Man and Other Mammals

Benzo(a)pyrene (page 2)			Chemical group: Benzopyrene		
concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
10 (+3.5ppm SO ₂)	more than 1 year (1 hour/ day)	inhal.	rat	squamous cell carcinomas of the lung	Laskin et al., 1970 (IARC, 1973, p.107)
0.003-0.216	more than 5 years	inhal.	human (employees in gas works industry, 40-65 years old)	increase in lung cancer (69%) and bronchitis mortality (126%) (8 years)	Lawther et al., 1965 (NAS, 1972, p.202)
0.002	more than 20 years	inhal.	human	increase in lung cancer (59%), stomach can- cer (67%), leukemia (68%), skin cancer (300%) and bladder cancer (68%), deaths	Bridbord and French, 1978 p.455

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Benzo(a)pyrene

Chemical group: Benzopyrene

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Sprague Dawley, 50 days old, female)	oral	500 (100mg)	single dose	mammary tumours	Huggins and Yang, 1962 (IARC, 1973, p.103)
mouse (ICR/Ha)	sub cut., intra- perit.	80 (2mg)	11th-15th day of gestation (daily)	lung adenomas, skin carcinomas in the off- spring	Bulay and Wattenberg, 1970 (IARC, 1973, p.113)
rat (Wistar)	intra- perit.	50 (10mg)	single dose	mammary and uterine carcin- omas (1 year)	Payne, 1958 (IARC, 1973, p.112)
mouse (18-30 days)	oral (diet)	50 (250ppm)	140 days (daily)	leukaemias, lung adenomas, stomach tumours	Rigdon and Neal, 1969 (IARC, 1973, p.103)
hamster	oral (intub.)	17 (2mg)	6 months (2x/week)	stomach- papillomas and carcinomas	Dontenwill and Mohr, 1962 (IARC, 1973, p.104)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Benzo(a)pyrene (page 2)

Chemical group: Benzopyrene

CARCINOGENICITY (contd.)

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
hamster	intra- tracheal	4 (0.5mg)	5 months (1x/week)	bronchial tumours (9 months)	Herrold and Dunham, 1962 (IARC, 1973, p.108)
mouse (C3H)	sub cut.	2.5 (0.062mg)	single dose	local sarcomas	Bryan and Shimkin, 1943 (IARC, 1973, p.110)
rat	intra- tracheal	0.05 (0.01mg+ India ink and blood substitute BK-8)	10 months (1x/month)	lung tumours (34 months)	Yanisheva, 1971 (IARC, 1973, p.108)
description of organism	route	concentration in mg/m ³ (conc. cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	inhal.	10 (+3.5ppm SO ₂)	more than 1 year (1 hour/day)	squamous cell carcinomas of the lungs	Laskin et al., 1970 (IARC, 1973, p.107)

A comprehensive evaluation of the known studies designed to assess the possible carcinogenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"B(a)P has produced tumours in all of the nine species for which data are reported following different administrations including oral, skin and intratracheal routes. It has both a local and a systematic carcinogenic effect. In sub-human primates, there is convincing evidence of the ability of B(a)P to produce local sarcomas following repeated subcutaneous injections and lung carcinomas following intratracheal instillation. It is also an initiator of skin carcinogenesis in mice, and it is carcinogenic in single-dose experiments and following prenatal exposure." (IARC, 1973, p.115)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Benzo(a)pyrene (page 3)

Chemical group: Benzopyrene

CARCINOGENICITY (contd.)

"No epidemiological studies on the significance of B(a)P exposure to man are available, and the studies reported in section 3.3 are insufficient to prove that B(a)P is carcinogenic for man. However, coal-tar and other materials which are known to be carcinogenic to man may contain B(a)P. The substance has also been detected in other environmental situations. The possible contribution of polycyclic aromatic hydrocarbons from some environmental sources to the overall carcinogenic risk to man is discussed in the preamble.

Similarities of metabolism of B(a)P in human and mouse cells cultured in vitro have been reported. The relevance of this finding for evaluating the risk for man cannot yet be assessed." (IARC, 1973, p.116)

MUTAGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
hamster (Chinese)	intra- perit.	500	single dose	no increase of micronuclei in bone marrow cells	Bayer, 1978, p.424
hamster (Chinese, 8-20 weeks old)	intra- perit.	100	single dose	no chromosome aberrations in bone marrow cells	Bayer, 1978, p.424
hamster (Chinese)	intra- perit.	40	single dose	increase in sister chrom- atide exchanges in bone marrow cells	Bayer, 1978, p.425

These studies, designed to evaluate the possible effects of the substance on gene mutation, chromosomal mutations, on DNA repair or recombination or on transformation, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Benzo(a)pyrene (page 4)

Chemical group: Benzopyrene

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Benzo(a)pyrene

Chemical Group: Benzopyrene

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Calanus heligolan- dicus (Zooplank- ton)	Adult	0.004	-	Mortality	-	Lee, R.F. (Un- published) quoted in Lee, R.F. et al., 1972
Gyrodinium sp. (Marine dino- flagellate)	-	0.005	12 days	Cell division period in- creased, mitotic index increased.	12 days	Ishio, S. et al., 1977
Antithamion plumula (Marine red algae)	-	0.01	96 hrs.	Increased number of cells	96 hrs.	Boney, A.D. and Corner, E.D.S., 1962
Porphyra tenera (Marine algae)	-	1.0	1-5 hrs.	Decrease in cell size	1-5 hrs	Boney, A.D., 1974

Toxic or Other Effects on Marine Organisms and Ecosystems

Benzo(a)pyrene (page 2)

Chemical Group: Benzopyrene

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Porphyra tenera (Marine algae)	-	1.0	1-5 hrs.	Tumorous growth on marginal area of frond	36 days	Boney, A.D., 1974
Paracentrotus lividus (Sea urchin)	Unfert. egg	5.0	3 hrs.	Abnormal egg cleavage, abnormal development.	3 hrs.	de Lima-Zanghi, C., 1968
Paracentrotus lividus (Sea urchin)	Unfert. egg	4.9-5.2	3 hrs.	Abnormal development	3 hrs.	Ceas, M.P., 1974
Sphaerechinus granularis (sea urchin)	Unfert. egg	5.0	3 hrs.	Eggs cleaved abnormally and developed into irregular morulae	3 hrs.	Ceas, M.P., 1974

Toxic or Other Effects on Marine Organisms and Ecosystems

Benzo(a)pyrene (page 3)

Chemical Group: Benzopyrene

System Organism Ecosystem Non-living	Life Stage	Concentration	Exposure Time	Effect	Time of Observation	Citation
mg/L						
Arbacia granulatis (Sea urchin)	Egg	5.0	3 hrs.	Eggs cleaved abnormally and developed into irregular morulae	3 hrs.	Ceas, M.P., 1974
Paracentrotus lividus (Sea urchin)	Fert. egg	0.0252-25.2	-	Fertilisation normal and identical to controls	-	Ceas, M.P., 1974
Paracentrotus lividus (Sea urchin)	Unfert. egg	5.0	-	Eggs cleaved abnormally and developed into irregular morulae	-	de Angelis, E. and Giordano, G.G., 1974

Analysis

Benzo(a)pyrene

Chemical group: Benzopyrene

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
liquid and gas chromatography plus mass spectroscopy (1ppb)	not very sensitive/ closed system procedure, rapid, apparatus available in well-equipped laboratories	May et al., 1975
gas chromatography (ppb-range)	great care must be given to preparation of standard samples/sensitive, inexpensive, reliable method	Junk et al., 1974
high pressure liquid chromatography (10ng)	low resolution may cause errors in quantification/ rapid, selective, inexpensive routine method	Dong and Locke, 1976

Legislation for the Protection of Man
and the Marine Environment

Benzo(a)pyrene

Chemical Group: Benzopyrene

general classifi- cation of control mechanism	country or political sub-division	description of control mechanism	quantitive information (analytical method(s))	citation (as reported in)
Control of substances in water	Yugoslavia	maximum permissible concentrations of dangerous substances in interrepublic watercourses	0.0002mg/l of total carcinogenic polynuclear aromatic hydrocarbons in Class I and Class II waters ^a	IDHL, 1978 (awaiting publication)

^a Class I: waters which, in their natural state, where necessary after disinfection, may be used for drinking purposes and in the food industry and, in the case of surface waters, for breeding Salmonidae. Class II: waters which, in their natural state, may be used for bathing and recreation, water sports, breeding of Cyprinidae, or which, after treatment, may be used for drinking purposes and in the food industry.

Benzo(a)pyrene

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MEDITERRANEAN DATA PROFILE

ZINC

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OUTLINE - GENERAL SUMMARY FOR ZINC

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GENERAL SUMMARY FOR ZINC

I. INTRODUCTION

Zinc is usually found in nature as the sulphide; it is often associated with sulphides of other metals, especially lead, copper, cadmium and iron. It also occurs as a silicate complex and carbonate. Furthermore, zinc is an essential constituent of many metallo-enzymes, proteins and structural cellular components (Bowen, 1966). High concentrations of zinc in the sea may result from the discharge of industrial wastes from mining, electroplating and synthetic fibre production (Bryan, 1971). A slow but continual process of mobilisation occurs as a result of metal complexing and certain other microbiological processes.

In sea water zinc can exist in several different stable or meta-stable forms. One of these forms has been called the "complexed" fraction, which appears to be relatively stable and can only be broken down at low pH. In addition, this fraction resists recombination with the ionic and "particulate" fraction. (Fowler and Heyraud, 1974)

Increasing mortality with increased temperature and decreased salinity has been demonstrated with various organisms.

The concentration of zinc in open sea waters of the Mediterranean appears to be similar to those of other oceans and seas.

II. OCCURRENCE

A. Production

CEC/EOA (1977) has reported that the zinc recovered annually from minerals has been more or less constant since 1970, and is about 5,000,000 tons worldwide.

France produced 218,000 tons and Italy produced 140,000 tons in 1971. Thermal production processing and wet processing are the two main methods of zinc production (CEC-EOA, 1977).

B. Use

In France the 1972 consumption of zinc was 264,000 tons, and in Italy it was 203,000 tons. The total world consumption for 1970 was 5,000,000 tons (CEC-EOA, 1977).

The major industrial uses of zinc are in the production of copper alloys, galvanising, the manufacture of light alloys, rolled and wire drawn zinc, sheet products and in the production of thermoplastic products (CEC-EOA, 1977).

III. ZINC IN THE ENVIRONMENT

A. Sources

1. Natural

Dissolution and weathering are calculated to release 720,000 tons/year of zinc worldwide (GESAMP, 1976). Precipitation in the Baltic Sea has been estimated to contribute 4×10^3 tons/year (Somer, 1977). Surface run off in the Southern California Bight contributes 100 metric tons/year, 74% of which is particulate. Dry aerial fallout in the same area has been estimated at 150 metric tons/year (Young et al., 1977).

2. Anthropogenic

Concentrations of zinc in surface waters are correlated with man's activities and with urbanisation and run off (Durum, 1974).

The industries that are most likely to discharge large quantities of zinc include steel works using galvanising processes, manufacturers using electroplating processes of zinc and bronze, manufacturers of silver plating, rayon viscose production, production of papers and magazines, etc. Quantities of zinc are also found in mining waste waters (CEC-EOA, 1977).

Durum et al. (1971) have reported that in mining areas surface water concentrations as high as 50mg/liter can be found.

B. Transformation

1. Abiotic

The sedimentation of Zn is not very strong except under anaerobic conditions, where insoluble zinc sulphide is formed. In this case, however, the precipitation of copper is favoured far more than zinc. Much of the zinc in sea water is found as dissolved Zn. The tendency to form complexes is not as high as for copper (Somer, 1977).

Lowman et al. (1966), in a study of a Puerto Rican river outflow, noted that the linear precipitation of Zn with time in a mixture of river water and sea water was reflected in the uniform distribution of zinc from the outflow. The coprecipitant for zinc in this mixture was iron.

Lu and Chen (1977) showed that for zinc and some other heavy metals the type of sediment (i.e. clay, silt or sand) does not control the direction of metal migration.

It is regulated mainly by the chemistry of the immediate overlying water as well as that of the interstitial water. The redox condition is the principal factor. The amount of Zn released increases as the redox conditions become more oxidising.

Sedimentation through the association of zinc with bacterial cells has also been demonstrated with mixed cultures of marine bacteria (McLerran and Holmes, 1974).

2. Biotic

The "particulate fraction", owing to its stability, might form a sink with only limited availability to marine biota. If zinc or other metals which exist in a complexed state are biologically derived, the importance of marine biota as metal processors, as well as accumulators, becomes evident. Different chemical forms of zinc excreted by zooplankton as well as polarographically by shrimp have been reported.

Some marine organisms are capable of forming zinc complexes and excrete such complexes with other waste products (Fowler and Heyraud, 1974).

C. Bioaccumulation

The uptake of Zn by phytoplankton is high; furthermore, zinc is enriched on the surface of macrophytes. Invertebrates and fish have lower concentrations than phytoplankton. There are no indications of magnification through the food chain (Somer, 1977).

For both zinc and iron, the food chain is the major source of metal in the tissues, the input from food being approximately two orders of magnitude greater than that from sea water (Young, 1977).

The absorption of zinc has been studied in brown seaweed (Laminaria digitata), but no evidence for the regulation of zinc has been found. Absorption is a gradual process of accumulation not accompanied by the exchange of zinc. Once absorbed, zinc shows little tendency to be lost from the plant. Over a period of 21 days a biomagnification coefficient of 2000 was recorded for the growing region (Bryan, 1969). In the shore crab, Carcinus maenas, the concentration of zinc in the body is regulated and does not change appreciably when the concentration in the water is increased from 1 to 100ug/l. Over a period of 22 days a biomagnification factor of 300 was demonstrated for the gills of this organism. (Bryan, 1966)

A biomagnification coefficient of 10 has been reported for the flounder (Hoss, 1964). The highest biomagnification coefficient found in the literature reviewed was 20,950 for the oyster, Crassostrea Virginica (Shuster and Pringle, 1969).

Aubert et al. (1974) found a biomagnification coefficient of 3,400 in plankton exposed to 0.03mg/l of zinc for 8 days.

Fowler and Oregoni (1976) determined the concentration of Zn in mussels from Sète to Genoa. They found that near ports and river discharges, the zinc content of the mussels increased. Seasonal variation in the concentration of zinc was evident and may in part have been due to the great changes in biomass during the life of the mussel.

IV. MONITORING

A. Analysis

Atomic absorption spectroscopy (Greig, 1975), Zeeman atomic absorption spectrometry (Koizumi and Yasuda, 1976), and differential pulse anodic stripping voltametry (Abdullah et al., 1976) are all suitable methods for the monitoring of zinc.

B. Amount in the Mediterranean

Concentrations of Zn in open sea samples from the Mediterranean are similar to those of other marine samples. Grancini et al. (1975) found 0.0364mg/l of zinc in sea water from the N. Adriatic. Sea water from Haifa Bay, Israel, contained 0.0436mg/l (Roth and Hornung, 1977).

Fukai and Huynh-Ngoc (1976) have investigated the concentration of Zn in coastal and offshore waters of the N.W. Mediterranean. Except for areas of significant anthropogenic inputs they observed no significant difference between the concentration in coastal and offshore waters. Levels of non-particulate zinc ranged from 0.0019-0.007mg/l.

Levels of zinc in sediments from various regions of the Mediterranean are as follow: Adriatic, 131mg/kg dry weight (Paul and Meischner, 1976); Tel Aviv, Israel, 80mg/kg (Amiel and Navrot, 1978); Ligurian Sea, 70.6mg/kg dry weight (Renfro and Oregioni, 1974).

Organisms from various areas of the Mediterranean show a wide variance in zinc concentration, depending on species and

origin. The mussel, Mytilus galloprovincialis, has been the object of many studies. Samples from Yugoslavia contained 0.178mg/kg dry weight (GFCM, 1978); Mytilus from the Saronikos Gulf contained 872mg/kg dry weight (Papadopoulos and Kanas, 1976a). Commercial fish from Haifa Bay, Israel, contained an average of 27.2mg/kg dry weight of zinc (Roth and Hornung, 1977).

C. Amount Entering the Mediterranean

The total annual zinc pollution load of the Mediterranean is 25,000 tons, 18,000 tons/year of which is carried by rivers. 5,000 tons/year is produced by coastal industry. 8,600 tons/year originates in the Adriatic and about 5,200 tons/year originates in the Liguro-Provencal (UNEP, 1977).

D. Regulations

Italy has recommended limits for industrial and urban effluents of 1.0mg/l of zinc discharged into public sewers, and 0.5mg/l as Zn discharged into surface waters. Yugoslavia allows a maximum permissible concentration of 1.0mg/liter for water used or intended for use as drinking water, for the production of food stuffs, fish breeding, watering of animals or public bathing. The Libyan Arab Republic has proposed standards of 1.0mg/l for effluents discharged into surface water resevoirs, for direct use in agriculture, discharged into aquifiers used for public water supply and for effluents discharged into urban sewage systems. The proposed standard for effluents discharged into the sea is 2.0mg/l (WHO/UNEP, 1976). Spain, Tunisia and Turkey also have legislation dealing with the discharge of zinc (IDHL, 1978; Kratel, unpublished).

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

It should be noted that many concentrations used in toxicity tests are higher than the saturation concentration for Zn, which is 1.2mg/l (Bernhard and Zattera, 1975).

A concentration of 100ug/l resulted in a 25 hour LC50 in the polychaete Ophryotrocha (Brown and Ahsanullah, 1971). Inhibition of larval development was observed with Paracentrotus lividus at a concentration of 30ug/l (Bernhard and Zattera, 1975).

The LC50 value for the brine shrimp is 100ug/l, over an exposure time of 150 hours (Brown and Ahsanullah, 1971).

Jones (1975) tested the synergistic effects of salinity, temperature and zinc sulphate on different species of isopods. He found increased mortality when the temperature increased or when the salinity decreased. Acutely toxic concentrations induced cellular breakdown of the gills and possible clogging of the gills with mucous. Chronically toxic concentrations of zinc compounds, in contrast, caused general enfeeblement and widespread histological changes to many organs, but not to gills. Growth and maturation were retarded (EPA, 1976).

Negilski (1976) observed increased mucous secretions and marked erosion of anal and caudal fins at a concentration of 7.2ug/l of Zn over an exposure time of 96 hours, with Aldricheta forestti (yellow eye mullet).

Eisler and Hennekey (1977) have reported an LC50 of 0.4ug/l over 96 hours for the adult crab, Pagurus longicarpus.

B. Toxic Effects on Man and Other Mammals

NIOSH (1978) reports the lowest lethal dose (LDLo) known for a human is 500ug/kg bw/day. The toxic dose low (TDLo) for zinc oxide is 600ug/m³. In this case the zinc oxide was inhaled and affected the pulmonary system. ITII (1975) has reported an LD50 of 630ug/kg bw/day for the rat.

Adverse effects of zinc include acute metal fume fever by the inhalation of fumes, throat irritation, coughing, dyspnea, muscle and joint pain (Lehmann, 1910), gastric irritation (Chrometzka, 1936), peptic ulcers and various liver effects (Guja, 1973).

Zinc has not been implicated in any human diseases derived from the eating of seafoods (Osterberg and Keckes, 1977).

There have been reports of human cases of zinc poisoning associated with the prolonged consumption of water from galvanised pipes. In two adults who drank water containing 40mg/l of Zn, irritability, muscular stiffness and pain, loss of appetite and nausea were reported. There is no evidence that zinc in excess is carcinogenic, mutagenic, or teratogenic (NAS, 1977).

Total Production

Zinc (metal)		Chemical Group: Zinc		
year	area	amount	trend	citation (as re- ported in)
1967	World	4 120 000 tons	-	Mc Mahon, 1971 (CEC/EOA, 1977, p.58)
1968	World	4 630 000 "		
1969	World	4 970 000 "		
1970	World	4 880 000 "		
1971	World	4 610 000 "		
1967	France	187 000 tons	-	IGS, 1973 (CEC/EOA, 1977, p.59)
1968	France	207 000 "		
1969	France	253 000 "		
1970	France	224 000 "		
1971	France	218 000 "		
1967	Italy	88 000 "		
1968	Italy	113 000 "		
1969	Italy	131 000 "		
1970	Italy	142 000 "		
1971	Italy	140 000 "		

Total Consumption

Zinc (generic)			Chemical Group: Zinc	
year	area	amount	trend	citation (as re- ported in)
1967	France	202 000 tons		CEC/EOA, 1977, p.60
1968	France	202 000 "		
1969	France	239 000 "		
1970	France	220 000 "		
1971	France	225 000 "		
1972	France	264 000 "	increasing	
1967	Italy	141 000 "		
1968	Italy	155 000 "		
1969	Italy	167 000 "		
1970	Italy	178 000 "		
1971	Italy	170 000 "		
1972	Italy	203 000 "	increasing	

Production Process(es)

Zinc (metal)

Chemical Group: Zinc

process (major or minor by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as re- ported in)
Zinc metallurgy (thermal process): roasting ZnS minerals, calcination, reduction, condensation, distillation	-	ZnO/-/SO ₂ , silicon oxides, Zn,Pb,Cu,Cd, Fe,As	CEC/EOA, 1977, p.56,71
Zinc hydrometallurgy (wet process): roasting ground blends, neutral lixiviation, decantation, purification by cementation, filtration, electrolysis, re-smelting	-	ZnO, SO ₄ Zn/-/ Zn,Cd,Cu,As,Fe	CEC/EOA, 1977, p.57,72

Use

Zinc (generic)		Chemical Group: Zinc		
use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as re- ported in)
copper alloys	France, 1970 (major) Italy, 1970 (major)	-	-	CEC/EOA, 1977, p.66
galvanizing	France, 1970 (major) Italy, 1970 (major)			
light alloys	France, 1970 (major) Italy, 1970 (major)			
rolled and wire drawn zinc	-			
sheet products	France, 1970 (major) Italy, 1970 (minor)			
zinc oxide	France, 1970 (minor)			

Pathways Leading to Marine Pollution

Zinc (Zn^{2+})		Chemical Group: Zinc	
Pathway	Quantity	Area	Citation
Dissolution and weathering	720 000 tons/yr	World	GESAMP, 1976
Precipitation	4000 tons/yr	Baltic Sea	Somer, E., 1977
Dry aerial fallout	150 metric tons/yr	Southern California Bight, U.S.A.	Young, D.R. et al., 1977
Surface runoff	100 metric tons/yr (74% particulate)	Southern California Bight, U.S.A.	Young, D.R., et al., 1973
Rivers and streams	857 kg/day (soluble)	Lougher Estuary, U.K.	Chubb, C.J., and Stoner, J.H. 1977
Direct sewage outfall into sea	-	Yafo, Tel Aviv	Amiel, A.J. and Navrot, J., 1978

Transformation in the Marine Environment

Zinc (Zn^{2+})

Chemical Group: Zinc

Process	Medium	Parameters	Effect	Citation
Sedimentation	Water, Clyde Estuary	Increasing salinity (8%-32%) Low fresh water flow	Decreasing zinc level in the water	MacKay, D.W. and Leatherland, T., 1976
Desorption	Sediment along Rhine estuary to Wadden Sea	Increasing salinity	Increasing desorption	de Groot, A.J. et al., 1976
Leaching with acetic acid	Mediterranean sediment laboratory	Decreased pH	10-80% desorption	Duursma, E. K., 1976
Adsorption with clay	Sea water, laboratory	18-23°C, pH 7.7-8.2	99% of zinc adsorbed in 3 days, 1% (0.02 mg/l) remaining in solution	Krauskopf, K.B., 1956
Oxidation	Sediment, laboratory	Increased redox potential	Increased release into sea water. Under oxidised conditions, $ZnCO_3$ and $ZnSiO_3$ controlling solid; under reduced conditions, ZnS controlling solid.	Lu, J.C.S. and Chen, K.Y., 1977
Oxidation	Reduced Mobile Bay sediment containing S-, laboratory	Decreased pH	Increased soluble zinc	Gambrell, R. P. et al., 1977

Transformation in the Marine Environment

Zinc (Zn²⁺) (page 2)

Chemical Group: Zinc

Process	Medium	Parameters	Effect	Citation
Oxidation	Mobile Bay reduced sediment containing no S ⁻	Increased pH	5-100x-less soluble zinc produced than from S ⁻ containing sediment	Gambrell, R. P. et al., 1977
Altered pH	Mobile Bay sediment, laboratory	Increased pH 5.0-8.0 Decreased pH	Decreased soluble and exchangeable zinc. Formation of ZnCO ₃ Increase in weakly or uncomplexed soluble zinc	Gambrell, R. P. et al., 1977
Precipitation with Fe(3)OH	River water mixed with filtered sea water, laboratory	-	67% zinc precipitated in 2 hours	Lowman, F.G. et al., 1966
Sedimentation	Mixed cultures of marine bacteria	-	17% zinc associated with bacterial cells; 68% zinc precipitated in 120 hours	McLerran, C. J. and Holmes, C.W., 1974

Behaviour of a Chemical Substance in Marine Organisms

Zinc (Zn²⁺)

Chemical Group: Zinc

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn. mg/l	Time	Tissue/ Organ	% Biomagnification Coefficient	%	Time	Name	Quantity	
Gobius sp. (goby)	F+ SW	(Zn-65)	96 days	WH	100	25	-	-	-	Renfro, W.C. et al., 1974
Paralichthys sp. (flounder)	F	(Zn-65)	5 days	WH	100	10	-	-	-	Hoss, D.E., 1964
Crassostrea virginica (oyster)	W	0.1	4 weeks	WH	100	20 950	-	-	-	Shuster, C.N., Jr. and Pringle, B.H., 1969
Nucella lapillus (dogwhelk)	W	0.014	20 days	S T	250	-	-	-	-	Young, M.L., 1977
Mytilus edulis (mussel)	W	5.0	7 days	G	-	100 (d.w.)	-	-	-	Brown, B.E., 1972
Mya arenaria (soft shell)	W	0.2	50 days	S T	-	85	-	-	-	Pringle, B.H. et al., 1968
Scrobicularia plana (bur- rowing bivalve)	F	455	-	D G	75	16	-	-	-	Bryan, G.W. and Uysal, H., 1978

Behaviour of a Chemical Substance in Marine Organisms

Zinc (Zn²⁺) (page 2)

Chemical Group: Zinc

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn. Time mg/l	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
<i>Carcinus maenas</i> (shore crab)	W	0.0073 22 days	G	-	300	-	-	-	-	Bryan, G.W., 1966
<i>Lysmata seticaudata</i> (shrimp)	SW	(Zn-65) 4 days	WH	100	80	-	-	-	-	Fowler, S.W. and Heyraud, M., 1974
<i>Palaemon serratus</i> (pink shrimp)	SW	0.017 10 days	WH	100	40	-	-	-	-	Fraizier, A., 1973
<i>Laminaria digitata</i> (brown seaweed)	W	0.0024 21 days	G R	-	2,000	-	-	-	-	Bryan, G.W., 1969
<i>Ascophyllum nodosum</i> (brown seaweed)	W	0.1 24 hours	tip	-	30	-	-	-	-	Skipnes, O. et al., 1975

Behaviour of a Chemical Substance in Marine Organisms

Zinc (Zn²⁺) (page 3)

Chemical Group: Zinc

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn. mg/l	Time	Tissue/ Organ	% Biomagnification Coefficient	%	Time	Name	Quantity	
Palaemon serratus (Pink shrimp)	SW	0.1	10 days	WH	100	34	-	-	-	Fraizier, A., 1973
Mytilus edulis (Mussel)	art- if. SW	0.45- 0.75	10 days	-	-	75	50	20 days	-	Calapaj, G.G., 1974
Gammarus locusta (Amphipod)	SW	-	27 days	-	-	400	50	70 days	-	Fowler, S.W. et al. 1974
Nereis diversicolor (Polychaete)	SW	0.0327	7 days	WH	100	1235.4	-	-	-	Aubert, M. et al., 1976
Plankton	art- if.	0.03	8 days	WH	100	3 400	-	-	-	Aubert, M. et al., 1974

SW Seawater
W Water
G Gill

S T Soft tissue

d.w. BMC calculated from dry weight of organism

F Food
D G Digestive gland
G R Growing region
WH Whole

Behaviour of the Substance in Man and Other Mammals

Zinc chloride

Chemical Group: Zinc

description of organism	exposure		retention tissue/percent/time	clearance rate		metabolite name/amount hazard	citation (as reported in)	
	route	concentration		duration of exposure	percent/time			
human (patients)	intra-venous	100uCi	single dose	liver/3.8%/174 days	-	-	Siegel et al., 1961 (FIRL, 1978, p.55)	
human (patients)	intra-venous	100uCi	single dose	% dose/g wet tissue: liver: 0.061/1 day, 0.015/71 days kidney: 0.040/1 day, 0.004/71 days spleen: 0.012/1 day, 0.002/71 days lung: 0.004/1 day, 0.001/71 days intestine: 0.004/1 day, - stomach: 0.001/1 day, - skeletal muscle: 0.001/1 day, 0.002/71 days pancreas: 0.011/1 day, 0.001/71 days adrenal: 0.009/1 day, 0.002/71 days prostate: 0.002/1 day, 0.003/71 days			-	Spencer et al., 1965 (FIRL, 1978, p.57)

Behaviour of the Substance in Man and Other Mammals

Zinc chloride (page 2)

Chemical Group: Zinc

description of organism	exposure		retention tissue/percent/time	clearance rate		metabolite name/amount hazard	citation (as re- ported in)
	route	concentration		percent/time	rate		
human (29-48 years old)	oral	0.6-1.0 uCi	-	-	50%/154 days	-	Richmond et al., 1962 (FIRL, 1978, p.57)
human	intra- venous	-	-	-	18%/30 days in faeces, 1%/30 days in urine	-	Prasad, 1966 (FIRL, 1978, p.57)
human	oral	-	-	-	19-76%/15 days in faeces, 0.7-2.1%/15 days in urine	-	Prasad, 1966 (FIRL, 1978, p.57)

Behaviour of the Substance in Man and Other Mammals

Zinc chloride (page 3)

Chemical Group: Zinc

description of organism	exposure		retention tissue/percent/time	clearance rate		metabolite name/amount hazard	citation (as re- ported in)
	route	concentration		percent/time	name/amount hazard		
dog	intra- venous	6.5-13 ug	-	-	-	-	Sheline et al., 1943a (FIRL, 1978, p.63)
			% dose/hour: whole blood: 3.2/3, 4.1/170 pancreas: 2.3/3, 0.69/170 liver: 38/3, 3.5/170 kidney: 3.2/3, 0.9/170 stomach: 0.88/3, 0.81/170 small intestine: 5.2/3, 2.8/170 colon + cecum: 0.81/3, 1.0/170 heart: 0.58/3, 0.98/170 skeletal muscle: 9.5/3, 36/170 thyroids: 0.017/3, 0.0052/170 adrenals: 0.027/3, 0.014/170 pituitary: 0.12/3, 0.002/170 brain: 0.067/3, 0.62/170 lungs: 0.63/3, 0.71/170 spleen: 0.37/3, 0.31/170 intestinal lymph nodes: 0.07/3, 0.064/170 peripheral lymph nodes: 0.24/3, 0.32/170				

Behaviour of the Substance in Man and Other Mammals

Zinc chloride (page 4)

Chemical Group: Zinc

description of organism	exposure		retention tissue/percent/time	clearance rate		metabolite name/amount hazard	citation (as re- ported in)
	route	concentration		percent/time	name/amount		
dog	intra- venous	5.7ug	-	25%/12-14 days in faeces, 1.2-4.7%/15 days in urine	-	-	Sheline et al., 1943b (FIRL, 1978, p.63)
mouse	intra- venous	0.33ug	-	50%/170 hours in faeces	-	-	Sheline et al., 1943b (FIRL, 1978, p.63)

Behaviour of the Substance in Man and Other Mammals

Zinc sulphate

Chemical Group: Zinc

description of organism	exposure		retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as re- ported in)
	route	concentration				

Nothing found in the literature reviewed.

Behaviour of the Substance in Man and Other Mammals

Zinc oxide		Chemical Group: Zinc					
description of organism	route	exposure		retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)
		concentration	duration of exposure				
human	oral	-	-	-	-	zinc chloride (by hydrochloric acid of the gastric juice)	Arena, 1974, p. 241

Concentrations in Water, Sediments and Biota

Zinc (Zn ²⁺)		Chemical Group: Zinc			
Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Water	Sorfjorden, Norway	XFS	0.313 mg/l (75% in solution)	1972-1975	Melhuus, A. et al., 1978
Water	Gulf of Fos, North-West Mediterranean	DPASV	0.063 mg/l (soluble ionic)	1975	Benon, P. et al., 1978
Water	Baltic Sea	DPASV	0.005 mg/l (dissolved)	1975	Kremling K. and Petersen, H., 1978
Surface sediment	Tamar Estuary, U.K.	AAS	455 mg/kg dry wt.	1974	Bryan, G.W. and Uysal, H., 1978
Sediment and coal ash (1 cm)	Western Baltic Sea	AAS	340 mg/kg dry wt.	1971	Erlenkeuser, H. et al., 1974
Sediment	Queensland Ni outfall, Coral Sea	AAS	44 mg/kg dry wt.	1975	Knauer, G. A., 1977
Mytilus gallo-provincialis (Mussel - soft parts)	Gulf of La Spezia, Italy	AAS	381 mg/kg dry wt.	1975	Capelli, R. et al., 1978
Ulva pertusa (Edible green alga)	Kizang, Korea	AAS	95 mg/kg	1974	Pak, C.K. et al., 1977

Concentrations in Water, Sediments and Biota

Zinc (Zn²⁺) (page 2)

Chemical Group: Zinc

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Scomber japonicus (Mackerel-otolith)	Cyclades Islands, Aegean Sea	INAA	67 mg/kg dry wt.	1961	Papadopoloucol C. et al., 1978
Chorda filum (alga)	Sorfjorden, Norway	XFS	6950 mg/kg dry wt.	1974	Melhuus, A. et al., 1978
Mytilus edulis (Mussel gonad)	Newport Harbour, U.K.	OES	360 mg/kg dry wt.	1974	Young, D.R. and Alexander, G.V., 1977
Platichthys flesus (Flounder)	Northern Adriatic Sea	-	25.4 mg/kg	1975-1976	Majori, L. et al., 1978
Sediment (Mud - 165m)	Adriatic	AAS	131 mg/kg dry wt.	1973	Paul, J. and Meischner, D., 1976
Sediment	Haifa Bay, Israel	AAS	7.0 mg/kg dry wt.	1974	Roth, I and Hornung, H., 1977
Sediment	Athens sewage outfall area	NAA	45-1800 mg/kg dry wt.	1973	Papakostidis, G. et al., 1975
Sediment	Tel Aviv, Israel	AAS	80 mg/kg	1973-1974	Amiel, A.J. and Navrot, J., 1978
Sediment	Ligurian Sea	AAS	70.6 mg/kg dry wt.	1973	Renfro, W.C. and Oregioni, B., 1974

Concentrations in Water, Sediments and Biota

Zinc (Zn²⁺) (page 3)

Chemical Group: Zinc

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Seawater	Gulf of Fos, N.W. Mediterranean	DPASV	0.063 mg/L (soluble, ionic)	1975	Benon, P. et al., 1978
Seawater	Monaco, (Surface)	S	0.0075 mg/L (total) 0.0025 mg/L (extractable)	1970	Fukai, R. et al., 1973
Seawater	N.W. Mediterranean 5-50m	ASV	0.0019-0.007 mg/L (non-particulate)	1974	Fukai, R. and Huynh-Ngoc, L., 1976b
Seawater	Menton	NAA	0.006 mg/L	-	May, S. et al., 1975
Seawater	N. Adriatic	NAA	0.0364 mg/L	1972	Grancini, G. et al., 1975
Seawater	Haifa Bay, Israel	AAS	0.0436 mg/L	1974	Roth, I. and Hornung, H., 1977
Seawater	Alexandria	AAS	0.0182 mg/L	-	Ibragim, A.M. and Patin, S. A., 1976
Seawater	Suez	AAS	0.0096 mg/L	-	Ibragim, A.M. and Patin, S. A., 1976
Paracentrotus lividus (Sea urchin - soft parts)	Bay of Naples	AAS	120 mg/kg wet wt.	1973	Sheppard, C.R. C. and Bellamy, D.J., 1974

Concentrations in Water, Sediments and Biota

Zinc (Zn²⁺) (page 4)

Chemical Group: Zinc

<u>Description of Sample</u>		<u>Analytical Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material Sampled</u>	<u>Origin</u>				
Microcosmus sulcatus (Tunicate - whole)	Keratsini Bay	NAA	180 mg/kg dry wt.	1974	Papadopoulou, C. and Kanias, G.D., 1977
Acartia clausi (Zooplankton)	Elefsis Bay, upper Saronikos Gulf, Greece	NAA	1600 mg/kg dry wt.	1974	Zafiropoulos, D. and Grimanis, A.P., 1977
Microplankton	N.W. Mediterranean	AAS	413 mg/kg dry wt.	1974	Fowler, S.W. et al., 1976
Tapes decussatus (Shellfish - soft part)	Cakalburnu fishery, Izmir Bay, Turkey	AAS	106 mg/kg dry wt.	-	Geldiay, R. and Uysal, H., 1975
Tapes decussatus (Shellfish - digestive gland)	Izmir Bay, Turkey	AAS	177.65 mg/kg dry wt.	-	Geldiay, R. and Uysal, H., 1976
Mytilus galloprovincialis (Mussel)	Yugoslavia	-	0.178 mg/kg dry wt.	1977	GFCM, 1978
Mytilus galloprovincialis (Mussel - whole)	Saronikos Gulf	AAS	872 mg/kg dry wt.	1969	Papadopoulou, C. and Kanias, G.D., 1976
Ostrea edulis (Oyster - whole)	Saronikos Gulf	AAS	10710 mg/kg dry wt.	1969	Papadopoulou, C. and Kanias, G.D., 1976
Mytilus galloprovincialis (Mussel)	N.W. Mediterranean	AAS	209 mg/kg dry wt.	1974	Fowler, S.W. and Orgeioni, B., 1976
Mytilus galloprovincialis (Mussel)	Sicily	AAS	250 mg/kg	1976	Castagna, A. and Sarro, F., 1977

Concentrations in Water, Sediments and Biota

Zinc (Zn²⁺) (page 5)

Chemical Group: Zinc

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Engraulis encrasicolus (Anchovy)	Savona, Ligurian Sea	-	21.53 mg/kg	1974	Ciusa, W. et al., 1974
Mullus surmuletus (Red mullet - muscle)	Seyhan delta, Ankara	-	3.07 mg/kg wet wt.	1977	GFCM, 1978
Sargus annularis (Fish - liver)	Mytelene Harbour, Aegean Sea	RS	111 mg/kg dry wt.	1973-1974	Grimanis, A.P. et al., 1978
Gobius niger (Fish - flesh)	Keratsini Bay, Aegean Sea	NAA	58 mg/kg dry wt.	1973-1974	Grimanis, A.P. et al., 1978
Commercial fish	Haifa Bay, Israel	AAS	27.2 mg/kg dry wt.	1974	Roth, I. and Hornung, H., 1977
Tapes decussatus (Shellfish - soft parts)	Tuzla, Izmir Bay, Turkey	AAS	211.4 mg/kg dry wt.	-	Geldiay, R. and Uysal, H., 1975

S	Spectroscopy
NAA	Neutron activation analysis
AAS	Atomic adsorption spectrophotometry
ASV	Anodic stripping voltametry
DPASV	Differential pulse anodic stripping voltametry
INAA	Instrumental neutron activation analysis
RS	Radiochemical separation
OES	Optical emission spectrometry
XFS	X-ray fluorescence spectrometry

Array of Toxic Effects on Man and Other Mammals

Zinc chloride

Chemical Group: Zinc

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
500	single dose	oral (gavage)	rat	stomach and liver damage, pyloric stenosis, death	Hahn and Schunk, 1955 (FIRL, 1978, p.30)
350	-	oral	rat	LD50	NIOSH, 1978, p.26
200	-	oral	guinea pig	LD50	NIOSH, 1978, p.26
50	-	oral	human	LDLo	NIOSH, 1978, p.26
20	11 days during gestation	intra- perit.	mouse	TDLo, terato- genic effects	NIOSH, 1978, p.26
-	-	dermal contact	human (using zinc chloride as a flux in soldering, handling railway ties im- pregnated with zinc chloride)	skin irrita- tion	Uotila and Noro, 1957 (Patty, 1963, p.1187)
6.3 (0.6mg Zn)	20 days (alternate days)	intra- perit.	rat (Wistar)	central nervous system effects	Fazzari and Catini, 1968 (FIRL, 1978, p.33)
4.8 (1.2mg)	20 days (alternate days)	intra- perit.	rat (Wistar)	kidney effects	Fazzari and Catini, 1966 (FIRL, 1978, p.32)

Array of Toxic Effects on Man and Other Mammals

Zinc chloride (page 2)

Chemical Group: Zinc

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
2 (10mg/l)	5 months	oral	mouse (water)	increase in bone marrow and uterine cancer	De Szilvay, 1964 (FIRL, 1978, p.38)
-	single dose	oral	human (6 1/2 year old boy who ingested soldering paste con- taining 96% ZnCl ₂)	abdominal pain, vomit- ing, cyanosis, coma, corr- osive gast- ritis, hep- atic necro- sis, death	Jacobziner and Raybin, 1962 (FIRL, 1978, p.25)
-	4 years	dermal	human (worker who exposed hands to a ZnCl ₂ - solution)	fatigue, weight loss, pain in bones, anorexia	Du Bray, 1937 (FIRL, 1978 p.24)
concentration in mg/m3 (conc. cited)	total exposure time; brief description	route	description in organism	effect (observation time)	citation (as reported in)
120000	30 minutes	inhal.	human (70 persons exposed to smoke from smoke pots)	respiratory effects, epi- gastric pain, eye irritat- ion, cyanosis, broncho-pneu- monia, pulmon- ary edema, brain, abdom- inal viscera, liver and kidney effects, death	Evans, 1945 (FIRL, 1978, p.20)

Array of Toxic Effects on Man and Other Mammals

Zinc chloride (page 3)

Chemical Group: Zinc

concentration in mg/m3 (conc. cited)	total exposure time; brief description	route	description in organism	effect (observation time)	citation (as reported in)
4800	30 minutes	inhal.	human	TCLo, pulmon- ary system effects	ITII, 1975, p.563
120	2 minutes	inhal.	human (volunteers)	nose, throat and chest irritation, cough, nausea	Collumbine, 1957 (FIRL, 1978, p.19)
80	2 minutes	inhal.	human (volunteers)	nausea, cough	Collumbine, 1957 (FIRL, 1978, p.19)
-	-	inhal.	human (20 year old sailor)	acute respir- atory dis- tress, cardiac en- largement	Whitaker, 1945 (FIRL, 1978, p.20)

Array of Toxic Effects on Man and Other Mammals

Zinc sulphate

Chemical Group: Zinc

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
643 (45g)	single dose	oral	human	death	Grieser, 1975, p.64
429 (30g)	single dose	oral	human	death	Arena, 1974, p.241
106	-	oral	human	TDLo, systemic effects	NIOSH, 1978, p.26
106	-	oral	human	TDLo, blood pressure effects	NIOSH, 1978, p.26
50	-	oral	human	LDLo	NIOSH, 1978, p.26
29	-	intra- perit.	mouse	LD50	NIOSH, 1978, p.26
6.17	5 days	sub. cut	rabbit	TDLo, neo- plastic effects	NIOSH, 1978, p.26
2.9 (200mg)	single dose	oral	human	vomiting	Grieser, 1975, p.64

Array of Toxic Effects on Man and Other Mammals

Zinc oxide

Chemical Group: Zinc

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
630	-	oral	rat	LD50	ITII, 1975, p.565
500	-	oral	human	LDLo	NIOSH, 1978, p.26
250 (50mg)	single dose	intra- trach- eal	rat	microscopic changes in lungs, peri- bronchial pneumonia (12 months)	Mogilevskaya, 1959 (NIOSH, 1975, p.32)
200 (0.4% of diet)	6 weeks	oral (diet)	rat	reduced cyto- chrome oxid- ase activity due to zinc- induced cop- per deficien- cy	Witham, 1963 (NIOSH, 1975 p.35)
-	-	oral	human	gastro- enteritis	Arena, 1974, p.241
-	-	-	human (packing zinc oxide)	exzema	Downing, 1935 (Patty, 1963, p.1187)

Array of Toxic Effects on Man and Other Mammals

Zinc oxide (page 2)

Chemical Group: Zinc

concentration in mg/m3 (conc. cited)	total exposure time; brief description	route	description in organism	effect (observation time)	citation (as reported in)
1060	1 hour	inhal.	guinea pig	abnormal temperature, increased respiration, microscopic changes in lungs (46 hours)	Turner and Thompson, 1926 (NIOSH, 1975, p.29)
1024	3 days - 2 days break - 6 days (1 hour/day)	inhal.	guinea pig	respiratory irritation, irregular heart action, weight loss	Turner and Thompson, 1926 (NIOSH, 1975, p.29)
747 (600mg Zn/m3)	10.5 minutes	inhal.	human (who had experienced metal fume fever)	fever, leukocytosis, decreased vital capacity	Sturgis et al., 1927 (NIOSH, 1975 p.19)
600	-	inhal.	human	TDLo, pulmonary system effects	NIOSH, 1978, p.26
110	15 minutes	inhal.	cat, rat, rabbit	temperature depression, increase in polymorphonuclear leukocytes	Drinker and Drinker, 1928 (NIOSH 1975, p.30)
100	-	inhal.	human (volunteers)	fever, throat irritation, coughing, dyspnea, muscle and joint pain, general malaise	Lehmann, 1910 (NIOSH 1975, p.13)

Array of Toxic Effects on Man and Other Mammals

Zinc oxide (page 3)

Chemical Group: Zinc

concentration in mg/m3 (conc. cited)	total exposure time; brief description	route	description in organism	effect (observation time)	citation (as reported in)
65 (52mg Zn/m3)	5 hours, 1st day	inhal.	human (technician in a brass foundry)	fever	Drinker et al., 1927 (NIOSH, 1975 p.20)
411 (330mg Zn/m3)	3 hours, 2nd day			no fever, short term tolerance to zinc fume fever	
50	-	inhal.	human (workers)	peptic ulcer liver effect, high urinary uropepsin levels, weight loss, heart burn, acid rebound, abdominal pain, debility	Guja, 1973 (NIOSH, 1975 p.25)
-	-	inhal.	human (elec- tric welders)	fever, gas- tric irrita- tion	Chrometzka, 1936 (NIOSH, 1975, p.24)
-	2-3 years	inhal.	human (wor- kers in zinc powder fac- tories)	inflammation of upper re- spiratory tract	Mogilevskaya, 1959 (NIOSH, 1975, p.18)
-	-	inhal.	human (wor- ker in a zinc oxide produc- tion plant)	fibrous changes of lungs	Dzukaev and Kochetkova, 1970 (NIOSH, 1975, p.18)

Toxic Effects from Special Studies on Mammals and Other
Non-Marine Experimental Systems

Zinc chloride

Chemical Group: Zinc

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	oral (water)	2 (10mg/l)	5 months (daily)	increase in bone marrow and uterine cancer	De Szilvay, 1964 (FIRL, 1978, p.38)

This study, designed to evaluate the possible carcinogenic effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

MUTAGENICITY

description of system	reported results	citation (as reported in)
Bacillus subtilis strain H ₁₇ (Rec ⁺ , arg ⁻ , trp ⁻) and M ₄₅ (Rec ⁻ , arg ⁻ , trp ⁻) exposed to 0.05M ZnCl ₂	no mutagenic effects found	Nishioka, 1975 (FIRL, 1978, p.38)

This study, designed to evaluate the possible effects of the substance on gene mutation, chromosomal mutations, on DNA repair or recombination or on transformation, was found in the literature reviewed. It did not result in a report of any of these effects. No comprehensive evaluation of this information was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and Other

Non-Marine Experimental Systems

Zinc chloride (page 2)

Chemical Group: Zinc

NEUROTOXICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Wistar)	intra-perit.	6.3 (0.6mg Zn)	20 days (alternate days)	paresis of hind-legs and anal sphincters, morphological changes of neurons	Fazzari and Catini, 1968 (FIRL, 1978, p.33)

This study, designed to evaluate the possible neurotoxic effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
rat	copper	prevented anemia	Van Reen, 1966 (FIRL, 1978, p.33)
-	calcium, phosphorous	reduced zinc uptake	Van Reen, 1966 (FIRL, 1978, p.33)
mouse	cadmium	increased zinc retention	Cotzias et al., 1962 (FIRL, 1978, p.33)

These studies, designed to evaluate the possible effects which could result from the combination of this substance with one or more other substances, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and Other

Non-Marine Experimental Systems

Zinc chloride (page 3)

Chemical Group: Zinc

PRIMARY IRRITATION

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rabbit	eye appl.	-	-	corneal damage	Johnstone, 1973 (FIRL, 1978, p.30)

This study, designed to evaluate the possible primary irritation effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

REPRODUCTIVE EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	oral (diet)	250 (5g/kg diet)	2 generations	no reproductive effects found	Heller and Burke, 1927 (FIRL, 1978, p.31)

This study, designed to evaluate the possible effects of this substance on reproduction, was found in the literature reviewed. It did not result in a report of effects on reproduction. No comprehensive evaluation of this information was found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and Other
Non-Marine Experimental Systems

Zinc sulphate

Chemical Group: Zinc

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

Nothing found in the literature reviewed.

MUTAGENICITY

Nothing found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and Other
Non-Marine Experimental Systems

Zinc oxide

Chemical Group: Zinc

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

Nothing found in the literature reviewed.

MUTAGENICITY

Nothing found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Zinc (Zn²⁺)

Chemical Group: Zinc

System Organism Ecosystem Non-living	Life Stage	Concn. mg/l	Exposure Time	Effect	Time of Observation	Citation
<i>Mya arenaria</i> (clam)	A	5.2	96 hours	LC50	96 hours	Eisler, R., 1977
<i>Mytilus edulis</i> (mussel)	A	7.8	96 hours	LC50	96 hours	Abel, P.D., 1976
<i>Pagurus longi- carpus</i> (crab)	A	0.4	96 hours	LC50	96 hours	Eisler, R., and Hennekey, R.J., 1977
<i>Artemia salina</i> (brine shrimp)	E	0.089	48 hours	50% dec. in hatching rate	48 hours	Jorgensen, K.F. and Jensen, K., 1977
<i>Crassostrea gigas</i> (oyster)	21 day	0.125	5 days	Delay in settling of larvae. Dec. numbers of larvae settling	5 days	Boyd, C.R. et al., 1975
<i>Mercenaria mercenaria</i> (hard clam)	L	0.195	8-10 days	38.4% reduced growth	8-10 days	Calabrese, A. et al., 1977

Toxic or Other Effects on Marine Organisms and Ecosystems

Zinc (Zn²⁺) (page 2)

Chemical Group: Zinc

System Organism Ecosystem Non-living	Life Stage	Concn. mg/l	Exposure Time	Effect	Time of Observation	Citation
Gymnodinium splendens (dino-flagellate)	-	1.0	39 days	Dec. max. cell density to 3.5% of control	39 days	Kayser, H., 1977
Scrippsiella faeroense (dino-flagellate)	-	1.0	(immed.)	Morphological aberrations	(immed.)	Kayser, H., 1977
Laminaria hyperborea (brown seaweed)	Z	1.0	28 days	Sporophyte formation time double	18 days	Hopkins, R. and Kain, J.M., 1971
Mytilus edulis (mussel)	A	1.6	10-12 minutes	50% reduction in filtration rate	10-12 minutes	Abel, P.D., 1976
Mytilus edulis (mussel)	A	1.8	7 days	50% dec. byssal thread production	7 days	Martin, J.M. et al., 1975
Aldrichetta foresti (yellow-eye mullet)	J	7.2	96 hours	Mucous secretions Marked erosion of anal and caudal fins	96 hours	Negilski, D.S., 1976

Toxic or Other Effects on Marine Organisms and Ecosystems

Zinc (Zn²⁺) (page 3)

Chemical Group: Zinc

System Organism Ecosystem Non-living	Life Stage	Concn. mg/l	Exposure Time	Effect	Time of Observation	Citation
Jaera albifrons (isopod)	A	10.0	120 hours	Red. osmoregulation ability in dilute saline	120 hours	Jones, M.B., 1975
Fundulus hetero- clitus (mummichog)	A	10.0	2 weeks	Liver ALA-D activity inc. 29%	2 weeks	Jackim, E., 1973
Artemia salina (brine shrimp)	E	5	3 days	15% hatch	3 days	Saliba, L. and Krzyk, R., 1976
Palaemon serratus (Pink shrimp)	A	7	30 days	LC50	30 days	Fraizier, A., 1973
Artemia salina (Brine shrimp)	L	30	60 hours	LC50	60 hours	Aubert, M. et al., 1972
Palaemon serratus (Pink shrimp)	A	50	96 hours	LC50	96 hours	Fraizier, A., 1973
Carassius auratus (Goldfish)	-	375-750	9 days	LC50	9 days	Aubert, M. et al., 1972

Toxic or Other Effects on Marine Organisms and Ecosystems

Zinc (Zn²⁺) (page 4)

Chemical Group: Zinc

System Organism Ecosystem Non-living	Life Stage	Concn. mg/l	Exposure Time	Effect	Time of Observation	Citation
Carcinus maenas (Shore crab)	-	0.8175 (threshold)	8 days	Toxicity	8 days	Aubert, M. et al., 1976
Nereis diversicolor (Annelid)	-	3.265 (threshold)	8 days	Toxicity	8 days	Aubert, M. et al., 1976
Asterionella japonica (Diatom)	-	4-8 (threshold)	-	Growth inhibition	-	Aubert, M. et al., 1972
Asterionella japonica (Diatom)	-	4-8 (threshold)	-	Growth inhibition	-	Pesando, D. and Aubert, M., 1975

E Egg
A Adult
J Juvenile
L Larva
Z Zoospore

Red. Reduced
Dec. Decreased
immed. immediately
max. maximum
ALA-D 6-aminolevulinate dehydrase

Analysis

Zinc (II)

Chemical Group: Zinc

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
atomic absorption spectroscopy (10ug)	sample work-up variability causes determination errors/ inexpensive routine method, available in normal laboratories	Greig, 1975
differential pulse anodic stripping voltametry (20ng)	copper ions may cause interferences/rapid inexpensive procedure, selective	Abdullah et al., 1976
Zeeman atomic absorption spectrometry (1ng)	apparatus more sophisticated than normal A.A.S. equipment, individual assembly possible, very sensitive and selective method, very rapid, inexpensive	Koizumi and Yasuda, 1976

Legislation for the Protection of Man
and the Marine Environment

Zinc (generic)

Chemical Group: Zinc

general classification of control mechanisms	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as re- ported in)
control of substances in effluents	Italy	recommended limits for industrial and urban effluents discharged into waters	1mg/l as Zn into water- courses, the sea and sewers 0.5mg/l as Zn into lakes	WHO/UNEP, 1976, p. Italy-4
control of substances in water	Italy	regulation concerning acceptable limits for discharges into surface and public sewers	0.5 mg/l as Zn in surface waters 1 mg/l as Zn in public sewers	IDHL, 1977, p.630
control of substances in effluents	Spain	regulation concerning discharges from submarine outfalls	3.5 mg/l in not more than 50% of samples 7.0 mg/l in not more than 10% of samples	IDHL, 1978, p.193
control of substances in effluents	Libyan Arab Republic	proposed standards for effluents discharged	1mg/l into surface water reservoirs for direct use in agriculture, into aquifers used for public water supply and into urban sewage systems 2mg/l into the sea	WHO/UNEP, 1976, p. Libyan Arab Republic-2

Legislation for the Protection of Man
and the Marine Environment

Zinc (generic) (page 2)

Chemical Group: Zinc

general classification of control mechanisms	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as re- ported in)
control of substances in effluents	Tunisia	proposed recommended values for discharges into surface waters and public sewers	2 mg/l as Zn for Kratel surface waters (unpublished) 5 mg/l as Zn for public sewers (1. Spectrophoto- metry with di- thizone 2. Atomic absorp- tion spectro- photometry)	
control of substances in effluents	Turkey	prohibition of discharges when the concentrat- ion exceeds the tolerance level	0.003 mg/l as Zn ions	Turkish Law of 10 October 1971
control of substances in effluents	Yugoslavia	maximum per- missible con- centrations of dangerous sub- stances dis- charged into water used or intended for use as drinking water, for pro- duction of food- stuffs, fish breeding, water- ing of animals or public bathing	1.0mg/l, 0.01mg/l when discharged into water used for breeding of Salmonidae	WHO/UNEP, 1976, p. Yugoslavia-4

Legislation for the Protection of Man
and the Marine Environment

Zinc (generic) (page 3)

Chemical Group: Zinc

general classification of control mechanisms	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as re- ported in)
control of substances in water	Yugoslavia	maximum per- missible concentrations of dangerous substances in interrepublic watercourses	0.2 mg/l in class I and class II waters ^a 1.0 mg/l in class III and class IV waters ^b	IDHL, 1978, (awaiting publication)

a Class I: waters which, in their natural state, where necessary after disinfection, may be used for drinking purposes and in the food industry and, in the case of surface waters, for breeding Salmonidae. Class II: waters which, in their natural state, may be used for bathing and recreation, water sports, breeding of Cyprinidae, or which, after treatment, may be used for drinking purposes and in the food industry.

b Class III: waters which may be used for irrigation and, after treatment, in industry other than the food industry. Class IV: waters which may be used for other purposes only after treatment.

Zinc

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GENERAL SUMMARY - CHROMIUM

I. INTRODUCTION

Chromium (Cr) is an abundant element in the earth's crust, and occurs in oxidation states ranging from Cr^{+2} to Cr^{+6} . The most common form in nature is Cr^{+3} , which is also the valence which is considered essential as a trace element in humans (EPA, 1976).

Marine organisms are able to concentrate Cr to various degrees, and a wide range of toxic effects have been noted for chromium in the hexavalent state, the stable form in sea water (EPA/ORNL, 1978).

Large amounts of Cr are used by industry, and sources to the environment include fossil fuel combustion, metal plating, ore refining, the leather industry, etc. In the Mediterranean, the Liguro-Provencal region receives the highest Cr load from land-based sources, mostly due to river run off (UNEP, 1977b).

II. OCCURRENCE

A. Production

Chromate and dichromate are the major chromium compounds produced in the chemical industry. Sodium monochromate is produced by roasting finely ground chromite ore with sodium carbonate and calcium carbonate and then leaching with hot water. Addition of dilute sulfuric acid produces sodium dichromate. These compounds serve as starting substances for the manufacture of all other chromium chemicals (EPA/ORNL, 1978).

Mediterranean countries producing chromium include Turkey and Albania (EPA/ORNL, 1978).

Though no production figures were provided in the literature searched for the Mediterranean region, the world production of chromites in 1971 has been estimated at 6.3×10^6 tons, which represents a 5% increase over 1970 (CEC-EOA, 1977).

Consumption of chromites in Italy in 1971 was 201,000 tons; France consumed 340,000 tons the same year (CEC-EOA, 1977). No consumption figures for other Mediterranean countries were available in the literature reviewed.

B. Use

NAS (1974) reports that in the U.S., where all chromite has been imported for use since 1961, approximately 57% is used in the metallurgic industry, 30% in refractory materials and 13% in the chemical industry.

Chromium is used in metal alloys to impart resistance to oxidation, wear and heat (IARC, 1973). Ores used for ferrochrome production contain at least 50% chromic oxide. Ferrochrome is used primarily in stainless steel and alloy steels; over 60% of chromium used by the metallurgic industry is used for stainless steel production. Other applications in this industry include austenite steel, high-speed steels, other alloy steels, high temperature steels, and non-ferrous alloys (NAS, 1974).

The refractory industry uses chromite as a furnace lining because of its high melting point and chemical inertness. Chromium chemicals are used in leather tanning, pigments, catalysts, for chrome plating and in wood preservatives (NAS, 1974).

III. CHROMIUM IN THE ENVIRONMENT

A. Sources

1. Natural

The natural level of Cr in soils is generally high and quite variable, with 64% in the range of 25-85 ppm total chromium. Very little chromium is released from soil by leaching, due to its insoluble nature, but surface run off carries some Cr to receiving waters, where it is mainly deposited in sediments (EPA/ORNL, 1978).

Sea water concentrations of Cr range from 0-0.36 ppb, mostly as hexavalent Cr. The trivalent form also exists in water, but it may eventually precipitate or be absorbed (EPA/ORNL, 1978).

The natural concentration of Cr in air, as indicated by measurements made at rural stations, seldom reaches $0.01\mu\text{g}/\text{m}^3$ (NAS, 1974).

2. Anthropogenic

About 68% of the Cr emitted to the atmosphere is estimated to be derived from ferrochrome production. Ore refining, chemical and refractory processing, and indirect sources also contribute to the atmospheric Cr burden. The combustion of coal is by far the largest of the indirect sources, with emissions being dependent on the Cr content in the coal being burned, which varies widely with source. Atmospheric Cr concentration closely parallels geographic areas of high population and industrial activity (EPA/ORNL, 1978).

Chromium is removed from the air by precipitation and fallout, being deposited on both land and in water. Terrestrial fallout will eventually be carried to surface waters by run off.

The plating and finishing industries discharge large amounts of Cr in the form of wastewaters. Only about 10-20% of the chromium used in chrome plating processes ends up in the product. The textile industry, using Cr to control algae, prevent corrosion, and in the dying process, also discharges effluents containing chromium. The tanning industry discharges wastes primarily as chromium (III) sulfate (NATO, 1976).

B. Transformations

1. Abiotic

Cr deposited in sediments is not readily mobilised. Most of the Cr^{+3} in water is found in the sediments, where it is effectively adsorbed and/or precipitated, and is unavailable for uptake by marine organisms. A.J. de Groot et al. (1976) found that increased salinity caused increased desorption of Cr from Rhine estuary sediments.

Krauskopf (1956) found significant absorption of Cr with MnO_2 in sea water. 90% of Cr present had been adsorbed after 4 days. Chromium showed very little absorption to iron oxide. The valence of the Cr used in these studies was not provided.

Though Cr doesn't form a sulfide in water, H_2S in the ocean will reduce Cr to the trivalent form, which precipitates as the hydroxide. This mechanism may be responsible for the low levels of chromium which occur in sea water (Krauskopf, 1956).

2. Biotic

No information on biotic transformations of chromium in the marine environment was found in the literature searched.

3. Bioaccumulation

Aubert et al. (1972, 1974) found biomagnification coefficients for Cr in two species of marine phytoplankton: Diogenes sp. was able to concentrate Cr 92 times over an ambient level of 0.025mg/l in 8 days; Asterionella japonica magnified an ambient concentration of 0.7mg/l by a factor of 18.2 in 15 days.

A biomagnification factor of 27 was found for the mussel, Mytilus edulis, in an 18 day exposure to a sea water concentration of 0.3mg/l of Cr (Calapaj, 1973).

IV. MONITORING

A. Analysis

NAS (1977) reports that only two analytic techniques, neutron activation and shielded-arc emission spectrography, are accurate enough for determination of Cr at the low concentrations that exist in many environmental media, especially plant and animal tissue. Due to expense and complexity, neither method is considered to be applicable to large scale environmental studies.

Other specific analytic methods include polarographic techniques, diphenylcarbazide method, gas-liquid chromatography and atomic-absorption spectrophotometry (NAS, 1974).

B. Amount in the Mediterranean

Sea water samples from the W. Mediterranean contained Cr concentrations (tri- and hexavalent) in the range of 0.39-0.41ug/l (Bernhard and Zattera, 1975).

Fukai and Vas (1967) found Cr levels of 0.1-0.57ug/l from coastal waters near Monte Carlo. Coastal sea water samples from Menton, France, contained 3.3ug/l of Cr (May et al., 1975).

Paul and Meischner (1976) examined Cr concentrations in sediments from the Adriatic. The median values reported were: 14mg/kg dry weight for sand; 75mg/kg dry weight for silty sand; 75.5mg/kg dry weight for muddy sand; and, 112mg/kg dry weight for mud. High Cr concentrations in sediments from the S.E. Adriatic were explained by natural river inputs.

In a study on trace metal distribution in seven mollusc species from the Saranikos Gulf in Greece, Papadopoulou and Kaniaris (1976a) found Cr concentrations of 7.8mg/kg dry weight in the mussel, Mytilus galloprovincialis, and 12.5mg/kg dry weight in the oyster, Ostrea edulis. Fowler and Oregioni (1976) found a comparable level of 7.5mg/kg dry weight in Mytilus from the N.W. Mediterranean.

C. Amount Entering the Mediterranean

UNEP (1977b) estimates the total input of Cr to the Mediterranean from land-based sources at 2,760 tons per year. The Liguro-Provencal region receives about 36%, or 1000 tons per year, of this amount. Rivers carry 54% of the total load to this region; 37% comes from coastal industrial discharges, and 9% from coastal domestic sources.

A potential Cr input of 0.02 million tons per year to the world oceans from atmospheric washout has been reported by UNEP (1977a).

D. Regulations

Standards relating to chromium discharged into waterways were found for 5 countries in the Mediterranean region; France, Italy, the Libyan Arab Republic, Spain and Yugoslavia. Depending on the country, control mechanisms apply to industrial and refinery effluents, levels entering public water supplies, discharges into urban sewers, and discharges into the sea (CEC, 1976; WHO/UNEP, 1976).

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

In its trivalent state Cr is an essential trace element at very low concentrations. At elevated concentrations, however, Cr can display toxic effects, especially in its hexavalent state (EPA, 1976).

A four day exposure to 5.0mg/l of hexavalent chromium caused a 50% reduction in photosynthesis in the giant kelp, Macrocystis pyrifera (Clendenning and North, 1960).

Fish appear to be relatively tolerant of chromium, but some aquatic invertebrates are quite sensitive (EPA, 1976). The spawning of a polychaete, Neanthes arenaceodentate, was totally inhibited by 0.1mg/l of Cr (Mearns et al., 1976).

A 96 hour LC50 for Cr in a crab, Pagurus longicarpus, was found to occur at 10.0mg/l (Eisler and Hennekey, 1977).

In a study on a soft shell clam, Mya cirenaria, Capuzzo and Sasner (1977) found decreased gill tissue oxygen consumption and decreased filtering activity, with slower, more erratic cilia movement, at Cr concentrations of 1.0mg/l.

B. Toxic Effects on Man and Other Mammals

Cr occurs in most biological material in the trivalent form, which is associated with proteins, nucleic acids and a variety of low molecular weight ligands. The hexavalent form is more toxic than the trivalent because of its oxidising potential and its easy permeation of biologic membranes (NAS, 1974).

An LDLo for humans, or the lowest dose reported to have been lethal, was established in the case of a child who orally ingested 26mg/kg bw/day of chromium (NIOSH, 1978). The high toxicity of hexavalent chromium was evident in the death of a 14 year old boy who ingested a single dose of 10mg Cr(VI)/kg BW. Blood effects and coma preceeded the death (Kaufman et al., 1970). Industrial exposure to chromium reportedly caused destruction of mucous membranes, perforation of nasal septum and lung cancer (Sullivan, 1969).

Hunter and Roberts (1933) reported that a single sub-cutaneous dose of 16mg/kg bw/day was lethal to a monkey (Macacus chesus) within 12 hours. Acute kidney damage was noted. NIOSH (1978) lists several experiments with rats and mice establishing carcinogenic effects of chromium.

Total Production

Chromites		Chemical group: Chromium		
year	area	amount	trend	citation (as reported in)
1971	World	6 300 000 tons	-	CEC/EOA, 1977, p.23

Total Production

Sodium dichromate + sodium chromate

Chemical Group: Chromium

year	area	amount	trend	citation (as reported in)
1971	USA	276 400 000 pounds	-	IARC, 1973, p.106

Total Consumption

Chromites		Chemical Group: Chromium			
year	area	amount	trend	citation (as reported in)	
1969	France	330 000	tons	-	CEC/EOA, 1977, p.23
1970	France	421 000	"		
1971	France	340 000	"		
1969	Italy	160 000	"		
1970	Italy	142 000	"		
1971	Italy	201 000	"		

Total Consumption

Dichromates

Chemical Group: Chromium

year	area	amount (estimated)	trend	citation (as reported in)
1969	EEC countries	137 500 tons	-	CEC/EOA, 1977, p.30
1970	EEC countries	140 000 "		
1971	EEC countries	142 000 "		

Production Process(es)

Sodium dichromate

Chemical Group: Chromium

process (major or minor by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
roasting finely ground chromite ore with sodium carbonate and calcium carbon- ate, leaching with hot water, addition of dilute sulfuric acid	-	-	EPA/ORNL, 1978, p.204

Production Process(es)

Calcium chromate

Chemical Group: Chromium

process (major or minor by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
reaction of calcium chloride with sodium chromate	-	-	IARC, 1973, p.104

Production Process(es)

Potassium dichromate

Chemical Group: Chromium

process (major or minor by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
reaction of sodium dichromate with potassium chloride	-	-	NATO, 1976, p.M6-5
roasting chrome ore with potassium carbonate	-	-	IARC, 1973, p.106

Use

Sodium dichromate

Chemical Group: Chromium

Use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as re- ported in)
lead chromate pigment production	-	-	-	NATO,1976, p.M6-5
chromic acid and potassium dichromate production				
wood preservatives				
oxidant in dye industry				
electroforming				
photography				
photocopying				

Use

Calcium chromate

Chemical Group: Chromium

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
corrosion inhibitor	-	-	-	IARC, 1973, p.104
depolarizer in batteries				

Use

Potassium dichromate

Chemical group: Chromium

use(s)	geographic area (major or minor)	substance (s) added	trend	citation (as reported in)
electroforming	-	-	-	NATO, 1976, p.M6-5
wood preservatives				
lead chromate pigment production				
oxidant in dye industry				
photography				
photocopying				

Pathways Leading to Marine Pollution

Chromium (Cr⁶⁺)

Chemical Group: Chromium

Pathway	Quantity	Area	Citation
River discharges	236,000 tons/yr	World	GESAMP, 1976
Rainwater	720 tonnes/yr (total)	North Sea	Cambray, R.S. et al., 1976
Municipal wastewater	576 metric tons/ yr (total)	Southern California Bight, U.S.A.	Young, D.R. et al., 1977
Storm runoff	25 metric tons/yr	Southern California Bight, U.S.A.	Young, D.R. et al., 1977
Dry aerial fallout	6.6 metric tons/yr (total)	Southern California Bight, U.S.A.	Young, D.R. et al., 1977
Direct sewage outfall into the sea	-	Tel Aviv-Yafo, Israel	Amiel, A.J. and Navrot, J., 1978

Transformation in the Marine Environment

Chromium

Chemical Group: Chromium

Process	Medium	Parameters	Effect	Citation
Desorption	Rhine estuary sediment	Increased salinity	Increased desorption	de Groot, A.J. et al., 1976
Adsorption with $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ (300mg/l)	Sea water, laboratory	18-23°C, pH 7.7-8.2	47% chromium adsorbed in 2 days. 53% (0.05mg/l) remaining in solution	Krauskopf, K.B., 1956
Adsorption with $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ (100mg/l)	Sea water laboratory	18-23°C, pH 7.7-8.2	90% chromium adsorbed in 4 days. 10% (0.05mg/l) remaining in solution	Krauskopf, K.B., 1956
Apatite (500mg/l) (Adsorption with)	Sea water laboratory	18-23°C, pH 7.7-8.2	15% chromium adsorbed in 2 days. 85% (3.4mg/l) remaining in solution	Krauskopf, K.B., 1956
Oxidation	Sediment, laboratory	Increased redox potential	No effect	Lu, J.C.S. and Chen, K.Y., 1977
Reduction	Sediment, laboratory	Decreased redox potential	No effect	Lu, J.C.S. and Chen, K.Y., 1977

Behaviour of a Chemical Substance in Marine Organisms

Chromium		Chemical Group: Chromium				
Organism	Route	Exposure Concn. Time mg/l	Accumulation and Distribution Tissue %	Biomagnification %	Loss Time	Citation
Citharichthys stigmaeus (Speckled sanddab- intestine)	W	1.0 44 days	Wh 100	40(d.w.)	- - -	Sherwood, M.J. and Wright, J.L., 1976
Mya arenaria (Soft shell clam)	W	1.0 4-6 weeks	Wh 100	765	- - -	Capuzzo, J.M. and Sasner, J.J., Jr., 1977
Crassostrea virginica (Oyster)	W	Cr-51 110 hours	Wh 100	9.94	- - -	Preston, E.M., 1971
Crassostrea virginica (Oyster)	W	0.05 10 weeks	Wh 73		- - -	Shuster, C.N., Jr. and Pringle, B.H., 1969
Neanthes arenaceoden- tata (Poly- chaete)	W	0.0045 45 days	Wh 100	3340 (d.w.)	- - -	Oshida, P.S., 1977

Behaviour of a Chemical Substance in Marine Organisms

Chromium (page 2)

Chemical Group: Chromium

Organism	Route	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
		Concn.	Time	Tissue	%	Biomagnification	%	Time	Name	Quantity	
mg/l											
Diogenes sp. (Phytoplank- ton)	W	0.025	8 days	Wh	100	92	-	-	-	-	Aubert, M. et al., 1974
Asterionella japonica (Phytoplank- ton)	W	0.7	15 days	Wh	100	18.2	-	-	-	-	Aubert, M. et al., 1972
Tapes decussatus (Clam)	W	Cr-51 0.01	10 days	F	-	12.9	-	-	-	-	Chipman, W.A., 1966
Mytilus ed- ulis (Mussel)	W	0.3	18 days	-	-	27	19	24 days	-	-	Calapaj, G.G., 1973
Nereis diver- si Color (Worm)	W	0.26	7 days	Wh	100	69.2	-	-	-	-	Aubert, M. et al., 1976

d.w. - BMC calculated from dry weight of organism;

F - Flesh;
W - Water;
Wh - Whole

Behaviour of the Substance in Man and Other Mammals

Sodium dichromate

Chemical Group: Chromium

description of organism	route	concentration	exposure duration of exposure	retention tissue/percent/time	clearance rate		metabolites name/amount/hazard (as reported in)	citation
					percent/time			

Nothing found in the literature reviewed.

Behaviour of the Substance in Man and Other Mammals

Calcium chromate		Chemical Group: Chromium					
description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)

Nothing found in the literature reviewed.

Behaviour of the Substance in Man and Other Mammals

Potassium dichromate			Chemical Group: Chromium			
description of organism	exposure		retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)
	route	concentration				
human abdominal skin	-	720mg/l	2 days (37°C, pH 4.5)	-	reduced chromium	Samitz and Katz, 1964 (NIOSH, 1975, p.33)

Concentrations in Water, Sediments and Biota

Chromium (Cr6+)		Chemical Group: Chromium			
Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Sampled Origin				
Seawater	Menton, France Mediterranean	NAA	0.0033 mg/l	-	May, S. et al., 1975
Water	Kure, Japan	AAS	0.0012 mg/l (hexavalent ion)	1974	Hiio, K. et al., 1976
Water	Tolo Harbour, Hong Kong	AAS	n.d.	-	Wang, M.H. and Li, M.W., 1977
Sediment (41 cm)	Gulf of Mexico	PIXE	74 mg/kg dry wt.	-	Pilotte, J. O. et al., 1978
Sediment	Tamar Estuary, U.K.	AAS	64 mg/kg dry wt.	1974	Bryan, G.W. and Uyssal H., 1978
Sediment (top 4 cm)	Dumpsite, New York Bight, USA	AAS	58.0 mg/kg dry wt.	1971	Greig, R.A. et al., 1977
Pomatomus saltatrix (Bluefish-liver)	New Jersey coast, U.S.A.	AAS	160 mg/kg dry wt.	1971	Mears, H.C. and Eisler, R., 1977
Pitar morrhuana (Widgeon clam-soft part)	Narragansett Bay, U.S.A.	AAS	14.2 mg/kg dry wt.	1973	Eisler, R. et al., 1978
Fucus vesiculosus (Brown seaweed)	Menai Straits, U.K.	AAS	4.5 mg/kg dry wt.	1972	Foster, P., 1976
Mytilus galloprovincialis (Mussel-soft tissue)	Gulf of La Spezia, Italy	AAS	19.5 mg/kg dry wt.	1975	Capelli, R. et al., 1978

Concentrations in Water, Sediments and Biota

Chromium (Cr⁶⁺) (page 2)

Chemical Group: Chromium

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Sand sea trout-flesh	South Texas Outer Continental Shelf	AAS	6.9 mg/kg	-	Horowitz, A. and Presely, B.J., 1977
Tapes decussatus (Shellfish-digestive gland)	Izmir Bay, Turkey	AAS	5.3 mg/kg dry wt.	-	Geldiay, R. and Uysal, H., 1976
Seawater	N. Adriatic	NAA	0.0838mg/l	1972	Grancini, G. et al., 1975
Sediment	Sewage outfall, Tel Aviv, Israel	AAS	60mg/kg	1973-1974	Amiel, A.J. and Navrot, J., 1978
Sediment	Ligurian Sea	AAS	18.8mg/kg (dry)	1973	Renfro, W.C. and Oregioni, B., 1974
Sediment (mud, 165m)	Adriatic	AAS	222mg/kg (dry)	1973	Paul, J. and Meischner, D., 1976
Sediment	N. Adriatic	NAA	106.8mg/kg (dry)	1972	Grancini, G. et al., 1975
Sediment	Sewage outfall area Athens	NAA	35-1,000mg/kg (dry)	1973	Papakostidis, G. et al., 1975
Sediment	Bay of Naples, Italy	AAS	714mg/kg (dry)	-	Griggs, G. B. and Johnson, S., 1978

Concentrations in Water, Sediments and Biota

Chromium (Cr⁶⁺) (page 3)

Chemical Group: Chromium

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Mytilus galloprovincialis (Mussel)	Saronikos Gulf	AAS	7.8mg/kg (dry)	1969	Papadopolou, C. and Kanas, G. D., 1976a
Ostrea edulis (Oyster)	Saronikos Gulf	AAS	12.5mg/kg	1969	Papadopolou, C. and Kanas, G. D., 1976a
Mytilus galloprovincialis (Mussel)	N.W. Mediterranean	AAS	7.5mg/kg (dry)	1974	Fowler, S.W. and Oregioni, B., 1976
Ophioderma longicauda (Echinoderm)	Saronikos Gulf	NAA	0.83mg/kg (dry)	1974	Papadopolou, C. and Kanas, G. D., 1976b
Arabacia lixula (Echinoderm)	Saronikos Gulf	NAA	13.0mg/kg (dry)	1974	Papadopolou, C. and Kanas, G. D., 1976b
Balanus amphitrite (Barnacle)	N. Adriatic lagoon	AAS	2.1-3.89 mg/kg(dry)	1975	Barbero, A. et al., 1978

Concentrations in Water, Sediments and Biota

Chromium (Cr⁶⁺) (page 4)

Chemical Group: Chromium

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Microcosmus sulcatus (Tunicate, whole)	Keratsini Bay	NAA	6.6mg/kg (dry)	1974	Papadopo- ulou, C. and Kanas, G. D., 1977
Acartia clausi (Zooplankton)	Elefsis Bay, upper Saronikos Gulf, Greece	NAA	3.71mg/kg (dry)	1974	Zafiropou- los, D. and Grimanis, A.P., 1977

AAS Atomic absorption spectrophotometry
 NAA Neutron activation analysis
 PIXE Proton induced X-ray emission
 n.d. Not detectable

Array of Toxic Effects on Man and Other Mammals

Sodium dichromate

Chemical Group: Chromium

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation) (time)	citation (as re- ported in)
140	69 weeks (intermit- tant)	intra- musc.	rat	TDLo, neo- neoplastic effects	ITII, 1975, p.476
50	-	oral	human	LDLo	NIOSH, 1978, p.9
-	-	dermal contact and in- hal.	human	irritant and caustic to skin and mucous mem- branes	Sullivan, 1969, (EPA/QRNL 1978, p.172)
-	-	dermal contact	human	primary dermatoses ("chrome holes")	Schwartz et al., 1957, (NAS, 1974 p.63)

Array of Toxic Effects on Man and Other Mammals

Sodium dichromate (page 2)

Chemical Group: Chromium

concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
0.01-2.8 (chromate)	sodium chromate and sodium dichromate	inhal.	human (wor- kers at a chromate producing plant)	nasal ir- ritation, septal perfor- ation	Machle and Gregorius, 1948 (NIOSH, 1975, p.43)
0-0.5	sodium chromate and sodium dichromate	inhal.	human (wor- kers at a chromate producing plant)	nasal sep- tum perfor- ations, chronic chemical rhinitis, chronic chemical pharyngitis	Mancuso, 1951 (NIOSH, 1975, p.44)
0.068 (Cr(VI), average value)	probably sodium chromate and sodium dichromate	inhal.	human (wor- kers in chro- mium produc- ing industry in USA)	nasal mu- cosal irri- tation and ulceration, nasal sep- tal perfor- ation, ear disorders, liver- enlargement, lung cancer, blood cells and casts in urine	US Public Health Service, 1953 (NIOSH, 1975, p.44)

Array of Toxic Effects on Man and Other Mammals

Calcium chromate

Chemical Group: Chromium

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as repor- ted in)
375	-	oral	rat	LD50	NIOSH, 1978, p.7
76	20 weeks (in- termittant)	intra- musc.	rat	TDLo, car- cinogenic effects	NIOSH, 1978, p.7
50	-	sub cut.	mouse	TDLo, car- cinogenic effects	NIOSH, 1978, p.7
50	-	implan- tation	mouse	TDLo, car- cinogenic effects	NIOSH, 1978, p.7
25	-	implan- tation	rat	TDLo, car- cinogenic effects	NIOSH, 1978, p.7
3.6 (5mg/week)	2 weeks	intra- musc.	rat	severe local in- flammation	Roe and Carter, 1969
0.36 (0.5mg/week)	18 weeks total 20 weeks	"	"	injection site sar- comas	(NIOSH, 1975, p.841)

Array of Toxic Effects on Man and Other Mammals

Calcium chromate (page 2)

Chemical Group: Chromium

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as repor- ted in)
0.17 (2mg/2 months)	10 months	intra- trach- eal instil- lation	rat	pulmonary complica- tions, mal- ignant tumours (most at in- stillation site), death	Hueper and Payne, 1962 (NIOSH, 1975, p.80)
0.12 (0.1mg/week)	15 weeks	intra- trach- eal injec- tion	hamster	lung paren- chyma, em- physema, goblet cell hyperplasia in the lungs, pulmonary ademonas	Nettesheim et al., 1971 (NIOSH, 1975, p.87)
concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observ. time)	citation (as repor- ted in)
13	6 months	inhal.	mouse	growth-re- duction, increase in pulmonary adenosarco- mas, lymph node hyper- plasia, lung effects	Nettesheim et al., 1970 (NRCC, 1976, p.97)
2.0	891 days (589x)	inhal.	rat (100 animals)	4 carcino- mas, muco- sal changes	Laskin, 1972 (NIOSH, 1975, p.86)
0.01-0.05	calcium and chromium- chromates and dichro- mates; trace amounts of other metals	inhal.	human (workers at a chromate- producing plant)	increase in lung-cancer	Machle and Gregorius, 1948 (NIOSH, 1975, p.114)

Array of Toxic Effects on Man and Other Mammals

Potassium dichromate

Chemical Group: Chromium

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effects (observation time)	citation (as reported in)
430 (30g)	single dose	internally	human	fatal with- in 35 min.	Sullivan, 1969 (EPA/ORNL, 1978, p.172)
280 (1g Cr)	3 months	oral	dog	fatal	Brard, 1935 (NAS, 1974, p.81)
50	-	oral	human	LDLo	NIOSH, 1978, p.9
28 (10mg Cr/kg)	single dose	oral	human (14 year- old boy)	blood effects, coma, death	Kaufmann et al., 1970 (NRCC, 1976, p.112)
26	-	oral	child	LDLo	NIOSH, 1978, p.9
16 (10cc of 2% solution)	single dose	sub cut.	monkey (Macacus rhesus, 2 animals)	death with- in 12 hrs., acute kidney damage	Hunter and Roberts, 1933 (NIOSH, 1975, p.74)
1.6 (1cc of 2% solution)	160 days (1x/7 weeks)	sub cut.	monkey (Macacus rhesus, 4 animals)	kidney da- mage	Hunter and Roberts, 1933 (NIOSH, 1975, p.74)
0.35	3 weeks	oral (water)	human	vomiting	ITII, 1975, p.431

Array of Toxic Effects on Man and Other Mammals

Potassium dichromate (page 2)

Chemical Group: Chromium

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as repor- ted in)
-	acute oral poisoning	oral	human (25-year- old woman)	paroxysm of vomiting, nephritis, hepatitis erythematous skin erup- tion	Goldman and Karotkin, 1935 (NIOSH, 1975, p.56)
-	-	-	human (F) (woman en- gaged in blueprint- production for 6 weeks)	allergic dermatitis	Parkhurst, 1925 (NIOSH, 1975, p.29)
(0.5% solution)	-	dermal appl.		hypersensit- ivity (positive patch test)	
-	-	dermal contact	human	primary dermatoses ("chrome holes")	Schwartz et al., 1957 (NAS, 1974, p.63)
-	-	indus- trial contact	human	destruction of mucous membranes, perforation of nasal septum, lung cancer	Sullivan, 1969 (EPA/ORNL, 1978, p.172)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Sodium dichromate

Chemical Group: Chromium

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Bethesda Black)	intra-pleural	10 (2mg)	16x	1/39 adeno-sarcinoma of the lung (2 years)	Hueper and Payne, 1962 (IARC, 1973 p.115)
rat	intra-musc.	10 (2mg)	16 month (1x/month)	no increase in tumours (2 years)	Hueper and Payne, 1962 (NIOSH, 1975, p.80)
rat (Partom Wistar)	implantation in left lung	10 (2mg)	-	1/100 fibro-sarcoma of upper left lung (no bronchial carcinomas)	NIOSH, 1975, p.88

A comprehensive evaluation of the known studies designed to assess the possible carcinogenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"In many experiments, various chromium compounds have been shown to induce tumours in mice and rats. Calcium chromate has been found to be carcinogenic by several routes of administration, producing epithelial tumours of the lung by intrabronchial implantation and sarcomas by intramuscular and intrapleural administration to rats.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Sodium dichromate (page 2)

Chemical Group:Chromium

Of the other chromium salts tested in the rat by intramuscular and intrapleural administration, chromic chromate and zinc chromate hydroxide were highly evocative of sarcomas at the site of injection in the rat, whilst barium chromate, lead chromate, chromic acetate and sodium dichromate were inactive or practically inactive. Strontium chromate was tested only by intramuscular implantation and evoked many local sarcomas." (IARC, 1973, p.119)

"There is an excessive risk of lung cancer among workers in the chromate-producing industry. It is likely that exposure to one or more chromium compounds is responsible, but the identity of this or these is not known.

There is no evidence that non-occupational exposure to chromium constitutes a cancer hazard." (IARC, 1973, p.120)

MUTAGENICITY

Nothing found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Sodium dichromate (page 3)

Chemical Group: Chromium

PRIMARY IRRITATION

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
human (with cement exzema)	dermal appl.	(0.5% solution)	-	hypersensitivity (positive patch test)	Jaeger and Pelloni, 1950 (NIOSH 1975, p.53)
human (workers in locomotive repair shop, incapacitated by chromate dermatitis)	dermal appl.	(0.25% solution)	-	hypersensitivity (positive patch test)	Winston and Walsh, 1951 (NIOSH, 1975, p.49)

A comprehensive evaluation of the known studies designed to assess the possible primary irritation effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"Certain effects such as contact dermatitis, skin ulcers, irritation and ulceration of the nasal mucosa, and perforation of the nasal septum have been reported and have resulted from contact with many different chromium (VI) materials. Since there is no evident demarcation of categories of such compounds, it is concluded that all chromium (VI) materials can cause these effects." (NIOSH, 1975, p.133)

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Calcium chromate

Chemical Group: Chromium

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	thigh muscle implantation	400 (10mg)	-	implantation site tumours (13 months)	Payne, 1960 (EPA/ORNL, 1978, p.182)
rat	pleural implantation	62.5 (12.5mg)	-	malignant implantation site tumours	Hueper and Payne, 1962 (NIOSH, 1975, p.81)
rat	thigh muscle implantation	62.5 (12.5mg)	-	malignant tumours (mostly at implantation site)	Hueper and Payne, 1962 (NIOSH 1975, p.81)
rat (Parton Wistar)	implantation in the lung	10 (2mg)	-	8/100 bronchial tumours (mostly squamous cell carcinomas) (2 years)	NIOSH, 1975 p.88
rat	intra-musc.	25 (5.0mg) 2.5 (0.5mg)	2 weeks (1x/wk) 18 weeks (1x/wk) total 20 weeks	injection site sarcomas	Roe and Carter, 1969 (NIOSH, 1975, p.84)

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Calcium chromate (page 2)

Chemical Group: Chromium

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
hamster	intra-tracheal	0.83 (0.1mg)	15 weeks (1x/wk)	pulmonary adenomas, goblet cell hyperplasia in the lungs	Nettesheim et al., 1971 (NIOSH, 1975, p.87)
description of organism	route	concentration in mg/m ³ (conc. cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	inhal.	13	lifetime (5hr/day, 5x/wk)	pulmonary adenomas	Nettesheim et al. 1971 (NAS, 1974, p.78)
hamster (100 animals)	inhal.	2.0	891 days (589x)	1 laryngeal carcinoma, 1 laryngeal papilloma, laryngeal metaplasia and hyperplasia	Laskin, 1972 (NIOSH, 1975, p.86)
rat (100 animals)	inhal.	2.0	891 days (589x)	1 lung carcinoma, 1 laryngeal carcinoma, laryngeal hyperplasia and metaplasia, 1 malignant peritruncal tumour	Laskin, 1972 (NIOSH, 1975, p.86)

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Calcium chromate (page 3)

Chemical Group: Chromium

A comprehensive evaluation of the known studies designed to assess the possible carcinogenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"In many experiments, various chromium compounds have been shown to induce tumours in mice and rats. Calcium chromate has been found to be carcinogenic by several routes of administration, producing epithelial tumours of the lung by intrabronchial implantation and sarcomas by intramuscular and intrapleural administration to rats." (IARC, 1973, p.119)

"There is an excessive risk of lung cancer among workers in the chromate-producing industry. It is likely that exposure to one or more chromium compounds is responsible, but the identity of this or these is not known.

There is no evidence that non-occupational exposure to chromium constitutes a cancer hazard." (IARC, 1973, p.120)

MUTAGENICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Potassium dichromate

Chemical Group: Chromium

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

Nothing found in the literature reviewed.

MUTAGENICITY

Nothing found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Potassium dichromate (page 2)

Chemical Group: Chromium

PRIMARY IRRITATION

description of organism	route	dose in mg (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
human (lithographers and tanners with no signs of dermatitis)	dermal appl.	(1% solution)	-	hypersensitivity (positive patch test)	McCord et al., 1930 (NIOSH, 1975, p.50)
human (woman engaged with production of blue-print)	dermal appl.	(0.5% solution)	-	hypersensitivity (positive patch test)	Parkhurst, 1925 (NIOSH, 1975, p.29)
human (with cement exzemy)	dermal appl.	(0.5% solution)	-	hypersensitivity (positive patch test)	Jaeger and Pelloni, 1950 (NIOSH 1975, p.53)
human (welders exposed to aerosols of hexavalent chromium)	dermal appl.	(0.1% solution)	-	hypersensitivity (positive patch test)	Fregert and Ovrum, 1963 (NIOSH, 1975, p.101)

A comprehensive evaluation of the known studies designed to assess the possible primary irritation effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"Certain effects such as contact dermatitis, skin ulcers, irritation and ulceration of the nasal mucosa, and perforation of the nasal septum have been reported and have resulted from contact with many different chromium (VI) materials. Since there is no evident demarcation of categories of such compounds, it is concluded that all chromium (VI) materials can cause these effects." (NIOSH, 1975, p.133)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Potassium dichromate (page 3)

Chemical Group: Chromium

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Chromium

Chemical Group: Chromium

System: Organism Ecosystem Non-living	Life Stage	Concn. mg/l	Exposure Time	Effect	Time of Observation	Citation
Aldrichetta fosteri C + V (yellow-eye mullet)	J	31.2	96 hours	LC50	96 hours	Negilski, D.S., 1976
Pagurus longicarpus (crab)	A	10.0	96 hours	LC50	96 hours	Eisler, R. and Hennekey, R.J., 1977
Sicyonia ingentis (penaeid shrimp)	A	30.0-45.0	96 hours	LC50	96 hours	Oshida, P.S. and Wright, J.L., 1976
Meanthes arenaceo- dentata (polychaete)	J	0.0125	J - A	48% decrease in blood size	100 days	Mearns, A.J. et al., 1976
Meanthes arenaceo- dentata (polychaete)	J	0.1	J - A	Spawning totally inhibited	-	Mearns, A.J. et al., 1976
Meanthes arenaceo- dentata (nereid polychaete)	J	0.5	3 days	EC50 for tube building	3 days	Mearns, A.J., 1974

Toxic or Other Effects on Marine Organisms and Ecosystems

Chromium (page 2)

Chemical Group: Chromium

System: Organism Ecosystem Non-living	Life Stage	Concn. mg/l	Exposure Time	Effect	Time of Observation	Citation
Mya arenaria (soft shell clam)	A	1.0	4-6 weeks	Decreased filtering activity, slower, more erratic movement of cilia	4-6 weeks	Capuzzo, J.M. and Sasner, J.J., jr., 1977
Mya arenaria (soft shell clam)	A	1.0	4-6 weeks	Decreased gill-tissue oxygen consumption	4-6 weeks	Capuzzo, J.M. and Sasner, J.J., 1977
Citharichthys stigmaleus (sanddab)	3.7-12.0 grams	2.2	21 days	EC50 for feeding response	21 days	Sherwood, M.J., 1975
Mytilus edulis (mussel)	A	3.9	7 days	EC50 for byssal thread	7 days	Martin, J.M. et al., 1975
Asterionella japonica (diatom)	-	15-30 (threshold)	10 days	Growth inhibition	10 days	Aubert, M. et al., 1972
Atherinasoma microstoma (hardy head)	P A	19.1	6 days	Loss of appetite	6 days	Negilski, D.S., 1976

L Larva

P A Pre-adult

J Juvenile

A Adult

Toxic or Other Effects on Marine Organisms and Ecosystems

Chromium (page 3)

Chemical Group: Chromium

System: Organism Ecosystem Non-living	Life Stage	Concn. mg/l	Exposure Time	Effect	Time of Observation	Citation
Artemia salina (Brine shrimp)	L	15	6 days	LC50	6 days	Aubert, M. et al., 1972
Carassius auratus (Goldfish)	-	60-160	9 days	LC50	9 days	Aubert, M. et al., 1972
Trachurus mediterraneus (Fish)	A	15.0	5 days	100% mortality	5 days	GFCM, 1978
Carcinus maenas (Shore crab)	-	1.3 (threshold)	8 days	Toxicity	8 days	Aubert, M. et al., 1976
Nereis diversicolor (Polychaete)	-	2.6 (threshold)	8 days	Toxicity	8 days	Aubert, M. et al., 1976
Asterionella japonica (Diatom)	-	58-60 (threshold)	-	Growth inhibition	-	Pesando, D. and Aubert, M., 1975

A Adult J Juvenile P A Pre-adult L Larva

Analysis

Chromium (generic)

Chemical Group: Chromium

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
neutron activation	expensive, time consuming, requires considerable experi- ence/ accurate at low Cr con- centrations	NAS, 1977, p.245
shielded-arc emission spectrography	expensive, time consuming, requires considerable experi- ence/ accurate at low Cr con- centrations	NAS, 1977, p.245

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and the Marine Environment

Chromium(VI)

Chemical Group: Chromium

general classifica- tion of con- trol mecha- nism	country or political sub-division	description of control mecha- nism	quantitative information (analytical method)	citation (as reported in)
control of substances in effluent	France	emission norm for surface treating industry	0.1mg/l	CEC, 1976, p.13-16
control of substances in effluent	France	regulation on refineries' effluents	0.05mg/l	CEC, 1976, p.13-17
control of substances water	Italy	recommended li- mits for indust- rial and urban effluents dis- charged into waters	0.1mg/l as Cr into watercour- ses and lakes, 0.5mg/l as Cr into the sea, 0.2mg/l as Cr into sewers	WHO/UNEP, 1976, p.Italy-4
control of substances in water	Italy	regulation concerning acceptable limits for discharges into surface water and public sewers	0.2mg/l as Cr	IOHL, 1977, p.630
control of substances in effluents	Libyan Arab Republic	proposed stan- dards for efflu- ents discharged	0.1mg/l into surface water reservoirs for direct use in agriculture 0.005mg/l into aquifers used for public water supply 0.05mg/l into the sea 0.2mg/l into urban sewage system	WHO/UNEP, 1976, p.Libyan Arab Republic-2

Legislation for the Protection of Man
and the Marine Environment

Chromium(VI) (page 2)

Chemical Group: Chromium

general classifica- tion of con- trol mecha- nism	country or political sub division	description of control mecha- nism	quantitative information (analytical method)	citation (as reported in)
control of substances in water	Spain	limits for recei- ving watercour- ses, that are not to be exceeded due to effluents	0.05mg/l	WHO/UNEP, 1976, p.Spain-2
control of substances in effluents	Tunisia	proposed recommended values for discharges into surface waters and public sewers	0.1mg/l into waters 0.5mg/l into public sewers (1. photometry with diphenyl- carbazide 2. atomic absorption spectometry)	Kratel (unpublished)
control of substances in effluents	Turkey	prohibition of discharges when the concentration exceeds the tolerance level	0.05mg/l (as ions, but valency not stated)	Turkish law of 1 October 1971
control of substances in water	Yugoslavia	maximum permissible concentrations of dangerous substances in interrepublic watercourses	0.05mg/l in class I and class II waters ^a 0.1mg/l in class III and class IV waters ^b	IDHL, 1978 (awaiting publication)

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and the Marine Environment

Chromium(VI) (page 3)

Chemical Group: Chromium

general classifica- tion of con- trol mecha- nism	country or political sub division	description of control mecha- nism	quantitative information (analytical method)	citation (as reported in)
control of substances in effluents	Yugoslavia	maximum permiss- ible concentra- tions of danger- ous substances discharged into water used or in- tended for use as drinking-water, for production of food stuffs, fish breeding, watering of animals or pub- lic bathing	0.05mg/l	WHO/UNEP, 1976, p.Yugoslavia-4

a Class I: waters which, in their natural state, where necessary after disinfection, may be used for drinking purposes and in the food industry and, in the case of surface waters, for breeding Salmonidae. Class II: waters which, in their natural state, may be used for bathing and recreation, water sport, breeding of Cyprinidae, or which, after treatment, may be used for drinking purposes and in the food industry.

b Class III: waters which may be used for irrigation and, after treatment, in industry other than the food industry. Class IV: waters which may be used for other purposes only after treatment.

Chromium

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GENERAL SUMMARY - LEAD

I. INTRODUCTION

The main sources leading to environmental contamination by lead arise from the industrial and other technological uses of lead by man. Though lead, as an element, occurs naturally in all phases of the environment, inputs from natural sources to the marine environment are insignificant compared to atmospheric washout, river input and industrial effluents which result from man's activities.

Lead serves no known biological function. The ability of many marine organisms to accumulate lead presents a potential hazard to humans through ingestion of contaminated marine produce. The toxic effects of lead in humans have been well documented, as lead has been used extensively by man for thousands of years.

II. OCCURRENCE

A. Production

The production of lead includes mining of ores as well as the recycling of used lead products. Ryan (1971) reports that in 1971, 42% of the total lead consumption in the U.S. came from recycled lead. Galena (PbS), is by far the most important mineral mined for its lead content. Galena occurs primarily in deposits which contain other minerals, especially zinc (EPA, 1976).

WHO-EHE (1977) reports a world mining production in 1975 of 3.6 million tonnes of lead. Mediterranean countries producing lead in 1975 were: France, 150,000 tonnes; Italy, 70,000 tonnes; Spain, 85,000 tonnes; Yugoslavia, 130,000 tonnes. In 1974, Morocco produced 1,000 tonnes of lead.

The consumption of refined lead by most of these countries was considerably higher than production, due to imports (WHO-EHE, 1977).

B. Use

The percentages of total consumption which are listed below are based on the use of lead by 6 industrialised countries, according to data assimilated by Stubbs (1975) and reported in (WHO-EHE, 1977).

Lead used in electric storage batteries accounts for 44% of total consumption. Recycling of batteries, which are used mainly in automotive applications, provides the major proportion of secondary lead production (WHO-EHE, 1977).

Alkyllead compounds used as antiknock additives in gasoline represent 12% of the lead market, though recent restrictions on lead additives are expected to decrease demand. The International Lead and Zinc Study Group (1973) estimates that only 6% of European lead consumption is for alkyllead additives, as contrasted by the U.S., where alkyllead manufacture is, after batteries, the largest lead consuming industry.

12% of the lead used in the 6 industrialised countries is for the chemical industry, mainly as pigments and drying agents in paint. Lead in paint has been responsible for a large number of poisonings, especially in children, and is being substituted by less toxic pigments (WHO-EHE, 1977).

Other major uses of lead are for cable sheathing, especially in Europe (9.8%); in alloys (10.8%); and in semi-manufactured components (12%), which include lead-coated metals used in construction for anticorrosion applications (WHO-EHE, 1977).

III. LEAD IN THE ENVIRONMENT

A. Sources

1. Natural

The contribution of natural sources of lead to present day concentrations in the environment is apparently insignificant (WHO-EHE, 1977).

Gases diffusing from the earth's crust and airborne dust containing an average 10-15ppm of lead are estimated to provide natural atmospheric concentrations of about 0.0005ug/m^3 of air. Greenland ice field studies indicate that present day atmospheric concentrations are about 400 times higher than natural background levels. The pre-industrial lead content of marine water has been estimated at 0.02-0.04ug/kg. Present levels in surface water samples from some areas of the Mediterranean contain approximately 10 times that amount (NAS, 1972).

2. Anthropogenic

Combustion of motor fuels containing alkyllead additives accounts for the major source of lead to the environment. About 70% of the alkyllead enters the environment immediately after combustion, mostly as particulate lead. The rest is trapped in crankcase oil and exhaust systems, and will enter the environment through different pathways (Huntzicker et al., 1975). The degree of pollution from the combustion of alkyllead varies from country to country, depending on the number of motor vehicles, and is a highly localised phenomenon.

In a study by Huntzicker et al. (1975), it was reported that most of the lead emitted from automobiles remained in the urban area of Los Angeles. Only 24% of the total lead discharged to the atmosphere was estimated to remain "airborne", that is, transferred out of the Los Angeles Basin (WHO-EHE, 1977). Atmospheric levels in the Northern Hemisphere have, however, substantially increased since 1940 as a result of alkyllead, as indicated by concentrations in Greenland ice fields (NAS, 1972).

The combustion of fossil fuels, especially coal, also contributes to the atmospheric lead burden. The lead content of fossil fuels varies widely, and determines the concentration of lead in the emissions (WHO-EHE, 1977).

Mining, smelting and refining lead can also cause local pollution. In Yugoslavia, a zone of air pollution extended up to 10km away from a lead smelter stack, soil was grossly contaminated as far as 7km away, and water courses were also heavily polluted (Djuric et al., 1971; Kerin, 1972, 1973).

The dispersion of lead in the environment has many other sources. Disposal of lead containing products, weathering of paint and galvanised metals, the manufacture of alkyllead fuel additives and chemicals and the recovery of lead from secondary smelters all contribute to the environmental lead burden (WHO-EHE, 1977).

B. Transformation

1. Abiotic

Due to the poor solubility of most lead compounds in water, much of the lead entering marine systems via

precipitation and run off will be removed by sedimentation. The factors which affect the stability and solution of lead in water are pH, solubility, adsorption characteristics, hydration, coprecipitation, colloidal dispersion and the formation of complexes (NAS, 1977). Lead forms stable complexes with organic matter, as well as with clay particles which are carried in river discharges. Desorption of lead from sediments is facilitated by increased salinity (deGroot et al., 1976).

A study by Gambrell et al. (1977) determined that increasing the pH caused an increased proportion of organically complexed lead and a decrease in exchangeable lead in sediments.

2. Biotic

Though it is generally accepted that the soluble forms of lead are most toxic to marine life, a study by Ellis (1937) found that finely divided lead sulphide (insoluble) was lethal to fish in two months. NRCC (1973) attributes these findings to the possibility of particulate, colloidal or organic lead being adsorbed to the gills of the fish. Lower pH at the gill surface due to respired CO₂ may dissolve lead to a soluble form, which could diffuse into the gill tissue.

Lead is classified as one of the "metals having metal alkyls which are stable in aqueous systems (that) have been reported to be biomethylated", as reported in UNEP (1977a). No other reference to possible biomethylation of lead was found in the literature searched.

C. Bioaccumulation

Many marine organisms have the ability to concentrate lead present in sea water. Bernhard and Zattera (1975) report that the first trophic levels, phytoplankton, zooplankton and macrophytes can enrich lead to a considerable extent over surrounding sea water. The authors also state that further enrichment by higher trophic levels is negligible, since the lead concentration in crustaceans, molluscs and fishes in apparently uncontaminated areas is not higher than in the first trophic levels. Aubert et al. (1974) report a biomagnification coefficient of 4,605 in phytoplankton.

However, Pringle et al. (1968) showed the ability of eastern oyster, Crassostrea virginica, to concentrate lead 960 times from an initial level of 0.025 mg/l. The mussel, Mytilus edulis, concentrated lead 19,370 times over an ambient level of 0.01 mg/l in a 35 day exposure (Schulz-Baldes, 1974).

IV. MONITORING

A. Analysis

Lead is difficult to measure in marine systems, and according to Patterson and Settle (1976), the determination of lead in most marine samples has been overestimated by several orders of magnitude owing to contamination during sampling, sample preparation and analysis.

Another problem considered in the literature is whether the total lead content should be measured, or only the soluble, particulate, or organic fraction. Distinction of different physio-chemical forms measured are often useful in predicting effects. NIOSH (1978b) reports a

dithizone colorimetry method for measuring arsenic that has a detection limit of 0.2 ± 0.1 ug. The most popular method for analysis of lead is probably atomic absorption spectroscopy. There is a wide variety of other analytical techniques for the determination of lead. (WHO-EHE, 1977).

B. Amount in the Mediterranean

Lead concentrations in sea water samples from various regions of the Mediterranean are as follows: South Lebanon, 0.95 mg/l (Shiber et al., 1978); Suez, 0.039 mg/l (Ibragim and Patin, 1976); Adriatic coast, 0.000068 mg/l; and, La Spezia, Italy, 0.001189 mg/l (Nürnberg et al., 1976).

Sediments are the ultimate sink for most of the lead entering the Mediterranean. As expected, trace metal concentrations, including lead, are higher in estuarine sediments. High lead concentrations in sediments were found in the Bay of Naples, Italy, where 200 mg/kg dry weight was measured (Griggs and Johnson, 1978). The Gulf of Trieste yielded sediment samples containing 300 mg/kg of lead (Majori et al., 1977a). The average lead concentration in sediments from Haifa Bay, Israel, was 8.4 mg/kg dry weight (Roth and Hornung, 1977).

The type of sediment is perhaps more important than the concentration of lead, since sorption, ion exchange, complexation and chelation are determined by physical characteristics of the sediment, i.e. sand, silt, clay and organic composition (UNEP, 1977a).

Roth and Hornung (1977) report that commercial fish from Haifa Bay, Israel, contained 1.8 mg/kg dry weight of lead. Mytilus galloprovincialis, a mussel, has been studied by several authors. Fowler and Oregioni (1976) found 21.5 mg/kg dry weight in samples from the N.W. Mediterranean. Castagna and Sarro (1977) found mussels from Sicily to contain 27.0 mg/kg of lead.

C. Amount Entering the Mediterranean

Approximately 4,820 tonnes of lead per year enter the Mediterranean from land-based sources. The Liguro-Provencal basin and the Adriatic receive 28% and 30%, respectively, of the total load. In the Liguro-Provencal, 59% of the lead comes from river discharge, while 41% is due to industrial and domestic effluents originating in the coastal zone. In the Adriatic, 91% comes from river discharge, the remainder also originating from coastal effluents (UNEP, 1977b). Atmospheric delivery of lead to the world's oceans has been estimated at 0.3 million tonnes per year, compared to only 0.1 million tonnes carried by rivers (UNEP, 1977a).

D. Regulations

There is a great deal of legislation dealing with the discharge of lead in effluents in the Mediterranean states. Standards range from a low of 0.05mg/l in Yugoslavia to a recommended maximum in Italy of 1.0mg/l (as Pb) for lead discharged into the sea (WHO/UNEP, 1976). The discharge of tetraethyl lead is prohibited in Yugoslavia. CEC (1978) has issued a directive limiting the lead content in petrol to 0.4 g/l, effective on January 1, 1981.

V. TOXICITY

A. Toxic or other Effects on Marine Organisms and Ecosystems

The toxicity of lead in water is affected by pH, hardness, organic materials, and the presence of other metals, as well as by the chemical form of the lead itself. The ability of many marine organisms to accumulate lead also

affects its potential toxicity. Calabrese et al. (1973) found a 48 hour LC50 of 2.45 mg/l of lead for embryos of the oyster, Crassostrea virginica. A 96 hour LC50 for lead in the softshell clam, Mya arenaria, was found to occur at 27.0 mg/l (Eisler, 1977).

Sub-lethal effects were found at much lower concentrations of lead. Eriphis spinifrons, a crustacean, showed reduced protein synthesis after 30 days in water containing 0.3mg/l of lead (D'Amelio et al., 1974).

B Toxic Effects on Man and Other Mammals

The biologic effects of lead in man have been well documented, based largely on studies of persons with acute lead poisoning and on experience with occupational exposure to lead. The lead intake of the general population is derived mainly through food sources and the ambient air.

Lead accumulates in the tissues of man and other mammals, and may cause intoxication over a prolonged period. The well known cases of lead poisoning in children who ingest flaking particles of lead-containing paint are manifested by brain damage, anemia, renal impairment and neurological dysfunction. Children are much more susceptible to toxic effects of lead than are adults (EPA, 1976).

An intravenous LD50 for lead in rats has been reported to occur at 120 mg/kg bw/day (ITIL, 1975). Oral doses of 0.025 mg/kg bw/day for 3 days caused reproductive effects in a rat (Hilderbrand et al., 1972). Benign and malignant renal neoplasms were observed in a mouse which consumed 200 mg/kg bw of lead (Van Esch and Kroes, 1969).

Total Production

Metallic lead		Chemical Group: Lead		
Year	Area	Amount	Trend	Citation (as reported in)
1975	World	3 600 000 tonnes		WHO-EHE, 1977, p.33
1973	France	186 000 tonnes	-	WHO-EHE, 1977, p.34
1974	"	178 000 "		
1975	"	150 000 "		
1973	Italy	100 000 tonnes		
1974	"	112 000 "		
1975	"	70 000 "		
1973	Morocco	1 000 tonnes		
1974	"	1 000 "		
1975	"	-		
1973	Spain	120 000 tonnes		
1974	"	102 000 "		
1975	"	85 000 "		
1973	Yugoslavia	97 000 tonnes		
1974	"	115 000 "		
1975	"	130 000 "		

Production Process(es)

Lead acetate		Chemical Group: Lead	
Process (major or minor by geographic area)	Workers exposed	Intermediate, impurities and waste products	Citation (as reported in)
Reaction of lead oxide with acetic acid	-	-	NATO, 1976, p. M2-7

Use

Lead (generic)		Chemical Group: Lead		
Use(s)	Geographic area (major or minor)	Substance(s) added	Trend	Citation (as reported in)
alkyllead (gasoline additives)	6 countries+ 1974 (major) Europe 1973 (minor)	-	-	WHO-EHE, 1977, p. 36
batteries	6 countries+ 1974 (major)	-	-	
cable sheating	6 countries+ 1974 (minor)	-	decreasing	
chemical pigments	6 countries+ 1974 (major)	-	-	
alloys	6 countries+ 1974 (major)	-	-	
semi-manu- facturers	6 countries+ 1974 (major)	-	-	
insecticide	-	-	decreasing	WHO-EHE, 1977, p.38

(+ France, Germany, Italy, Japan, UK, USA)

Use

Lead acetate		Chemical Group: Lead		
Use(s)	Geographic area (major or minor)	Substance(s) added	Trend	Citation (as reported in)
drying agent in paints	-	-	-	NATO, 1976, p.M2-7
lead salts, lead chromate and lead carbonate production				
metal coating				
medicine	-	-	-	EPA, 1977, Table 2
textile-dyeing				
waterproofing				
varnishes				
gold cyanidation process				
insecticide				
antifouling paints				
analytical reagent				

Pathways Leading to Marine Pollution

Lead (Pb ²⁺)		Chemical Group: Lead	
Pathways	Quantity	Area	Citation
Atmosphere	15 000 tons/yr.	North Sea	GESAMP, 1976
Rivers and domestic waste water.	approx. 10 ³ tons/yr. (total).	Baltic Sea	Somer, E., 1977
Precipitation	approx. 10 ³ -10 ⁴ tons/yr. (total)	Baltic Sea	Somer, E., 1977
Surface runoff.	90 metric tons/yr. (89% particulate)	Southern California Bight, U.S.A.	Young, D.R. et al., 1973
Ocean dumping	28 metric tons/yr.	Southern California Bight, U.S.A.	Young, D.R. et al., 1973
Atmosphere	-	Gulf of Trieste, N. Adriatic	Favretto, L. et al., 1977
Direct sewage outfall	-	Yafo, Tel Aviv	Amiel, A.J. and Navrot, J., 1978
Automobile exhaust	-	Ras Beirut, Lebanon	Shiber, J.G. and Shatila, T.A., 1978
Sewage from Beirut river	-	Ras Beirut, Lebanon	Shiber, J.G. and Shatila, T.A., 1978
Land drainage after pesticide spraying	-	Ras Beirut, Lebanon	Shiber, J.G. and Shatila, T.A., 1978

Transformation in the Marine Environment

Lead (Pb²⁺)

Chemical Group: Lead

Process	Medium	Parameters	Effect	Citation
Complex formation	North Sea water, laboratory	pH 8.1	Complex formation with organic material within 30 minutes.	Duinker, J.C. and Kramer, C.J.M., 1977
Oxidation	Barataria Bay sediment, laboratory	Increased pH	Increased proportion of organically complexed lead and decreased exchangeable lead	Gambrell, R.P. et al., 1977
Oxidation	Reduced Barataria Bay sediment, containing S, laboratory	Decreased pH	Increase in soluble and exchangeable lead	Gambrell, R.P. et al., 1977
Oxidation	Sediment, laboratory	Increased redox potential	Increased desorption of lead. Under oxidised conditions, PbCO ₃ controlling solid; under reduced conditions, PbS controlling solid.	Lu, J.C.S. and Chen, K. Y., 1977
Adsorption with Fe ₂ O ₃ .nH ₂ O (30mg/l)	Sea water, laboratory	18-23°C, pH 7.7-8.2	86% lead adsorbed 2 days, 14% (0.07 mg/l) remaining in solution	Krauskopf, K. B., 1956
Adsorption with clay (20g/l)	Sea water, laboratory	18-23°C, pH 7.7-8.2	96% lead adsorbed in 3 days, 4% (0.02 mg/l) remaining in solution.	Krauskopf, K. B., 1956
Desorption	Rhine estuary sediment	Increased salinity	Increased desorption	Groot, A. J. de et al., 1976
Leaching with acetic acid	Mediterranean sediment, laboratory	Decreased pH	50% desorption	Duursma, E.K., 1976

S - sulphide.

C-Pb-18

Behaviour of a Chemical Substance in Marine Organisms

Lead (Pb²⁺)

Chemical Group: Lead

Organism	Exposure		Accumulation and Distribution				Loss		Metabolites		Citation
	Route	Concn. mg/l	Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
Gillichthys mirabilis (estuarine teleost)	W	0.265	8 days	SP	-	117	-	-	-	-	Somero, G.N. et al., 1977a
Gillichthys mirabilis (estuarine teleost)	W	0.265	21 days	I	-	86 (d.w.)	13	30 days	-	-	Somero, G.N. et al., 1977a
Mytilus edulis (muschel)	W	0.01	35 days	K	62.8	19,370	30	28 days	-	-	Schulz-Baldes, M., 1974
Mytilus sp. (muschel)	SW	4.0	8 hours	S T	-	12.5	-	-	-	-	Guidone, R. and Mazzara, M.A., 1973
Crassostrea virginica (oyster)	W	0.5	2 weeks	S T	-	328	-	-	-	-	Shuster, C.N. Jr. and Pringle, B.H., 1969
Mya arenaria (Soft shell)	W	0.2	40 days	S T	-	1,175	-	-	-	-	Pringle, B.H. et al., 1968
Crassostrea virginica (oyster)	W	0.025	-	-	-	960	75	21 days	-	-	Pringle, B.H. et al., 1968

Behaviour of a Chemical Substance in Marine Organisms

Lead (Pb²⁺) (page 2)

Chemical Group: Lead

Organism	Exposure		Accumulation and Distribution					Loss	Metabolites		
	Route	Concn. mg/l	Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	Citation
<i>Haliotis rufescens</i> (abalone)	F	3.0	6 weeks	K	-	8	-	-	-	-	Stewart, J. and Schulz-Baldes, M., 1976
<i>Egria laevigata</i> (brown algae)	W	0.1	-	T	-	30	-	-	-	-	Stewart, J. and Schulz-Baldes, M., 1976
<i>Asterionella japonica</i> (phyto-plankton)	SW	5.0	15 days	WH	100	615.9	-	-	-	-	Aubert, M. et al., 1972
<i>Platymonas subcordiformis</i> (flagellate)	W	0.1	7 days	WH	100	0.8	-	-	-	-	Schulz-Baldes M. and Lewin R.A., 1976
Phytoplankton	SW	0.1	8 days	WH	100	4,605	-	-	-	-	Aubert, M. et al., 1974

Behaviour of a Chemical Substance in Marine Organisms

Lead (Pb²⁺) (page 3)

Chemical Group: Lead

Organism	Exposure		Accumulation and Distribution					Loss		Metabolites	
	Route	Concn. mg/l	Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	Citation
Mytilus galloprovincialis (Mussel)	art-tif. SW	0.05	8 days	ST	-	198.8	-	-	-	-	Majori, L. and Petronio, F., 1973a
Mytilus galloprovincialis (Mussel)	SW	0.1mg/l	30 days	ST	-	320	3.1	27 days	-	-	Majori, L. and Petronio, F., 1973a
Mytilus galloprovincialis (Mussel)	art-tif. SW	0.005 mg/l	40 days	ST	-	1,200	-	-	-	-	Majori, L. and Petronio, F., 1973b
Mya arenaria (Clam)	SW	0.05 (calc.)	-	-	-	1,075 (calc.)	-	-	-	-	Majori, L. and Petronio, F., 1973b
Crassostrea virginica	SW	0.05 (calc.)	-	-	-	700 (calc.)	-	-	-	-	Majori, L. and Petronio, F., 1973b

Behaviour of a Chemical Substance in Marine Organisms

Lead (Pb²⁺) (page 4)

Chemical Group: Lead

Organism	Exposure		Accumulation and Distribution				Loss		Metabolites		Citation
	Route	Concn. mg/l	Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
Nereis diversicolor (polychaete worm)	SW	0.1036	7 days	WH	-	66.6 (from wet wt.)	-	-	-	-	Aubert, M. et al., 1976
Mytilus galloprovincialis (Mussel)	art- if.	0.005	40 days	-	-	1,000	-	-	-	-	Majori, L. et al., 1978b

C-Pb-22

F Food, W Water
I Intestine, K Kidney
SP Spleen, S T Soft Tissue
T Thallus, WH Whole
d.w. BMC calculated from dry wt. of organism
SW Seawater

Behaviour of the Substance in Man and Other Mammals

Lead acetate		Chemical Group: Lead				
description of organism	route	concentration	exposure duration of	retention		clearance rate percent/time
				tissue/percent/time	metabolites name/amount/hazard	
dog	oral (diet)	0.32Pb mg/kg bw	15-356 days	high retention in bone, kidney and liver	-	-
						Calvery et al., 1938 (NAS, 1972, p.258)

Concentrations in Water, Sediments and Biota

Lead (Pb ²⁺)		Chemical Group: Lead			
Description of Sample Material	Origin	Analytical Method	Level(s)	Date(s)	Citation
Seawater	South Lebanon	AAS	0.95 mg/l	1974	Shiber, J. et al., 1978
Water	Sorfjorden, Norway	XFS	0.0089 mg/l (total)	1972-1975	Melhuus, A. et al., 1978
Seawater	Gulf of Fos	DPASV	0.0063 mg/l	1975	Benon, P. et al., 1978
Sediment	Gulf of Mexico, U.S.A.	PIXE	739 mg/kg	-	Pilotte, J.O. et al., 1978
Sediment	Tamar Estuary, U.K.	AAS	249 mg/kg dry wt.	1974	Bryan, G.W. and Uysal, H., 1978
Sediment (top 4 cm)	Dump site, New York Bight, U.S.A.	AAS	97 mg/kg dry wt.	1971	Greig, R.A. et al., 1977
Sargassum horneri (edible brown algae)	Arimyondo, Korea	AAS	8.9 mg/kg dry wt.	1974	Pak, C.K. et al., 1977
Thunnus alalunga (Albacore epidermis)	Southern California coast, U.S.A.	HRMS	1.7 mg/kg wet wt.	1971	Chow, T.J. et al., 1974
Engraulis encrasicolus (Anchovy)	Gulf of Trieste	-	1.44 mg/kg wet wt.	1974-1975	Majori, L. et al., 1978

Concentrations in Water, Sediments and Biota

Lead (Pb²⁺) (page 2)

Chemical Group: Lead

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Enteromorpha sp.	Sorfjorden, Norway	XFS	301.5 mg/kg dry wt.	1974	Pilotte, J.O. et al., 1978
Mytilus galloprovincialis (Mussel)	La Spezia, Italy	AAS	50.0 mg/kg dry wt.	1975	Capelli, R. et al., 1978
Brown shrimp (exoskeleton)	South Texas Outer Continental Shelf, U.S.A.	AAS	17.1 mg/kg dry wt.	-	Horowitz, A. and Presley, B.J., 1977
Commercial fish	Haifa Bay, Israel	AAS	1.8mg/kg dry	1974	Roth, I. and Hornung, H., 1977
Pleuronectes laterna (Flatfish)	Ligurian Sea	-	1.5mg/kg	1974	Ciusa, W. et al., 1974
Patella coerula (Mussel)	Ras Beirut,	AAS	37.8mg/kg dry wt.	1977	Shiber, J.G. and Shatila, T.A., 1978
Mytilus galloprovincialis nean (Mussel)	N.W. Mediterranean	AAS	21.5mg/kg dry wt.	1974	Fowler, S.W. and Oregioni, B., 1976
Mytilus galloprovincialis (Mussel)	Sicily	AAS	27.0mg/kg	1976	Castagna, A. and Sarro, F., 1977
Mytilus galloprovincialis (Mussel)	Yugoslavia	-	0.08mg/kg dry wt.	1977	GFCM, 1978

Concentrations in Water, Sediments and Biota

Lead (Pb²⁺) (page 3)

Chemical Group: Lead

<u>Description of Sample</u>		<u>Analytical Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material</u>	<u>Origin</u>				
Mussels	Gulf of Thessalonikis	AAS	480 mg/kg dry wt.	-	Kovatsis, A. V. and Nitsas, C.V., 1973
Seawater	Ras Beirut, Lebanon	AAS	0,36mg/L	1977	Shiber, J.G. and Shatila, T.A., 1978
Seawater	Haifa Bay, Israel	AAS	0.0072mg/L	1974	Roth, I. and Hornung, H., 1977
Seawater	Alexandria	AAS	0.0067mg/L	-	Ibragim, A.M. and Patin, S.A., 1976
Seawater	Suez	AAS	0.0039mg/L	-	Ibragim, A.M. and Patin, S.A., 1976
Seawater	Jade Bay	DPASV	0.000015mg/L	1975	Nürnberg, H. W. et al., 1976
Seawater	Adriatic coast	DPASV	0.000068mg/L	1975	Nürnberg, H. W. et al., 1976
Seawater	La Spezia, Italy	DPASV	0.001189mg/L	1975	Nürnberg, H. W. et al., 1976
Seawater	Mediterranean	C	0.0002mg/L	-	Tatsumoto, M. and Patterson, C.C., 1963

Concentrations in Water, Sediments and Biota

Lead (Pb²⁺) (page 4)

Chemical Group: Lead

<u>Description of Sample</u>		<u>Analytical Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material</u>	<u>Origin</u>				
Seawater	Gulf of Trieste	AAS	0.001mg/L	1976	Favretto, L. et al., 1977
Seawater	W. Mediterranean	PP	0.0045	Dec 1976	Cambon, J.P. et al., 1977
Mytilus gall- oprovincialis (Mussel)	Marseilles	AAS	117mg/kg dry wt.	1973-74	Fowler, S. and Oregioni, B., 1975
Mytilus gall- oprovincialis (Mussel)	Gulf of Trieste	-	4.0mg/kg wet wt.	1972-75	Majori, L. et al., 1977b
Tapes decuss- atus (Shell- fish)	Deniz Bostanh, Izmir Bay, Turkey	AAS	20.6mg/kg dry wt.	-	Geldiay, R. and Uysal, H., 1975
Tapes decuss- atus (Shell- fish)	Cakalburnu Fishery, Izmir Bay, Turkey	AAS	7.8mg/kg dry wt.	-	Geldiay, R. and Uysal, H., 1975
Paracentrotus lividus (Sea urchin) - soft parts	Bay of Naples	AAS	58.6mg/kg wet wt.	1973	Sheppard, C.R.C. and Bellamy, D.J., 1974
Marine algae	Haifa Bay, Israel	AAS	22.2mg/kg dry wt.	1974	Roth, I. and Hornung, H., 1977
Dunaliella (Blue algae)	Ligurian Coast	DPASV	1.6mg/kg	1975	Nürnberg, H.W. et al., 1976
Blue algae II	Ligurian Coast	DPASV	90mg/kg	1975	Nürnberg, H.W. et al., 1976

Concentrations in Water, Sediments and Biota

Lead (Pb²⁺) (page 5)

Chemical Group: Lead

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Sediment 165m	Adriatic	AAS	16.0mg/kg dry	1973	Paul, J. and Meischner, D., 1976
Sediment	Tel Aviv, Israel	AAS	27.0mg/kg	1973-74	Amiel, A.J. and Navrot, J., 1978
Sediment	Bay of Naples, Italy	AAS	200mg/kg dry	-	Griggs, G.B. and Johnson, S., 1978
Sediment	Gulf of Trieste	AAS	300mg/kg	1972-75	Majori, L. et al., 1977a
Sediment	Haifa Bay, Israel	AAS	8.4mg/kg dry	1974	Roth, I and Hornung, H., 1977

PP Pulse polarography
AAS Atomic absorption spectrophotometry
DPASV Differential pulse anodic stripping voltametry
HRMS High resolution mass spectrometry
PIXE Proton induced X-ray emission
XFS X-ray fluorescence spectrometry
C X-ray fluorescence spectrometry

Array of Toxic Effects on Man and Other Mammals

Lead acetate

Chemical Group: Lead

dose in mg/kg bw/ day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as report- ed in)
8 524	78 weeks	oral	rat	TDLo, carcinogenic effects	NIOSH, 1978, p.15
3 660 (4% Pb in diet)	30 days	oral (mater- nal diet)	rat	decreased aminolevu- linic acid dehydratase in liver, brain and blood in suckling rat	Millar et al., 1970 (NAS, 1972, p.259)
2 000 (10mg/ml)	40 days from birth	oral (water)	mouse (Swiss Webster, CD-1)	delayed walk- ing, weaning, eye opening and hair growth	Silbergeld and Gold- berg, 1974 (NIOSH, 1976, p.75)
400 (2mg/ml)	life time	oral (water)	mouse	increased motor activity	Silbergeld and Gold- berg, 1973 (NIOSH, 1976, p.77)

Array of Toxic Effects on Man and Other Mammals

Lead acetate (page 2)

Chemical Group: Lead

dose in mg/kg bw/ day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as report- ed in)
350 (70mg)	40 days	oral	rat	hypertension, death	Griffith and Land- auer, 1944 (WHO-EHE, 1977, p.92)
125 (0.1% in diet)	2 years	oral (diet)	hamster (male)	kidney effects	Van Esch and Kroes, 1969 (IARC, 1972, p.46)
120	-	intra- venous	rat	LD50	ITII, 1975, p.299
120	-	intra- perit.	mouse	LD50	ITII, 1975, p.299
114 (500ul of a 0.24M solution/ 2 days)	10 days	dermal appl.	rat (4 months old Wistar)	decreased erythrocyte aminolevu- linic acid activity	Rastogi and Clausen, 1976 (NIOSH, 1978b, p.XI-61)
25.6 (512mg/kg diet)	70 days	oral (diet)	rat	decreased rate of protein catabolism	Lightbody and Calvery, 1938 (NAS, 1972, p.256)
17	16 days (5x 30mg Pb/kg)	oral	rabbit	increase in basophilic cells	Bradley and Fredrick, 1941 (NAS, 1972, p.257)

Array of Toxic Effects on Man and Other Mammals

Lead acetate (page 3)

Chemical Group: Lead

dose in mg/kg bw/ day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as report- ed in)
12 (10.4g Pb in 160 days)	160 days	oral	dog	increased coproporphyrin excretion and porphyrinuria, death	Salomon and Cowgill, 1948 (NAS, 1972, p.257)
0.59 (0.32mg Pb/kg)	15-356 days	oral (diet)	dog	behavioural and central nervous system effects, death	Calvery et al., 1938 (NAS, 1972, p.258)
0.4 (20mg/kg of 2% solution)	single dose	intra- venous	rabbit	erythrocyte and throm- bocyte effects	Hacirov, 1972 (WHO- EHE, 1977, p.88)
0.078 (3mg Pb)	4 years	oral	human	no clinical symptoms, increased lead content in blood and urine	Kehoe, 1961 (NAS, 1972, p.257)
0.025 (5ug)	3 days	oral	rat	reproductive effects	Hilderbrand et al., 1972 (NSF, 1977, p.189)
0.020	21 days	oral	human (volunteers, 18-26 years old)	increased blood lead level, increased protoporphyrin IX content of erythrocytes (female)	Stuik and Zielhuis, 1975 (WHO-EHE, 1977, p.98)

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Lead acetate

Chemical Group: Lead

BEHAVIOURAL EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time: brief description	effect (observation time)	citation (as reported in)
mouse (Swiss Webster CD-1)	oral (water)	2000 (10mg/ml)	40 days from birth (daily)	delayed walking, weaning, eye opening, hair growth	Silbergeld and Goldberg, 1974 (NIOSH, 1976, p.75)
mouse	oral (water)	400 (2mg/ml)	lifetime (daily)	increased motor activity	Silbergeld and Goldberg, 1973 (NIOSH, 1976, p.77)
rat	oral	81	3rd-21st day of life (daily)	altered drug response	Sobotka and Cook, 1974 (NIOSH, 1976, p.80)

These studies, designed to evaluate the possible effects of the substance on behaviour, resulted in reports of effects on behaviour, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Lead Acetate (page 2)

Chemical Group: Lead

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time: brief description	effect (observation time)	citation (as reported in)
mouse (Swiss)	oral (diet)	200 (0.1% in diet)	(daily)	benign and malignant renal neoplasms	Van Esch and Kroes, 1969 (IARC, 1972, p.45)
rat (Wistar)	oral (diet)	15 (2 months), 20 (16 months) (3mg and 4mg)	18 months (daily)	prostate, pituitary, testis, adrenal, thyroid, kidney and leyding cell tumours	Zawirska and Medras, 1968 (IARC, 1972, p.45)

A comprehensive evaluation of the known studies designed to assess the possible carcinogenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"Lead acetate is carcinogenic in rats and mice; lead subacetate and lead phosphate are carcinogenic in the rat. Given orally, they produce benign and malignant tumours of the kidney. The observation that exposure of rats to lead subacetate may result in an increased frequency of gliomas needs confirmation, as well as the observation of a high frequency of tumours of the testis, adrenal, thyroid, pituitary and prostate, together with renal tumours, in rats receiving lead acetate. No induction of tumours was reported to occur following exposure to lead arsenate or lead carbonate, but the evidence cannot be held as conclusive.

There is no evidence to suggest that exposure to lead salts causes cancer of any site in man. However, only one epidemiological study of the relationships between exposure to lead and the occurrence of cancer has been reported. It must be noted that the level of human exposure equivalent to the levels of lead acetate producing renal tumours in rats is 810 mg per day (550 mg Pb). This level appears to exceed by far the maximum tolerated dose for man." (IARC, 1972, p. 47-48.)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Lead acetate (page 3)

Chemical Group: Lead

MUTAGENICITY

Nothing found in the literature reviewed.

NEUROTOXICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time: brief description	effect (observation time)	citation (as reported in)
mouse (Swiss Webster CD-1)	oral (water)	2000 (10mg/ml)	40 days from birth (daily)	delayed walking, weaning, eye opening, hair growth	Silbergeld and Goldberg, 1974 (NIOSH, 1976, p.75)
mouse	oral (water)	400 (2mg/ml)	lifetime (daily)	increased motor activity	Silbergeld and Goldberg, 1973 (NIOSH, 1976, p.77)
rat	intra-perit.	100	3 days	locomotor problems	Brown et al., 1971 (NSF, 1977, p.188)
rat	oral (nursing)	- (4% in maternal diet)	-	tremors, deformed cerebellum	Krall et al., 1972 (NSF, 1977, p.188)

These studies, designed to evaluate the possible neurotoxic effects of the substance, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Lead acetate (page 4)

Chemical Group: Lead

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
mouse	lindane	slight syner- gistic effect on urinary copro- porphyrin concentration	Cress, 1970 (NRCC, 1973, p.66)
rat	magnesium	reversed depression in mitochondrial phosphorylation	Krall et al., 1972 (NSF, 1977, p.188)

These studies designed to evaluate the possible effects which could result from the combination of this substance with one or more other substances, resulted in reports of the above effect, but no comprehensive evaluation of this material was found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Lead acetate (page 5)

Chemical Group: Lead

REPRODUCTIVE EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time: brief description	effect (observation time)	citation (as reported in)
sheep (pregnant ewes)	-	9	1st 45 days of gestation (daily)	abortion, death	James et al., 1966 (NRCC, 1973, p.65)
sheep (pregnant ewes)	-	5	1st 45 days of gestation (daily)	no effect found	James et al., 1966 (NRCC, 1973, p.65)
rat	oral	0.025 (5 ug)	30 days (daily)	prostate and testicle effects, seminiferous tubules damage, halted spermatogenesis, irregular estrus, males refused to copulate	Hildebrand et al., 1972 (NSF, 1977, p.189)

These studies, designed to evaluate the possible effects of the substance on reproduction, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Lead Acetate (page 6)

Chemical Group: Lead

TERATOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time: brief description	effect (observation time)	citation (as reported in)
sheep (pregnant ewes)	-	9	1st 45 days of gestation (daily)	abortion, death	James et al., 1966 (NRCC, 1973, p.65)
sheep (pregnant ewes)	-	5	1st 45 days of gestation (daily)	no effect found	James et al., 1966 (NRCC, 1973, p.65)

These studies, designed to evaluate the possible teratogenic effects of the substance, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Lead (Pb²⁺)

Chemical Group: Lead

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Mercenaria mercenaria (hard clam)	Em	0.78	42-48 hours	LC50	42-48 hours	Calabrese, A. and Nelson, D.A., 1974
Mya arenaria (softshell clam)	A	27.0	96 hours	LC50	96 hours	Eisler, R., 1977
Crassostrea virginica (oyster)	Em	2.45	48 hours	LC50	48 hours	Calabrese, A. et al., 1973
Crassostrea virginica (oyster)	A	0.1-0.2	12 weeks	Tissue changes in gonad and mantle	12 weeks	ICES, 1978
Eriphia spinifrons (crustacean)	-	0.3	30 days	Decrease in protein synthesis	30 days	D'Amelio V. et al., 1974
Mytilus galloprovincialis (mussel)	Em	0.5	2 days	Inhibition of embryonic development	2 days	Hrs-Brenko, M. et al., 1977
Dunaliella salina (marine Green flagellate)	-	0.9	12 days	Decreased total pigment per cell	12 days	Pace, F. et al., 1977

Toxic or Other Effects on Marine Organisms and Ecosystems

Lead (Pb²⁺) (page 2)

Chemical Group: Lead

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Fundulus heteroclitus (mummichog)	Em	1.0	Stage 12 embryo through to larva	80% skeletal malforma- tion of fry at hatching	hatching time	Weis, J.S. and Weis, P., 1977
Prorocentrum micans (dinoflagellate)	-	1.0	10 days	50% decrease in photosynthesis	10 days	Saifullah, S. M., 1976
Mytilus edulis (mussel)	A	2.5	7 days	50% reduction in byssal thread production	7 days	Martin, J.M., et al., 1975
Gillichthys mirabilis (estuarine fish)	A	2.65	60 days	Increased oxygen con- sumption and activity	60 days	Somero, G.N. et al., 1977b
Dunaliella tertiolecta (flagellate)	-	3.0	8 days	Stopped growth	8 days	Stewart, J., 1977
Artemia salina (brine shrimp)	E	5.0	3 days	35% decrease in hatch.	3 days	Saliba, L.J. and Krzyz, R. H., 1976

Toxic or Other Effects on Marine Organisms and Ecosystems

Lead (Pb²⁺) (page 3)

Chemical Group: Lead

System Organism Ecosystem Non-Living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Pseudopleuronectes americanus (winter flounder)	A	10.0	7 days	66% decrease in liver ALA-D activity	7 days	Jackim, E., 1973
Artemia salina (Brine shrimp)	-	500	24 hr	75% mortality	24 hr	Aubert, M. et al., 1972
Carassius auratus (Gold- fish)	-	375-750	9 days	LC50	9 days	Aubert, M. et al., 1972
Nereis diversicolor (Polychaete worm)	-	10.36 (threshold)	8 days	toxicity	8 days	Aubert, M. et al., 1976
Carcinus maenas (Crab)	-	10.36 (threshold)	8 days	toxicity	8 days	Aubert, M. et al., 1976
Heterothrix sp (Unicell- ular algae)	-	2.0 (minimum)	17 days	lethal	17 days	Berland, B.R. et al., 1976

Toxic or Other Effects on Marine Organisms and Ecosystems

Lead (Pb²⁺) (page 4)

Chemical Group: Lead

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Natural phytoplankton community	-	0.1	short term	10% decrease in photosynthesis	short term	Ibragim, A.M. and Patin, S. A., 1976
Perinereis cultrifera (Annelid)	-	0.2	8 days	-amino-levulinic acid decreased	8 days	Geraci, F. et al., 1977
Asterionella japonica (Diatom)	-	0.82 (threshold)	-	growth inhibition	-	Pesando, D. and Aubert, M., 1975
Cylindrotheca closterium (Unicellular alga)	-	1.0 (minimum)	17 days	growth inhibition	17 days	Berland B.R. et al., 1976
Asterionella japonica (Diatom)	-	3-7 (threshold)	-	growth inhibition	-	Aubert, M. et al., 1972

A Adult

E Egg

Em Embryo

ALA-D -aminolevulinic acid dehydratase

Analysis

Lead (generic)		Chemical group: Lead
analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
dithizone colorimetry (0.2+0.1ug)	requires meticulous attention to details/ equipment found in most chemical laboratories	NIOSH, 1978b, p.V-10

Legislation for the Protection of Man
and the Marine Environment

Lead (generic)

Chemical Group: Lead

general classification of control mechanism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as report- ed in)
control of substances in petrol	CEC	directive concerning the maximum permitted lead compound content of petrol, effective on 1 January 1981	0.40g/l as Pb	CEC, 1978, p.19
control of substances in effluents	Egypt	standard for industrial waste- water discharged into drainage canals	-	WHO/UNEP, 1976, p.Egypt-3
control of substances in effluents	France	regulation on refineries' effluents	0.1mg/l	CEC, 1976, p.13-17
control of substances in effluents	Italy	recommended limits for industrial and urban effluents discharged into waters	0.1mg/l as Pb into watercourses and lakes, 1mg/l as Pb into the sea 0.2mg/l as Pb into sewers	WHO/UNEP, 1976, p.Italy-4
control of substances in water	Italy	regulation concerning acceptable limits for discharges into surface water and public sewers	0.2mg/l as Pb in surface waters 0.3mg/l as Pb in public sewers	IDHL, 1977, p.630

Legislation for the Protection of Man
and the Marine Environment

Lead (generic) (page 2)

Chemical Group: Lead

general classification of control mechanism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as report- ed in)
control of substances in effluents	Libyan Arab Republic	proposed stand- ards for effluents discharged	0.2mg/l into surface water reservoirs for direct use in agriculture, into aquifers used for public water supply and into urban sewage systems 0.1mg/l into the sea	WHO/UNEP, 1976, p.Libyan Arab Republic-2
control of substances in effluents	Spain	regulation concerning discharges from submarine outfalls	7.5mg/l in not more than 50% of samples 15.0mg/l in not more than 10% of samples	IDHL, 1978, p.193
control of substances in water	Spain	limits for receiving public watercourses, that are not to be exceeded due to effluents	0.1mg/l	WHO/UNEP, 1976, p.Spain-2
control of substances in effluents	Tunisia	proposed recommended values for discharges into surface waters and public sewers	0.5mg/l as Pb for surface waters 2mg/l as Pb for public sewers (1. Spectro- photometry with dithizone 2. Atomic absor- ption spectro- photometry)	Kratel (unpublish- ed)

Legislation for the Protection of Man
and the Marine Environment

Lead (generic) (page 3)

Chemical Group: Lead

general classification of control mechanism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as report- ed in)
control of substances in effluents	Yugoslavia	maximum permis- sible concentrat- ions of danger- ous substances discharged into water used or intended for use as drinking water, for production of food stuffs, fish breeding, watering of animals or public bathing	0.05mg/l (discharge of tetraethyl lead is prohibited)	WHO/UNEP, 1976, p.Yugoslavia- 2
control of substances in water	Yugoslavia	maximum permissible concentrations of dangerous substances in interrepublic watercourses	0.05mg/l in class I and class II waters ^a 0.1mg/l in class III and class IV waters ^b 0.0001mg/l of tetraethyl lead in class III and class IV waters ^b	IDHL, 1978, (awaiting publication)

^a Class I: waters which, in their natural state, where necessary after disinfection, may be used for drinking purposes and in the food industry and, in the case of surface waters, for breeding Salmonidae. Class II: waters which, in their natural state, may be used for bathing and recreation, water sports, breeding of Cyprinidae, or which, after treatment, may be used for drinking purposes and in the food industry.

^b Class II: waters which may be used for irrigation and, after treatment, in industry other than the food industry. Class IV: waters which may be used for other purposes only after treatment.

Lead

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MEDITERRANEAN DATA PROFILE

SELENIUM

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^a Nothing found in the literature reviewed

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GENERAL SUMMARY FOR SELENIUM

I. INTRODUCTION

The chemical properties of selenium (Se) are similar to those of sulphur. It exists in nature in several oxidation states : -2, 0, +4 and +6 (NAS, 1976). However, it differs from sulphur in that it is more reactive and its compounds are less stable (Gosink and Reynolds, 1975).

Under alkaline soil conditions selenium can be transformed by a process of oxidation. A process of biotic reduction is also known to occur.

Overall, it is the weathering of selenite containing rocks that provides the main oceanic input. However, as a result of known anthropogenic additions of this highly toxic element to the marine environment, selenium is beginning to receive attention as a potential marine pollutant. The low solubility of elemental selenium, however, serves to lower its potential environmental toxicity.

Selenium can be accumulated to relatively high levels in marine biota and in some instances is strongly correlated with the concentration of mercury and other metals.

II. OCCURRENCE

A. Production

Se can be produced, by way of extraction, from the lead chamber sludge that forms during sulphuric acid production or from the anode sludge from the electrolytic purification of copper (NATO, 1976).

The worldwide Se production for 1973 was about 1,100 tons (IARC, 1975). No production figures for the Mediterranean were found in the literature reviewed.

B. Use

Se use includes various electronic applications such as rectifiers, xerographic copying machines and photoelectric cells. It is also used by the glass and ceramics industry in the manufacture of pigments, as a component of plating solutions (NAS, 1976) and in the production of pharmaceutical and cosmetic products (IARC, 1975). At present the chief agricultural use of Se is in the prevention of selenium deficiency in livestock (IARC, 1975), although it is also used in insecticides (Merck Index, 1968), fungicides (Innes et al., 1969) and veterinary medicine (Elkin and Margrave, 1968).

III. SELENIUM IN THE ENVIRONMENT

A. Sources

1. Natural

NAS (1977) states that there is little indication in the literature that selenium is present in surface waters at toxic concentrations. In fact, the data of Cannon (1974) indicates that in some circumstances it may occur at sub-nutritional levels.

On a worldwide scale, Bertine and Goldberg (1971) estimated that 8,000 tons per year are discharged into the oceans from rivers. Fowler and Benayoun (1976b) have pointed out that selenium enters the marine environment primarily through the weathering of selenite containing rocks. The selenium content in various rocks has been reported as being in the range of 0.3 - 3.7ppm (Schnepe and Flanagan, 1973). Cannon (1974) has recorded a concentration as high as 178ppm in phosphate containing rock.

Klayman and Gunther (1973) indicate that problems of environmental contamination are very likely minimised, because nearly all organic selenium is in the -2 oxidation state; upon decomposition elemental selenium is formed, very little of which can be absorbed. Compounds of major concern to environmental toxicologists are selenite (Se^{+4}) and selenate (Se^{+6}). These are the forms that occur most often in water. The +2 oxidation state has not been reported to occur naturally (NAS, 1977).

2. Anthropogenic

The natural weathering cycle accounts for most of the selenium mobilised into the environment; however, anthropogenic fluxes originating from fossil fuel consumption (450 tons/yr) and agricultural and industrial usage will add to the levels derived from natural processes (Bertine and Goldberg, 1971).

NATO (1976) has stated that selenium containing waste does not occur in large amounts. However, Schafer (1976) has reported that in 1975, 17.1 metric tons of selenium were discharged into Southern Californian coastal waters in municipal waste water.

Other major sources include the manufacture and repair of xerox drums, the sludge from paint production, and the flue dusts from power plants and incinerators. Considerable amounts of selenium are also contained in newsprint (NATO, 1976).

Recognition of an anthropogenic component in the total environmental selenium flux has lead some authors to consider this highly toxic element as a potential pollutant in the marine environment (Ketchum, 1975).

B. Transformation

1. Abiotic

On burning, selenium is oxidised to selenium dioxide, which sublimates and forms selenious acid on solution in water. Selenite (Se^{+4}) has an affinity for iron and aluminium sesquioxides, with which it forms stable adsorption complexes. Alkaline and oxidising conditions favour the formation of selenate (Se^{+6}). This oxidative transformation is known to occur in alkaline soils by a process of chemical weathering (NAS, 1976).

The coexistence of the hexa- and tetravalent ions in aqueous solutions has been confirmed by Sugimura et al. (1976). There are a large number of studies indicating that the selenium content of sea water is very low, due mainly to the precipitation of selenite by the oxides of iron and manganese (NAS, 1977).

2. Biotic

Selenium is metabolised by a combination of reduction and methylation processes. Methylated metabolites of selenium include trimethyl selenonium, the major urinary metabolite of selenium, and dimethyl selenide, the volatile selenium metabolite produced under conditions of selenium toxicity. Several microorganisms are able to biosynthesize selenomethione from inorganic selenium salts, but evidence for the formation of seleno-cystine is much less certain. Although many microorganisms produce methylated selenium metabolites, these compounds are less toxic than the soluble inorganic salts of selenium. This is in contrast to the situation with mercury (NAS, 1976).

C. Bioaccumulation

Organic forms of selenium are retained by the body to a greater degree than inorganic forms (Smith et al., 1938). There is some evidence that a homeostatic mechanism operates at physiologic levels of inorganic selenium intake to limit the amounts of selenium retained in the tissues (Burk et al., 1972).

Selenium can be accumulated by euphasids both directly from water and through the food chain. Fowler and Benayoun (1976c) demonstrated a biomagnification coefficient of 400 over 7 days with Meganyctiphanes norvegica. In their work on the bioaccumulation of the radioisotope Se-75, the same authors suggested that non-metabolic processes were involved in the direct uptake of Se-75 by external surfaces, such as shell and exoskeleton. A biomagnification coefficient of 20 was recorded for the exoskeleton of the shrimp, Lysmata seticaudata (Fowler and Benayoun, 1976a).

Kosta et al. (1975) have suggested that some sort of Hg-Se linkage exists, such that even slightly increased mercury levels seem capable of raising the selenium content in those organs which accumulate and retain mercury (i.e., thyroid, pituitary, kidney and brain).

The highest tissue concentration found in the literature reviewed was 22mg/kg wet weight in the spleen of the albacore, Thunnus alalunga (Folsom et al., 1972).

No evidence indicating magnification of selenium in the food web was found in the literature reviewed.

IV. MONITORING

A. Analysis

Virtually every instrumental method has been adapted for selenium determination. For marine samples the following methods have been developed: neutron activation (Schutz and Turekian, 1965), fluorimetry (Rankin, 1973), isotopic labeling (Sandholm et al., 1973), gas phase chromatography (Talmi and Andren, 1974), and atomic absorption spectrometry (Ihnat, 1976; Pierce et al., 1976).

B. Amount in the Mediterranean

No information concerning the concentration of selenium in the waters or sediments of the Mediterranean was found in the literature reviewed. However in sediment from the Southampton Estuary, U.K., the selenium concentration was found to be 6.6mg/kg wet weight. The average seawater concentration of Se is estimated at 4.0ug/l by Gaskell (1971).

Grimanis et al. (1978) found 6.6mg/kg dry weight of selenium in the liver of Sargus annularis, taken from the Petallon Gulf in the Aegean Sea. The same authors found 2.6mg/kg dry weight in the liver of the Goby, Gobius niger, from Keratsini Bay in the Aegean. Papadopoulou and Kanas (1976) measured selenium levels in two echinoderm species from the Saronikos Gulf in Greece. Shaerechinus granularis contained 0.8mg/kg dry weight; Echinaster sepositus had a selenium concentration of 4.4mg/kg dry weight.

C. Amount Entering the Mediterranean

No information on this topic was found in the literature reviewed.

D. Regulations

The EEC, Egypt, Italy, Spain, Turkey, the Libyan Arab Republic and Yugoslavia have all legislated for the control of selenium levels in water or effluents. The lowest limit set is 0.01mg/l, by both the EEC and Yugoslavia. The highest is 0.05mg/l, by Spain and Turkey (WHO/UNEP, 1976).

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

The LC50 for adult British Oysters (*Ostrea edulis*) was 50.1mg/l after 7 days (Wrench, 1977). No other information on this topic was found in the literature reviewed.

B. Toxic Effects on Man and Other Mammals

Selenium inhaled as a dust or vapour is toxic and causes severe irritation of the mucous membrane and respiratory tract. On the skin selenium may cause blisters and other skin sores (NATO, 1976).

Biologically, selenium is an essential element recognised as a metabolic requirement in trace amounts for animals, but toxic when ingested in amounts ranging from about 0.1 - 10mg/kg of food (EPA, 1976). No information on the minimal toxic dose for man was found in the literature reviewed.

An oral dose of 5mg/kg bw/day is the lowest dose known to have a lethal effect on a human (NIOSH, 1978).

NIOSH (1978) reports that 70mg/kg bw/day over a period of 49 weeks, fed to rats, produced cancer.

Total Production

Selenium (generic)

Chemical Group: Selenium

year	area	amount	trend	citation (as reported in)
1973	world	1 100 tonnes	-	Baltrusaitis, 1974 (IARC, 1975, p.247)

Production Process(es)

Selenium (generic)		Chemical Group: Selenium	
process (major or minor- by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
by-product of the electrolytic refining of copper - decopperised slimes are smelted in a rotary kiln with sodium bi- sulphate, selenium dioxide is volatized and collected in a scrubber - Cottrell system (USA) purified selenium may be obtained by dissolving the dioxide in water and precipit- ating selenium with sulphur dioxide	-	-	Elkin and Margrave, 1968 (IARC, 1975, p.246)

Use

Selenium (generic)		Chemical Group: Selenium		
use(s)	geographic area (major or minor)	substance (s) added	trend	citation (as reported in)
additive in natural and synthetic rubbers	-	-	-	Elkin and Margrave, 1968, (IARC, 1975, p.247)
catalysts, oxidizing and reducing agents				
paint, plastics and ceramics industry				
photoelectric cells				
veterinary medicines				
feed additives	-	-	-	IARC, 1975 p.248
fungicide	-	-	-	Innes et al., 1969 (IARC, 1975, p.248)
additive to improve machinability and reduce porosity of steels	-	-	-	Baltrusaitis, 1974 (IARC, 1975, p.247)

Use

Selenium (generic) (page 2)		Chemical Group: Selenium		
use(s)	geographic area (major or minor)	substance (s) added	trend	citation (as reported in)
manufacture of glass	-	-	-	Baltrusaitis, 1974 (IARC, 1975, p.247)
pharmaceutical and cosmetic products				
rectifiers				
selenium- coated photo- receptors				

Use

Sodium selenate

Chemical Group: Selenium

use(s)	geographic area (major or minor)	substance (s) added	trend	citation (as reported in)
feed additive	-	-	-	IARC, 1975, p.248
veterinary medicine	-	-	-	Elkin and Margrave, 1968 (IARC, 1975, p.248)
insecticide	-	-	-	Merck Index, 1968, p.965

Pathways Leading to Marine Pollution

Selenium		Chemical Group: Selenium	
Pathway	Quantity	Area	Citation
Weathering of selenite-containing rocks	7 200 tons/yr	World oceans	Fowler, S.W., and Benayoun, G., 1976c
Municipal waste dischargers	17.1 metric tons/yr (total)	Southern California coastal water, U.S.A.	Schafer, H.A., 1976
Rainfall	105 tonnes/yr (total)	North Sea	Cambray, R.S., et al., 1976

Transformation in the Marine Environment

Selenium

Chemical Group: Selenium

Process	Medium	Parameters	Effect	Citation
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Nothing found in the marine environment.

Behaviour of a Chemical Substance in Marine Organisms

Selenium

Chemical Group: Selenium

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn. mg/l	Time	Tissue/ Organ	% Biomagnification Coefficient	%	Time	Name	Quantity	
Mytilus gallo-provincialis (Mussel)	W	-	13 days	Wh	-	46	-	-	-	Fowler, S.W. and Benayoun, G., 1976a and b
Ostrea edulis (Oyster)	W	-	24 hours	S T	-	2.36	-	-	-	Wrench, J.J., 1977
Meganyctiphanes norvegica (euphausiid)	F+W	-	7 days	Wh	-	400	-	-	-	Fowler, S.W. and Benayoun, G., 1976c
Lysmata seticaudata (shrimp)	W	-	6 days	Ex	60%	20	-	-	-	Fowler, S.W. and Benayoun, G., 1976a
Mytilus galloprovincialis (Mussel)	W	-	23 days	G	12%	100	84	97 days	-	Fowler, S.W. and Benayoun, G., 1976a and b
Lysmata seticaudata (Shrimp)	W	-	6 days	Ex	60%	20	95	82 days	-	Fowler, S.W. and Benayoun, G., 1976a and b

Behaviour of a Chemical Substance in Marine Organisms

Selenium (page 2)

Chemical Group: Selenium

Organism	Exposure		Accumulation and Distribution					Loss		Metabolites		Citation
	Route	Concn. mg/l	Time	Tissue/ Organ	% Biomagnification Coefficient	% Biomagnification Coefficient	% Biomagnification Coefficient	Time	Name	Quantity		
Meganycti- phanes norvegica (Euphuasiid)	F+W	-	7 days	Wh	-	400	50	37 days	-	-	Fowler, S.W. and Benayoun, G., 1976c	

Ex Exoskeleton
G Gills
S T Soft tissue
Wh Whole
W Water
F Food

Behaviour of the Substance in Man and Other Mammals

Sodium selenate

Chemical Group: Selenium

description of organism	exposure		retention tissue/percent/amount	clearance rate		metabolites name/amount/hazard in)	citation (as reported in)
	route	concentration		percent/time	metabolites name/amount/hazard in)		
rat	-	-	-	-	dimethyl selenide	McConnel and Portman, 1952 (NAS, 1977, p.353)	
rat	-	-	-	-	trimethyl selenonium ion	Palmer and Olson, 1974 (NAS, 1977, p.353)	
rat	sub cut.	-	single dose	40%/24 hours in urine, 3-6%/24 hours in faeces	-	McConnel, 1941 (NAS, 1976, p.56)	
rat	sub cut.	-	single dose	highest concentrations in liver, kidneys, muscle mass, gastrointestinal tract and blood	-	McConnel, 1941 (NAS, 1976, p.53)	
dog	injection	-	single dose	2%/7 hours in bile	-	McConnel and Martin, 1952 (NAS, 1976, p.57)	

Concentrations in Water, Sediments and Biota

Selenium		Chemical Group: Selenium			
Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Water	Southampton Estuary, U.K.	ECGC	0.019 mg/l	1974	Gosink, T.A. and Reynolds, D.J., 1975
Surface water	English Channel	S	0.0005 mg/l (total)	-	Chau, Y.K. and Riley, J.P., 1965
Surface water	Western North Pacific Ocean	F	0.00012 mg/l (total)	1976	Sugimura, Y. and Suzuki, Y., 1977
Sediment	Southampton Estuary U.K.	ECGC	6.6 mg/kg wet wt.	1974	Gosink, T.A. and Reynolds, D.J., 1975
Sediment (9 cm)	Outfall area, Palos Verdes, U.S.A.	NAA	6.0 mg/kg dry wt.	1971	Young, D.R., 1974
Sediment	Long Island Sound U.S.A.	NAA	3.0 mg/kg dry wt.	1972	Greig, R.A. et al., 1977
Thunnus alalunga (Albacore -spleen)	Southern California U.S.A.	NAA	22 mg/kg wet wt.	1971	Folsom, T.R. et al., 1972
Homarus vulgaris (Lobster - roe)	Norway	AAS	4.43 mg/kg dry wt.	-	Egaas, E. and Braekkan, O.R., 1977
Thunnus albacares (Yellowfin tuna -muscle)	New South Wales, Australia	SF	0.5 mg/kg wet wt.	-	Bebbington, G. N. et al., 1977

Concentrations in Water, Sediments and Biota

Selenium (page 2)

Chemical Group: Selenium

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Prototheca staminea (Clam)	Prince William Sound Alaska	ECGC	0.2-0.4 mg/kg wet wt.	-	Gosink, T.A. and Reynolds, D.J., 1975
Pelagophycus porra (Elk Kelp - outermost layer of bladder)	San Diego, U.S.A.	NAA	≤ 2.2 mg/kg wet wt.	-	Folsom, T.R. et al., 1972
Gadus virens (Coalfish)	Norway	AAS	1.23 mg/kg dry wt.	-	Egaas, E. and Braekkan, O.R., 1977
Sargus annularis -liver	Petallion Gulf, Aegean Sea	RS	6.6mg/kg dry wt.	1973-74	Grimanis, A.P. et al., 1978
Gobius niger (Goby) -liver	Keratisini Bay, Aegean Sea	RS	2.6mg/kg dry wt.	1973-74	Grimanis, A.P. et al., 1978
Microcosmus sulcatus (Tunicate) -whole	Keratsini Bay, Aegean Sea	NAA	5.1mg/kg dry wt.	1974	Papadopoulou, C. and Kanias, G.D., 1977
Shaerechinus granularis (Echinoderm)	Saronikos Gulf	NAA	0.8mg/kg dry wt.	1974	Papadopoulou, C. and Kanias, G.D., 1976
Echinaster sepositus (Echinoderm)	Saronikos Gulf	NAA	4.4mg/kg dry wt.	1974	Papadopoulou, C. and Kanias, G.D., 1976

Concentrations in Water, Sediments and Biota

Selenium (page 3)

Chemical Group: Selenium

<u>Description of Sample</u>		<u>Analytical Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material Sampled</u>	<u>Origin</u>				
Acartia clausi (zooplankton)	Saronikos Gulf	NAA	2.4mg/kg dry wt.	1974	Zafiropoulos, D. and Grimanis, A.P., 1977

AAS Atomic Adsorption Spectroscopy
 ECGC Electron Capture Gas Chromotography
 F Fluorometry
 NAA Neutron Activation Analysis
 SF Spectrophotofluorometry
 S Spectrophotometry
 RS Radiochemical Separation

Array of Toxic Effects on Man and Other Mammals

Sodium selenate

Chemical Group: Selenium

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
70	49 weeks	oral	rat	TDLo (carcinogenic effects)	NIOSH, 1978, p.23
5	-	oral	human	LDLo	NIOSH, 1978, p.23
4	-	oral	rabbit	LD ₅₀	NIOSH, 1978, p.23
4	13 days	intra- perit.	rat	histologic changes of epiphyseal plate	Campo and Bieln, 1971 (NAS, 1977, p.358)
2.9 (0.2g/70kg)	-	oral	human	estimated fatal dose	Arena, 1974, p.138
2.5	-	oral	rat	LD ₅₀	NIOSH, 1978, p.23
0.6 (3ppm in water)	lifetime	oral (water)	mouse	decreased lifespan in females	Schroeder and Mitchener, 1972 (NAS, 1977, p.359)
0.2 (4mg/kg diet)	100 days	oral (diet)	rat (Wistar)	toxic hepatitis, death	Harr et al., 1967 (IARC, 1975, p.252)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Sodium selenate

Chemical Group: Selenium

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Long-Evans)	oral (diet)	0.15 (3mg/l)	-	higher incidence of tumours	Schroeder and Mitchener, 1971 (IARC, 1975, p.251)
mouse (Swiss)	oral (water)	0.6 (3mg/l)	-	no increase in tumours	Schroeder and Mitchener, 1972 (IARC, 1975, p.250)

These studies, designed to evaluate the possible carcinogenic effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

MUTAGENICITY

Nothing found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Sodium selenate (page 2)

Chemical Group: Selenium

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Selenium		Chemical Group: Selenium			
System	Life Stage	Concentration mg/l	Exposure Time	Effect	Citation
Organism Ecosystem Non-living					
Ostrea edulis (Native British oyster)	A	50.1	7 days	LC50	Wrench, J.J., 1977

A - Adult

Analysis

Selenium (0, IV, VI)

Chemical group: Selenium

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
atomic absorption spectrometry with carbon furnace atomization (25ng/g)	many experimental parameters must be optimized: this could affect reproductability /sensitive, commercially available apparatus	Ihnat, 1976
atomic absorption spectroscopy with hydride generation (19ng/l)	extreme accuracy in system monitoring required, interference from copper possible/ extremely fast, sophisticated technique, high sensitivity	Pierce et al., 1976

Analysis

Selenium (IV)

Chemical group: Selenium

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
gas chromatography with microwave emission spectrometry (40pg)	precise chemical pretreatment of sample necessary (time consuming)/ high sensitivity and selectivity, apparatus commercially available	Talmi and Andren, 1974

Legislation for the Protection of Man
and the Marine Environment

Selenium (generic)

Chemical group: Selenium

general classifica- tion of con- trol mecha- nism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in water	EEC	guideline covering quality requirements to be met by surface water used to provide drinking water	0.01mg/l	NATO, 1976, p.M7-1
control of substances in effluents	Egypt	standard for industrial waste-water discharged into drainage canals	-	WHO/UNEP, 1976, p.Egypt-3
control of substances in effluents	Italy	recommended limits for industrial and urban effluents discharged into waters	0.03mg/l as Se into water- courses, 0.01mg/l as Se into lakes, 0.1mg/l as Se into the sea, 0.05mg/l as Se into sewers	WHO/UNEP, 1976, p.Italy-4
control of substances in effluents	Libyan Arab Republic	proposed stand- ards for effluents discharged	0.02mg/l into surface water reservoirs for direct use in agriculture and into aquifers used for public water supply, 0.03mg/l into urban sewage systems	WHO/UNEP, 1976, p.Libyan Arab Republic-2

Legislation for the Protection of Man
and the Marine Environment

Selenium (generic) (page 2)

Chemical group: Selenium

general classifica- tion of con- trol mecha- nism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in water	Spain	limits for receiving public water courses, that are not to be exceeded due to effluents	0.05mg/l	WHO/UNEP, 1976, p.Spain-2
control of substances in effluents	Turkey	prohibition of discharges when the concen- tration exceeds the tolerance level	0.05mg/l as selenium ion	WHO/UNEP, 1976, p.Turkey-4
control of substances in effluents	Yugoslavia	maximum permiss- ible concentra- tions of danger- ous substances discharged into water used or intended for use as drinking water, for production of food-stuffs, fish-breeding, watering of animals or public bathing	0.01mg/l	WHO/UNEP, 1976, p.Yugoslavia- 2

Selenium

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MEDITERRANEAN DATA PROFILE

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GENERAL SUMMARY FOR ARSENIC

I. INTRODUCTION

Arsenic and its compounds are ubiquitous in nature, and display both metallic and non-metallic properties. The trivalent and pentavalent cations are the most common oxidation states, though elemental arsenic also occurs. Trivalent arsenic is much more toxic to both mammals and aquatic organisms, and industrially produced arsenic is in the toxic trivalent (inorganic) state (Schroeder and Balassa, 1966).

Although arsenic itself is insoluble, many of its compounds are soluble in water, leading to average sea water concentrations of 2.0-3.0ug/l (EPA, 1976). Marine organisms, especially invertebrates, are able to concentrate arsenic from sea water to very high levels. Most of the arsenic is in the organic form in marine organisms, which is much less toxic than the trivalent inorganic compounds (Bernhard, 1978).

II. OCCURRENCE

A. Production

Arsenic trioxide (As_2O_3) is produced commercially as a by-product of metal refining operations. It is recovered from the flue dusts which are evolved in the roasting of non-ferrous ores, especially copper. Metallic arsenic is produced by the reduction of arsenic trioxide with charcoal, and oxidation of As_2O_3 yields arsenic pentoxide (IARC, 1973).

No information on the amount of arsenic produced in the Mediterranean countries was found in the literature reviewed.

IARC (1973) reports that France is one of the major arsenic trioxide producing countries in the world, along with Sweden, USSR, Mexico and South-West Africa.

The world production of arsenic trioxide in 1962 was 55,000 tons (Lisella et al., 1972).

B. Use

Arsenic and its compounds have many diversified industrial uses, including in lead and copper alloys, as corrosion inhibitors in oil well piping, in glass and cloth manufacture, and in electrical semiconductors. Arsenicals have also found use in medicines, pesticides, herbicides and wood preservatives (EPA, 1976; IARC, 1973).

Lisella et al. (1972) report that the use of arsenicals as herbicides and insecticides outside the U.S. apparently hasn't increased or declined significantly in recent years.

No figures on the consumption of arsenic in the Mediterranean countries were found in the literature reviewed.

III. ARSENIC IN THE ENVIRONMENT

A. Sources

1. Natural

Natural sources, including the erosion of surface rocks, probably account for a significant portion of arsenic found in surface waters and groundwater (NAS, 1977). GESAMP (1976) estimates that 72,000 tons/year of arsenic (as arseneious oxide) is weathered from the earth's crust.

Arsenic concentrations in the earth's crust average 2ppm, and volcanic gases have been reported to contain up to 700ppb. (Fleischer, 1973)

Rainwater is a direct source of arsenic to the ocean. Though no figures were available for the Mediterranean, Cambray et al. (1976) estimate that 420 tonnes/year of arsenic is delivered to the North Sea in rainwater.

2. Anthropogenic

The smelting of non-ferrous ores, especially copper, is largely responsible for environmental arsenic contamination from man-made sources. Since arsenic vaporises as As_2O_3 well below the melting temperatures of these ores, the flue dusts may contain large amounts of arsenic (IARC, 1973). A large copper smelter in the region of Puget Sound, Washington, releases about 300 tons of arsenic to the atmosphere per year, and about the same amount in liquid effluent directly into the ocean (NAS, 1977).

Recent analyses of petroleum show a median arsenic concentration of 90ppb, but there are few data (NAS, 1977).

Superphosphate fertilizers contain as much as 0.1% arsenic, which is taken up by plants and leached into groundwaters (NAS, 1977). Soil concentrations of arsenic can reach levels of several hundred parts per million after years of spraying with lead arsenate and other arsenicals (Lisella et al., 1972).

B. Transformations

1. Abiotic

Arsenates (inorganic pentavalent arsenicals) are usually formed and found in oxidation zones in contact with the free oxygen of the atmosphere. The uppermost layers of aerated soils probably contain arsenic as the arsenate ion (Schroeder and Balassa, 1966), and oxic sea waters would also be expected to contain arsenic in primarily the pentavalent state, based on purely thermodynamic considerations (Haywood and Riley, 1976).

A study by de Groot et al. (1976) found that desorption of trivalent arsenic from sediments increased with increased salinity.

2. Biotic

Although thermodynamic considerations suggest that arsenic should exist in oxic sea waters practically entirely in the pentavalent state, equilibrium rarely appears to be attained, probably because of the existence of biologically mediated reduction processes. For this reason, arsenic in most of these waters exists to an appreciable extent in the trivalent state, and, indeed, As (III):As (V) ratios as high as 1:1 have been found in a number of instances (Haywood and Riley, 1976).

Arsenic found in biological tissue presumably occurs primarily in the pentavalent form, due to the presence of oxygen (Schroeder and Balassa, 1966).

C. Bioaccumulation

In a study with two species of green algae, Lunde (1973) found concentration factors of 200-3000 over arsenic concentration in the medium. The arsenic salts in the water for this study had a 1:1 ratio of trivalent: pentavalent arsenic, and the arsenic in the algae had been converted to organic arseno compounds.

Although the EPA (1976) reports that arsenic is "evidently not progressively concentrated along a food chain" (in aquatic organisms), Lunde (1973) states that algae appear to be an important source of the arseno organic compounds found in higher marine organisms.

IV. MONITORING

A. Analysis

IARC (1973) reports three main methods for the analysis of arsenic, along with their corresponding detection limits; spark source mass spectrometry (60pg), neutron activation (0.1ng), and atomic absorption (0.1ng).

B. Amount in the Mediterranean

Due to the difficulties in determining heavy metals in sea water, few measurements of arsenic have been made in the Mediterranean Sea. Distinction between different physico-chemical forms of arsenic is important in determining participation in biogeochemical cycles and effects on marine organisms. (Bernhard, 1978)

May et al. (1975) found 0.48ug/l of arsenic in sea water from Menton, France. Papadopoulou (1972) measured arsenic concentrations in polluted and non-polluted waters near Greece. The Saronikos Gulf yielded samples containing 3.5ug/l of arsenic, and samples from coastal waters near Rhodes Island contained 2.0ug/l arsenic. Levels in fish muscle tissues from the areas reflected these concentration differences.

A sediment sample taken from a sewage outfall area near Athens contained 0.7-70mg/kg dry weight of arsenic (Papakostidis et al., 1975). Carpenter (1972) found arsenic concentrations in the upper layers of Pacific Ocean sediments to be several orders of magnitude higher than in the cores of the samples.

Zafiropoulos and Grimanis (1977) found arsenic concentrations of 3.1mg/kg dry weight in zooplankton from the Saronikos Gulf, Greece. Oysters, Ostrea edulis, taken from the same location contained 83.0mg/kg dry weight, and the soft parts of the mussel, Mytilus galloprovincialis, contained 25.5mg/kg dry weight (Papadopoulou and Kanas, 1976).

C. Amount Entering the Mediterranean

No information on the amount of arsenic entering the Mediterranean was found in the literature reviewed.

D. Regulations

The NAS (1972) recommends a minimal risk concentration for arsenic in sea water of 10.0ug/l.

The EPA (1976) recommends a criteria of 50ug/l of arsenic in domestic water supplies.

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

Like mercury, most of the arsenic found in marine organisms is in an organic form. However, in contrast to methyl-mercury, the methylated forms of arsenic are much less toxic than inorganic arsenic compounds, which may explain the high tissue concentrations found in some marine organisms (Bernhard, 1978).

Nelson et al. (1976) reports a 96 hour LC50 for trivalent arsenic of 3.49mg/l in the Bay scallop, Argopecten irradians. The pink salmon, Oncorhynchus gorbuscha, displayed a 96 hour LC50 for trivalent arsenic at 9.0mg/l (Holland et al., 1960). The development of red algae, Plumaria elegans, was inhibited by 85% when exposed to a concentration of 1.0mg/l of trivalent arsenic for 18 hours (Boney et al., 1959).

B. Toxic Effects on Man and Other Mammals

The toxic effects of arsenic have been recognised by man for thousands of years. Its use as a poison is well known, and an epidemic associated with arsenic contamination in beer caused 1,000 deaths in England in 1900 (Lisella et al., 1972).

Occupational exposure to arsenic is associated with increased risk of cancer, especially of the lungs. Evidence has come from studies on smelter and mining workers, factory workers where arsenic containing pesticides are manufactured, and vineyard workers (IARC, 1973).

Mutagenic effects of arsenic were found in a study by Paton and Allison (1972). Cultured human leucocytes and fibroblasts displayed chromatid breaks when treated with $0.29-1.8 \times 10^{-8} \text{M}$ sodium arsenite.

The symptoms of severe arsenic intoxication in man include gastrointestinal catarrh, kidney degeneration, tendency to edema, polyneuritis, liver cirrhosis, bone marrow injury, exfoliate dermatitis and altered skin pigmentation. Trivalent arsenic accumulates mainly in bone muscle and skin, and to a lesser extent in the liver and kidneys, during chronic exposure (EPA, 1976).

Total Production

Sodium arsenite			Chemical group: Arsenic	
year	area	amount	trend	citation (as reported in)
1962	World	55 000 tons	-	Lisella et al., 1972

Total Consumption

Sodium arsenite			Chemical Group: Arsenic	
year	area	amount	trend	citation (as reported in)
1954	USA	4 500 000 pounds	decreasing	IARC, 1973, p.54

Production Process(es)

Sodium arsenite

Chemical Group: Arsenic

process (major or minor by geographic area)	workers exposed	intermediates, impurities and waste products	citation (as reported in)
reaction of arsenic trioxide with sodium carbonate or sodium hydroxide	-	-	IARC, 1973, p.54

Use

Sodium arsenite		Chemical Group: Arsenic		
use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
herbicide	(major)	-	decreasing	IARC, 1973, p.54
pesticide	(major)	-	decreasing	
corrosion inhibitor in oil well piping	(major)	-	decreasing	
arsenic containing medicinal production	-	-	-	
arsenical soap production				
copper acetoarsenite production				
copper arsenite production				
wood preserv- ation				
pigment usage				
high preserv- ation				
textile dyeing				
tree and stump killing				
bark removal				

Pathways Leading to Marine Pollution

Arsenic (As^{3+})

Chemical Group: Arsenic

Pathway	Quantity	Area	Citation
Weathering of earth's crust (arsenious oxide)	72 000 tons/yr	World	GESAMP, 1976
River Rhine discharge	1 000 tonnes/yr	North Sea	Cambray, R.S. et al., 1976
Rainwater	420 tonnes/yr	North Sea	Cambray, R.S. et al., 1976
Municipal waste dischargers	12.2 metric tons/yr (total)	California coastal waters	Schafer, H.A., 1976
Recreational vessels antifouling paint	1.4 metric tons/yr	Southern California Bight, U.S.A.	Young, D.R. et al., 1973

Transformation in the Marine Environment

Arsenic (As ³⁺)			Chemical Group: Arsenic	
Process	Medium	Parameters	Effect	Citation
Desorption	Rhine estuary sediment	Increased salinity	Increased desorption	de Groot, A.J. et al., 1976

Behaviour of a Chemical Substance in Marine Organisms

Arsenic (As³⁺)

Chemical Group: Arsenic

Organism	Exposure		Accumulation and Distribution				Loss		Metabolites		Citation
	Route	Concn. mg/l	Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
Pleuronectes platessa (Plaice)	W	0.002	42 days	K	-	0.89	-	-	-	-	Pentreath, R.J., 1977
Argopecten irradians (Bay scallop)	W	4.0	96 hours	S T	-	10.1	-	-	-	-	Nelson, D.A. et al., 1976
Mytilus edulis (Mussel)	W	1 dose of 0.1 mg	14 days	B	-	30	-	-	-	-	Sautet, J. et al., 1964
Phaeodactylum tricornutum (Green alga)	W	As-74	-	Wh	100	2900	-	-	-	-	Lunde, G., 1973

B Byssus
K Kidney
S T Soft tissue
W Water
Wh Whole

Behaviour of the Substance in Man and Other Mammals

Sodium arsenite

Chemical Group: Arsenic

description of organism	exposure		duration of exposure	retention tissue/percent/time	clearance rate		metabolites name/amount/hazard in)	citation (as reported in)
	route	concentration			percent/time	name/amount/hazard		
rabbit	intra- muscu- lar	-	-	mainly in liver, kidneys and lungs	-	-	-	Ducoff et al., 1948 (NAS, 1977, p.319)
human (volunteers)	intra- venous	-	-	-	99%/15 hours	-	-	Mealey et al., 1959 (NAS, 1977, p.320)
human (1 patient)	injec- tion	4mg	single dose	highest levels in liver and kidneys after 20 hours	-	-	-	Ducoff et al., 1948 (IARC, 1973, p.63)
human (2 patients)	intra- venous	-	single dose	-	60%/6-7 days (predominantly in urine)	-	-	IARC, 1973, p.64

Concentrations in Water, Sediments and Biota

Arsenic (As ³⁺)			Chemical Group: Arsenic		
Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Water	Velsao Bay, Arabian Sea	-	0.6998/ 0.0075 mg/l (inorganic)	1973/1974	Singbal, S.Y. S. et al., 1976
Water	Brest Har- bour, Atlan- tic Ocean	NAA	0.001 mg/l	-	May, S. et al., 1975
Water 100m below surface	San Diego Trough, USA	GC and AAS	6x10 ⁻⁵ mg/l (As ³⁺)	1976	Andreae, M.O., 1977
Sediment (5-8 cm)	(Historical mining area) Hayle Estuary, U.K.	Colorimetry	768 mg/kg dry wt.	-	Yim, W.W.S., 1976
Sediment	Rhine-Meuse Estuary	-	220 mg/kg	1970	de Groot, A.J. et al., 1976
Sediment	Bridgeport, Long Island Sound	AAS	12.2 mg/kg	-	Brannon, J.M. et al., 1976
Sargassum fulvellum (Brown alga)	Yamaguchi, Japan	-	79.0 mg/kg dry wt.	1974	Tagawa, S. and Kojima, Y., 1976
Pleuronectes platessa (Plaice - muscle)	Ling Bank, Scotland, U.K.	AAS	43.2 mg/kg wet wt.	1975-1976	Shepherd, R. J. and Topping, G., 1977
Cancer pegurus (Crab-white meat)	Firth of Forth, Scotland, U.K.	AAS	22.3 mg/kg wet wt.	1975-1976	Shepherd, R. J. and Topping, G., 1977

Concentrations in Water, Sediments and Biota

Arsenic (As³⁺) (page 2)

Chemical Group: Arsenic

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Panulirus argus (Florida lobster)	North Atlantic Ocean	AAS	14.0 mg/kg dry wt.	1971	Windom, H.L., 1972
Busycon canaliculatum (Channelled whelk)	Long Island Sound, USA	AAS	9.0 mg/kg wet wt.	1971-1972	Greig, R.A. et al., 1977
Acanthorpagrus australis (Yellowfin bream, muscle)	New South Wales, Australia	S	1.1 mg/kg wet wt.	-	Bebbington, G.N. et al., 1977
Seawater	Menton, France	NAA	0.00048 mg/l	-	May, S. et al., 1975
Sediment	Sewage outfall area, Athens	NAA	0.7-70mg/kg dry wt.	1973	Papakostidis, G. et al., 1975
Sargus annularis (Liver)	Petallon Gulf, Aegean Sea	RS	30mg/kg dry wt.	1973-1974	Grimanis, A.P. et al., 1978
Gobius niger (Goby)	Keratsini Bay, Aegean Sea	RS	142mg/kg dry wt.	1973-1974	Grimanis, A.P. et al., 1978
Mytilus galloprovincialis (Mussel, soft parts)	Saronikos Gulf, Greece	AAS	25.5mg/kg dry wt.	1969	Papadopoulou, C. and Kaniias, G.D. 1976
Ostrea edulis (Oyster)	Saronikos Gulf, Greece	AAS	83.0mg/kg dry wt.	1969	Papadopoulou, C. and Kaniias, G.D. 1976

Concentrations in Water, Sediments and Biota

Arsenic (As³⁺) (page 3)

Chemical Group: Arsenic

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Mytilus gallo-provincialis (Mussel)	"Typical" Mediterranean	-	5.0mg/kg wet wt.	-	Bernhard, M., 1978
Pagellus erythrinus	"Typical" Mediterranean	-	4.5mg/kg wet wt.	-	Bernhard, M., 1978
Mytilus gallo-provincialis (Mussel)	Yugoslavia	-	0.015mg/kg dry wt.	1977	GFCM, 1978
Acartia clausi (Zooplankton)	Elefsis Bay, NAA Upper Saronikos Gulf, Greece		3.1mg/kg dry wt.	1974	Zafiropoulos, D. and Grimanis, A.P., 1977

AAS Atomic absorption spectrophotometry
 GC Gas Chromatography
 NAA Neutron activation analysis
 S Spectrophotometry
 RS Radiochemical separation

Array of Toxic Effects on Man and Other Mammals

Sodium arsenite

Chemical Group: Arsenic

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
41	-	oral	rat	LD50	NIOSH, 1978, p.3
10.8 (125ppm As)	2 years	oral (diet)	dog	weight loss, early mortality	Byron et al., 1967 (IARC, 1973, p.60)
10	9th day of gestation	intra- perit.	mouse	implantations resorbed or dead, fetal malformations (18th day of gestation)	Hood and Bishop, 1972 (NAS, 1977, p.340)
5	-	oral	human	LDLo	NIOSH, 1978, p.3
0.63 (5ppm)	lifetime	oral (water)	rat (Long Evans)	increase in unspecified "pretumour- ous" lesions of liver	Kanisawa and Schroeder, 1969 (IARC, 1973, p.60)
-	-	dermal	human (spilled 10% NaAsO ₂ on his foot)	peripheral neuritis	NIOSH, 1976, p.308
concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
0.254- 0.696	10-50 years	inhal.	human (workers in a sheep-dip factory)	29% of 75 deaths due to cancer (mostly lung and skin), 13% of control group	Hill and Fanning, 1948 (NAS, 1977, p.327)

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Sodium arsenite

Chemical Group: Arsenic

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Osborne-Mendel)	oral (diet)	21.6 (250ppm As)	2 years (daily)	no increase in tumours	Byron et al., 1967 (IARC, 1973, p.60)
mouse (Swiss)	oral (water)	1.73 (5ug As/ml)	lifetime (daily)	no increase in tumours	Kanisawa and Schroeder, 1969 (IARC, 1973, p.58)
rat (Long Evans)	oral (water)	0.63 (5ppm)	lifetime (daily)	increase in unspecified "pretumorous" lesions of liver	Kanisawa and Schroeder, 1969 (IARC, 1973, p.60)

A comprehensive evaluation of the known studies designed to assess the possible carcinogenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"Adequate oral studies on arsenic trioxide in the mouse and on lead arsenate, calcium arsenate, sodium arsenate, arsenic trioxide and sodium arsenite in the rat gave negative results.

The studies designed to detect cocarcinogenicity to mouse skin by potassium arsenite, sodium arsenate or arsenic trioxide gave negative results." (IARC, 1973, p.68)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Sodium arsenite (page 2)

Chemical Group: Arsenic

CARCINOGENICITY

"Human data

The available studies point consistently to a causal relationship between skin cancer and heavy exposure to inorganic arsenic in drugs, in drinking-water with a high arsenic content, or in the occupational environment.

The risk of lung cancer is clearly increased in certain smelter workers who inhale high levels of arsenic trioxide. However, the causative role of arsenic is uncertain, since the influence of other constituents of the working atmosphere cannot be determined. An increased relative frequency of deaths from lung cancer has been found in other occupational groups exposed to high levels of inorganic arsenic compounds (e.g., sheep-dip workers, certain mining and vineyard workers).

Cases of lung cancer occurring after the medicinal use of inorganic arsenic compounds, and of liver haemangioendothelioma following various kinds of exposure to arsenic have been reported, but these may be chance associations.

No evidence exists that other forms of cancer occur excessively with heavy arsenic exposure." (IARC, 1973, p.69)

MUTAGENICITY

description of system	reported results	citation (as reported in)
Escherichia coli (WP) cultures plated in presence or absence of NaAsO ₂ after exposure to UV-light	significantly decreased survival, suggesting inhibition of DNA repair	Rossman et al., 1976 (NAS, 1977, p.332)

description of system	reported results	citation (as reported in)
cultured human leucocytes and fibroblasts treated with 0.29-1.8x10 ⁻⁸ M NaAsO ₂	chromatid breaks	Paton and Allison, 1972 (NAS, 1977, p.332)

These studies, designed to evaluate the possible effects of the substance on gene mutation, chromosomal mutations, on DNA repair or recombination or on transformation, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Sodium arsenite (page 3)

Chemical Group: Arsenic

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	intra- perit.	10	9th day of gestation	implantations resorbed or dead, fetal malformations (18th day of gestation)	Hood and Bishop, 1972 (NAS, 1977, p.340)

This study, designed to evaluate the possible teratogenic effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic and Other Effects on Marine Organisms and Ecosystems

Arsenic (As³⁺)

Chemical Group: Arsenic

System Organism Ecosystem Non-living	Life Stage	Concentration mg/L	Exposure Time	Effect	Time of Observation	Citation
Oncorhynchus gorbuscha (Pink salmon)	F (27 days)	9.0	96 hours	LC50	96 hours	Holland, G.A. et al., 1960
Argopecten irradians (Bay scallops)	J	3.49	96 hours	LC50	96 hours	Nelson, D.A. et al., 1976
Crassostrea virginica (Oyster)	Em	7.5	48 hours	LC50	48 hours	Calabrese, A. et al., 1973
Plumaria elegans (Red alga)	S	1.0	18 hours	85% inhibition of development	7 days	Boney, A.D. et al., 1959
Nassarius obsoletus (Mud snail)	-	3.0	72 hours	Decreased oxygen consumption and signs of distress	72 hours	MacInnes, J.R. and Thurberg, F.P., 1973

Em Embryo
F Fry
J Juvenile
S Sporeling

Analysis

Arsenic (generic)

Chemical group: Arsenic

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
spark source mass spectrometry (60pg)	-	Morrison, 1972 (IARC, 1973, p.55)
neutron activation (0.1ng)	-	Morrison, 1972 (IARC, 1973, p.55)
atomic adsorption (0.1ng)	-	IARC, 1973, p.55

Legislation for the Protection of Man
and the Marine Environment

Arsenic (generic)

Chemical group: Arsenic

general classification of control mechanism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in effluents	Egypt	standard for industrial waste-water discharged into drainage canals	-	WHO/UNEP, 1976, p. Egypt-3
control of substances in effluents	Italy	recommended limits for industrial and urban effluents discharged into waters	0.2mg/l as As into water- courses and lakes, 0.5mg/l as As into the sea and sewers	WHO/UNEP, 1976, p. Italy-4
control of substances in effluents	Libyan Arab Republic	proposed standards for effluents discharged	0.05mg/l into surface water reservoirs for direct use in agriculture, into aquifers used for public water supply and into the sea, 0.1mg/l into urban public sewage systems	WHO/UNEP, 1976, p. Libyan Arab Republic-2
control of substances in water	Spain	limits for receiving public water- courses, that are not to be exceeded due to effluents	0.2mg/l	WHO/UNEP, 1976, p. Spain-2
control of substances in in effluents	Turkey	prohibition of discharges when the concen- tration exceeds the tolerance level	1.0mg/l for arsenic ion, 1.0mg/l for arsenic tri- oxide	WHO/UNEP, 1976, p. Turkey-4

Legislation for the Protection of Man
and the Marine Environment

Arsenic (generic)

Chemical group: Arsenic

general classification of control mechanism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in effluents	Yugoslavia	maximum per- missible con- centrations of dangerous sub- stances dis- charged into water used or intended for use as drinking water, for pro- duction of food- stuffs, fish breeding, water- ing of animals or public bathing	0.05mg/l	WHO/UNEP, 1976, p. Yugo- slavia-2

Arsenic

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MEDITERRANEAN DATA PROFILE

THALLIUM

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^a Nothing found in the literature reviewed.

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GENERAL SUMMARY FOR THALLIUM

I. INTRODUCTION

Thallium (Tl) is widely distributed in the earth's crust, and is released to the environment mainly as a result of the mining and processing of other metals (e.g. Cu, Pb, Zn). The toxicity of thallium is very high, both in aquatic systems and in man. Tl occurs as either a monovalent or trivalent cation, forming compounds which are generally soluble in seawater. Some organisms are capable of accumulating Tl, which may lead to food web magnification and possible hazards to man through consumption of contaminated marine produce. Though present industrial uses are too limited to generate significant pollution, local contamination may occur due to effluents from mines, ore processing and coal burning plants (Zitko, 1975).

II. OCCURRENCE

A. Production

The average concentration of thallium in the earth's crust is $7 \times 10^{-5}\%$ (Merck, 1968). Thallium ores, however, are rare, and the metal is recovered primarily during the processing of sulfide ores of lead, copper and zinc, which contain up to 10mg/g of Tl. The world production of Tl has been estimated at 10-12 t/year, but potential emissions to the environment are much greater, due to the large amount of unrecovered Tl in mining wastes (Zitco, 1975).

No figures on the production or consumption of Tl in the Mediterranean states were found in the literature searched.

B. Use

The uses of thallium include: in rodent poisons, fungicides, optical systems, photoelectric cells, in high density liquids, selenium rectifiers, low range glass thermometers (8.5% Tl) and for insect proofing. A potential use is as an antiknock additive for gasoline (Patty, 1963).

III. THALLIUM IN THE ENVIRONMENT

A. Sources

1. Natural

As an element, thallium occurs naturally in all phases of the environment. The average content of igneous rocks is 30g/ton of thallium (Patty, 1963), which will be gradually released to the aquatic environment through geological processes. In the Mediterranean region (Greece), thallium occurs naturally as $TlAsS_2$ (Merck, 1968). Glasby (1973) reports that relatively high levels of thallium are found in manganese nodules.

2. Anthropogenic

As with other elements, human activity does not change the concentration of thallium on a global scale, but localised pollution may occur from man made sources.

Tl is usually not recovered from mining effluents, due to its limited market. In addition, the processes used to treat mining effluents, aimed at the removal of heavy metals such as copper and zinc, would not remove thallium (Zitco, 1975).

Zitco et al. (1975) reported Tl concentrations of 1-80ug/l in two rivers draining base metal mining properties in Canada.

Atmospheric emissions in flue dusts from pyrite burners and Pb and Zn smelters and refineries usually contain thallium as the sulphate. Emissions as a by-product from Cd production are estimated at "a few 1000 lbs. per year" (Patty, 1963).

Davison et al. (1974) and Natusch et al. (1974) report that thallium is emitted in the fly ash of coal burning power plants. The concentration increases from 5-45ug/g in larger particles to 29-76ug/g in airborne fly ash.

B. Transformation

1. Abiotic

Thallium metal undergoes rapid superficial oxidation in air to form Tl_2O (Merck, 1968). Most of the Tl in seawater is found as a monovalent cation, which is more stable than the trivalent cation. The solubility of thallium (I) hydroxide in water is 259g/l (Lange and Forker, 1967).

2. Biotic

Burger and Starke (1969) have suggested that hypertension, as a symptom of thallium poisoning in humans and fish, may be caused by the oxidation of thallium (I) to thallium (III), which inhibits the ATPase of amine-storing granules, thus causing alterations in the catecholamine metabolism.

The uptake of thallium by yeast mitochondria and the formation of thallium (III) oxide in these organisms confirm that oxidation of thallium in vivo takes place (Lindegren and Lindegren, 1973).

C. Bioaccumulation

The accumulation factors of thallium in fish are somewhat higher than for other metals, excluding methylmercury. Concentration factors of Tl in a test on Atlantic salmon were 130 in muscle tissue, 170 in the liver and 480 in gills (Zitco et al., 1975).

Zitco and Carson (1975) concluded that clams and mussels do not concentrate thallium to the levels which some other heavy metals are concentrated in shellfish. The authors state that the low levels of thallium accumulated by these shellfish precludes the possibility that significant amounts of Tl will enter the food web from this source. A biomagnification coefficient of 10.9 was found in the mussel, Mytilus edulis, in a 40 day exposure to 0.1 mg/l of Tl. over 90% of the Tl in the soft tissues had been lost after 29 days.

Thallium (I) can be actively taken up by marine algae, presumably by the potassium "pump". Oxygen evolution is sensitive to Tl^+ , which is transported through the cellular membrane to the chloroplast, where photosynthesis is inactivated. These effects were noted at concentrations which cause no damage to the cell membrane, as reflected by potassium leakage (Overnell, 1975).

Zitco (1975), reports that thallium concentrations of 9.5 to 162ug/g dry weight were found in algae and moss from two rivers containing 1-80ug/l of Tl.

IV. MONITORING

A. Analysis

Curry et al. (1969) consider atomic absorption spectrophotometry a rapid, reliable and sensitive technique by which thallium can be accurately determined in biological samples. A detection limit of $\leq 2.0\text{ng}$ has been reached for water samples, and $\leq 1.0\text{ng}$ for urine samples. Flameless atomic adsorption spectrophotometry, though susceptible to interference, is very sensitive, with a detection limit of 0.1ng of Tl (Hauck, 1973)

B. Amount in the Mediterranean

The average concentration of Tl in seawater is 0.00001 mg/l (Gaskell, 1971; Skinner and Turekian, 1973). No information on thallium levels in the Mediterranean was found in the literature reviewed.

C. Amount Entering the Mediterranean

No information on the amount of thallium entering the Mediterranean was found in the literature reviewed.

D. Regulations

No legislation dealing with the control of thallium in the Mediterranean states was found in the literature reviewed.

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

Zitko (1975) considers thallium and its compounds to be highly toxic substances. In fish, Tl is as acutely toxic as copper on a weight basis, and 3 to 4 times as toxic on a molar basis.

The toxic effects may be related to thallium's ability to substitute monovalent cations, especially potassium, in enzymatic reactions.

Thallium kills fish quite slowly, and species differences may affect toxicity. Water hardness, which strongly affects the toxicity of metals to fish, may not have much effect on the toxicity of thallium because of its low complexing ability. The acute toxicities of copper and thallium, and of zinc and thallium to fish are not additive (Zitko, 1975).

A test on Atlantic salmon by Zitko et al. (1975) established an LC50 for thallium of 0.03mg/l.

A 96 hour LC50 for thallium in Brown shrimp, Crangon crangon, was determined to occur at 10ppm (Portman and Wilson, 1971).

In a study with two species of marine algae, Overnell (1975) found that thallium (and mercury) may be transported through the outer membrane of the cell to the chloroplast, where photosynthesis is inactivated at concentrations which cause no damage to the cell membrane as reflected in potassium leakage. Thallium can be actively taken up, presumably by the cell's potassium pump.

Thallium is toxic to bacteria, but generally only at quite high doses. Nitrification by Nitrobacter agilis was inhibited by thallium (Tandon and Mishra, 1969).

Little is known about the toxicity of organothallium compounds. Diphenyl thallium chloride and cyanate were toxic to a number of pathogenic fungi (Srivastava et al., 1973).

B. Toxic Effects on Man and Other Mammals

In humans, thallium is absorbed through the mucous membranes and the skin, is widely distributed throughout the body, and accumulates in bones, renal medulla and, eventually, in the central nervous system. Thallium passes through the placenta, occurs in milk, and is excreted mainly in the urine (Oehme, 1972).

Symptoms of thallium poisoning include hypertension, gastro-intestinal distress, and neurological manifestations. Pain in the legs, inability to walk as a result of tender soles, and personality changes are also associated with thallium poisoning (Curry et al. 1969).

Thallium administered orally to a rat at doses of 0.8mg/kg bw/day caused neoplastic effects (ITII, 1975).

Zitko (1975) states that the toxicity of thallium in mammals is slightly greater than mercury, and is exceeded only by methylmercury for the group of metals compared.

Total Production

Thallium			Chemical Group: Thallium	
year	area	amount	trend	citation (as reported in)
yearly	world	10-12 t	-	Zitko, 1975, p.185

Production Process(es)

Thallium		Chemical Group: Thallium	
process (major or minor by geographic area)	workers exposed	intermediates impurities and waste products	citation (as reported in)
precipitation of crude thallium onto Zn or Al	-	-	Patty, 1963, p.1138
electrolysis of carbonate, sulphate or perchlorate solutions	-	-	Patty, 1963, p.1138

Use

Thallium (generic)

Chemical Group: Thallium

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
rodent poison	-	-	-	Patty, 1963, p.1138
lenses, plates and prisms				
fungicide				
low-range glass thermometers				
separation of mineralogic specimens				
photoelectric cells				
high-density liquids				
special glasses				
Se rectifiers				
insect proofing				
phosphor activator				

Pathways Leading to Marine Pollution

Thallium

Chemical Group: Thallium

Pathway	Quantity	Area	Citation
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Nothing found in the marine environment

Transformation in the Marine Environment

Thallium

Chemical Group: Thallium

Process	Medium	Parameters	Effect	Citation
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Nothing found in the marine environment

Behaviour of a Chemical Substance in Marine Organisms

Thallium		Chemical Group: Thallium					
Organisms	Exposure		Accumulation and Distribution		Loss		Citation
	Route	Concn. Time mg/l	Tissue/ Organ	% Biomagnification Coefficient	% Time	Name Quantity	
Mytilus edulis (mussel)	W	0.1 40 days	S T	10.9	90 29 days	- -	Zitko, V., and Carson, W.V., 1975

S T Soft tissue
W Water

Behaviour of the Substance in Man and Other Mammals

Thallium

Chemical Group: Thallium

description of organism	route	concentration	exposure	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)
human	-	-	-	-	-	15.4%/ 5.5 days in urine, 3.2%/ day of remaining body burden	-	Barclay et al., 1953 (Patty, 1963, p.1141)
dog	oral	-	-	single dose	-	60%/36 days	-	Heyroth, 1947 (Patty, 1963, p.1141)
rabbit	-	-	-	-	-	24.4%/23 days in faeces, 31.9%/23 days in urine	-	Truhaut, 1959 (Patty, 1963, p.1141)

Concentrations in Water, Sediments and Biota

Thallium		Chemical Group: Thallium			
Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material	Origin				
Water	Ocean	-	0.00001 mg/l	-	Gaskell, T.F., 1971
Water	Ocean	-	0.00001 mg/l	-	Skinner, B.J., and Turekian, K.K., 1973
Fundulus heteroclitus (Mummichog)	Rhode Island USA	AAS	n.d.	-	Eisler, R., and La Roche, G., 1972

AAS Atomic Absorption Spectrophotometry
n.d. Not Detectable

Array of Toxic Effects on Man and Other Mammals

Thallium			Chemical Group: Thallium		
dose in mg/kg bw/day	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
0.8	continuous days -	oral	rat	TDLo, neo- plastic effects	ITII, 1975, p.515
-	-	-	human (72 cases of thallium poisoning)	permanent central nervous system damage, death	Arena, 1974, p.124

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Thallium

Chemical Group: Thallium

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

Nothing found in the literature reviewed.

MUTAGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	-	-	-	mitosis-inhibition of the intestinal mucosa cells	Marras and Nanetti, 1954 (Patty, 1963, p.1142)

This study, designed to evaluate the possible effects of the substance on gene mutation, chromosomal mutations, on DNA repair or recombination or on transformation, resulted in a report of one or more of these effects, but no comprehensive evaluation of this material was found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
rat	cystine, 1-20% in diet	delayed development of alopecia, increased survival period	Gross et al., 1948 (Patty, 1963, p.1142)

This study designed to evaluate the possible effects which could result from the combination of this substance with one or more other substances, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Thallium (page 2)

Chemical Group: Thallium

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Thallium

Chemical Group: Thallium

System Organism Ecosystem Non-living	Life Stage	Concn. mg/L	Exposure Time	Effect	Time of Observation	Citation
Crangon crangon (Brown shrimp)	A	10.0	96 hours	LC50	96 hours	Portmann, J.E., and Wilson, K.W., 1971
Dunaliella tertio- lecta (marine flagel- late)	-	2.0	15 minutes	Reduced photosynthetic activity	15 minutes	Overnell, J., 1975
Dunaliella tertio- lecta (marine flagel- late)	-	20.4	15 minutes	35% loss of cell potassium content	15 minutes	Overnell, J., 1975

A Adult

Analysis

Thallium		Chemical group: Thallium
analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
atomic adsorption spectrophotometry - tantalum boat technique - ($<2\text{ng}$ in water, $<1\text{ng}$ in urine)	susceptible to interference/rapid, available in well- equipped laboratories, sensitivity: $6\text{ng}/50\text{ul}$ water, $3\text{ng}/50\text{ul}$ urine	Curry et al., 1969
flameless atomic adsorption spectro- photometry (0.1ng)	susceptible to interference/ sensitive	Hauck, 1973

Legislation for the Protection of Man
and the Marine Environment

Thallium

Chemical group: Thallium

general classifica- tion of con- trol mechan- ism	country or political sub-division	description of control mech- anism	quantitative information (analytical methods)	citation (as reported in)
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Nothing found in the literature reviewed.

Thallium

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MEDITERRANEAN DATA PROFILE

CARBAMATE

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GENERAL SUMMARY FOR CARBARYL

I INTRODUCTION

Carbaryl (1-naphthyl-N-methylcarbamate) is a moderately toxic carbamate insecticide which is effective against a variety of insect pests. It is the most heavily used of the carbamate insecticides, representing two-thirds of the U.S. market in 1971. The present use of carbaryl is probably greater, as it is a useful substitute for DDT (NAS, 1977).

Though carbaryl can be degraded both chemically and biologically in sea water, the products of these reactions may be toxic to various marine organisms.

II. OCCURRENCE

A. Production

Carbaryl can be synthesised by reacting phosgene with 1-naphthol, followed by reaction with methylamine. An alternate method is the reaction of 1-naphthol with methyl isocyanate, which is believed to be the method currently used in the U.S. (IARC, 1976).

The U.S. produced an estimated 24,000 tonnes of carbaryl in 1972, over half of which was exported (IARC, 1976).

B. Use

The major use of carbaryl is as a wide spectrum insecticide used to control pests on fruits, vegetables, cotton, tobacco, corn, rice and sugar beets (NAS, 1977).

Applications also include home and garden insecticides, on animals and in forests. In the United States, carbaryl is also registered as an acaricide and molluscicide (IARC, 1976; NAS, 1977). WHO (1976) reports that carbamates have been used in residual applications for malaria control.

Italy uses about 600 tonnes of carbaryl annually (IARC, 1976).

III. CARBARYL IN THE ENVIRONMENT

A. Sources

1. Natural

No evidence was found in the literature reviewed for the natural occurrence of carbaryl.

2. Anthropogenic

The use of carbaryl pesticides will naturally be a source of possible environmental contamination. Increasing levels of carbaryl in food samples from the U.S. is reported by IARC (1976). Pathways to the marine environment include industrial effluents, agricultural run off (Coppage, 1977) and direct application (Karinen et al., 1967).

The EPA (1976) states that carbaryl should always be submitted to alkaline hydrolysis before disposal, to prevent the formation of methylisocyanate under the influence of sunlight. Methylisocyanate is considered a poisonous and highly reactive substance. Procedures for the disposal of carbaryl containers are also detailed in the EPA (1976) report.

B. Transformation

1. Abiotic

Carbaryl is slightly soluble in water (40ppm at 30°C). Though hydrolysis is slow in neutral solutions, carbaryl is rapidly hydrolysed in strong alkali. Karinen et al. (1967) found the amount of carbaryl hydrolysed by sea water (at pH 8) in four days to be 44% at 17°C, 55% at 20°C, and 93% at 28°C. A study by Faust (1975) found that 50% of the carbaryl present in sea water was hydrolysed in 10.5 days at pH 7, and in 2.5 hours at pH 9.

A study of the persistence of carbaryl in estuarine water and mud in laboratory aquaria revealed approximately 50% disappearance of carbaryl in 38 days at 8°C. At 20°C after 17 days, almost all of the carbaryl had disappeared. Hydrolysis was accelerated by increasing temperature and exposure to sunlight (NAS, 1977).

The primary hydrolysis product from carbaryl is 1-naphthol, though methyl amine and alkaline carbonate may also be formed. 1-naphthol is reported to be more toxic than carbaryl to young clams and fish. It is also known that 1-naphthol itself is unstable in sea water, being degraded to carbon dioxide and numerous other products. The main decomposition product is a precipitate containing a stable free radical that is toxic to certain estuarine species (EPA, 1976).

Chemical oxidation of carbaryl is poorly understood, and cannot be considered as a disposal method (EPA, 1976).

Crosby (1969) has found that carbaryl is converted to 1-naphthol and methylisocyanate under the influence of sunlight. Methylisocyanate is a highly reactive, poisonous substance.

2. Biotic

Hughes (1971) found that the addition of bacterial isolates to pond water caused increased degradation of carbaryl and 1-naphthol. Degradation by marine fungi removed 90% of the carbaryl present in 3 days (Sikka et al., 1975). 100% transformation of carbaryl occurred in 17 days in non-sterile sea water, and 90% transformation in 10 days in non-sterile seawater and mud (Karinen et al., 1967).

The degradation of carbaryl in microorganisms, plants, insects and mammalian systems has been well studied. The compound is readily metabolised in most systems, forming 1-naphthol and its conjugates as the predominant metabolites. All the metabolites are less toxic to both insects and mammals than carbaryl (NAS, 1977). 1-naphthol, however, is more toxic than carbaryl to young clams and fish (Lamberton and Claeys, 1970).

Studies on the decomposition of carbaryl in plants and animals have established that oxidation is directed primarily at the methyl group attached to the nitrogen atom (EPA, 1976).

C. Bioaccumulation

Carbaryl is highly soluble in organic solvents (EPA, 1976). In a 96 hour exposure to 2.0mg/l of carbaryl, a biomagnification coefficient of 2.99 was found for the cockle clam, Clinocardium nuttali. 97% of the amount accumulated was lost after 12 hours (Butler et al., 1968). Sikka and Rice (1974) found a 24 hour biomagnification coefficient of 0.08 in the marine algae, Thalassiosira pseudomona, exposed to 2.0mg/l carbaryl.

IV. MONITORING

A. Analysis

IARC (1976) lists the following analytical methods for the determination of carbaryl, along with the corresponding detection limits: colorimetry (0.1-1.0 ug/20 mg sample); gas chromatography and electron-capture detection (40-2000 ng); thin layer chromatography (0.01 ug); and, high pressure liquid chromatography (7ng).

B. Amount in the Mediterranean

No information on the concentrations of carbaryl in the water, sediments or biota of the Mediterranean was found in the literature reviewed.

In a study on carbaryl treated mud flats in Oregon, U.S.A., Karinen et al. (1967) found levels of 5.4mg/kg dry weight 2 hours after treatment; 0.1mg/kg dry weight of carbaryl was found 42 days after treatment.

Chambers (1969) studied carbaryl concentrations in biota from the coast of Washington, U.S.A. The values below are all given in wet weight, and were measured after direct application: pacific oyster, Crassostrea gigas, 0-0.27mg/kg; crab, Cancer magister, 0-0.87 mg/kg; Nereid worms, 8.12-9.16mg/kg.

C. Amount Entering the Mediterranean

No information on the amount of carbaryl entering the Mediterranean was found in the literature reviewed.

D. Regulations

Italy recommends a limit of 0.1 mg/l for carbamates discharged into rivers, 0.05 mg/l for lake discharges, and 0.2 mg/l for carbamates discharged into the sea and sewers. Turkey prohibits discharges when the concentration exceeds the tolerance level of 1.3ug/l (WHO/UNEP, 1976).

FAO/WHO (1977) recommends maximum residue limits for carbaryl in meats (0.2 mg/kg), feed (100 mg/kg feed), and milk and milk products (0.1 mg/kg).

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

In studies on the mussel, Mytilus edulis, Liu and Lee (1975) found a 96 hour LC50 for carbaryl of 22.7mg/l. A 50% reduction in shell growth occurred after a 48 hour exposure to 1.5mg/l, and a 96 hour exposure to 10.3mg/l caused a 50% decrease in byssal thread attachment. The authors also found a 10% decrease in growth after 10 days at 0.33mg/l of carbaryl.

A 15 hour exposure to 1.33mg/l of carbaryl caused 79% inhibition of acetylcholinesterase in the Pinfish, Lagodon rhomboides (Coppage, 1977). In studies on the Killifish, Fundulus heteroclitus, Weis and Weis (1975) found cardiac malformations after a 4.5 day exposure to 10.0mg/l. A 14 day exposure to 0.01mg/l of carbaryl caused a decreased rate of regeneration of amputated caudal fins.

Butler (1963) found a 16.8% decrease in productivity in natural phytoplankton communities exposed to 1.0mg/l of carbaryl for 4 hours.

Lamberton and Claeys (1970) report that 1-naphthol, the primary degradation product in aquatic systems, is more toxic to young clams and fish than carbaryl. Furthermore, 1-naphthol is unstable in sea water, and one of its degradation products is a precipitate containing a stable free radical that is toxic to certain estuarine species.

B. Toxic Effects on Man and Other Mammals

Carbaryl exerts its toxicity on insects, as well as mammals, by inhibiting cholinesterase enzymes. This leads to the accumulation of endogenous acetylcholine, the principle choline ester which has demonstrated physiologic significance in humans (NIOSH, 1976).

A study on rats found that 18 mg/kg of carbaryl for two years in the diet caused reduced growth and liver and kidney effects (NAS, 1977). An oral LD50 for male rabbits was found to occur at 707 mg/kg bw/day (FAO/WHO, 1967).

A single oral dose of 2.8 mg/kg bw in a human caused epigastric pain and sweating (Hayes, 1963). NIOSH (1978) reports that the oral TDLo in humans, the lowest dose reported to cause a toxic effect, is 2.8 mg/kg bw/day.

Carcinogenic, behavioural, mutagenic, teratogenic and reproductive effects have been found for carbaryl in studies on mice and rats (FAO/WHO, 1975; NIOSH, 1976).

Total Production

Carbaryl		Chemical Group: Carbamate		
year	area	amount	trend	citation (as reported in)
1972	USA	24 000 tonnes	-	IARC, 1976, p.38

Total Consumption

Carbaryl		Chemical Group: Carbamate		
year	area	amount	trend	citation (as reported in)
yearly	Italy	600 tonnes	-	IARC, 1976, p.39

Production Process(es)

Carbaryl

Chemical Group: Carbamate

process (major or minor - by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
reaction of phosgene with 1-naphthol followed by reaction with methylamine (USA)	-	-/2-naphty-N-methyl- carbamate (affects crop flavour, may be cataractogenic)/-	Fitzhugh and Bushka, 1949 (NAS, 1977, p.643)
reaction of 1-naphtol with methyl isocyanate	-	-	von Rumker et al., 1974 (IARC, 1976, p.38)

Use

Carbaryl		Chemical Group: Carbamate		
use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
insecticide acaricide molluscicide	(major)	-	-	IARC, 1976, p.38

Pathways Leading to Marine Pollution

Carbaryl		Chemical Group: Carbamate	
Pathways	Quantity	Area	Citation
Industrial Effluent	-	World	Coppage, D.L., 1977
Run off from agricultural land	-	World	Coppage, D.L., 1977
Direct application	-	World	Karinen, J.F. et al., 1967

Biotic Transformation in the Marine Environment

Carbaryl

Chemical Group: Carbamate

Process	Transformation		Products		Citation
	%	time	name	quantity	
Degradation by marine fungi	90	3 days	Water soluble metabolites	-	Sikka, H.C. et al., 1967
Hydrolysis in non-sterile seawater	100	17 days	1-naphthol	43%	Karinen, J.F. et al., 1967
Hydrolysis in non-sterile mud and seawater	90	10 days	1-naphthol	-	Karinen, J.F. et al., 1967

Abiotic Transformation in the Marine Environment

Carbaryl

Chemical Group: Carbamate

Process	Location	Conditions		Products Name	Quantity	Transformation		Citation
		Temp C.	pH			%	Time	
Hydrolysis	Seawater in laboratory	20	8	-	Natural 1-naphthol light	-	50 82 hrs.	Liu, D.H.W. and Lee, J.M., 1975
Hydrolysis	Seawater in laboratory	-	7	-	1-naphthol	-	50 10.5 days	Faust, S.D., 1975
Hydrolysis	Seawater in laboratory	-	9	-	1-naphthol	-	50 2.5hr	Faust, S.D., 1975
Adsorption onto mud	Seawater and mud in laboratory	8	8	-	warm white	slight	-	8-12 days Karinen, J.F. et al., 1967

Behaviour of a Chemical Substance in Marine Organisms

Organism	Carbaryl		Chemical Group: Carbanate						
	Route	Exposure Concn. mg/l	Time	Accumulation and Distribution			Loss Time	Metabolites	
				Tissue/ Organ	%	Biomagnification Coefficient		Name	Quantity
Clinocardium nutalli (Cockle clam)	W	2.0	96 hours	Wh	-	2.99	97 12 hours	1-naphthol	-
Butler, J.A. et al., 1968									
Thalassiosira pseudomona (Algae)	W	2.0	24 hours	Wh	-	0.08	-	none	-
Sikka, H.C. and Rice, C.P., 1974									

W - Water
Wh - Whole

C-Car-18

Behaviour of the Substance in Man and Other Mammals

Carbaryl		Chemical Group: Carbamate					
Description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard (as reported in)	citation
rat	oral (gavage)	9.0mg/kg	C-14 labelled carbaryl	-	94%/7 days	-	Knaak et al., 1965 (NIOH, 1976, p.79)
guinea pig	intra-perit.	750mg/kg bw (150mg)	naphtyl- and methyl-labelled carbaryl	-	85%/24 hours in urine	4-hydroxycarbaryl glucuronide; 1-naphtyl methyl-imidocarbonate-o-glucuronide; 1-naphtyl glucuronide; 1-naphtyl sulfate; 1-naphtyl methyl-carbamate N-glucuronide	Knaak et al., 1965 (NIOH, 1976, p.79)
dog (beagle)	oral	25mg/kg	C-14 labelled carbaryl	-	almost half of total carbaryl excreted in faeces	1-naphtyl methyl-imidocarbonate -o-glucuronide	Knaak and Sullivan, 1967 (NIOH, 1976, p.81)
rat	-	-	-	-	-	s-(4-hydroxy-1-naphtyl) cysteine, s-(5-hydroxy-1-naphtyl) cysteine	Bend et al., 1971 (IARC, 1976, p.43)

Behaviour of the Substance in Man and Other Mammals

Carbaryl (page 2)

chemical Group: Carbamate

Description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard (as reported in)	citation
cow (lactating)	oral (diet)	0.25 and 3.05mg/kg bw	single dose	-	11-15% re-covered in faeces 58-70% re-covered in urine 0.35% re-covered in milk	5,6-dihydro -5,6-dihydroxy-1-naphtyl N-methyl carbamate (milk)	Dorough, 1967 (FAO/WHO, 1968 p.16)
human (2 men)	oral	2mg/kg bw	-	-	26-28%/2 days in urine	1-naphtyl methyl-imido-carbonate-o-glucuronide; 4-hydroxycarbaryl glucuronide (4%); 1-naphtyl glucuronide (15%); 1-naphtyl sulfate (8%)	Knaak et al., 1967 (FAO/WHO 1968 p.15)

Behaviour of the Substance in Man and Other Mammals

Carbaryl (page 3)

Description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time	chemical Group: Carbamate	
						metabolites name/amount/hazard (as reported in)	citation (as reported in)
human	dermal appl.	4ug/cm ²	24 hours, C ¹⁴ -labelled carbaryl dissolved in acetone	-	73.9%/5 days in urine	-	Feldmann and Maibach, 1974 (NIOSH, 1976, p.23)
monkey (rhesus)	oral	300mg/kg	naphtyl- and methyl-labelled carbaryl	-	-	1-naphtyl methyl-imidocarbonate-o-glucuronide; 4-(methyl-carbamoyloxy) 1-naphtyl sulfate; 1-naphtyl sulfate; 4-hydroxycarbaryl-glucuronide	Knaak et al., 1968 (NIOSH, 1976, p.82)
steer	dermal appl.	2 gallons of a single dose 0.3% dispersion	perirenal fat/highest concentration/1 day; all tissues/no detectible residue/7 days	-	-	-	Hurwood, 1967 (NIOSH, 1976, p.77)

C-Car-21

Behaviour of the Substance in Man and Other Mammals

Carbaryl (page 4)

Chemical Group: Carbamate

Description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)
rabbit	oral	400mg/kg	single dose	brain:0.03mg/kg/ 48 hours; liver:0.075mg/kg/ 48 hours; bile:1.5mg/kg/ 48 hours; kidney fat:0.03mg/ kg/48 hours; other tissues:0mg/ kg/48 hours	-	-	Bukin and Filatov, 1965 (NIOSH, 1976 p.78)
C- rat liver microsomes	-	-	-	-	-	1-naphthyl-N-hydroxy-methyl carbamate; 4-hydroxy-1-naphthyl-N-methylcarbamate; 5-hydroxy-1-naphthyl-N-methyl-carbamate; 5,6-dihydroxy-5,6-dihydro-1-naphthyl-N-methyl carbamate	Dorough and Casida, 1964 (IARC, 1976, p.43)

Concentrations in Water, Sediments and Biota

Carbaryl		Chemical Group: Carbamate			
Description of Sample					
Material Sampled	Origin	Analytical Method	Level(s)	Date(s)	Citation
Mud in treated mud flats	Oregon, U.S.A.	S	5.4mg/kg dry wt.	2 hours after treatment	Karinen, J.F. et al., 1967
Mud in treated mud flats	Oregon, U.S.A.	S	0.1mg/kg dry wt.	42 days after treatment	Karinen, J.F. et al., 1967
Crassostrea gigas (Pacific oyster)	Washington Coast, U.S.A.	S	0-0.27mg/kg wet wt.	After direct application	Chambers, J.S., 1969
Cancer magister (Crab)	Washington Coast, U.S.A.	S	0-0.87mg/kg wet wt.	After direct application	Chambers, J.S., 1969
Nereid worms	Washington Coast, U.S.A.	S	8.12-9.16 mg/kg wet wt.	After direct application	Chambers, J.S., 1969

S - Spectroscopy

Array of Toxic Effects on Man and Other Mammals

Carbaryl			Chemical Group: Carbamate		
dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
5800	96 weeks intermittent	oral	rat	TDLo, neoplastic effects	ITII, 1975 p.357
5700 (0.5 liter of a Sevin 80 solution, possibly 400g of carbaryl)	single dose	oral	human (39-year- old man)	visual disturbance, skin effects, brain and kidney damage, pulmonary edema, blood congested viscera, blood cholinesterase inhibited, death	Farago, 1969 (NIOSH, 1976, p.29)
5700	95 weeks intermittent	oral	rat	TDLo, carcinogenic effects	NIOSH, 1978 p.7
707 (in 25% agar)	-	oral	rabbit (male)	LD50	FAO/WHO, 1967, p.35
89	-	oral	rat	LD50	ITII, 1975 p.357
50	-	oral	human	LDLo	NIOSH, 1978 p.7
18	2 years	oral (diet)	rat	growth re- duction, kidney and liver effects	NAS, 1977, p.646
8.2	"	"	"	no effects found	"

Array of Toxic Effects on Man and Other Mammals

Carbaryl (page 2)			Chemical Group: Carbamate		
dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
10 (200mg/kg diet)	50 days	oral (diet)	rat (Wistar)	neurotoxic effects	Dési et al., 1974 (IARC, 1976, p.42)
8.6 (total 6mg)	4 weeks (12 x)	intra- perit.	mouse	increase in lung tumours	Schimkin et al., 1969 (IARC, 1976, p.42)
7.6	11 months	oral	rabbit	biochemical changes in liver, depressed tissue cholin- esterase	Kagan et al., 1970 (FAO/WHO, 1975, p.142)
7.2	1 year (5 days/week)	oral	dog	kidney effects	Carpenter et al., 1961 (FAO/WHO, 1967, p.36)
6.25	62 days (throughout gestation)	oral (diet)	dog (beagle)	abnormal pups	Smalley et al., 1968 (NIOSH, 1976, p.59)
2.8	-	oral	human (man)	TDLo, central nervous system effects	NIOSH, 1978 p.7
2.8	single dose	oral	human	epigastric pain, sweating	Hayes, 1963 (NIOSH, 1976 p.23)

Array of Toxic Effects on Man and Other Mammals

Carbaryl (page 3)

Chemical Group: Carbamate

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
2	4 generations, 6 months/ generation	oral (in- tub.)	rat	reproductive effects	Shtenberg and Ozhovan, 1971 (NIOSH, 1976 p.71)
0.76	11 months	oral	rabbit	blood effects, depressed tissue cholinesterase	Kagan et al., 1970 (FAO/WHO, 1975, p.142)
0.7	3.5 months	oral	mouse	induced tension and stimulation of thyroid activity	Stenberg, 1970 (FAO/WHO, 1975, 142)
0.56	single dose	intra- perit.	rat	decreased physical activity	Singh, 1973 (NIOSH, 1976, p.57)
0.12	6 weeks	oral	human	decreased ability of the kidney to reabsorb amino acids	Wills et al., 1968 (NIOSH, 1976, p.32)
-	-	oral	human (19-year-old man, who ingested water-melon sprayed with 80% carbaryl)	vomiting, hyperflexia, pallor, intestinal colic, nasal dis- charge	Lopez, 1970 (NIOSH, 1976, p.30)
(several milliliters of a 80% carbaryl solution)	-	oral	human (33-year- old man)	salivation, headache, lacrimation, tremors	Lopez, 1970 (NIOSH, 1976, p.30)

Array of Toxic Effects on Man and Other Mammals

Carbaryl (page 4)

Chemical Group: Carbamate

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as re- ported in)
-	single dose	oral	human (19-month- old child)	constricted pupils, excessive salivation, muscle in- coordination	Best and Murray, 1962 (FAO/WHO, 1967, p.35)

Array of Toxic Effects on Man and Other Mammals

Carbaryl (page 5)

Chemical Group: Carbamate

concentration in mg/m ³ (conc. cited)	total exposure time; brief	route	description of organism	effect (observation)	citation (as re- ported in)
390	4 hours	inhal.	guinea pig	nasal and local ocular irritation, hemorrhagic areas of lungs (14 days)	Carpenter et al., 1961, (NIOSH, 1976, p.43)
196 (230mg/m ³ of a powder containing 85% carbaryl)	4 hours	inhal.	guinea pig	slight weight loss (14 days)	Carpenter et al., 1961 (NIOSH, 1976, p.43)
40.6-50.9	2 days	inhal.	human (workers)	increased urinary, naphtol concent- ration, no notice- able effects found	NIOSH, 1976, p.27
40	2 months (6 hours/day)	inhal.	cat	deteriorated conditioned reflexes, cholinester- ase inhib- ition	Yakim, 1967 (NIOSH, 1976, p.45)
20	6 hours	inhal.	cat	serum and erythrocyte cholinester- ase inhib- ition	Yakim, 1967 (NIOSH, 1976, p.44)
2	3-4 days (4-6 hours/ day)	inhal.	human (agriculture workers)	reduced blood cholinester- ase activity	Yakim, 1967 (NIOSH, 1976, p.28)

Array of Toxic Effects on Man and Other Mammals

Carbaryl (page 6)

Chemical Group: Carbamate

concentration in mg/m ³ (conc. cited)	total exposure time; brief	route	description of organism	effect (observation)	citation (as re- ported in)
0.23	-	inhal.	human (men)	whole blood cholinesterase activity slightly depressed, no clinical signs found	Best and Murray, 1962 (FAO/WHO, occasionally 1967, p.34)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Carbaryl

Chemical Group: Carbamate

BEHAVIOURAL EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time) qualification	citation (as reported in)
rat	sub cut.	10	2 weeks (1 x /week)	lowered motiv- ation, lowered electroshock avoidance	Sideroff and Santolucito, 1972 (NIOSH, 1976, p.56)
monkey (rhesus)	oral	1.0	18 months (daily)	no effects on behaviour found	Santolucito and Morrison, 1971 (NIOSH, 1976, p.56)
rat	intra- perit.	0.56	single dose	decreased physical activity	Singh, 1973 (NIOSH, 1976, p.57)

These studies, designed to evaluate the possible effects of the substance on behaviour, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Carbaryl (page 2)

Chemical Group: Carbamate

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time) qualification	citation (as reported in)
rat	oral (intub.)	30 (97.7% pure)	22 months (daily)	increase in fibrosarcomas and osteo- sarcomas	Andrianova and Alekseev, 1970 (IARC, 1976, p.41)
mouse	intra- perit.	20 (total 6mg)	4 weeks (12 x)	increase in lung tumours	Shimkin et al., 1969 (IARC, 1976, p.42)

These studies, designed to evaluate the possible carcinogenic effects of the substance, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Carbaryl (page 3)

Chemical Group: Carbamate

MUTAGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time) qualification	citation (as reported in)
mouse (male)	oral	1000	5 days (daily)	no effects found (dominant lethal assay)	Epstein et al., 1972 (NIOSH, 1976, p.57)
mouse	oral	0.5	-	chromosomes stuck together	Vashakidze, 1970, (FAO/WHO, 1975, p.146)
description of system	reported results			citation	
Drosophila melano- gaster	low rate of recessive sex- linked lethal and sublethal mutation			Brzekij and Vaskov, 1971 (NIOSH, 1976, p.58)	
cultured human embryonic fibroblasts treated with 20.80ug/ml of a technical product containing 84% carbaryl	inhibition of mitosis and spindle fibre formation			Vasilos et al., 1972 (IARC, 1976, p.46)	

A comprehensive evaluation of the known studies designed to assess the possible mutagenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"Mutagenic studies have been carried out in mammalian (mouse) and bacterial systems (E coli, H influenzae, and B subtilis) and on yeast (S cerevisiae). These studies indicate that, under the experimental conditions used, carbaryl did not demonstrate any mutagenic effects. Experiments on an insect (Drosophila) showed only weak mutagenicity. These studies do not warrant a conclusion that carbaryl is a mutagen." (NIOSH, 1976, p.127)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Carbaryl (page 4)

Chemical Group: Carbamate

NEUROTOXICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time) qualification	citation (as reported in)
chicken (Rhode Island Red)	sub cut.	2000	single dose	leg weakness	Carpenter et al., 1961 (NIOSH, 1976, p.52)
dog	intra- venous	30	single dose	lacrimation, salivation, occasional tremors	Miller et al., 1973 (NIOSH, 1976 p.55)
rat (Wistar)	oral (diet)	10 (200mg/kg diet)	50 days (daily)	effects on learning, per- formance and EEG patterns, inhibited erythrocyte and brain acetyl-cholin- esterase activity, functional deviations of central nervous system	Dési et al., 1974 (IARC, 1976, p.42)

A comprehensive evaluation of the known studies designed to assess the possible neurotoxic effects of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"The results obtained with chickens and dogs show that apparently only very high doses of carbaryl will produce neuromuscular effects, eg, leg weakness, in these species, probably as a consequence of cholinesterase inhibition. Since no demyelination occurred in the swine nor in the chicken, which is the animal of choice for demonstrating demyelinating effects, it may be concluded that carbaryl is unlikely to produce demyelinating paralytic effects in humans." (NIOSH, 1976, p.130)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Carbaryl (page 5)

Chemical Group: Carbamate

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
dog	atropine sulfate	protective against the carbaryl effects	Carpenter et al., 1961 (NIOSH, 1976, p.41)
mouse	obidoxime and P2S	synergistic	Natoff and Reiff, 1973 (FAO/WHO, 1975, p.142)
rat	$\frac{1}{4}$ -dimethylamino- ethyl-diphenyl- propyl-acetate	increases the behavioural effects	Goldberg et al., 1965 (FAO/WHO, 1967, p.34)

These studies designed to evaluate the possible effects which could result from the combination of this substance with one or more other substances, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Carbaryl (page 6)

Chemical Group: Carbamate

PRIMARY IRRITATION

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time) qualification	citation (as reported in)
rabbit	eye appl.	50	single dose	transient miosis, hyperemia	Yakim, 1967 (NIOSH, 1976, p.46)
rabbit (albino)	intra- cut.	(0.1ml of 0.1% dis- persion)	3 weeks (8x, 3x/week), single dose after 3 weeks pause	weak sensitisation	Carpenter et al., 1961 (NIOSH, 1976, p.47)

A comprehensive evaluation of the known studies designed to assess the possible primary irritation effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"Adverse local ocular effects have not been reported in humans, but minor eye irritation has been demonstrated in animals after local application of carbaryl. It is therefore concluded that dermal and eye exposure are factors to be considered in the workplace environment." (NIOSH, 1976, p.130)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Carbaryl (page 7)

Chemical Group: Carbamate

REPRODUCTIVE EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time) qualification	citation (as reported in)
rat	oral (intub.)	2	4 generations (6 months/ generation)	effects on testicular and ovarian tissues, spermato- genesis and sperms; de- crease in estrus duration, litter size and surviving pups	Shtenberg and Ozhovan, 1971 (NIOSH, 1976, p.71)
mouse	oral	1	(6 month experiment)	sterility	Vashakidze, 1970 (FAO/WHO, 1975, p.146)

A comprehensive evaluation of the known studies designed to assess the possible effect of this substance on reproduction in experimental systems has been carried out. The evaluation reached was as follows:

"The above studies indicate that carbaryl has an effect on several aspects of reproduction in rodents administered carbaryl." (NIOSH, 1976, p.127)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Carbaryl (page 8)

Chemical Group: Carbamate

TERATOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time) qualification	citation (as reported in)
rat	oral (diet)	500	throughout gestation (daily)	no gross or teratogenetic anomalies, 2/3 of pups dies within 4 days after birth	Weil et al., 1972 (NIOSH, 1976, p.62)
guinea pig	oral	300	single dose (12th-16th day of gestation)	malformed fetuses, mostly vertebral malformations, increased maternal mortality	Robens, 1969 (NIOSH, 1976, p.63)
dog (beagle)	oral (diet)	6.25	throughout gestation (62 days, daily)	abnormal pups	Smalley et al., 1968 (NIOSH, 1976, p.59)

A comprehensive evaluation of the known studies designed to assess the possible teratogenic effect of this substance in experimental systems has been carried out. The evaluation reached was as follows:

"It may be concluded from the above studies that carbaryl in doses as low as 6.25mg/kg is teratogenic in only one species, ie the beagle dog." (NIOSH 1976, p.125)

Toxic or Other Effects on Marine Organisms and Ecosystems

Carbaryl		Chemical Group: Carbamate					
System	Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
	Morone saxatilis (Striped bass)	J	1.0	96 hours	LC50	96 hours	Korn, S. and Earnest, R., 1974
	Mytilid edulis (Mussel)	A	22.7	96 hours	LC50	96 hours	Liu, D.H.W. and Lee, J.M., 1975
	Palaemon macro- dactylus (Korean shrimp)	A	0.007	96 hours	LC50	96 hours	Earnest, R., 1970
	Diaptomus sp. (Microcrustacean)	-	0.001	24 hours	LC50	24 hours	Ruber, E. and Baskar, J., 1978
	Fundulus heteroclitus (Killifish)	A	0.01	14 days	Decreased rate of re- generation of amputated caudal fin	14 days	Weis, J.S. and Weis, P., 1975
	Leiostomus xanthurus (Spot)	J	0.1	5 months	Pathological changes in liver	5 months	Katz, M., 1961

Toxic or Other Effects on Marine Organisms and Ecosystems

Carbaryl (page 2)

Chemical Group: Carbamate

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Mytilus edulis (Mussel)	L	0.33	10 days	10% decreased growth	10 days	Liu, D.H.W. and Lee, J.M., 1975
Natural phyto- plankton communities	-	1.0	4 hours	16.8% decrease in product- ivity	4 hours	Butler, P.A., 1963
Lagodon rhomboides (Pinfish)	A	1.33	15 hours	79% inhibition of acetyl- cholinesterase	15 hours	Coppage, D.L., 1977
Mytilus edulis (Mussel)	Em	1.5	48 hours	50% decrease in shell growth	48 hours	Liu, D.H.W. and Lee, J.M., 1975
Mytilus edulis (Mussel)	1st polar body	5.3	1 hour	Abnormal development	-	Armstrong, D.A. and Millemann, R.E., 1974
Fundulus hetero- clitus (Killifish)	Em	10.0	4.5 days	Cardiac malform- ations	4.5 days	Weis, P. and Weis, J.S., 1974

Toxic or Other Effects on Marine Organisms and Ecosystems

Carbaryl (page 3)

Chemical Group: Carbamate

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Mytilus edulis (Mussel)	A	10.3	96 hours	50% decrease in byssal thread attachment	96 days	Liu, D.H.W. and Lee, J.M., 1975

A - Adult
J - Juvenile
L - Larvae
Em - Embryo

C-Car-40

Analysis

Carbaryl		Chemical Group: Carbamate
analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
colorimetry (0.1-1ug/20mg sample)	-	Rangaswamy and Majumder 1974 (IARC, 1976, p.39)
gas chromatography and electron-capture detection (40-2000ng)	-	Sherma and Shafik, 1975 (IARC, 1976, p.40)
thin-layer chromatography (0.01ug)	-	Malinin, 1974 (IARC, 1976, p.40)
high-pressure liquid chromatography (> 7ng)	-	Colvin et al., 1974 (IARC, 1976, p.40)

Legislation for the Protection of Man
and the Marine Environment

Carbaryl

Chemical Group: Carbamate

general classifica- tion of con-	country or political sub-division	description of control mech- anism	quantitative information	citation (as reported in)
control of substances in food	FAO/WHO	recommended maximum residue limits in meat, feed milk and milk products	0.2mg/kg meat (of cattle, sheep and goats), 100mg/kg feed, 0.1mg/kg milk and milk products	FAO/WHO, 1977, p.84

Legislation for the Protection of Man
and the Marine Environment

Carbamate (generic)

Chemical Group: Carbamate

general classifica- tion of con-	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in effluents	Italy	recommended limits for industrial and urban effluents discharged into waters	0.1mg/l into water-courses 0.05mg/l into lakes, 0.2mg/l into the sea and sewers	WHO/UNEP, 1976, p. Italy-4
control of substances in effluents	Turkey	prohibition of discharges when the concen- tration exceeds the tolerance level	1.3ug/l	Turkish Law of 1 October 1971

Carbaryl

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MEDITERRANEAN DATA PROFILE

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^a Nothing found in the literature reviewed.

OUTLINE - GENERAL SUMMARY FOR ORGANOSILICON COMPOUNDS

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GENERAL SUMMARY FOR ORGANOSILICON COMPOUNDS

I. INTRODUCTION

Organic compounds of silicon are defined as compounds containing at least one silicon-carbon bond per molecule. Commercially, the most important of these substances are the silicones, which occur as liquids, resins, or elastomers. These compounds are siloxane polymers and copolymers, containing $-R_2-Si-O-$ as a structural unit, where R represents an organic radical at least once in the polymer. The silicone resins and elastomers exhibit rigid matrices as a result of cross-linking of the polymers through reactive sidechains (e.g. vinyl). The silicone fluids (also called siloxanes or polysiloxane fluids, etc.), consist mainly of high molecular weight, linear molecules, usually identified in terms of viscosity.

II. OCCURRENCE

A. Production

EPA (1975) lists three processes used in the manufacture of organosilicon compounds; a direct process, in which silicium is reacted with alkylchloride, separated by distillation, and hydrolysed; Grignard process, the reaction of chloro- or organochlorosilanes with $C_6H_5 MgCl$, followed by hydrolysis of the resulting organochlorosilanes; and an olefin process, which adds olefin to chlorosilanes, followed by hydrolysis.

There are nine firms in continental Europe which produce silicones, listed by country and number of sites: Belgium (1), France (2), Italy (1), East Germany (2), and West Germany (3). There are also several sites in Czechoslovakia and the USSR (EPA, 1975). The location of these sites may be important with relation to production wastes reaching the Mediterranean. No information on the amount of organosilicon produced was found in the literature reviewed.

B. Use

The wide range of applications for PDMS and other polysiloxane fluids are directly related to their physical and chemical properties: resistance to degradation by high or low temperatures, ozone, weather or corona discharge; low variability of physical constants with temperature; good dielectric properties; film-forming ability; hydrophobic behaviour; release action; surface activity; high compressibility and physiological inertness (EPA, 1975). Though expensive, the fluids may be used in very low concentrations in many applications, including: waxes, polishes, antifoams, foamers for polyurethanes, protective coatings (for textiles, glass and leather), cosmetics, pharmaceutical preparations, lubricants and release applications (adherents). Bulk applications of PDMS fluids include use in damping devices, dielectric applications and heat exchange media.

Elastomers and resins exhibit properties similar to the fluids, and are used as synthetic rubber for electrical insulation, electrical adhesives and caulking compounds; for moulding and extruding applications in the food, plastic, rubber, and ceramic industries; as medical "spare parts", due to their inert qualities, and for specialty products, such as "Silly Putty". (Merck Index, 1968)

The silicon "chemicals" are non-polymeric compounds, usually containing one or two Si atoms per molecule, that are used as monomers, intermediates and cross-linking agents in production of polysiloxanes. They also find use as ancillary chemicals for other industries. The largest class of chemicals from this category is the methylchlorosilanes (SACSA, 1977).

In 1970, it was estimated that Europe used 27,000 tonnes of silicones, which represents 27% of the world market for that

year. An accurate breakdown for production of individual chemicals in Europe was not found, but based on relative production in the U.S., about 33% of the total market was PDMS fluids and elastomers (SACSA, 1977).

III. ORGANOSILICON COMPOUNDS IN THE ENVIRONMENT

A. Sources

1. Natural

No information on the natural occurrence of organosilicon compounds was found in the literature reviewed

2. Anthropogenic

Synthesis of organosilicon compounds may result in liquid waste products which contain silicone. The liquid wastes are disposed of by clarification, biological treatment, incineration and neutralisation (EPA, 1975). Resulting products are judged to be minor contributors to possible environmental contamination (e.g. SiO_2 and CO_2 from incineration). Solid wastes are landfilled, which may result in leaching of silicones into ground water. This process is poorly understood. (EPA, 1975). Accidental spills during production or transport are not considered a major source of possible contamination, and the inert nature of silicones precludes hazard from storage leaks.

The primary pathway by which silicones may be reaching the marine environment is through use. Due to their often fluid nature and use as antifoams, waxes, polishes, cosmetics, lubricants and release or protective agents, a large percentage of silicone fluids may be discharged with

sewage into rivers which flow into the Mediterranean. Treatment baths for glass and textile industries may be major sources of contamination (EPA, 1975).

The vapour pressure of PDMS fluids (10^{-5} - 10^{-6} mm Hg) is similar to DDT's (10^{-5} - 10^{-7}) and PCB's (10^{-4} - 10^{-5}), providing the possibility of atmospheric transport as a major pathway into the environment (EPA, 1975).

Use of elastomers and resins should not result in discharge of silicones to the marine environment, except in very low amounts (e.g. from the use of articles moulded in silicone coated molds).

The disposal of organosilicon containing products (such as polyurethane foam with residues from foaming agents, electrical insulation, etc.) is usually accomplished by means of incineration or landfill, which are believed to contribute little to marine pollution.

B. Transformation

1. Abiotic Transformation

The siloxane fluids are resistant to oxidation, ozone and photochemical degradation. Hydrolysis, however, has been shown to occur in contact with a wide variety of soils, and soluble hydrolysis products in water are demethylated when dilute aqueous solutions are exposed to an ordinary sun lamp. Low concentrations (10ppb) of nitrate ions cause potentiation of this process, presumably by enhancing photolytic formation of hydroxyl radical, which is believed to be the actual cleavage agent (Frye, 1978). The Si-O bond is about 50% ionic, and is susceptible to heterolytic cleavage by acids or bases. Since sea water is normally pH 8.0-8.5,

some hydrolysis may occur by this process. Hydrolysis is also thought to be facilitated by a large interface between water and silicone, for example, in an emulsion (EPA, 1975).

Despite the well-known oxidative resistance of bulk PDMS, the isolated individual molecules do not appear to present any exceptional resistance to environmental chemical degradation (Frye, 1978).

2. Biotic Transformation

No evidence for biotic transformation was found in the literature reviewed. The silicon-methyl bond appears to be resistant to biodegradation, and PDMS fluids exhibit no anti-bacterial or fungicidal properties. Siloxane fluids appear to be virtually non-biodegradable by the organisms tested (EPA, 1975).

C. Bioaccumulation

No evidence for bioaccumulation in marine organisms has been found. However, in a study with humans exposed to PDMS antifoams, only 1.8-3.3% of the dose was excreted, presenting the possibility of accumulation (WHO/FAO, 1975).

IV. MONITORING

A. Analysis

Technology for determining silicone levels in the sea must be specific due to the high occurrence of silicone in nature. Dow Corning has developed an extraction procedure that is sensitive in the ppb range, according to preliminary reports (EPA, 1975).

Horner et al. (1960) report a selective extraction with infrared quantification method for measuring PDMS in food and biological samples.

B. Amount in the Mediterranean

No information on concentrations of organosilicon in the Mediterranean was found in the literature reviewed.

C. Amount Entering the Mediterranean

No monitoring of silicone levels in effluents reaching the Mediterranean was found in the literature reviewed.

D. Regulations

Tunisia has a proposal limit for silicon discharged into waters of 0.01mg/l, and 0.1mg/l for discharges into public sewers (Kratel, unpublished). No other legislation for the Mediterranean countries was found in the literature reviewed.

WHO/FAO (1975) has recommended an estimated acceptable daily intake for man of 0-1.5mg/kg bw of PDMS fluids and antifoams.

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

Hobbs et al. (1975) have studied the effects of 1000mg/l of PDMS on several marine organisms. A 96 hour LC50 was found for the mummichog, Fundulus heteroclitus; the cockle, Prothaca spamina; and the Brown shrimp, Panaeus oxtectus.

High mortality of Daphnia exposed to emulsified siloxane fluids may or may not have actually been caused by the silicone content of the emulsions (EPA, 1975).

B. Toxic Effects on Man and Other Mammals

NIOSH (1978) reports a sub-cutaneous TDLo, or the lowest dose reported to have caused a toxic effect, of 1,500mg/kg bw in the rat. Neoplastic effects were observed. PDMS antifoams used in extracorporeal circulation of blood in operations on humans have been associated with the formation of emboli (Kimura et al., 1964).

Carcinogenic effects have been noted in studies on mice and rats injected with PDMS fluids. A greater incidence of teratogenic effects has been indicated in studies on rabbits and rats injected with 20mg/kg bw/day of the PDMS fluid, DC 360 (EPA, 1975)

Subchronic dermal applications of a phenylmethyldisiloxane mixture on male rabbits caused testicular atrophy and spermatogenic depression. Estrogen-like activity in female rats was also found for many of the materials causing estrogen depression in males. Effects noted in females included changes in uterine weight, production of uterine hyperemia and uterine histology. These results were found with phenylmethyl substituted linear disiloxanes. Cyclosiloxanes were most active. Tests with other siloxane fluids, including PDMS fluids, were negative (OLSON, 1972).

A highly circumstantial association between PDMS and decreased activity of anticoagulant drugs has been reported (EPA, 1975).

Total Production

Polydimethylsiloxane
fluids and antifoams

Chemical group: Organosilicon compounds

year	area	amount	trend	citation
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Nothing found in the literature reviewed.

Total Consumption

Silicones (generic)

Chemical Group: Organosilicon compounds

year	area	amount (estimated)	trend	citation (as reported in)
1970	World	100 000 tonnes	-	SACSA, 1977 (table 1)
1970	Europe	27 000 "	-	

(reported as estimated world market)

Production Process(es)

Silicone fluids	Chemical Group: Organosilicon compounds		
process (major or minor by geographic)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
Direct Process: reaction of silicium with alkylchloride, seperation by distillation followed by hydrolysis of the resulting organochlorosilanes	-	-	EPA, 1975, p.18
Grignard Process: reaction of chlorosilanes or organochlorosilanes with C ₆ H ₅ MgCl, followed by hydrolysis of the resulting organochlorosilanes	-	magnesium chloride	EPA, 1975, p.18
Olefin Process: olefin addition to chlorosilanes, followed by hydrolysis of the resulting organochlorosilanes	-	-	EPA, 1975, p.18

Use

Silicone fluids

Chemical Group: Organosilicon compounds

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
antifoams	-	-	-	EPA, 1975, p.23-27
cosmetics				
damping devices				
dielectric fluids				
foaming of polyurethane				
food additives				
heat transfer media				
lubricants				
polishes				
protective coatings (textiles, glass and leather)				
release agents				
textile finishings				
waxes				

Use

Silicones (generic)

Chemical Group: Organosilicon compounds

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
caulking compounds	-	-	-	Merck Index, 1968, p.946
electrical adhesives				
electrical insulation				
enamels				
paints				
pharmaceutical preparations				
speciality products (i.e. Silly Putty)				
varnishes				
"spare parts" for the human body	-	-	-	SACSA, 1977

Pathways leading to Marine Pollution

Polydimethylsiloxane
fluids and antifoams

Chemical Group: Organosilicon compounds

Pathway	Quantity	Area	Citation
Industrial waste	-	World	Taylor, D., 1972
Ocean dumping of products	-	World	Taylor, D., 1972
Sewage	-	World	EPA, 1975, p.31
Leaching of landfills	-	World	EPA, 1975, p.32
Atmospheric transport	-	World	EPA, 1975, p.51
Accidental spillage	-	World	EPA, 1975, p.29

Biotic Transformation in the Marine Environment

Polydimethylsiloxane Chemical Group: Organosilicon compounds
fluids and antifoams

Process	Transformation		Name	Production		Citation
	%	Time		Quantity		

Nothing found in the marine environment.

Abiotic Transformation in the Marine Environment

Polydimethylsiloxane
fluids and antifoams

Chemical Group: Organosilicon compounds

Process	Location	Temp C.		Conditions		Products		Transformation		Citation
				pH	Chem. Cata.	Light	Name	Quantity	% Time	
Hydrolysis						acid/base	low M.W. fragments terminated with silanol group (-Si (CH ₃) ₂ -OH)		-	EPA, 1975, p.51

Behaviour of a Chemical Substance in Marine Organisms

Polydimethylsiloxane
fluids and antifoams

Chemical Group: Organosilicon compounds

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn. Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	

Nothing found in the marine environment.

Behaviour of the Substance in Man and Other Mammals

Polydimethylsiloxane
fluids and antifoams

Chemical Group: Organosilicon compounds

description of organism	exposure		duration of exposure	retention		clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)
	route	concentration		tissue	percent/time			
monkey	oral	21.8 mg/kg/bw 41.8 mg/kg/bw (C14 labelled PDMS)	-	-	93-97% recovered in faeces	no chemical change of silicones in faeces	WHO/FAO, 1975, p.169	
human	oral	100 mg/kg or 30 mg/kg (PDMS A and M, A contains low M.W. polymers, M does not)	single dose	-	PDMS A: 1.8-3.3%/72 hours in urine (25% in the form of organo-soluble silicon) 0.35%/8 hours was exhaled PDMS M: no increase in urinary silicon during 72 hours, no PDMS was exhaled	octomethyl cyclo- tetrasiloxane, decamethylcyclo- pentasiloxane (exhaled)	WHO/FAO, 1975, p.173	

Behaviour of the Substance in Man and Other Mammals

Polydimethylsiloxane (page 2)
fluids and antifoams

Chemical Group: Organosilicon compounds

description of organism	exposure		duration of exposure	retention		clearance rate percent/time	metabolites		citation (as reported in)
	route	concentration		tissue	percent/time		name/amount	hazard	
monkey (rhesus, 3 animals)		1.15-18.0 mg/kg/bw (C14- labelled PDMS)	single dose	bile/ hours	0.1-0.3%/24	80-90%/92 hours in faeces, 0.5-0.9% in expired air (half- life 4-6 hours), 2.0-2.5% in urine (half-life 24 hours)	-		WHO/FAO, 1975, p.168
rat	intra- cist- ernal	6 μ Ci (C14- labelled silicone)	single dose	brain/ vertebral column/ 31.4%/45 days, spinal cord/9.9%/45 days, fat/7.9%/45 days, liver/1.19%/45 days, spleen/0.21%/45 days, lungs/0.16%/45 days, gastrointestinal tract/ 0%/45 days, whole blood/0%/45 days, total tissues/91.86/ 45 days	41.1%/45 days	-	-		Hine et al., 1969 (EPA, 1975, p.48)

Behaviour of the Substance in Man and Other Mammals

Polydimethylsiloxane (page 3)
fluids and antifoams

Chemical Group: Organosilicon compounds

description of organism	route	concentration	exposure duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)
rat	intra- perit.	15 μ Ci (C^{14} - labelled silicone)	single dose	fat/51.0%/25 days, gastrointestinal tract/ 27.25%/25 days, liver/14.8%/25 days, spleen/1.56%/25 days, testes/0.98%/25 days, kidney/0.63%/25 days, muscle/0.1%/25 days, skin/0.09%/25 days, lungs/0.07%/25 days, brain/0.04%/25 days, heart/0%/25 days, whole blood/0%/25 days, total tissues/96.52%/25 days	-	-	Hine et al., 1969 (EPA, 1975, p.47)
human	oral	753 mg	-	-	108-118.5% recovered in faeces	-	EPA, 1975, p.42
rat	oral	270 mg	-	-	99% recovered in faeces	-	EPA, 1975, p.42

Concentrations in Water, Sediments and Biota

Polydimethylsiloxane
fluids and antifoams

Chemical Group: Organosilicon compounds

<u>Description of Sample</u>		<u>Analytical</u> Method	Level(s)	Date(s)	Citation
Material	Origin				

Nothing found in the marine environment.

Array of Toxic Effects on Man and Other Mammals

Polydimethylsiloxane
fluids and antifoams

Chemical Group: Organosilicon compounds

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
313 000	8 months (DC 151)	-	dog (male, 2 animals)	no effects found	WHO/FAO, 1975, p. 172
311 000 (8 ml, 350 cSt.)	single dose	sub cut.	mouse	no toxic effects found	Rees et al., 1967 (EPA, 1975, p.77)
60 000 (300 g/day)	8 months, 5 days/week (DC 151)	oral (diet)	monkey (4 animals)	no toxic effects, slight diarrhoea	WHO/FAO, 1975, p.172
48 600 (10 ml, 350 cSt.)	single dose	intra- perit.	rat	granuloma formation	Brody and Frey, 1968 (EPA, 1975, p.78)
39 000 (1 ml, 350 cSt.)	single dose	sub cut.	mouse	phagocytosis, phagocyte accumulation near adrenal glands, no inflammatory response or tumour form- ation evident	Ben-Hur et al., 1967 (EPA, 1975, p.78)
9 500 (10 ml/kg, 350 cSt.)	single dose (DC 200)	oral	guinea pig	laxative effect	Rowe et al., 1948 (EPA, 1975, p.64)

(cSt. = centistroke)

Array of Toxic Effects on Man and Other Mammals

Polydimethylsiloxane (page 2) Chemical Group: Organosilicon compounds
fluids and antifoams

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
9 100 (9.4 ml/kg, 100 cSt.)	24 hours	dermal appl. (abraded skin)	rabbit	pulmonary focal hemorrhage and edema, kidney, heart and brain damage, 2/3 deaths, surviving rabbits showed no changes	Treon, et al., 1954 (EPA, 1975, p.74)
1 500	single dose	sub cut.	rat	TDLo, neoplastic effect	NIOSH, 1978 p.20
1 000 (20 000 ppm)	4 months (DC Antifoam A)	oral (diet)	rat	no toxic effects found	Cutting, 1952 (EPA, 1975, p.69)
650 (48 ml)	3-13 months, divided doses (DC 151)	-	human (27 patients)	no toxic effects, occasional nausea	WHO/FAO, 1975, p.173
333 (1% in diet)	8 months (2% silicone emulsion consisting of 50% Antifoam A and 2% penta- erythritol distearate)	oral (diet)	rabbit	no toxic effects found	Carson et al., 1966 (WHO/FAO, 1975, p.171)
324 (1 ml, 200 cSt.)	single dose	inject- ion into synovial cavity of knee joint	rabbit	mild trans- itory inflammation after leaving synovial cavity	Murray, 1972 (EPA, 1975, p.81)

Array of Toxic Effects on Man and Other Mammals

Polydimethylsiloxane (page 3) Chemical Group: Organosilicon compounds
fluids and antifoams

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
243 (1.25 ml 500, 1000, 2000 cSt.)	single dose (DC 360 medical grade)	intra- vitre- ous	monkey	irreversible cellular damage to and loss of the ganglion cells in the retina, receptor cell damage (1 year)	Lee et al., 1969 (EPA, 1975, p.80)
150 (3 g/kg diet)	6 months (DC Antifoam A)	oral (diet)	dog	bile deposits in Kupffer and hepatic cells and in inter- lobular bile ducts	Child et al., 1951 (EPA, 1975, p.68)
24 (10 ml)	single dose	sub cut. (abdom- inal)	ape	phagocytic histocytes, degenerative connective tissue, cavities filled with siloxanes lined by foreign body giant cells	Winer et al., 1964 (EPA, 1975, p.78)
0.02	(DC Antifoam A)	carot- id artery	dog	LD50, necrosis due to impeded blood flow to the brain	Reed and Kittle, 1959 (EPA, 1975, p.79)

Array of Toxic Effects on Man and Other Mammals

Polydimethylsiloxane (page 4) Chemical Group: Organosilicon compounds
fluids and antifoams

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
(400 ml)	(DC 360 Medical Grad Fluid, with possible organic additives)	inject- ion into breast	human	adverse tissue response	Symmers, 1968 (EPA, 1975, p.60)
-	PDMS/silica preparations antifoaming agents in pump-oxygenators	-	human (patients treated with extra- corporeal circulation)	associated with emboli formation	Kimura et al., 1964 (EPA, 1975, p.59)
-	-	inject- ion	human (1 woman)	multicystic masses (containing pure PDMS) surrounded by foreign body giant cells (2.5 years after exposure)	Delage et al., 1973 (EPA, 1975, p.61)

Toxic Effects from Special Studies on Mammals and Other

Non-Marine Experimental Systems

Polydimethylsiloxane
fluids and antifoams

Chemical Group: Organosilicon compounds

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse (22 males)	sub cut.	15 600 (0.4 ml, 350 cSt.)	20 months (DC 360)	1 fibrosar- coma, 1 neurofibr- oma, 1 dif- fuse lymphoma, 1 ulcerating benign hyperplasia of skin	EPA, 1975, p.86
mouse (22 females)	intra- perit.	15 600 (0.4 ml, 350 cSt.)	18 months (DC 360)	1 malignant histiocytic prolifera- tion of the liver, 1 fibrosar- coma, 1 clear wal- led siloxane cyst	EPA, 1975, p.86
mouse	oral (diet)	5 000 (2.5% PDMS 1000 cSt. in diet)	80 weeks (daily)	tumour frequency equal to controls	EPA, 1975, p.86
rat (36 females)	intra- perit.	4 860 (1.0 ml, 350 cSt.)	17 months (DC 360)	8 reticulum cell sar- comas, 1 local adenocarci- noma	EPA, 1975, p.86

These studies, designed to evaluate the possible carcinogenic effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

(cSt. = centistroke)

Toxic Effects from Special Studies on Mammals and Other

Non-Marine Experimental Systems

Polydimethylsiloxane (page 2) Chemical Group: Organosilicon compounds
fluids and antifoams

MUTAGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse (Albino)	intra- perit	10 000	single dose (DC 700 Fluid)	no effect (dominant lethal assay)	Kennedy et al., 1976

This study, designed to evaluate the possible effects of the substance on gene mutation, chromosomal mutations, DNA repair or recombination or on transformation, was found in the literature reviewed. It did not result in a report of any of these effects. No comprehensive evaluation of this information was found.

NEUROTOXICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (male)	inj. spin- ally	-	(DC MF 360)	no neurolo- gical effect found (90 days)	Hine et al., 1969 (WHO/FAO,1974, p.169)
rabbit (New Zealand White)	inj. spin- ally	-	(DC MF 360)	no neurolo- gical effect found (90 days)	Hine et al., 1969 (WHO/FAO,1975, p.169)
monkey (female cynomolgus)	inj. spin- ally	-	(DC MF 360)	no neurolo- gical effect found (90 days)	Hine et al., 1969 (WHO/FAO,1975, p.169)

These studies, designed to evaluate the possible neurotoxic effects of this substance, was found in the literature reviewed. It did not result in a report of neurotoxic effects. No comprehensive evaluation of this information was found.

Toxic Effects from Special Studies on Mammals and Other

Non-Marine Experimental Systems

Polydimethylsiloxane (page 3) Chemical Group: Organosilicon compounds
fluids and antifoams

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
mouse	sub cut.	115 000 (3.0 ml, 20, 100, and 1 000 cSt.)	-	no gross tissue reaction, inflammatory or foreign body reaction, but cyst formations and fluid losses from injection site noted	Ben-Hur and Neuman, 1965 (EPA, 1975, p.77)
human	dermal (20, 50 and appl. 100 cSt.)		repeated insult patch tests	not fatigu- ing, irri- tating or sensitising to human skin	EPA, 1975, p.54
rabbit	eye (dir- ect)	(DC 200, 0.65-50 cSt. and DC 550, 75 cSt.)	single dose	irritation	Rowe et al., 1948 (EPA, 1975, p.75)

These studies, designed to evaluate the possible primary irritation effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and Other

Non-Marine Experimental Systems

Polydimethylsiloxane (page 4) Chemical Group: Organosilicon compounds
fluids and antifoams

REPRODUCTIVE EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	sub cut.	1 000	6-16th day of gestation (daily) (DC 360)	no effects found	Kennedy et al., 1976
rabbit	dermal appl.	1 000 (1.5 cSt.)	28 days (daily) (DC 200)	no effects found	Hobbs et al., 1972
rat	sub cut.	200	male: 10 weeks prior to mating, (3 x/week) female: 2 weeks prior to mating, continued until 21 days after parturition (daily) (DC 360)	no effects found	Kennedy et al., 1976
rat	sub cut.	200	from day 15 of gestation throughout lactation, (daily) (DC 360)	increase in utero mortality	Kennedy et al., 1976
rabbit	dermal appl.	200 (50, 350 and 12 500 cSt.)	28 days (DC 200)	no effects found	Hobbs et al., 1972

These studies, designed to evaluate the possible effects of the substance on reproduction, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and Other

Non-Marine Experimental Systems

Polydimethylsiloxane (page 5) Chemical Group: Organosilicon compounds
fluids and antifoams

TERATOGENICITY

description of organism	route	dose in mg/kg bw/day (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	sub cut.	20 (350 cSt.)	day 6-16 gestation (daily) (DC 360)	indication of a greater incidence of teratog- enic effects	EPA, 1975, p.83
rabbit	sub cut.	20 (350 cSt.)	day 6-18 gestation (daily) (DC 360)	indication of a greater incidence of teratog- enic effects	EPA, 1975, p.83

These studies, designed to evaluate the possible teratogenic effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Polydimethylsiloxane
fluids and antifoams

Chemical Group: Organosilicon compounds

System Organism Ecosystem Non-living	Life Stage	Concentration mg/L	Exposure Time	Effect	Time of Observation	Citation
Fundulus hetero- clitus (Mummichog)	Adult	1 000	96 hours	LC50	96 hours	Hobbs, E.J. et al., 1975
Prothaca spamina (Cockle)	Adult	1 000	96 hours	LC50	96 hours	Hobbs, E.J. et al., 1975
Penaeus oxtectus (Brown shrimp)	Adult	1 000	96 hours	LC50	96 hours	Hobbs, E.J. et al., 1975
Fundulus hetero- clitus (Mummichog)	Adult	1 000	96 hours	Quiescence and surfacing	96 hours	Hobbs, E.J. et al., 1975
Penaeus oxtectus (Brown shrimp)	Adult	1 000	96 hours	Loss of equilibrium	96 hours	Hobbs, E.J. et al., 1975

Analysis

Polydimethylsiloxane
fluids and antifoams

Chemical Group: Organosilicon
compounds

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
selective extraction with infrared quantification	-	Horner et al., 1960 (EPA, 1975, p.31)

Legislation for the Protection of Man and the

Marine Environment

Polydimethylsiloxane
fluids and antifoams

Chemical Group: Organosilicon compounds

general classifica- tion of con- trol mech- anism	country or political	description of control mechanism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in food	WHO/FAO	recommended estimated accep- table daily in- take for man	0-1,5 mg/kg bw	WHO/FAO, 1975, p.174
control of substances in effluents	Tunisia	proposed recommended values for discharges into surface waters and public sewers	0.01mg/l as Si into waters 0.1 mg/l into public sewers (gas chromat- ography)	Kratel (unpub- lished)

Organosilicon compounds

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MEDITERRANEAN DATA PROFILE

ACRYLONITRILE (CYANIDE)

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^a Nothing found in the literature reviewed

OUTLINE-GENERAL SUMMARY FOR ACRYLONITRILE

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- II. OCCURRENCE
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- III. ACRYLONITRILE IN THE ENVIRONMENT
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 - B. Transformation
 - 1. Abiotic
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GENERAL SUMMARY FOR ACRYLONITRILE

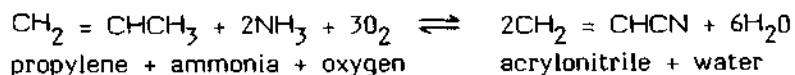
I. INTRODUCTION

Acrylonitrile (vinyl cyanide, propenenitrile) is a chemical intermediate used in the production of plastics, elastomers and a wide variety of synthetic fibers. It is highly reactive chemically and is subject to biodegradation. Concern has been generated by the low levels of acrylonitrile (AN) which enter the environment during production, storage and use. AN has been shown to be carcinogenic in animals, and possibly humans. Teratogenic effects have been noted in studies on rats; and some strains of bacteria undergo mutations when exposed to low levels of AN. Toxicity in humans occurs when AN is inhaled, ingested or applied to the skin. Marine fish and invertebrates are also sensitive to low levels of AN. The U.S. International Trade Commission (1976) reports the production of acrylonitrile in 1976 was about 682,000 tonnes in the United States, which represents a 53% increase since 1966. This trend is expected to continue, especially as a result of increased plastics demand. Increasing production and high toxicity in low concentrations present the possibility of contamination in marine systems.

II. OCCURRENCE

A. Production

Idol (1974) reports that acrylonitrile is produced by a catalytic vapor phase oxidation of propylene and ammonia, which can be expressed as follows:



No figures on the total production of AN in the Mediterranean countries were found in the literature reviewed.

However, Olson (1977) reports that in 1977, France had a production capacity of 330×10^6 lbs. of AN; Italy had a total capacity of about 511×10^6 lbs.; and Spain's production capacity was 198×10^6 lbs.

In addition to domestic production, an estimated 105,877 tonnes of AN were exported from the U.S. to Western Europe in 1976 (U.S. Bureau of Census, 1972-1976). Information concerning the proportion of this amount that was consumed by Mediterranean states was not found in the literature reviewed.

B. Uses

EPA (1978) reports that the major uses of AN in the United States include acrylic and modacrylic fibers (50%), acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins (20%), adiponitrile (10%), nitrile rubber (5%), and miscellaneous applications (5%). The remaining 10% of production was exported. It is unknown if the percentages indicating relative use can be applied to the Mediterranean states.

Acrylic fibers contain at least 85% AN, by definition, and modacrylic fibers 35-85% of polymerised acrylonitrile (Holker, 1975). Acrylics closely resemble wool, and compete with wool in the carpet, knitwear and woven good markets (Stobaugh et al., 1971).

25-35% of the raw material used in producing ABS and SAN resins is acrylonitrile. These resins are used in compounding, housewares, moulded packaging, automotive applications, small appliances and for miscellaneous uses (EPA, 1978)

Adiponitrile is used in the synthesis of nylon 6,6.

The AN content of nitrile rubbers imparts resistance to gas and oil. These nitrile rubbers are used in hoses, seals, gaskets, moulded goods, adhesives, sealants, coated fabrics, plastics-blends, rubber covered rolls, footwear and for miscellaneous applications (Idol, 1974).

Miscellaneous uses of AN include the production of acrylamide and as a fumigant. Acrylamides are used in water treatment (clarification and treatment of effluents, food, etc.,) paper chemistry, oil well stimulation, mineral processing and soil stabilisation. Acrylamide is also used in packaging, but was banned from use in beverage containers by the FDA in 1977 (Kennedy, 1977). A small amount of AN is used as a fumigant against insects and nematodes, and has been used particularly as a grain fumigant (EPA, 1978).

III. ACRYLONITRILE IN THE ENVIRONMENT

A. Sources

EPA (1978) reports that the acrylonitrile monomer can enter the environment during its production, waste handling, storage, transfer, transport and end-use. The total emissions during production are estimated at an average of 0.888 g/kg of AN produced. Waste handling includes gaseous, liquid and solid wastes which occur during production. The liquid wastes in the U.S. are disposed of by deep well injection, which is no longer considered a viable disposal method. Alternative treatments have been discussed by Lowenback et al., (1978). EPA (1978) reports that 590 gallons of wastewater are deep well injected for each 1000lbs. of AN produced; this water contains about 175 ppm AN.

An additional 130 gallons per 1000 lb. of AN produced are sent to a biopond, with an AN concentration of 120 ppm (EPA, 1978).

Transportation losses may occur at sea or on land. NAS (1975) estimates that 41 tons of acrylonitrile were discharged into the sea from transport and handling in 1970. Spills on land will contaminate soils and groundwater. The end-use release of AN includes possible leaching from fabrics during laundering, disposal of AN containing products, residues of AN resulting from its use as a fumigant, as well as acrylimide products which are used in water treatment facilities (EPA, 1977).

B. Transformations

1. Abiotic

Though no controlled studies of chemical degradation of AN in the environment are known to be available, it is possible to predict the fate of AN based on physical properties. AN is a volatile compound; its high vapour pressure suggests considerable evaporation in spill situations. In the atmosphere, AN is subject to oxidation by atomic oxygen, hydroxyl radicals and ozone (Seinfeld, 1975).

The reactivity of AN in the atmosphere is contrasted by its behaviour in water. No appreciable dissociation occurs, and AN doesn't react with water. Persistence in water is, therefore, dependent on losses due to volatilisation and biodegradation (McKee and Wolfe, 1963).

2. Biotic

There is a limited amount of data which suggests that small amounts of AN are removed from water systems by biological degradation. Aerobic bacteria, especially if acclimated to acrylonitrile, are capable of breaking it down to products which include ammonia and acrylic acid (Mills and Stack, 1955). Acclimated anaerobic bacteria are also able to degrade AN (Lank, 1969). Biological oxidation by microorganisms is quite rapid in experimental conditions (EPA, 1978). Dow Chemical reports almost complete oxidation to ammonia 20 days after acrylonitrile was added to activated sludge seed (NAS, 1975).

Though microorganisms have the ability to degrade AN, the low concentrations which are toxic to most organisms may not be tolerated, especially high initial doses. The fate of AN in marine systems remains unclear (EPA, 1978).

C. Bioaccumulation

The cumulative effect of AN was noted in a long term study by Henderson et al. (1961) on fathead minnows.

No magnification of AN in the food chain was reported in the literature reviewed.

IV. MONITORING

A. Analysis

Acrylonitrile can be separated from water and from impurities in water by gas chromatography. Detection limits have been reported in the range of 50-100ppb by Livingston (1977).

Spectrophotometric methods (Hall and Stevens, 1977), azeotropic distillation and purge and trap techniques have also been used to measure AN levels in water and soil (MRI, 1977).

Acrylonitrile is not usually measured directly in biological samples. A metabolite of AN, thiocyanate, is often used as an index of AN exposure (e.g. Efremov, 1976).

B. Amount in the Mediterranean

No information on the levels of AN in the Mediterranean was found in the literature reviewed.

C. Amount Entering the Mediterranean

No information concerning the amount of AN entering the Mediterranean was found in the literature reviewed.

D. Regulations

Yugoslavia has a maximum permissible concentration of dangerous substances (AN) in interrepublic watercourses of 2.0 mg/l (IDHL, 1978). No other regulations pertaining to Mediterranean countries on acrylonitrile levels in air, water or food were found in the literature reviewed.

Acrylonitrile is restricted in the U.S. for use as a fumigant by the Food and Drug Administration (Costle, 1977).

V. TOXICITY

A. Toxic on other Effects on Marine Organisms and Ecosystems

Daugherty and Garrett (1951) reported on the acute toxicity of AN to pin perch, Lagodon rhomboides. 20mg/l was the maximum level at which no deaths occurred, and 30mg/l was the minimal lethal concentration. The median threshold limit (TLm) for 24 hours was interpolated at 24.5 mg/l.

The 24 hour LC₅₀ for AN in brown shimp, Crangon Crangon, is 10-33 mg/l (Portmann and Wilson, 1971).

No tainting of fresh water fish was observed in a study with blue gills, exposed to a sub-lethal dose of 50mg/l for 1-4 weeks (Henderson et al., 1961).

A balanced biota, including bacteria, diatoms, algae, protozoa and rotifers, developed in aerated river water, enriched with nitrogen and phosphorous, at AN concentrations of 10-25mg/l, reflecting the ability of microorganisms to degrade AN at sublethal concentrations. At 50mg/l, diversity decreased, and growth was primarily fungal (Cherry et al., 1956).

Evidence of the mutagenic potential of acrylonitrile has been provided by several tests on E. coli bacteria. Levels as low as $0.1 \times 10^{-3} M$ were reported by Green et al., (1976) to cause mutagenesis. Tests on other strains of bacteria have revealed no mutagenic effects (e.g. SRI, 1976).

B. Toxic Effects on Man and Other Mammals

There is evidence that exposure to acrylonitrile may present increased carcinogenic, mutagenic and teratogenic risks in humans. Du Pont reports excess incidence of cancer and cancer mortality among workers exposed to AN at a filter plant in Camden, South Carolina (O'Berg, 1977). Two studies on rats (Quast et al., 1975; Maltoni, 1976) indicate that prolonged exposure to AN causes a higher incidence of tumours and carcinomas. Acrylonitrile was positively mutagenic in some bacterial assays, but not others (EPA, 1978).

Teratogenic effects have been studied in gravid rats by Murray et al., (1976). Maternal and fetal toxicity occurred at doses of 65mg/kg of AN, administered orally during gestation. Scheufler (1976) showed embryotoxic effects of AN on mice. There are a wide range of toxic effects associated with AN, including altered breathing, central nervous system impairment, convulsions, membrane irritation, etc. It is unknown whether ingestion of marine produce contaminated with AN would be a hazard to humans (EPA, 1978).

Total Production

Acrylonitrile		Chemical group: Cyanide		
year	area	amount	trend	citation (as reported in)
1977	France	330 000 000 lbs.*	-	Olson, 1977 (EPA, 1978, p.21)
1977	Italy	511 000 000 lbs.*		
1977	Spain	198 000 000 lbs.*		

* reported as production capacity

Production Process(es)

Acrylonitrile

Chemical group: Cyanide

process (major or minor- by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
dehydration of either acrylamide or ethylene cyanohydrin with phosphorous pentoxide	-	-	Fugate, 1963 (EPA, 1978, p.9)
catalytic reaction acetylene and hydrogen cyanide in presence of a cuprous chloride catalyst	-	-	EPA, 1978, p.9
catalytic reactions of propylene with nitric oxide	-	-	EPA, 1978, p.9
catalytic vapour oxidation of propylene and ammonia (major- World)	-	-	Idol, 1974 (EPA, 1978, p.11)

Use

Acrylonitrile

Chemical group: Cyanide

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
acrylic and modacrylic fibres	(major)	-	-	EPA, 1978, p.25
acrylonitrile - butadiene - styrene, styrene- acrylonitrile	(major)			
adiponitrile	(major)			
nitrile rubber	(minor)			
miscellaneous applications e.g. pesticide	(minor)			
synthetic fibre production	USA (major)	-	-	US Tariff Comm. Rept., 1958 (Patty, 1963, p.2009)
various plastics	USA			
synthetic rubber	USA			
organic synthesis	USA			

Pathways Leading to Marine Pollution

Acrylonitrile

Chemical group: Cyanide

Pathways	Quantity	Area	Citation
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Nothing found in the marine environment

Transformation in the Marine Environment

Acrylonitrile

Chemical group: Cyanide

Process	Medium	Parameters	Effect	Citation
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Nothing found in the marine environment

Behaviour of a Chemical in Marine Organisms

Acrylonitrile		Chemical group: Cyanide				
Organism	Route	Exposure Concn.	Time	Accumulation and Distribution		Metabolites
				Tissue/ Organ	% Biomagnification Coefficient	Loss % Time
						Name Quantity Citation

Nothing found in the marine environment

Behaviour of the Substance in Man and Other Mammals

Acrylonitrile				Chemical group: Cyanide			
description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)
human (3 men)	inhal.	20ug/l	4 hours	46% in respiratory tract	-	-	Rogaczewska and Piotrowski, 1968 (EPA, 1978, p.93)
rat	oral	-	-	-	-	thiocyanate	Dahm, 1977 (EPA, 1978, p.96)
dog	inhal.	52mg/m ³ (24ppm)	4 hours	-	-	thiocyanate	Lawton et al. 1943 (EPA, 1978, p.97)
-	-	-	-	-	-	cyanide, cyanmethemoglobin	Benes and Cerna, 1959 (EPA, 1978, p.97)

Behaviour of the Substance in Man and Other Mammals

Acrylonitrile (page 2)

Chemical group: Cyanide

description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)
-	-	-	-	-	-	L-cysteine conjugate, L-glutathione conjugate	Hashimoto and Kanai, 1965 (EPA, 1978, p.100)
rat (Spartan, Charles River) monkey (rhesus)	oral	0.1mg/kg	-	-	-	N-acetylated cysteine, cysteine conjugate	Wright, 1977 (EPA, 1978, p.100)
rat (Wistar, male)	oral (gavage)	20.5mg/kg	single dose	-	-	D-glucuronic acid conjugate	Hoffman et al., 1976 (EPA, 1978, p.102)
rat	-	-	-	-	-	carbon dioxide	Young et al., 1977 (EPA, 1978, p.102)

Concentrations in Water, Sediments and Biota

Acrylonitrile

Chemical group: Cyanide

<u>Description of Sample</u>		<u>Analytical</u> <u>Method</u>	<u>Level(s)</u>	<u>Date(s)</u>	<u>Citation</u>
<u>Material</u>	<u>Origin</u>				

Nothing found in the marine environment

Array of Toxic Effects on Man and Other Mammals

Acrylonitrile			Chemical Group: Cyanide		
dose mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
93	-	oral	rabbit	LD ₅₀	NIOSH, 1978
65	6-15th days of of gestation	oral (gavage)	rat (Sprague- Dawley)	increase in fetal mal- formations	Murray et al., 1976 (EPA, 1978, p.178)
62	-	oral	rat	LD ₅₀	Knobloch et al., 1971 (EPA, 1978, p.177)
50 (10mg)	single dose	oral	rat (ARS- Sprague- Dawley)	adrenal haemorrhages	Szabo and Selye, 1971 (EPA, 1978, p.120)
50	3 weeks	intra- perit.	rat (Wistar)	reduced body weight blood, heart, liver, spleen and kidney effects, brain damage	Knobloch et al., 1971 (EPA, 1978, p.141)
30	368 days	oral (water)	rat (Sprague- Dawley, female)	alkaline phosphatase activity increased	Quast et al., 1977 (EPA 1978, p.148)
20	6 weeks	intra- perit.	rat	effects on Y-maze performance	Krysiak and Knobloch, 1971 (EPA, 1978, p.141)

Array of Toxic Effects on Man and Other Mammals

Acrylonitrile (page 2)

Chemical Group: Cyanide

dose mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
17	135 days	oral (water)	dog (Beagle)	biochemical changes in blood	Quast et al., 1975 (EPA, 1978, p.152)
16	182 days	oral (water)	dog (Beagle)	brain, kidney and lung effects	Quast et al., 1975 (EPA, 1978, p.152)
11 (85ppm)	90 days	oral (water)	rat (female)	urine specific gravity increased	Humiston et al., 1975 (EPA, 1978, p.138)
10	368 days	oral (water)	rat (Sprague- Dawley)	brain and heart effects	Quast et al., 1977 (EPA, 1978, p.148)
10	12 months	oral (water)	rat (Sprague- Dawley)	stomach damage, papillomas, ear canal tumours	Quast et al., 1977 (EPA, 1978, p.148)
5	10 days	sub cut.	rat	decreased protein content of liver and blood	Solovei, 1974, (EPA, 1978, p.142)
4	12 months	oral (water)	rat (Sprague- Dawley)	reduced body weight, kidney and liver damage, testicular edema, eye effects	Quast et al., 1977 (EPA, 1978, p.148)

Array of Toxic Effects on Man and Other Mammals

Acrylonitrile (page 3)

Chemical Group: Cyanide

dose mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
2.1 (5mg/kg bw 3x/week)	52 weeks	oral (gavage)	rat (Sprague- Dawley)	slight increase in tumours	Maltoni, 1976 (EPA, 1978, p.184)
1.5 (30mg/kg of a 5% solution)	single dose	intra- venous	rabbit	effects on sulphydryls in liver and brain	Hashimoto and Kanai, 1972 (EPA, 1978, p.127)
-	-	dermal appl. (head)	human (10 year old girl)	dizziness, headache, nausea, convulsions, death	Lorz, 1950 (EPA, 1978 p.78)
-	6 weeks	dermal	human (who had used a Plexidure finger splint)	allergic dermatitis	Balda, 1975 (EPA, 1978, p.75)
(0.1% solution)	-	dermal appl.	"	positive patch test	"
-	-	-	human (workers)	increased cancer incidence and cancer mortality	O'Berg, 1977 (EPA, 1978, p.90)
-	-	-	human (workers)	blood effects	Zotova, 1975 (EPA, 1978, p.85)

Array of Toxic Effects on Man and Other Mammals

Acrylonitrile (page 4)

Chemical Group: Cyanide

concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
990	4 hours	inhal.	guinea pig	LC ₅₀	Knobloch et al., 1971 (EPA, 1978, p.110)
900	0.5 hour	inhal.	mouse	increased activity and respiration	McOmie, 1949 (EPA, 1978, p.110)
660	2 hours	inhal.	rat	mucous membrane irritation	Dudley and Neal, 1942 (EPA, 1978, p.110)
470	4 hours	inhal.	rat	LC ₅₀	Knobloch et al., 1971 (EPA, 1978, p.110)
330	8 weeks (4 hr/day 5 days/week)	inhal.	rat (young)	weight loss, growth impairment, nasal and eye irritation, death	Dudley et al., 1942 (EPA, 1978, p.131)
220	8 weeks (4 hrs/day, 5 day/week)	inhal.	cat	vomiting, listlessness, weight loss, hind leg weakness, death	Dudley et al., 1942 (EPA, 1978, p.132)
198	4 hours	inhal.	monkey (rhesus)	weakness, redness of face, genitals, and oral mucosa	Dudley and Neal, 1942 (EPA, 1978, p.108)

Array of Toxic Effects on Man and Other Mammals

Acrylonitrile (page 5)

Chemical Group: Cyanide

concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
163	7 hours	inhal.	monkey	respiratory distress, eye effects, cyanosis, unconscious- ness	Brieger et al., 1952 (EPA, 1978, p.112)
163	7 hours	inhal.	dog	vomiting incoordi- nation, convulsions, respiratory paralysis	Brieger et al., 1952 (EPA, 1978, p.111)
140	4 hours	inhal.	monkey (rhesus)	stimulated respiration	Dudley and Neal, 1942 (EPA, 1978, p.108)
120	4 weeks (4 hrs/day, 5 days/week)	inhal.	dog (2 animals)	weakness, convulsions, death	Dudley et al., 1942 (EPA, 1978, p.132)
63	4 hours	inhal.	dog	salivation	Dudley and Neal, 1942 (EPA, 1978, p.107)
50	6 months (3 hrs/day, 6 days/week)	inhal.	rat (Wistar)	blood and kidney effects	Knobloch et al., 1972 (EPA, 1978, p.142)
<43.4 (< 20ppm)	0-10 years	inhal.	human (workers)	liver effects	Sakurai and Kusumoto, 1972 (EPA, 1978, p.85)

Array of Toxic Effects on Man and Other Mammals

Acrylonitrile (page 6)

Chemical Group: Cyanide

concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
35 (16ppm)	20 minutes	inhal.	human (workmen)	headache, fullness of chest, irritation of mucous membranes, nervous irritability	Wilson et al., 1948 (EPA, 1978, p.81)
10.8	52 weeks (4 hrs/day, 5 day/week)	inhal.	rat (Sprague- Dawley)	slight increase in tumours	Maltoni, 1976 (EPA, 1978, p.184)
2.5 (5x0.5mg/ m ³)	-	inhal.	human (workers)	blood and bone marrow effects	Shustov, 1968 (EPA, 1978, p.84)
-	5-15 minutes	inhal.	human (16 workers)	nausea, vomiting, headache, vertigo	Zeller et al., 1969 (EPA, 1978, p.81)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Acrylonitrile

Chemical group: Cyanide

BEHAVIOURAL EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	intra-perit.	20	6 weeks (daily)	effects on Y-maze performance	Krysiak and Knobloch, 1971 (EPA, 1978, p.141)

This study, designed to evaluate the possible effects of the substance on behaviour, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Sprague-Dawley)	oral (water)	10 (100ppm)	12 months (daily)	tumours of stomach, central nervous system and ear canal	Quast et al., 1977 (EPA, 1978, p.148)
rat (Sprague-Dawley)	oral (gavage)	5	52 weeks (3x/week)	slight increase in tumours	Maltoni, 1976 (EPA, 1978, p.184)
description of organism	route	concentration in mg/m ³ (conc. cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	inhal.	43.4 (20ppm)	2 years (6 hrs/day, 5 days/week)	mammary and brain tumours	EPA, 1978, p.142

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Acrylonitrile (page 2)

Chemical group: Cyanide

description of organism	route	concentration in mg/m ³ (conc. cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Sprague-Dawley)	inhal.	10.8	52 weeks (4 hrs/day, 5 days/week)	slight increase in tumours (131 weeks)	Maltoni, 1976 (EPA, 1978, p.184)

These studies, designed to evaluate the possible carcinogenic effects of the substance, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

MUTAGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Sprague-Dawley)	-	(500ppm)	90 days	no chromatid or chromosomal aberrations in bone marrow cells	EPA, 1978, p.178

description of system	reported results	citations
L5178Y thymidine kinase mouse lymphoma cell assay	no mutagenic activity found	Litton Bionetics, Inc., 1976 (EPA, 1978, p.177)
Escherichia Coli (trp-)	increased number of trp ⁺ -revertants	Venitt et al., 1977 (EPA, 1978, p.176)

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Acrylonitrile (page 3)

Chemical group: Cyanide

description of system	reported results	citations
Salmonella typhimurium exposed to acrylonitrile vapour	increased number of revertants not sensitive to base-pair substitutions	Milvy and Wolff, 1977 (EPA, 1978, p.174)

These studies, designed to evaluate the possible effects of the substance on gene mutation, chromosomal mutations, on DNA repair or recombination or on transformation, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

NEUROTOXICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	intra-perit.	20	6 weeks (daily)	effects on Y-maze performance	Krysiak and Knobloch, 1971 (EPA, 1978, p.141)

This study, designed to evaluate the possible neurotoxic effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
dog, rabbit	sodium nitrite	reduced effects, prevented death	Dudley and Neal, 1942 (EPA, 1978, p.158)
mouse	hydroxycobalamin	increased LD50-values	Graham, 1965 (EPA, 1978, p.159)

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Acrylonitrile (page 4)

Chemical group: Cyanide

description of organism	chemical substance(s)	effect	citation (as reported in)
mouse	sodium thiosulfate	increased LD50-values	Graham, 1965 (EPA, 1978, p.159)

These studies, designed to evaluate the possible effects which could result from the combination of this substance with one or more other substances, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

PRIMARY IRRITATION

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rabbit	dermal appl.	-	15 minutes	edema	Zeller et al., 1969 (EPA, 1978, p.115)
rabbit	dermal appl.	-	20 hours	necrosis	Zeller et al., 1969 (EPA, 1978, p.115)
rabbit	dermal appl. (abraded skin)	(1ml)	24 hours	erythema	Tullar, 1947 (EPA, 1978, p.114)
rabbit	eye appl.	(0.05ml)	single dose	edema, necrosis (8 days)	Zeller et al., 1969 (EPA, 1978, p.115)

These studies, designed to evaluate the possible primary irritation effects of the substance, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Acrylonitrile (page 5)

Chemical group: Cyanide

REPRODUCTIVE EFFECTS

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Sprague-Dawley)	oral (water)	62.5 (500ppm)	-	decreased fertility, gestation and viability	Svirbely and Floyd, 1961 (EPA, 1978, p.183)

This study, designed to evaluate the possible effects of the substance on reproduction, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

TERATOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat (Sprague-Dawley)	oral (gavage)	65	6-15 th day of gestation	increase in fetal malformations	Murray et al., 1976 (EPA, 1978, p.178)
mouse (AB Jena-Halle, C57BI and DBA)	intra-perit.	-	during gestation	embryo-toxicity	Scheufler, 1976 (EPA, 1978, p.183)

These studies, designed to evaluate the possible teratogenic effects of the substance, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Acrylonitrile		Chemical group: Cyanide			
System organism ecosystem non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of observation Citation
Lagodon rhomboides (Pinperch)	A	24.5	24 hours	TLm	- Daugherty, F.M. and Garrett, J.T., 1951
Teredo diegensis (Mollusc borer)	L	> 100	72 hours	LC100	- Vind, H.P. and Hochman, H., 1960
Crangon crangon (Brown shrimp)	A	10-33	24 hours	LC50	- Portmann, J.E. and Wilson, K. W., 1971
Limnoria tripunctata (Crustacean borer)	A	50	100 hours	LC50	- Vind, H.P. and Hochman, H., 1960
Gobius minutus (Goby)	A	14.0	96 hours	LC50	96 hours Adema, D.M.M., 1976
Crangon crangon (shrimp)	A	6.0	96 hours	LC50	96 hours Adema, D.M.M., 1976
A Adult L Larvae					

Analysis

Acrylonitrile

Chemical group: Cyanide

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
gas chromatography (50ppb for water)	-	Livingston, 1977 (EPA, 1978, p.71)
gas chromatography	sensitivity: 0.05ppm for air	NIOSH, 1976 (EPA, 1978, p.68)

Legislation for the Protection of Man
and the Marine Environment

Acrylonitrile		Chemical Group: Cyanide		
general classifica- tion of control mechanism	country or political sub-division	description of control mechanism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in water	Yugoslavia	maximum permissible concentrations of dangerous substances in interrepublic watercourses	2.0mg/l	IDHL, 1978 (awaiting publication)

Acrylonitrile

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MEDITERRANEAN DATA PROFILE

FLUORIDE

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^a Nothing found in the literature reviewed

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GENERAL SUMMARY FOR FLUORIDE

I. INTRODUCTION

Fluorine is the most electronegative and reactive of all the elements existing naturally in the form of fluoride. It is the 17th most abundant element in the earth's crust. Its soluble compounds can produce toxic effects at very low doses. However, the bulk of the element is locked up in relatively insoluble minerals, such as fluorite (CaF_2) and fluoroapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$). It appears to be ubiquitous throughout man's environment in trace amounts (Dobbs, 1972; NAS, 1977).

II. OCCURRENCE

A. Production

Sodium fluoride is prepared by fusing cryolite with NaOH or by adding equivalent amounts of sodium hydroxide or sodium carbonate to 40% hydrogen fluoride. The impurities are mainly sodium and aluminium fluosilicates (Merck Index, 1968). No information on the quantities of fluoride produced in Europe was found in the literature reviewed. U.S.A. marketable production in 1971 was almost 39 million tons (NIOSH, 1975).

B. Use

Sodium fluoride is used as an insecticide, as a constituent of vitreous enamel and glass mixes, as a steel degassing agent, in electroplating, in fluxes, in heat treating salt compositions, in the fluoridation of drinking water, for disinfecting fermentation apparatus in breweries and distilleries, preserving wood,

pastes and mucilage, manufacture of coated paper, frosting glass and in dental laboratories (Merck Index, 1968).

NIOSH (1975) reports that consumption for the U.S.A. in 1971 was almost 28 million tons.

III. FLUORIDE IN THE ENVIRONMENT

A. Sources

1. Natural

NRCC (1970) reports the total fluoride content of sea water to be in the range of 0.77 to 1.40ppm. Approximately 50% of the total sea water fluoride is bound as the double ion MgF^+ . Thus, the unbound ionic fluoride concentration in sea water appears to range between about 0.4 and 0.7ppm.

Dobbs (1974) states that most of the dissolved fluoride in surface waters and rivers must come from atmospheric precipitation, which, in turn, could derive from three sources: volcanic activity, industrial pollution and the sea. He further estimates that volcanoes and industry account for no more than 10-20% of the amounts commonly found in rain and snow.

2. Anthropogenic

Dobbs (1974) reports that man-made pollution with fluoride compounds from industrial processes include superphosphate works, aluminium smelters, steel, glass, brick, ceramic, ironstone and cryolite works. Many

forms of welding using fluoride as flux, and the burning of some coals, have long been known as sources of fluoride pollution. Treshow (1971) reports that estimated emissions of fluoride are expected to double between 1971 and 1980, even assuming 90% containment.

NAS (1977) reports that for more than 30 years, the practice of adding fluoride to drinking water has been practiced in the United States for the reduction of dental cavities. The principal chemicals used for this purpose are sodium fluoride, sodium silicofluoride, hydrofluorosilicic acid and ammonium silicofluoride. The usual dosage has been in the range of 1.0mg/liter. At the 1.0mg/liter concentration these chemicals dissociate almost completely. 30% of the total fluoride entering Narragansett Bay, U.S.A., is derived from domestic sewage as a result of the fluoridation of water supplies (NRCC, 1977).

B. Transformation

1. Abiotic

It has been estimated that, carbonate and phosphate precipitation in the sea occurs at about one-fifth to one-eighth of the rate at which it is being delivered by the rivers. Furthermore, some 80-90% of the dissolved fluoride in river water is believed to be cyclic (Dobbs, 1974).

2. Biotic

According to NRCC (1970), fluoride accumulates in the mineral phase of mammalian skeletal tissue by a

process of isoionic substitution of F^- for OH^- , so converting hydroxyapatite to fluoroapatite.

C. Bioaccumulation

Stewart et al. (1974) analyzed specimens from an uncontaminated estuarine coastal area of New Zealand. They report fluoride levels from 509 to 2885ppm (ash basis) in the skeleton, and from 31 to 209ppm in the exoskeletons of different species. Moore (1971) exposed the crab, Callinectes sapidus, to 128mg/l fluoride in water. A biomagnification coefficient of 25 was found for the exoskeleton after 30 days; 39% of the fluoride was lost after 20 days. Hemens et al. (1975) exposed three species of marine organisms to 5.88mg/l of fluoride for 68 days. Whole tissue biomagnification factors were as follows: mullet, Mugil cephalus, 172; the prawn, Penaeus indicus, 182.6; and, the mud crab, Tylodioplax blephariskios, 34.

NAS (1977) states that radiofluoride studies show the metabolism of fluoride in the body to be quite simple. Hence, fluoride is unlikely to give rise to intolerance by reason of disease or genetics. Accumulation has been found to occur only in the kidneys and calcified tissues. The reabsorption of water without the reabsorption of fluoride in the kidneys explains the increased concentration of fluoride in calcified tissues. However, the rate of such retention decreases with age, so that adults are nearly in balance.

The ash of the bones of a dog given 65mg of sodium fluoride for 65 months contained 10 times the amount of fluorine found in the bones of the control. Among the soft tissues, increased amounts were found only in the lungs and kidneys. They were found to contain 1.77 and 3.01mg/kg, respectively (Largent, 1949).

IV. MONITORING

A. Analysis

NIOSH (1975) has described a method using an ion-selective electrode with a detection limit of 0.02ppm.

B. Amount in the Mediterranean

Sea water samples from the Northern Adriatic contained 0.8-3.6mg/l of fluoride (Barbaro et al., 1978). A study on over-ocean dust by Bressan et al. (1974) found airborne fluoride concentrations ranging from 100ppm on the East coast of America to 730ppm over the sea in Greenland. No sediment concentrations were found in the literature reviewed.

Barbaro et al. (1978) found that the shell of the barnacle, Balanus amphitrite, from the Northern Adriatic, contained 77.5mg/kg wet weight; the soft parts contained 138-212mg/kg dry weight of fluoride.

C. Amount Entering the Mediterranean

No information on this topic was found in the literature reviewed.

D. Regulations

Italy has recommended limits for industrial and urban effluents, discharged into watercourses, lakes, and sewers, of 10mg/l and 20mg/l into the sea. In Spain, effluents discharged into public watercourses must not contain fluorides in amounts such as to raise the concentrations in the receiving waters above 1.5mg/litre. The Libyan Arab Republic and Yugoslavia also

have legislation concerning the discharge of fluoride into water (WHO/UNEP, 1976).

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

Hemens and Warwick (1972) and Hemens et al. (1975) studied the potential environmental effects of the "scrub water" from an aluminium smelter in South Africa. Brown mussels, Perna perna, were the most sensitive of the organisms tested. In this species, 30% mortality occurred at fluoride levels from 1.0-1.2mg/l in sea water after exposure for 15 days, but lack of food during the test period may have enhanced toxicity (NRCC, 1977).

Portman (1970) found a 48 hour LC50 for fluoride of 300mg/l in the shrimp, Crangon crangon. Decreased growth increment at the ecdysis of the crab, Callinectes sapidus, occurred after 5-15 days of the exposure to 20mg/l fluoride (Moore, 1971).

Dobbs (1974) states that fluorides are phytotoxic and fungitoxic, and can inhibit the development of some important fungal diseases of economic crops, such as rusts and mildews, at a concentration slightly below that at which they visibly damage the crop plant.

B. Toxic Effects on Man and Other Mammals

Initial symptoms of toxicity are a result of the local action of fluoride on the mucosa of the gastrointestinal tract. Vomiting, abdominal pain, nausea and diarrhea are followed by paresthesias, hyperactive reflexes and convulsions. Death is

usually due to respiratory paralysis or cardiac failure. Many of the signs and symptoms of acute fluoride toxicity are a result of the calcium-binding effects of fluoride (NAS, 1977).

NIOSH (1975) reports a case in which workers were exposed to $1.0\text{mg}/\text{m}^3$ of fluoride. Toxicity was manifested in the form of coughs, "horseness", sore throat, and congestion of the nose. Although an inverse relationship of these symptoms to the level of sodium fluoride exposure was found, the original authors concluded it was difficult to separate the independent effects of sodium fluoride, tar smoke and sulphur dioxide.

NIOSH (1978) reports on oral LDLo, or the lowest lethal dose, of $75\text{mg}/\text{kg}$ bw/day for humans. According to NAS (1977), there is no confirmation of the hypothesis that fluorides or fluoridation causes cancer.

Total Production

Fluoride (generic)

Chemical group: Fluoride

year	area	amount	trend	citation (as reported in)
1971	USA	39 000 000 tons	-	NIOSH, 1975, p.19

Production Process(es)

Sodium fluoride		Chemical group: Fluoride	
process (major or minor- by geographic area)	workers exposed	intermediate, impurities and waste products	citation (as reported in)
fusing cryolite with NaOH	-	sodium, aluminium fluosilicates/-/-	Merck Index, 1968, p.959
adding equivalent amounts of NaOH or Na ₂ CO ₃ to 40% HF	-	sodium, aluminium fluosilicates/-/-	Merck Index, 1968, p.959

Use

Sodium fluoride		Chemical group: Fluoride		
use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
wood preservative	-	-	-	ITII, 1975, p.477
insecticide				
fungicide				
rodenticide				
chemical cleaning				
electroplating				
glass manufac- ture				
coated paper				
steel degassing agent	-	-	-	Merck Index, 1968, p.959
fluxes				
heat-treating salt compositions				
fluoridation of drinking water				
disinfecting fermentation apparatus				
pastes and mucilage				
dental laboratories				
prophylaxis of dental caries				
veterinary uses				

Pathways Leading to Marine Pollution

Fluoride		Chemical group: Fluoride	
Pathway	Quantity	Area	Citation
Industrial effluent from aluminium smelting plant	-	Richards Bay, RSA	Hemens, J. and Warwick, R.J., 1972
Aeolian transport from continent to ocean	-	World	Bressan, D.J. et al., 1974
Fluoridation of domestic water supply; domestic sewage	36% of total fluoride entering Bay	Naragansett Bay, USA	NRCC, 1977
Effluent from phosphate mining operation	-	Texas, USA	Moore, D.J., 1971
Effluent from Inralco Aluminium Corporation	132.6 mg/l	Strait of Georgia, USA	Dube, M.A., 1977

Transformation in the Marine Environment

Fluoride

Chemical group: Fluoride

Process	Medium	Parameters	Effect	Citation
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Nothing found in the marine environment.

Behaviour of a Chemical Substance in Marine Organisms

Fluoride		Chemical group: Fluoride						
Organism	Route	Exposure		Accumulation and Distribution			Loss	
		Concn. mg/l	Time	Tissue/ Organ	% Biomagnification Coefficient	%	Time	Metabolites
Mugil cephalus W (Mullet)	W	5.88	68 days	Wh	100	172 (Calc.)	- -	- Hemens, J. et al., 1975
Penaeus indicus W (Prawn)	W	5.88	68 days	Wh	100	182.6 (Calc.)	- -	- Hemens, J. et al., 1975
Tylosidiplox ble- W phariskios (Mud crab)	W	5.88	68 days	Wh	100	34 (Calc.)	- -	- Hemens, J. et al., 1975
Callinectes sapidus (Blue crab)	W	128	30 days	Ex	-	25	39 20 days	- Moore, D.J., 1971
Callinectes sapidus (Blue crab)	W	100	25 days	M	-	1	- -	- Moore, D.J., 1971
W Water								
Wh Whole								
Ex Exoskeleton								
M Muscle								

Behaviour of the Substance in Man and Other Mammals

Sodium fluoride			Chemical Group: Fluoride				
description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard (as reported in)	citation
dog	-	65mg F	65 months	increased amounts found in lungs, kidney and bones	-	-	Largent, 1949 (Patty, 1963, p.837)
human	-	5mg F	single dose	-	20-25%/3 hours in urine, rest excreted in faeces and perspiration	-	Zipkin and Leone, 1957 (NIOSH, 1975, p.29)
human (children)	teeth brushing	0.15% dentifrice	single dose	whole body/30%	-	-	Winkler et al., 1953 (WHO, 1970, p.53)
human	-	4-9mg	-	-	0.19-0.33mg/day in faeces	-	Largent, 1961 (WHO, 1970, p.142)
human	mouth-wash	10ml	single dose	whole body/19% (children), whole body/30% (adults)	-	-	Hellstrom, 1960 (WHO, 1970, p.56)

Behaviour of the Substance in Man and Other Mammals

Sodium fluoride (page 2)				Chemical Group: Fluoride		
description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time name/amount/hazard (as reported in)	citation
human (3-6 years old)	oral	1.0mg	-	whole body/72%	400ug F/day in urine	- Stookey and Muhler, 1966 (WHO, 1970, p.47)
human	oral	1.0mg F	-	whole body/28.3%	10% in faeces, 61.7% in urine	WHO, 1970, p.41
human	oral	1mg F	-	-	75+/12 hours in urine	WHO, 1970, p.43
human	oral	2mg F	12-14 days	-	1.403-1.523mg F/day in urine	Muhler et al., 1966 (WHO, 1970, p.44)
rat	oral	-	-	skeleton/62.5%	-	WHO, 1970, p.50

Concentrations in Water, Sediments and Biota

Fluoride		Chemical group: Fluoride			
Description of Sample Material Sampled Origin		Analytical Method	Level(s)	Date(s)	Citation
Seawater	North Adriatic	-	0.8-3.6 mg/l	1974	Barbaro, A. et al., 1978
Seawater	New Zealand	FSIE	1.11 mg/l	-	Farrier, P.M. and Pullen, D. R., 1973
Seawater	Northumberland, UK	-	1.3-1.5 mg/l	-	Wright, D.A. and Davison, A.W., 1974
Seawater	Florida, USA	FE	43.0 mg/l	1973	Taft, W.H. and Martin, D.F., 1974
Seawater	Mid Atlantic	C	1.32 mg/l	1968-69	Bewers, J.M., 1971
Over ocean dust	Atlantic	PAA	700 ppm	-	Bressan, D.J. et al., 1974
Over ocean dust	Caribbean	PAA	330-540 ppm	-	Bressan, D.J. et al., 1974
Over ocean dust	Greenland sea	PAA	730 ppm	-	Bressan, D.J. et al., 1974
Over ocean dust	Pacific	PAA	510-640 ppm	-	Bressan, D.J. et al., 1974
Over ocean dust	East coast, USA	PAA	100 ppm	-	Bressan, D.J. et al., 1974
Blue cod - bone	New Zealand	FSIE	1,459 mg/kg dry wt.	-	Farrier, P.M. and Pullen, D. R., 1973

Concentrations in Water, Sediments and Biota

Fluoride (page 2)

Chemical group: Fluoride

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Leander serratus	Northumberland, UK	FSIE	5.66 mg/kg wet wt.	1972-73	Wright, D.A. and Davison, A.W., 1974
Pleuronectes flesus (Flounder)	Northumberland, UK	FSIE	99.74 mg/kg wet wt.	1972-73	Wright, D.A. and Davison, A.W., 1974
Crayfish - bone	New Zealand	FSIE	673 mg/kg dry wt.	-	Farrier, P.M. and Pullen, D. R., 1973
Oyster - bone	New Zealand	FSIE	59 mg/kg dry wt.	-	Farrier, P.M. and Pullen, D. R., 1973
Balanus amphitrite (Barnacle) - shell	North Adriatic	-	77.5 mg/kg wet wt.	1975	Barbaro, A. et al., 1978
Balanus amphitrite (Barnacle) - soft parts	North Adriatic	-	138-212 mg/ dry wt.	1975	Barbaro, A. et al., 1978

FSIE Fluoride specific ion electrode
 FE Fluoride electrode
 C Colorimetry
 PAA Photon activation analysis

Array of Toxic Effects on Man and Other Mammals

Sodium fluoride			Chemical group: Fluoride		
dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
250	single dose	sub cut.	rabbit	decreased glycogen in liver and skeletal muscle	Iwase, 1958 (WHO, 1970, p.171)
180	-	oral	rat	LD ₅₀	NIOSH, 1978, p.23
75	-	oral	human	LDL ₀	NIOSH, 1978, p.23
56 (763ppm F)	92 days	oral (diet)	rabbit	bone effects	Largent et al., 1943 (Patty, 1963, p.838)
50 (0.1% in diet)	30 days	oral (diet)	rat	decreased fatty acid metabolism, depressed glycogen turnover	Zebrowski et al., 1964 (WHO, 1970, p.171)
44 (20mg F/kg)	single dose	intra- venous	dog	approximate LD ₅₀ , vomiting, defecation, central ner- vous system effects	Leone et al., 1956 (WHO, 1970, p.229)
29 (2g)	-	-	human	fatal	Arena, 1974, p.123
28	11-21 days of gestation	oral	mouse	TDL ₀ , teratogenic effects	NIOSH, 1978, p.23

Array of Toxic Effects on Man and Other Mammals

Sodium fluoride (page 2)

Chemical group: Fluoride

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
10	3 months	oral	rabbit	degeneration of phosphory- lase in nec- rotic foci in myocardia and liver	Iwase, 1958 (WHO, 1970, p.171)
8.29 (1.658mg)	60 days	oral	rat	blood effects	Dibak et al., 1965 (ILO, 1976)
6 (150ppm)	18 weeks	oral (diet)	swine (Young)	reduced growth rate	Forsyth et al., 1972 (NRCC, 1977, p.49)
4	-	oral	human	TDL ₀ , central ner- vous system effects	ITII, 1975, p.477
3.1 (25ppm)	23 days	oral (water)	rat	striations on incisor teeth	Dean et al., 1934 (WHO, 1970, p.233)
1.4 (100mg)	10 days	intra- venous	human (patients)	thirst, excessive urination	Hodge and Smith, 1965 (WHO, 1970, p.252)
0.51 (36mg)	-	oral	human	decreased lactic dehy- drogenase	Frajola, 1959 (NIOSH, 1975, p.59)
0.21 (15mg)	single dose	-	human (allergic patients)	allergic reactions, (headache, nausea, vom- iting, epi- astric pain) (10 days)	Waldbott, 1963 (WHO, 1970, p.309)

Array of Toxic Effects on Man and Other Mammals

Sodium fluoride (page 3)

Chemical group: Fluoride

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
0.2 (10ug)	20 days	intra- perit.	rat (3-10 days old)	abnormal enamel form- ation	Bhussry, 1960 (WHO, 1970, p.234)
0.19 (13.2mg)	chronic intake	-	human	fluorosis, mottling of enamel of teeth	Arena, 1974, p.123
0.07 (5mg)	-	-	human	reduced alkaline phosphatase activity	Ferguson, 1971 (NIOSH, 1975, p.59)
(6ppm)	-	oral (water)	human (patients whose drink- ing water contained excessive concentrations of fluoride)	osteoscler- osis, album- inuria	Kumar and Harper, 1963 (WHO, 1970, p.252)
(3.2-13% in scrambled eggs)	-	oral	human (263 persons who acciden- tally in- gested NaF)	acute gastro- intestinal effects, death	Lidbeck et al., 1943 (NIOSH, 1975, p.43)
(0.03% solution)	dermal appl.	-	human	destroyed epithelium	Stanton and Kahn, 1915 (Patty, 1963, p.843)
-	-	-	human (hyperthy- roidic patients)	mild antithy- roidal effect	WHO, 1970, p.257

Array of Toxic Effects on Man and Other Mammals

Sodium fluoride (page 4)

Chemical group: Fluoride

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
-	-	oral	human	death due to altered calcium metabolism	Robinowitch, 1945 (WHO, 1970, p.227)
concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as repor- ted in)
2.2 (1.0mg F/m ³) + tar smoke, sulfur dioxide	-	inhal.	human (workers)	cough, hoarseness, sore throat, nose conges- tion	US Public Health Service, 1948 (NIOSH, 1975, p.73)
-	-	inhal.	human (exposed to aqueous mist of NaF)	death	Hayhurst, 1943 (WHO, 1970, p.64)

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Sodium fluoride

Chemical group: Fluoride

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

Nothing found in the literature reviewed.

MUTAGENICITY

description of system	reported results	citation (as reported in)
cow oocytes exposed to 10ppm NaF	clumping of chromosomes at meiosis	Jagiello and Ja-Shein, 1974 (NAS, 1977, p.394)
human lymphocytes exposed to 1mM NaF	no mutagenic effects found	Slacik-Erben and Obe, 1976 (NAS, 1977, p.393)

These studies, designed to evaluate the possible effects of the substance on gene mutation, chromosomal mutations, on DNA repair or recombination or on transformation, resulted in reports of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
rat	calcium, iron	reduced fluoride retention	WHO, 1970, p.52

This study, designed to evaluate the possible effects which could result from the combination of this substance with one or more other substances, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and
Other Non-Marine Experimental Systems

Sodium fluoride (page 2)

Chemical group: Fluoride

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Fluoride		Chemical group: Fluoride					
System	Organism Ecosystem Non-living	Life Stage	Concen- tration mg/l	Exposure Time	Effect	Time of Observation	Citation
	Crangon crangon (Shrimp)	-	300	48 hours	LC50	48 hours	Portmann, J.E., 1970
	Tylosidiplax blephariskios (Mud crab)	A	52.0	72 days	70% mortality com- pared to 10% of controls	72 days	Hemens, J. and Warwick, R.J., 1972
	Perna perna (Mussei)	A	1.0-1.2	15 days	30% mortality	15 days	Hemens, J. and Warwick, R.J., 1972
	Porphyra tenera	"very young"	0.9 by fumigation (critical)	4 hours	Toxic	4 hours	Ishio, S. and Nakagawa, H., 1971
	Mugil cephalus (Grey Mullet)	Juv.	5.5	113 days	No mortality	113 days	Hemens, J. et al., 1975
	Tylosidiplax blephariskios (Mud crab)	-	5.5	113 days	No mortality	113 days	Hemens, J. et al., 1975
	Mugil cephalus (Grey Mullet)	Juv.	100	96 hours	No mortality	96 hours	Hemens, J. and Warwick, R.J., 1972

Toxic or Other Effects on Marine Organisms and Ecosystems

Fluoride (page 2)		Chemical group: Fluoride					
System	Organism Ecosystem Non-living	Life Stage	Concen- tration mg/l	Exposure Time	Effect	Time of Observation	Citation
	Penaeus indicus (Prawn)	A	100	96 hours	No mortality	96 hours	Hemens, J. and Warwick, R.J., 1972
	Penaeus indicus (Prawn)	-	5.7	113 days	Increased growth	113 days	Hemens, J. et al., 1975
	Mugil cephalus (Grey Mullet)	Juv.	5.88	68 days	Decreased growth	68 days	Hemens, J. et al., 1975
	Callinectes sapidus (Blue crab)	A	20	5-15 days	Decreased growth increment at ecd- ysis	5-15 days	Moore, D.J., 1971
	Palaemon pacificus (Sand shrimp)	A	52	72 days	Reproductive proc- esses adversely affected	72 days	Hemens, J. and Warwick, R.J., 1972
	Mugil cephalus (Mullet)	A	52	72 days	Deterioration in physical condition	72 days	Hemens, J. and Warwick, R.J., 1972

Juv. Juvenile
A Adult

Analysis

Fluoride (generic)		Chemical group: Fluoride
analytical methods (detection limit)	limitations/benefits	citation (as reported in)
ion-selective electrode (0.02ppm)	-/no evaporation losses, rapid, potential inter- ferences easily minimized, minimal clean-up time	NIOSH, 1975, p.165

Legislation for the Protection of Man
and the Marine Environment

Fluoride (generic)		Chemical group: Fluoride		
general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method)	citation (as reported in)
control of substances in effluents	Italy	recommended limits for industrial and urban effluents discharged into waters	10mg/l as F-into watercourses, lakes and sewers 20mg/l as F-into the sea	WHO/UNEP, 1976, p.Italy-4
control of substances in effluents	Libyan Arab Republic	proposed standards for effluents discharged	4mg/l into surface water reservoirs for direct use in agriculture, 1mg/l into aquifers used for public water supply, 10mg/l into urban sewage systems	WHO/UNEP, 1976, p.Libyan Arab Republ- ic-2
control of substances in water	Spain	limits for re- lieving public watercourses, that are not to be exceeded due to effluents	1.5mg/l	WHO/UNEP, 1976, p.Spain-2
control of substances in water	Yugoslavia	maximum permiss- ible concentrations of dangerous sub- stances discharged into water used or intended for use as drinking-water, for production of food stuffs, fish- breeding, watering of animals or public bathing	1.5mg/l	WHO/UNEP, 1976, p.Yugosla- via-2

Fluoride

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MEDITERRANEAN DATA PROFILE

ALKYLBENZENE SULPHONATE (ABS)

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and the Marine Environment

ABS (generic) C-ABS-27

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^a Nothing found in the literature reviewed.

OUTLINE - GENERAL SUMMARY

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GENERAL SUMMARY - ALKYL BENZENE SULPHONATE

I. INTRODUCTION

Alkylbenzene sulphonate (ABS) is a group of surface-active ingredients used in household synthetic detergents, which largely replaced classical soaps in detergents in the 1950's. ABS compounds are anionic, branched chain hydrocarbons. Relatively resistant to normal sewage treatment procedures, as well as to degradation by microorganisms, ABS can accumulate in natural waterways. Several countries have discontinued manufacture of ABS in favour of more biodegradable substances, including linear alkylbenzene sulphonate (LAS). Generally occurring in low concentrations in marine organisms, the chronic and sublethal effects are probably more important than acute toxicity (Swedmark et al., 1971).

II. OCCURRENCE

A. Production

Prior to 1964, ABS accounted for about 70% of total surfactant production in the U.S. A production figure of 500,000 tons per year of ABS has been reported (Anon., 1964). The manufacture of ABS has been discontinued by several countries; Germany, 1962; Sweden, 1969; U.S., 1965. It has been replaced by LAS, which is easily biodegradable (Swedmark, 1971). Renzoni (1974) reports that LAS is more toxic than ABS to the larvae of some marine invertebrate species.

B. Use

ABS is used as a surface-active ingredient in synthetic detergents.

Ambe (1973) reports that about 10,000 tons of ABS in detergents is consumed by the 10 million inhabitants of Tokyo yearly. No information on the consumption of ABS in the Mediterranean countries was found in the literature reviewed.

III. ALKYL BENZENE SULPHONATE (ABS) IN THE ENVIRONMENT

A. Sources

1. Natural

No evidence that ABS occurs naturally was found in the literature reviewed.

2. Anthropogenic

ABS containing detergents that are used in household or industrial applications will be discharged with sewage into receiving waterways. Present methods of wastewater treatment are ineffective in breaking down the ABS fraction of these detergents - only about 50% of ABS is removed during the usual biologic treatment. Municipal sewage contains ABS concentrations of about 10ppm, and laundry wastes may contain 60-100ppm (Anon., 1964).

B. Transformation

1. Abiotic

ABS carried by rivers is expected to precipitate with particulate matter and be deposited in sediments when it reaches the sea (Ambe, 1973). Unlike soaps, ABS is not precipitated by magnesium or calcium ions in hard water (Anon., 1964).

Eisler (1965) reports that 40% of the original ABS present had been transformed at the end of 12 weeks, in a laboratory experiment conducted at 3.5°C.

2. Biotic

ABS is resistant to degradation by microorganisms. Cossa and Maggi (1973) found that no ABS had been biodegraded after 4 days; after 11 days, 61% had been transformed. Cook and Goldman (1974) found that 75% of the ABS present had been biologically oxidised after 11-20 days.

C. Bioaccumulation

No information on accumulation of ABS was found in the literature reviewed.

IV. MONITORING

A. Analysis

An infrared spectrometric technique is used as a standard method for the analysis of ABS in water. The colorimetric method by ABS and methylene blue complex is also used for water analysis (Ambe, 1973).

B. Amount in the Mediterranean

A sample of seawater from near Marseilles, France, contained 0.021mg/l of ABS (Cossa, 1973). In a study on organisms from the Italian coast, Bellassai and Sciacca (1973) found the following levels of ABS: mullet, 2.1mg/kg; mackerel, 0.25mg/kg; mussel, 1.2mg/kg. No ABS was detected in sardines.

C. Amount Entering the Mediterranean

No information on the amount of ABS entering the Mediterranean was found in the literature reviewed.

D. Regulations

Italy has recommended the following limits for anionic detergents in effluents: 2.0mg/l for watercourses and lakes; 6.0mg/l for the sea; and, 10.0mg/l for discharges into sewers (WHO/UNEP, 1976).

The Libyan Arab Republic has proposed the following standards for surfactants discharged into waterways: 1.5mg/l for surface waters used in agriculture; 0.5mg/l for waters used for public consumption; 5.0mg/l for discharges into the sea; and, 4.0 mg/l for urban sewage systems (WHO/UNEP, 1976).

Turkey and Yugoslavia have also set limits on the levels of dangerous substances discharged into waterways (WHO/UNEP, 1976).

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

Maggi and Cossa (1973) found the 96 hour LC50 for ABS in several marine organisms: eel, Anguilla anguilla, 2.9mg/l; limpet, Patella vulgata, 3.0mg/l; mussel, Mytilus edulis, 4.0mg/l; cockle, Cardium edule, 5.0mg/l.

Sub-lethal effects were found for the larva of the oyster, Ostrea edulis, at 0.05 mg/l of ABS, which caused a decreased growth rate. Abnormal development of fertilised eggs from the same organism occurred at ABS concentrations of 0.1mg/l (Renzoni, 1975).

Swedmark et al. (1971) found that fish were most susceptible to ABS (96 hour LC50 ranging from 0.8-6.5ppm), followed by bivalves (96 hour LC50 ranging from 5- 100ppm), and the much more resistant crustaceans (96 hour LC50 ranging from 25-100ppm). These differences in susceptibility are attributed to physiological and anatomical characteristics within each of these 3 systematic groups. The authors also found that, as a rule, the more active species are more susceptible than the more sluggish, and that developmental stages are especially sensitive.

Foaming of water caused by the presence of ABS may be of aesthetic significance. Water containing over 1ppm of ABS begins to show signs of foaming (Shuval, 1962).

B. Toxic Effects on Man and Other Mammals

The toxic effects of tetrapropylene benzenesulphonate, an ABS compound, have been reported by NIOSH (1978). An oral, 96 hour LC50 was found to occur at 1000mg/kg bw/day in studies on rats. The oral LDLo for humans, or the lowest dose reported to have been lethal, occurred at 500mg/kg bw/day.

Total Production

ABS (generic)

Chemical Group: ABS

year	area	amount	trend	citation (as reported in)
yearly	U.S.A.	↻ 500 000 000 pounds	-	Anon., 1964

Production Process(es)

Tetrapropylenebenzene sulphate

Chemical Group: ABS

process
(major or minor-by
geographic area)

workers
exposed

intermediate,
impurities
and waste products

citation
(as reported
in)

Nothing found in the literature reviewed.

Use

ABS (generic)

Chemical Group: ABS

Use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
Surface-active component in synthetic detergents	-	-	decreasing	Swedmark et al., 1971

Pathways Leading to Marine Pollution

ABS (generic)

Chemical Group: ABS

Pathway	Quantity	Area	Citation
Domestic effluent	10 000 tons/annum	Tokyo, Japan	Ambe, Y., 1973
Industrial effluent	-	-	Hidu, H., 1965

Biotic Transformation in the Marine Environment

ABS (generic)			Chemical Group: ABS		
Process	Transformation %	Time	Product Name	Quantity	Citation
-	0-64	7 days	-	-	Standard, P.G. and Ahearn, D.G., 1970
-	0 61	4 days 11 days	- -	- -	Maggi, P. and Cossa, D., 1973
Oxidation	75	11-20 days	-	-	Cook, T.M. and Goldman, C., 1974

Abiotic Transformation in the Marine Environment

ABS (generic)		Chemical Group: ABS				
Process	Location	Conditions		Products		Citation
		Temp C.	pH	Chem. Cata.	Light	
		Transformation %		Time		
-	laboratory	3.5	-	-	-	Eisler, R., 1965

Behaviour of a Chemical Substance in Marine Organisms

Organism	ABS (generic)		Chemical Group: ABS						
	Exposure		Accumulation and Distribution			Loss		Metabolites	Citation
	Route	Concn. mg/l	Time	Tissue/ Organ	%	Biomagnification Coefficient	%		

Nothing found in the marine environment.

Behaviour of the Substance in Man and Other Mammals

Tetrapropylenebenzene sulphonate

Chemical Group: ABS

description of organism	route	exposure concentration	duration of exposure	retention tissue/percent/time	clearance rate percent/time	metabolites name/amount/hazard (as reported in)	citation
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Nothing found in the literature reviewed

Concentrations in Water, Sediments and Biota

ABS (generic)		Chemical Group: ABS			
Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Surface water	Seine Estuary, France	AAS	0.0355 mg/l	1972	Cossa, D., 1973
Sea water	Marseilles, France	AAS	0.021 mg/l	1971-72	Cossa, D., 1973
Estuarine water	Maryland, U.S.A.	-	0.06 mg/l	-	Hidu, H., 1965
Bottom mud	Tokyo Bay	MB-ABS complex colorimetry + IS	11-80 mg/kg dry wt.	1971	Ambe, Y., 1973
Mugil cephalus (Mullet)	Italian Coast	MB-ABS complex colorimetry	2.1 mg/kg	1971	Bellassai, S. and Sciacca, S., 1973
Sardinus pilchardus (Sardine)	Italian Coast	MB-ABS complex colorimetry	0.0	1971	Bellassai, S. and Sciacca, S., 1973
Mytilus edulis (Mussel)	Italian Coast	MB-ABS complex colorimetry	1.2 mg/kg	1971	Bellassai, S. and Sciacca, S., 1973
Scomber scombrus (Mackerel)	Italian Coast	MB-ABS	0.25mg/kg	1971	Bellassai, S. and Sciacca, S., 1973
Mytilus edulis (Mussel)	Italian Coast	MB-ABS	1.2mg/kg	1971	Bellassai, S. and Sciacca, S., 1973

AAS Atomic Absorption Spectrophotometry
 IS Infra red Spectrophotometry
 MB-ABS Methylene blue-Alky benzene sulphonate

Array of Toxic Effects on Man and Other Mammals

Tetrapropylenebenzene sulphonate

Chemical Group: ABS

dose in mg/kg/ bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observa- tion time)	citation (as reported in)
1000	-	oral	rat	LD50	NIOSH, 1978, p.4
500	-	oral	human	LDLo	NIOSH, 1978, p.4

Toxic Effects from Special studies on
Mammals and Other Non-Marine
Experimental Systems

Tetrapropylenebenzene sulphonate

Chemical Group:ABS

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

Nothing found in the literature reviewed.

MUTAGENICITY

Nothing found in the literature reviewed.

NEUROTOXICITY

Nothing found in the literature reviewed.

POTENTIATION/ANTAGONISM

Nothing found in the literature reviewed.

PRIMARY IRRITATION

Nothing found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

ABS (generic)

Chemical Group: ABS

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Gadus morrhua (Cod)	A	3.5	96 hours	LC50	96 hours	Swedmark, M. et al., 1971
Cardium edule (Cockle)	A	20.0	96 hours	LC50	96 hours	Swedmark, M. et al., 1971
Crangon crangon (Shrimp)	A	100	96 hours	LC50	96 hours	Maggi, P. and Cossa, D., 1973
Ciona intesti- nalis (Sea squirt)	Spermat- zoa	0.1	1 hours	Decreased fertility	1 hour	Renzoni, A., 1974
Ciona intesti- nalis (Sea squirt)	Eggs + sperm	0.1	Development period	Reduced hatching index	-	Renzoni, A., 1974
Crassostrea gigas (Oyster)	L	1.0	6 hours	Decreased setting and metamorphosis	6 hours	Renzoni, A., 1974

Toxic or Other Effects on Marine Organisms and Ecosystems

ABS (generic) (page 2)

Chemical Group: ABS

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Mercenaria mercenaria (Clam)	Fert. eggs	1.55	10 days	Decreased development	10 days	Hidu, H., 1965
Macrocystis (Marine kelp)	-	2.0	48 hours	Decreased photosynthesis	48 hours	Clendenning, K. A., 1960
Phaeodactylum tricornutum (Algae)	-	3.4	10 days	50% decreased growth	10 days	Maggi, P. and Cossa, D., 1973
Gadus morhua (Cod)	A	5.0	-	Increased swimming activity	-	Swedmark, M. et al., 1971
Gadus morhua (Cod)	A	5-10	48 hours	Swollen gills, increased blood in liver	-	Swedmark, M., 1968
Gadus morhua (Cod)	A	10.0	-	Immobilisation	-	Swedmark, M. et al., 1971
Anguilla anguilla (Eel)	A	2.9	96 hours	LC50	96 hours	Maggi, P. and Cossa, D., 1973

Toxic or Other Effects on Marine Organisms and Ecosystems

ABS (generic) (page 3)

Chemical Group: ABS

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Patella vulgata (Limpet)	A	3.0	96 hours	LC50	96 hours	Maggi, P. and Cossa, D., 1973
Mytilus edulis (Mussel)	A	4.0	96 hours	LC50	96 hours	Maggi, P. and Cossa, D., 1973
Cardium edule (Cockle)	A	5.0	96 hours	LC50	96 hours	Maggi, P. and Cossa, D., 1973
Scolecopsis fuliginosa (Polychaete)	A	10.11	96 hours	LC50	96 hours	Stora, G., 1972
Ciona intestina- lis (Sea Squirt)	L	16.0	6 hours	LC50	6 hours	Renzoni, A., 1974
Crangon crangon (Shrimp)	A	18.5	96 hours	LC50	96 hours	Adema, D.M.M., 1976
Gobius minutus (Goby)	A	25	96 hours	LC50	96 hours	Adema, D.M.M., 1976

Toxic or Other Effects on Marine Organisms and Ecosystems

ABS (generic) (page 4)

Chemical Group: ABS

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
<i>Ostrea edulis</i> (Oyster)	L	2	6 hours	lethal	6 hours	Renzoni, A., 1973
<i>Carassius auratus</i> (Goldfish)	A	59 (threshold)	1-9 days	lethal	1-9 days	Donnier, B., 1971
<i>Artemia salina</i> (Brine shrimp)	Larva hatched in polluted water	60 (threshold)	9 days	lethal	9 days	Donnier, B., 1971
<i>Artemia salina</i> (Brine shrimp)	Larva hatched in clean water	8 (threshold)	9 days	lethal	9 days	Donnier, B., 1971
<i>Ostrea edulis</i> (Oyster)	L	0.05	-	Decreased rate of growth	-	Renzoni, A., 1975
<i>Crassostrea</i> <i>gigas</i> (Oyster)	Fert. egg	0.1	-	Abnormal development	-	Renzoni, A., 1975

Toxic or Other Effects on Marine Organisms and Ecosystems

ABS (generic) (page 5)

Chemical Group: ABS

System Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Ciona intestin- alis (Sea squirt)	Egg	0.1-10.0	through hatching and development	4-95% decrease in fertility index	-	Renzoni, A., 1974
Ciona intestin- alis (Sea squirt)	Egg	0.1-10.0	through hatching and development	5-100% decrease in in hatching	-	Renzoni, A., 1974
Ostrea edulis (Oyster)	L	1.0	6 hours	Decreased metamorphosis	6 hours	Renzoni, A., 1973
Asterionella japonica (Diatom)	-	4.0 (threshold)	-	Growth inhibition	-	Pesando, D. and Aubert, M., 1975
Asterionella japonica (Diatom)	-	4.0	-	Growth inhibition	-	Aubert, M. and Donnier, B., 1973
Diogenes sp (Microalgae)	-	30	3 days	Inhibition of development	3 days	Donnier, B., 1971

Toxic or Other Effects on Marine Organisms and Ecosystems

ABS (generic) (page 6)

Chemical Group: ABS

System	Organism Ecosystem Non-living	Life Stage	Concentration mg/l	Exposure Time	Effect	Time of Observation	Citation
Asterionella japonica (Diatom)		-	100	3 days	Inhibition of growth	3 days	Donnier, B., 1971
Artemia salina (Brine shrimp)		Egg	312	-	Prevention of hatching	-	Donnier, B., 1971

A Adult
L Larvae

C-ABS-25

Analysis

ABS (generic)

Chemical Group: ABS

analytical method(s) (detection limit)	Limitations/benefits	citation (as reported in)
methylene blue colorimetry combined with infrared spectrometry	-	Ambe, 1973

Legislation for the Protection of Man
and the Marine Environment

ABS (generic)		Chemical Group: ABS		
general classifica- tion of control mechanism	country or political sub-division	description of control mechanism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in effluents	Turkey	prohibition of discharges when the concentration exceeds the tolerance level	3ug/l of TBS 0.1ug/l of ABS	Turkish law of 1 October 1971
control of substances in effluents	Yugoslavia	maximum permissible concentrations of dangerous substances discharged into water used or intended for use as drinking water for production of foodstuffs, fish breeding, watering of animals or public bathing	0.5mg/l	WHO/UNEP, 1976, p.Yugoslavia-2
control of substances in water	Yugoslavia	maximum permissible concentrations of dangerous substances in interrepublic watercourses	0.4mg/l of ABS in class I and class II waters ^a 1.0mg/l of ABS in class III and class IV waters ^b	IDHL, 1978 (awaiting publication)

^a Class I: waters which, in their natural state, where necessary after disinfection, may be used for drinking purposes and in the food industry and, in the case of surface waters, for breeding Salmonidae. Class II: waters which, in their natural state, may be used for bathing and recreation, water sports, breeding of Cyprinidae, or which, after treatment, may be used for drinking purposes and in the food industry.

^b Class III: waters which may be used for irrigation and, after treatment, in industry other than the food industry. Class IV: waters which may be used for other purposes only after treatment.

Alkylbenzene sulphonate

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MEDITERRANEAN DATA PROFILE

PHOSPHORUS AND ITS INORGANIC COMPOUNDS

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^a Nothing found in the literature reviewed

OUTLINE-GENERAL SUMMARY

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GENERAL SUMMARY
PHOSPHORUS AND ITS INORGANIC COMPOUNDS

I. INTRODUCTION

Phosphorus occurring as phosphate is one of the major nutrients required by plants, and is essential for all forms of life. In the elemental form, phosphorus is extremely toxic, and is subject to bioaccumulation in marine organisms. Since virtually all phosphorus in sea water occurs as phosphates (PO_4^{3-}), due to oxidation and hydrolysis reactions, measurements are often given in terms of "total phosphate phosphorus", or "phosphorus as P". Evidence from Placentia Bay, Newfoundland, indicates that elemental P, discharged from a phosphorus production plant, was responsible for a large fish kill there, and that phosphorus in the elemental state shows some degree of persistence in sediments.

In spite of its high toxicity in the elemental form, the main problem in the Mediterranean stemming from contamination by phosphorus is probably eutrophication. Nutrient enrichment, as well as sewage effluents containing a high organic matter load, occurs mainly near large coastal cities and near the estuaries of large rivers. Aesthetic degradation and ecosystem alteration are probable results of severe eutrophication along some shores of the Mediterranean.

II. OCCURRENCE

A. Production

No figures on production levels of phosphorus in the Mediterranean region were found in the literature searched.

Phosphorus is a by-product and intermediate in the smelting of phosphate rock for production of phosphate fertilisers. In this process, phosphate rock, sand, and coke are heated in a furnace to produce yellow (elemental) phosphorus (Patty, 1963).

B. Uses

There are two commercially important forms of phosphorus, yellow (or white) and red phosphorus. Yellow phosphorus is extremely toxic and unstable, igniting spontaneously in contact with air. The red form is less toxic and more stable (Merck Index, 1968).

Yellow phosphorus is the most important commercially, being used in the production of phosphoric acid, which in turn is used to produce various chemicals used in detergents, cosmetics, shampoos, etc. Elemental phosphorus is also used in metal finishing, fertilisers, insecticides and rodent poisons (Jangaard, 1970).

III. PHOSPHORUS IN THE ENVIRONMENT

A. Sources

Though urban and industrial effluents contribute only 2% of total run off to the Mediterranean, an estimated 16% of P originates in coastal areas from these sources (UNEP, 1977). River run off carries the remainder of the P load, present in concentrations of much lower magnitude than coastal effluents. Only mild eutrophication is expected near river discharges, due to circulation, high primary production and relatively low levels of suspended organic matter.

The low water content of effluents tends to concentrate organic matter and nutrients in a narrow zone of eutrophication along polluted shorelines (UNEP, 1977).

Industrial effluents were responsible for 150-250 lbs./day of yellow phosphorus entering Placentia Bay, Newfoundland, in 1969-1970 (Ackman et al., 1972b).

B. Transformation

1. Abiotic

In the presence of oxygen, phosphorus is converted to phosphate. This process has a half-life of 240 hours at 0°C, which is close to the temperature near the bottom of the sea (Bullocks and Newlands, 1969). Discharge from a phosphorus plant at Placentia Bay, Newfoundland, caused significant poisoning of fish and lobsters in the area, indicating persistence of elemental phosphorus for relatively long periods under water (Jangaard, 1970).

Up to 20% of phosphate dissolved in fresh water entering the sea is deposited in sediments as silt. In sediments P occurs in four states: 1) interstitial phosphate, which can be leached into the water column 2) adsorbed phosphate, which can be released chemically 3) insoluble phosphate bound to cations (e.g. Ca^{+2} , Fe^{+3}) 4) phosphorus bound to organic matter (UNEP, 1977).

2. Biotic

Phosphorus bound to organic matter is released very rapidly, probably due to solubilisation by microorganisms. The deep ocean is the most important reserve of inorganic P (UNEP, 1977).

C. Bioaccumulation

Elemental phosphorus is subject to rapid bioaccumulation by marine organisms, including seaweed, fish and invertebrates. Being readily soluble in lipids, P is concentrated primarily in the fatty organs, especially the liver (Jangaard, 1970).

In one set of experiments, a cod swimming in water containing 0.0001 mg/l of P for 16 hours showed concentration factors of 50-130 in muscle tissue, and 15,000 in the liver (Dyer et al., 1970). Fletcher (1972) found a biomagnification coefficient of 1,000-2,000 in the lobster, Homarus vulgaris, in a 48 hour exposure to 0.015 mg/l of yellow phosphorus.

These effects are apparently irreversible in the fish studied, though an experiment with marine invertebrates and seaweed reported that P was eliminated from the organisms 7 days after return to clean sea water (Fletcher, 1971). The efficiency of concentration of P by cod is relatively greater at low levels of P than at high levels. This may be due to decreased adsorption due to gill damage by colloidal P at higher concentrations, or simply due to more efficient uptake by fatty tissue at the lower concentration gradient (Dyer et al., 1970).

IV. MONITORING

A. Analysis

A gas chromatographic method developed by Addison and Ackman (1970) for determination of elemental phosphorus has a sensitivity well below 1.0ppb and requires only 5 minutes per estimation. Another advantage of this technique is its specificity for yellow phosphorus, which isn't possible with benzene extraction followed by spectrophotometry. With benzene extraction techniques phospholipids can be extracted from organisms (e.g. plankton) in the sea water, giving total phosphorus levels, including phosphate (Bullock and Newlands, 1969).

B. Amount In the Mediterranean

Placentia Bay, Newfoundland, is the source of most of the information on phosphorus levels in marine systems. Addison et al. (1972) found sea water levels of 0.5 mg/l near the point of discharge, and 0.003 mg/l in the Bay itself. Coarse sand sediments in Placentia Bay contained 5,700 mg/kg dry weight of phosphorus (Peer, 1972). Ackman et al. (1972a) found the following phosphorus levels in biote from Placentia Bay: herring, Clupea harengus, 1.2 mg/kg in the viscera; cod, Gadus morhua, 0.0038 mg/kg; crab, 8.69 mg/kg.

Large cities and rivers are the main sources of nutrient supply to the Mediterranean. Concentrations of phosphates vary with the seasons, due to tidal flows, upwelling of bottom waters, temperature, light, etc. (UNEP, 1977).

The northern Adriatic, the coastal crescent between Barcelona and Naples, and the shores between Beirut and Alexandria are critically affected by eutrophication. Phosphorus-phosphate levels in the northern Adriatic reached 2.4ug-at $\text{PO}_4\text{-P/l}$, with levels decreasing progressively farther south. Near the mouth of the Rhone, 1.4 - 6.1ug-at $\text{PO}_4\text{-P/l}$ was recorded. These values compare to levels of 0.04ug-at $\text{PO}_4\text{-P/l}$ in offshore waters (open ocean) near Egypt (UNEP, 1977). Surface waters generally show lower concentrations of P than deep ocean waters, due largely to utilization in the euphotic zone by phytoplankton and other microorganisms (UNEP, 1977).

C. Amount Entering the Mediterranean

Rivers carry an estimated 300,000 tonnes of phosphorus into the Mediterranean each year.

An additional 57 tonnes come from coastal discharges by industry, municipal effluents, and agricultural runoff (UNEP, 1977). Annual per capita contribution of phosphorus as P is estimated at 1.6 kilograms, discharged in municipal sewage (EPA, 1976).

D. Regulations

No regulations concerning phosphorus-phosphate levels in the Mediterranean region were found in the literature reviewed. In the U.S.A., a recommended concentration of yellow phosphorus of 0.1 ug/l in marine or estuarine waters has been proposed by the EPA (1976).

V. TOXICITY

A. Toxic or Other Effects on Marine Organisms and Ecosystems

Elemental P is extremely toxic to marine organisms. Herring are sensitive at concentrations as low as 2.5ppb, and a study with trout, salmon and cod found lethal effects at concentrations of less than 10ppb. Hemolysis of the blood leading to a red tinge in fish, especially around the head and gills, is often a characteristic of P poisoning (Jangaard, 1970).

The effect of P on herring in Placentia Bay, Newfoundland, was found to be irreversible and cumulative (Jangaard, 1970).

A 96 hour LC50 for elemental phosphorus in the cod, Gadus morhua, was found to occur at 0.006 mg/l (Maddock and Taylor, 1976). A 130 hour LC50 in the herring, Clupea harengus, occurred at 0.0025 mg/l, and a 96 hour LC50 for yellow phosphorus was found to occur at 0.12 mg/l in the lobster, Homarus americanus (Zitco et al., 1970).

A more important problem for the Mediterranean which is associated with increased levels of both P and N is eutrophication in coastal areas. Increased primary production due to nutrient enrichment occurs in the euphotic layer. Most of the oxygen produced by increased photosynthesis in the surface layer finds its way to the atmosphere, and thus is lost to the marine system. Transport of this oxygen into deeper waters is hampered by stratification due to temperature and salinity gradients. As populations of saprophytic microorganisms increase to decompose the larger amount

of plant biomass, respiratory demand will bring about oxygen deficiencies in deep waters, and especially in sediments. Decomposition will proceed by anaerobic pathways, which characteristically produce foul-smelling gasses (e.g. H_2S , CH_4). This process is augmented by the frequent occurrence of high levels of organic matter in coastal effluents, especially in sewage wastewaters (UNEP, 1977).

The type of organism which responds to increased levels of P may be noxious in themselves. Algal blooms (red tides), produce neurotoxins which can cause fish kills, contamination of shellfish, and respiratory distress in susceptible members of the human population when onshore winds carry spray from red tides to inland areas (UNEP, 1977).

Decrease in species diversity as a result of the elimination of less resistant species in heavily polluted areas endangers the stability of the ecosystem as a whole. Benthic communities are especially sensitive to eutrophication, and mobile organisms, i.e. fish, are likely to avoid contaminated areas completely (UNEP, 1977).

Aesthetic degradation of coastal areas is of concern in the Mediterranean due to the large number of tourists visiting the area each year.

B. Toxic Effects on Man and Other Mammals

FIRL (1978) regards elemental phosphorus as a highly toxic substance. It is believed that intracellular oxidation processes are disturbed due to the potent reducing properties of P.

Doses as low as 0.2mg/kg bw may lead to adverse symptoms in humans, and the lethal oral dose is about 1.0mg/kg bw (Diaz-Rivera et al., 1950).

Severe burns occur when any part of the body is brought into direct contact with elemental phosphorus.

Chronic exposure to phosphorus typically results in necrosis of the bones, especially the jaw. Other effects of phosphorus in humans include possible liver and kidney effects, cardiovascular collapse, blood disorders, and gastrointestinal lesions (Diaz-Rivera et al., 1950).

Total Production

Yellow Phosphorus Chemical Group: Phosphorus and its inorganic compounds

year	area	amount in tons	trend	citation (as reported in)
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Nothing found in the literature reviewed.

Production Process(es)

Yellow Phosphorus Chemical Group: Phosphorus and its inorganic compounds

process (major or minor by geographic area)	workers exposed	intermediates impurities and waste products	citation (as reported in)
Phosphate rock, sand and coke heated in a furnace	-	-	Patty, 1963 p.2257

Use

Yellow Phosphorus Chemical Group: Phosphorus and its inorganic compounds

use(s)	geographic area (major or minor)	substance(s) added	trend	citation (as reported in)
fertiliser manufacture	-	-	-	Arena, 1974, p.133
fireworks				
insect and rodent poisons				
smoke screens	-	-	-	Merck Index, 1968, p.824
gas analysis				

Pathways Leading to Marine Pollution

Yellow Phosphorus Chemical Group: Phosphorus and its inorganic compounds

Pathway	Quantity	Area	Citation
Industrial effluent	-	Placentia Bay, Newfoundland	Chamut, P.S. et al. 1972
Industrial effluent	150-250 lb/day, 1969-1970	Placentia Bay, Newfoundland	Ackman, R.G. et al. 1972b.

Biotic Transformation in the Marine Environment

Yellow Phosphorus Chemical Group: Phosphorus and its inorganic compounds

Process	Transformation		Products		Citation
	%	Time	Name	Quantity	

Nothing found in the marine environment

Abiotic Transformation in the Marine Environment

Yellow Phosphorus

Chemical Group: Phosphorus and its inorganic compounds

Process	Location	Conditions			Product		Transformation		Citation
		Temp. C	pH	Chem. cata.	Light	Name	Quantity	% Time	
Oxidation	Lab. - Sea water	30 0	- -	- -	- -	- -	- -	50 hrs. 240 hrs.	Bullock, E. and Newlands, M.J. 1972
Oxidation	Lab. - Aqueous dispersion	-	-	-	-	Phosphates	-	50 2 hrs.	Zitko, V. et al. 1970
Oxidation	Lab. - phosphorus contaminated bottom mud	-	-	-	-	Phosphates	-	50 20 hrs.	Zitko, V. et al. 1970

Behaviour of a Chemical Substance in Marine Organisms

Yellow Phosphorus

Chemical Group: Phosphorus and its inorganic compounds

Organism	Exposure		Accumulation and Distribution			Loss		Metabolites		Citation
	Route	Concn.	Time	Tissue/ Organ	% Biomagnification Coefficient	%	Time	Name	Quantity	
Salmo salar (Atlantic salmon)	W	1.9 mg/L	2.8hrs.	L	3.8	26	50	0.9hr	-	Fletcher, G.L., 1974
Gadus morhua (Cod)	W	0.0111 mg/L	71.7hrs.	L	52.5	120	50	5.27 hrs.	-	Fletcher, G.L., 1974
Gadus morhua (Cod)	W	0.001 mg/L	16 hrs.	L M	- -	15,000 50-130	- -	- -	- -	Dyer, W.J. et al. 1970
Gadus morhua (Cod)	W	0.0244 mg/L	28 hrs.	L	66	100-300	50	1 hr.	-	Maddock, B.G. and Taylor, D. 1976
Mya arenaria (Clam)	W	0.015 mg/L	48 hrs.	Wh	-	22	100	7 days	-	Fletcher, G.L., 1972
Homarus vulga- ris (Lobster)	W	0.015 mg/L	48 hrs.	Wh	-	1,000- 2,000	-	-	-	Fletcher, G.L., 1972

Behaviour of a Chemical Substance in Marine Organisms

Yellow Phosphorus (page 2)

Chemical Group: Phosphorus and its inorganic compounds

Organism	Exposure		Accumulation and Distribution				Loss		Metabolites		Citation
	Route	Concn.	Time	Tissue/ Organ	%	Biomagnification Coefficient	%	Time	Name	Quantity	
Fucus distichus (Sea weed)	W	0.015 mg/L	48 hrs.	Wh	-	22	100	7 days	-	-	Fletcher, G.L., 1972

(W - Water; L - Liver; M - Muscle; Wh - Whole)

Behaviour of the Substance in Man and Other Mammals

Yellow Phosphorus

Chemical Group: Phosphorus and its inorganic compounds

description of organism	route	concentration	exposure	duration of exposure	tissue	retention percent/time	clearance rate percent/time	metabolites name/amount/hazard	citation (as reported in)
rat	oral	0.3 mg/kg bw	single dose			-	33%/5 days in faeces 46.7%/5 days in urine	organic and inorganic phosphates	Lee et al. 1975 (FIRL, 1978, p.60)
rat (female)	oral	0.3 mg/kg bw	single dose		gastrointestinal tract: 15.3%/1 day, 1.7%/5 days liver: 16.9%/1 day, 6.3%/5 days whole blood: 4.1%/1 day, 1.7%/5 days kidney: 0.8%/1 day, 0.4%/5 days spleen: 0.1%/1 day, 0.1%/5 days brain: 0.1%/1 day, 0.1%/5 days lungs: 0.3%/1 day, 0.2%/5 days skeletal muscle: 5.5%/1 day, 6.0%/5 days		-	-	Lee et al. 1975 (FIRL, 1978, p.55)

Concentrations in Water, Sediments and Biota

Yellow Phosphorus Chemical Group: Phosphorus and its inorganic compounds

Description of Sample		Analytical Method	Level(s)	Date(s)	Citation
Material Sampled	Origin				
Water	Placentia Bay, Newfoundland, point of effluent	GLC	0.5 mg/L	1969	Addison, R.F. et al., 1972
Water	Placentia Bay, Newfoundland	GLC	0.003 mg/L	1969	Addison, R.F. et al., 1972
Coarse sand	Placentia Bay, Newfoundland	GLC	5,700mg/kg dry wt.	1969	Peer, D.L., 1972.
Clupea harengus (Herring) - viscera	Placentia Bay, Newfoundland	GLC	1.2 mg/kg	1969	Ackman, R.G. et al. 1972a
Gadus morhua (Cod)	Placentia Bay, Newfoundland	GLC	0.0038mg/kg	1969	Ackman, R.G. et al. 1972a
Crab	Placentia Bay, Newfoundland	GLC	8.69 mg/kg	1970	Ackman, R.G. et al. 1972a

Array of Toxic Effects on Man and Other Mammals

Yellow phosphorus Chemical Group: Phosphorus and its inorganic compounds

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
16	-	oral	human	TDLo, systemic effects	NIOSH, 1978, p.20
4.82-4.85	-	oral	mouse	LD50, appetite loss, liver effects	Lee et al. 1975 (FIRL, 1978, p.43)
3.03-3.07	-	oral	rat	LD50, appetite loss, liver effects	Lee et al. 1975 (FIRL, 1978, p.43)
2.6	-	oral	human (woman)	TDLo, central nervous system effects	NIOSH, 1978, p.20
1.4	-	oral	human	LDLo	NIOSH, 1978, p.20
1.30	8 days	oral (diet)	rat (23 days old, Wistar, female)	abnormal remodelling of bones	Wahlen et al., 1973 (FIRL, 1978, p.37)
1	6x (every 3-5 days)	sub cut.	guinea pig	increase in circulating monocytes	Fleming and Collings, 1951 (FIRL, 1978, p.37)
0.6	4 months	oral	rabbit, guinea pig	liver effect	Mallory, 1933 (FIRL, 1978, p.45)

Array of Toxic Effects on Man and Other Mammals

Yellow phosphorus (page 2)		Chemical Group: Phosphorus and its inorganic compounds			
dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
0.3	117 days	oral	rabbit	reduced weight gain and bone growth)	Adams, 1940 (FIRL, 1978, p.44)
0.4	single dose	sub cut.	dog (1 year old female) (3 animals)	vascular engorgement in all organs, liver and kidney damage, gastrointest- inal lesions, death	Suchanan et al. 1954 (FIRL, 1978, p.34)
0.2	"	"	(1 animal)	liver and kidney damage, gastrointest- inal lesions, death	"
0.1	"	"	(12 animals)	liver and kidney effects (116 days)	"
1	single dose	oral	human	gastrointest- inal effects, cardiovasc- ular collapse, coma, oligurea, liver and kidney effects, death	Diaz-Rivera et al. 1950 (FIRL, 1978, p.23)
-	-	dermal	human (25 year old man, a white phos- phorus grenade exploded at his feet)	29% of body burned, massive hemolysis	Summerlin, 1967 (FIRL, 1978, p.26)

Array of Toxic Effects on Man and Other Mammals

Yellow phosphorus Chemical Group: Phosphorus and its inorganic compounds
(page 3)

dose in mg/kg bw/day (dose cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
-	-	dermal	human (38 year old woman with acute phosphorus burns)	skin burns, bone necrosis	Schautz, 1953 (FIRL, 1978, p.26)
-	-	dermal	human (46 year old man)	12.5% of body burned, hematuria, hemoglobin- urea, oligurea	Summerlin, 1967 (FIRL, 1978, p.26)
-	13 years	-	human (35 year old man packaging yellow phosphorus)	jaw bone necrosis	Heimann, 1946, (FIRL, 1978, p.28)

concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
500	10 minutes	inhal.	mouse	LCLo	ITII, 1975 p.420
150-160	60 days (0.5 hour/day)	inhal.	rabbit	decrease in hemoglobin and erythrocytes	Maruo, 1955, (FIRL, 1978, p.42)
150-160	60 days (0.5 hour/day)	inhal.	rat	effects on bone growth	Inuzuka, 1956 (FIRL, 1978, p.45)

Array of Toxic Effects on Man and Other Mammals

Yellow phosphorus (page 4)		Chemical Group: Phosphorus and its inorganic compounds			
concentration in mg/m ³ (conc. cited)	total exposure time; brief description	route	description of organism	effect (observation time)	citation (as reported in)
35 (+ 0.22 mg/l phosphor- us pent- oxide	- (2-6 hours at 7 hour inter- vals)	inhal.	human (5 workers cleaning a tank of "Cottrell Milk" without gas masks)	fever, hyper- emia of face and pharynx, tracheobron- chitis, toxic pneumonia, toxic hepatitis, leukocytosis, dysproteinemia, reduced acetyl- cholinesterase	Aizenshtadt et al., 1971 (FIRL, 1978, p.27)

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Yellow phosphorus Chemical Group: Phosphorus and its inorganic compound

BEHAVIOURAL EFFECTS

Nothing found in the literature reviewed.

CARCINOGENICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rat	oral	1.6	512 days (daily)	no tumours	Fleming et al. 1942 (FIRL, 1978, p.54)
rat	sub cut.	3.2	610 days (2x /week)	no tumours	Fleming et al. 1942 (FIRL, 1978, p.54)
dog	sub cut.	1	over 55 days (daily)	no tumours	Buchanan et al. 1954 (FIRL, 1978, p.54)

These studies, designed to evaluate the possible carcinogenic effects of the substance, was found in the literature reviewed. They did not result in reports of carcinogenic effects. No comprehensive evaluation of this information was found.

MUTAGENICITY

description of system	reported results	citation (as reported in)
L-cells	74% inhibition of the cell replication at 0.31 mg/l suspension, altered cellular morphology	Li et al., 1969, p.133

This study, designed to evaluate the possible effects of the substance on gene mutation, chromosomal mutations, on DNA repair or recombination or on transformation, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Yellow Phosphorus Chemical Group: Phosphorus and its inorganic compounds
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NEUROTOXICITY

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rabbit	intra- venous	(0.2-1.0 ml 1% oil solution)	15 weeks (2-3x/week)	pathological changes in brain	Ferraro et al. 1938 (FIRL, 1978, p.46)

This study, designed to evaluate the possible neurotoxic effects of the substance, resulted in a report of neurotoxic effects, but no comprehensive evaluation of this material was found in the literature reviewed.

POTENTIATION/ANTAGONISM

description of organism	chemical substance(s)	effect	citation (as reported in)
rat (Sprague Dawley, female)	glutathion and propyl gallate	protective against triglyceride infiltration of the liver and disaggregation of polyribosomes	Pani et al. 1972 (FIRL, 1978, p.37)

This study designed to evaluate the possible effects which could result from the combination of this substance with one or more other substances, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

Toxic Effects from Special Studies on Mammals and

Other Non-Marine Experimental Systems

Yellow Phosphorus Chemical Group: Phosphorus and its inorganic compounds
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PRIMARY IRRITATION

description of organism	route	dose in mg/kg bw (dose cited)	total exposure time; brief description	effect (observation time)	citation (as reported in)
rabbit (New Zeal- and white)	dermal appl.	10 000 (to 7.5 cm ²)	1 minute	10-20% of total body burned, decreased serum cal- cium, inc- reased serum phosphorus, death	Bowen et al. 1971 (FIRL, 1978, p.32)
rat	dermal (intro- duction into incision	10 000	-	skin burn, biochemical changes, liver and kidney damage, death	Ben Hur et al. 1973 (FIRL, 1978, p.33)
rabbit	dermal appl.	(1% sol- ution in peanut oil)	-	no primary skin irritation	Lee et al. 1975 (FIRL, 1978, p.32)

These studies, designed to evaluate the possible primary irritation effects of the substance, resulted in a report of the above effects, but no comprehensive evaluation of this material was found in the literature reviewed.

REPRODUCTIVE EFFECTS

Nothing found in the literature reviewed.

TERATOGENICITY

Nothing found in the literature reviewed.

Toxic or Other Effects on Marine Organisms and Ecosystems

Yellow Phosphorus

Chemical Group: Phosphorus and its inorganic compounds

System Organism Ecosystem Non-living	Life Stage	Concentration mg/L	Exposure Time	Effect	Time of Observation	Citation
Gadus morhua (Cod)	A	0.006	96 hrs.	LC50	96 hrs.	Maddock, B.G. and Taylor, D., 1976
Clupea harengus (Herring)	A	0.0025	130 hrs.	LC50	130 hrs.	Zitko, V. et al. 1970
Gadus morhua (Cod)	A	4.03	0.5 hrs.	LC50	29.9 hrs.	Fletcher, G.L. and Hoyle, R.J., 1972
Homarus americanus (Lobster)	A	0.12	96 hrs.	LC50	96 hrs.	Zitko, V. et al. 1970
Salvelinus fontinalis (Brook trout)	A	0.0005	50-100 hrs.	Decreased haematocrit	50-100 hrs.	Fletcher, G.L. et al. 1970
Gadus morhua (Cod)	A	0.00189	125 hrs.	LC50, no haemolysis	125 hrs.	Fletcher, G.L. and Hoyle, R.J., 1972
Clupea harengus (Herring)	A	0.0025	130 hrs.	Irreversible haemolysis red colour in all external areas	130 hrs.	Zitko, V. et al. 1970

Toxic or Other Effects on Marine Organisms and Ecosystems

Yellow Phosphorus (page 2)

Chemical Group: Phosphorus and its inorganic compounds

System Organism Ecosystem Non-living	Life Stage	Concentration mg/L	Exposure Time	Effect	Time of Observation	Citation
Homarus americanus (Lobster)	A	0.12	84 hrs.	Loss of all neuromuscular responses	84 hrs.	Zitko, V. et al. 1970
Homarus americanus (Lobster)	J	Contaminated mud	-	Degenerative changes in antennal gland and hepatopancreas	-	Aiken, D.E. and Byard, E.H., 1972
Clupea harengus (Herring)	A	Contaminated water	-	Leucocyte destruction, tissue damage	-	Aiken, D.E. and Byard, E.H., 1972

A - Adult
J - Juvenile

Analysis

Yellow phosphorus Chemical group: Phosphorus and its inorganic compounds

analytical method(s) (detection limit)	limitations/benefits	citation (as reported in)
gas-liquid chromatography (10 ⁻¹² g phosphorus)	-/requires only 5 minutes per estimation; specific for yellow phosphorus. Sensitivity 2 parts in 10 ¹²	Addison and Ackman, 1969

Legislation for the Protection of Man
and the Marine Environment

Yellow phosphorus Chemical group: Phosphorus and its inorganic compounds

general classifica- tion of con- trol mech- anism	country or political sub-division	description of control mech- anism	quantitative information (analytical method(s))	citation (as reported in)
control of substances in water	USA (EPA)	recommended concentration of yellow (elemental) phosphorus in marine or estuarine waters	0.1 ug/l	EPA, 1976, p.186

Yellow Phosphorus

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