MEDITERRANEAN ACTION PLAN
MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

ASSESSMENT OF ORGANOTIN COMPOUNDS AS MARINE POLLUTANTS IN THE MEDITERRANEAN

EVALUATION DES COMPOSES ORGANOSTANNIQUES EN TANT QUE POLLUANTS DU MILIEU MARIN EN MEDITERRANEE

In cooperation with

WHO IAEA

MAP Technical Reports Series No. 33

UNEP
Athens, 1989

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This volume is the thirty-third issue of the Mediterranean Action Plan Technical Report Series.

This series contains selected reports resulting from the various activities performed within the framework of the components of the Mediterranean Action Plan: Pollution Monitoring and Research Programme (MED POL), Blue Plan, Priority Actions Programme, Specially Protected Areas and Regional Oil Combating Centre.

Ce volume constitue le trente-troisième numéro de la série des Rapports techniques du Plan d'action pour la Méditerranée.

Cette série comprend certains rapports élaborés au cours de diverses activités menées dans le cadre des composantes du Plan d'action pour la Méditerranée: Programme de surveillance continue et de recherche en matière de pollution (MED POL), Plan Bleu, Programme d'actions prioritaires, Aires spécialement protégées et Centre régional de lutte contre la pollution par les hydrocarbures.

INTRODUCTION

The Mediterranean States meeting in Barcelona in 1975, adopted an Action Plan for the Protection of the Mediterranean Sea against pollution. The legal framework for this co-operative regional programme is the Convention for the Protection of the Mediterranean Sea against pollution (also known as Barcelona Convention) and its related protocols which has been ratified by 17 Mediterranean states and the European Economic Community. So far, four protocols have been adopted and entered into force one of them being the Protocol for the Protection of the Mediterranean Sea against pollution from Land-based Sources (LBS protocol).

The MED POL programme is the scientific/technical component of the Mediterranean Action Plan and is concerned with assessing and evaluating the environmental problems. The environmental assessment undertaken, provides a basis for assisting national policy makers to manage their natural resources in a more effective and sustainable manner.

The specific objectives of the MED POL programme are designed to provide the Contracting Parties to the Barcelona Convention, inter alia, with:

- information required for the implementation of the Convention and the protocols;
- indicators and evaluation of the effectiveness of the pollution prevention measures taken under the Convention and the protocols;
- scientific information which may lead to eventual revisions and amendments of the relevant provisions of the Convention and the protocols and for the formulation of additional protocols;
- information which could be used in formulating environmentally sound national, bilateral and multilateral management decisions essential for the continuous socio-economic development of the Mediterranean region on a sustainable basis.

One of the basic components of the MED POL porgramme is the implementation of the LBS protocol according to which Contracting Parties undertake to eliminate pollution from land-based sources by the substances listed in Annex I to the Protocol. Assessment documents have already been prepared and recommendations adopted for mercury and mercury compounds, cadmium and cadmium compounds, used lubricating oils, organohalogen compounds and organotin compounds. Assessment documents are already under preparation for the remaining groups of substances of Annex I, i.e.:

- organophosphorus compounds
- persistent synthetic materials which may float, sink or remain in suspension
- carcinogenic, teratogenic or mutagenic substances
- radioactive substances

The present document on the assessment of organotin compounds as marine pollutants in the Mediterranean, was presented to the First Meeting of the Scientific and Technical Committee (Athens, 23-27 May 1988) as document UNEP(OCA)/MED WG.1/7. The Annex of this document includes the report on the results of the FAO/UNEP/IAEA/WHO Pilot survey of organotins in selected Mediterranean areas which was prepared by the review meeting on the survey (Erdemli, Turkey, 7-9 November 1988) and published as document FIR/MEDPOL/OT/5.

Based on this assessment document, a set of recommendations on organotin compounds was adopted by the Sixth Ordinary Meeting of the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against pollution and its related protocols (Athens, 3-6 October, 1989).

INTRODUCTION

La réunion d'Etats méditerranéens tenue à Barcelone en 1975 a adopté un Plan d'action pour la protection de la mer Méditerranée contre la pollution. Le cadre juridique de ce programme de coopération régionale consiste en la Convention pour la protection de la mer Méditerranée contre la pollution (connue également comme Convention de Barcelone) avec les protocoles y relatifs qui a été ratifiée par 17 Etats méditerranéens et la Communauté économique européenne. Jusqu'à ce jour, quatre protocoles ont été adoptés et sont entrés en vigueur; l'un d'eux est le protocole relatif à la protection de la mer Méditerranée contre la pollution d'origine tellurique.

Le programme MED POL est la composante scientifique/technique du Plan d'action pour la Méditerranée et vise à évaluer les problèmes de l'environnement. L'évaluation de l'environnement qui est entreprise fournit une base permettant d'aider les décideurs nationaux à gérer leurs ressources nationales d'une manière plus efficace et judicieuse.

Les objectifs spécifiques du programme MED POL sont destinés à procurer notamment aux Parties contractantes à la Convention de Barcelone:

- les renseignements nécessaires pour l'application de la Convention et de ses protocoles;

- des indicateurs et une évaluation de l'efficacité des mesures de protection prises en vertu de la Convention et de ses protocoles;

- des renseignements scientifiques susceptibles d'aboutir à des révisions et modifications des dispositions concernées de la Convention et des protocoles et de permettre la formulation de protocoles supplémentaires;

- des renseignements pouvant servir à formuler des décisions de gestion au niveau national, bilatéral et multilatéral qui soient respectueuses de l'environnement et essentielles à la poursuite du développement socio-économique de la région méditerranéenne sur une base judicieuse.

L'une des composantes fondamentales du programme MED POL consiste en l'application du Protocole tellurique conformément auquel les Parties contractantes s'engagent à éliminer la pollution d'origine tellurique par les substances énumérées à l'annexe I au dit Protocole. Des documents d'évaluation ont déjà été établis et des recommandations adoptées pour le mercure et les composés de mercure, pour le cadmium et les composés de cadmium, pour les huiles lubrifiantes usées, pour les composés organohalogénés et pour les composés organostanniques. Des documents d'évaluation sont déjà en cour d'élaboration pour les groupes restants de substances de l'annexe I, à savoir:

- les composés organophosphorés
- matières synthétiques persistantes qui peuvent flotter, couler ou rester en suspension
- substances cancérigènes, tératogènes ou mutagènes
- substances radioactives

Le présent document sur l'évaluation des composés organostanniques en tant que polluants du milieu marin en Méditerranée, a été établi par l'Unité de coordination du Plan d'action pour la Méditerranée, en étroite coopération avec la FAO, l'OMS et l'AIEA. Il a été présenté à la première réunion du Comité scientifique et technique (Athènes, 23-27 mai 1988) sous la cote UNEP(OCA)/MED WG.1/7. En annexe de ce document figure le rapport sur les résultats de l'étude pilote FAO/PNUE/AIEA/OMS des organostanniques dans certaines zones de la Méditerranée, rapport rédigé par la réunion chargée de l'examen de l'étude pilote (Erdemli, Turquie, 7-9 novembre 1988) et qui a été publié sous la cote FIR/MEDPOL/OT/5.

Sur la base de ce document d'évaluation, un ensemble de recommandations sur les composés organostanniques ont été adoptées par la Sixième réunion ordinaire des Parties contractantes à la Convention pour la protection de la Méditerranée contre la pollution et aux Protocoles y relatifs (Athènes, 3-6 octobre 1989).

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ASSESSMENT OF ORGANOTIN COMPOUNDS AS MARINE POLLUTANTS IN THE MEDITERRANEAN

1. BACKGROUND

The Protocol for the Protection of the Mediterranean Sea against Pollution from Land-based Sources (LBS protocol) is the third Protocol to the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention); it was signed in May 1980 and entered into force in June 1983.

According to this Protocol, the Contracting Parties shall take all appropriate measures to prevent, abate, combat and control pollution of the Mediterranean Sea Area caused by discharges from rivers, coastal establishments or outfalls, or emanating from any other land-based sources within their territories.

Article 5 of this Protocol stipulates that:

- The Parties undertake to eliminate pollution of the Protocol Area from land-based sources by substances listed in Annex I to this Protocol;
- To this end they shall elaborate and implement, jointly or individually, as appropriate, the necessary programmes and measures;
- These programmes and measures shall include, in particular, common emission standards and standards for use.

Organotin compounds and substances which may form such compounds in the marine environment (with the exception of those which are biologically harmless or which are rapidly converted into biologically harmless substances) are included in Annex I to this Protocol.

The Meeting of Experts for the Technical Implementation of the LBS protocol (December, 1985) proposed that the measures to be recommended to the Contracting Parties for each group of substances should be based on an "assessment document" which should be prepared by the Secretariat. According to this proposal, which was adopted by the Fifth Ordinary Meeting of the Contracting Parties to the Barcelona Convention (September, 1987) such assessments should include inter alia chapters on:

- sources, point of entries and amounts of pollution for industrial, municipal and other discharges to the Mediterranean Sea;
- levels of pollution;
- effects of pollution;
- present legal, administrative and technical measures at national and international level.

Prior to the preparation of this assessment document a small ad-hoc meeting on organotin compounds was convened in Athens in October 1987 (FAO/UNEP/IAEA/WHO, 1987). The meeting agreed on an annotated outline of the assessment document and recommended proposals for control measures and for further research and monitoring work.

The present document, which was prepared by the Secretariat with the help of consultants and in close cooperation with FAO, WHO and IAEA, evaluates information on the contamination of the marine environment by organotin compounds, the ecological and human health significance of such contamination, and proposed measures for their control in the Mediterranean area.

2. HARMFUL ORGANOTIN COMPOUNDS

The increasing worldwide use of organotin compounds, and the known toxic potential of some of them, has given rise in recent years to increasing concern about the ecotoxicology of these chemicals. This concern is reflected in the inclusion of organotin compounds as a group in Annex I of the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources (UNEP, 1982) and in the 'priority list' of environmental contaminants prepared under the Toxic Substances Control Act (ToSCA) by the Environmental Protection Agency (EPA) of the USA (US EPA, 1982). Organotin compounds are chemicals containing tin-carbon bonds, with a general formula R_nSnX_{4-n}, where n = 1-4; R = alkyl or aryl group; X = halogen, OR', etc.

2.1 Production and use patterns

The wordwide production of organotin compounds had risen from a very low level in the late 1940's (UK DOE, 1986) to 5,000 tonnes in 1955, 24,000 tonnes in 1975 and to more than 30,000 tonnes per year at present (WHO, 1980; Blunden et al., 1984; Fig. 1).

In the late 1940's diorganotin derivatives were introduced as degradation inhibitors of polyvinyl chloride (PVC). In the 1950's triorganotin compounds were used extensively as biocides in agriculture and during the 1960's triorganotins began to be used in wood preservatives and in antifouling paints. The specific uses of various organotin compounds are given in Table I.

The uses of organotin compounds can be divided into two main categories: nonbiocidal and biocidal.

The nonbiocidal uses account for about 70% of the actual worldwide use of organotin compounds (Blunden et al., 1984; Thompson et al., 1985). The main nonbiocidal use (around 60-65% of total use and essentially diorgano-derivatives, (Table I) is for PVC stabilization; it was estimated that some 20,000 out of the 30,000 tonnes used in 1980 were for this purpose (UK DOE, 1986). Diorganotin derivatives, at concentrations ranging from 0.5 to 2% on polymer weight basis, are effective in preventing PVC degradation induced by UV light, prolonged exposure or heating (Evans, 1974; Blunden et al., 1984). Sulfurcontaining mercaptide compounds such as dibutyltin bis (isooctyl mercaptoacetate) are effective for heat stabilization; nonsulfur-containing compounds, such as dibutyltin dilaurate, are mainly used as protection against UV light (Thompson et al., 1985).

Another important nonbiocidal use of organotin compounds is as catalysts; dibutyltin derivatives (eg. dibutyltin dilaurate, dibutyltin diacetate) are used for this purpose in the production of polyurethane foams (Evans, 1974).

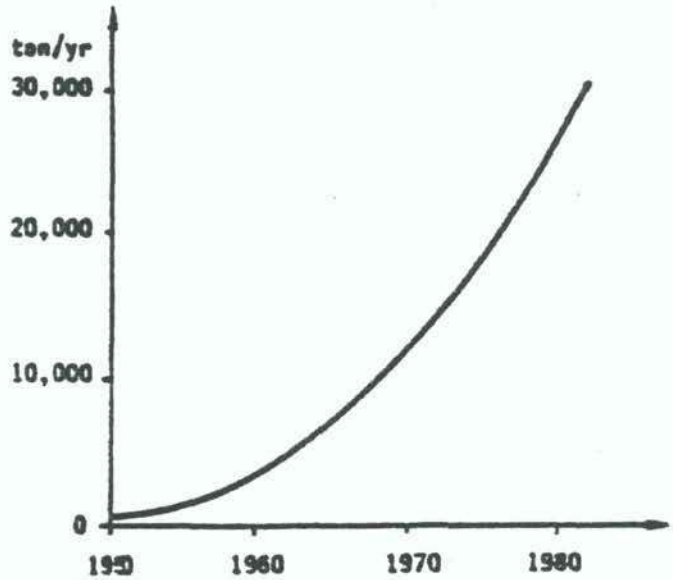

Fig. 1 Worldwide uses of organotin compounds

Table I

Uses of organotin compounds (from Blunden et al., 1984).

use	compound
	R_3SnX
Agriculture (fungicides, etc.)	Ph_3SnX (X=OH, OAc)
(acaricides)	(cyclo-C_6H_{11})$_3$SnX
	(X=OH, $-\overset{H}{N}-C=N-\overset{H}{C}=N$)
	$((PhMe_2CCH_2)_3Sn)_2O$
Antifouling paints (biocides)	Ph_3SnX (X=OH, OAc, F, Cl..)
	$Ph_3SnO.CO.CH_2CBr_2.CO.OSnPh_3$
	Bu_3SnX (X=F, Cl, OAc)
	$(Bu_3Sn)_2O$
	$Bu_3SnO.CO.CH_2CBr_2.CO.OSnBu_3$
	$Bu_3SnO.CO.(CH_2)_4.CO.OSnBu_3$
	$(-CH_2CMe(CO.OSnBu_3)-)_n$

Table I (continued)

use	compound
Wood preservative fungicides	$(Bu_3Sn)_2O$
	Bu_3Sn(naphthenate)
	$(Bu_3Sn)_3PO_4$
Stone preservation	$(Bu_3Sn)_2O$
Disinfectants	$Bu_3SnO.CO.Ph$
	$(Bu_3Sn)_2O$
Molluscicides	Bu_3SnF
	$(Bu_3Sn)_2O$
R_2SnX_2	
Heat and light stabilizers (PVC)	$R_2Sn(SCH_2.CO.OOct^i)_2$
	(R=Me,Bu,Oct,$BuO.CO.CH_2CH_2$) $(R_2SnO.CO.CH:CH.CO.O)_n$
	(R=Bu,Oct)
	$R_2Sn(O.CO.CH:CH.CO.OR')_2$
	(R=Bu; R'=Oct)
	$Bu_2Sn(O.CO.C_{11}H_{23})_2$
	$Bu_2Sn(SC_{12}H_{25})_2$
Catalysts (silicones, polyurethane	$Bu_2Sn(O.CO.R')_2$
foams, transesterification	(R'=Me, Oct, $C_{11}H_{23}$)
reactions)	$(Bu_2SnO)_n$
Antihelminthics (for poultry)	$Bu_2SN(O.CO.C_{11}H_{23})_2$
$RSnX_3$	
Heat stabilizers (PVC)	$RSn(SCH_2.CO.OOct^i)_3$
	(R=Me,Bu,Oct,$BuO.CO.C_2H_4$)
	$(BuSnS_{1.5})_4$
Catalysts (transesterification react.)	$(BuSn(O)OH)_n$
	$BuSn(OH)_2Cl$

In addition there are minor uses, essentially related to industrial activities, including heat stabilization of material other than PVC (transformer and lubricating oils, rubber paints, cellulose acetate, polyethylene and polypropylene) by diorganotin compounds (Thompson et al., 1985), as well as the waterproofing of paper and textiles (Luijten, 1972; UK DOE, 1986).

The biocidal applications are estimated to account for about 30% of total present use. In agriculture some organotin compounds (triphenyl- and tricyclohexyl-derivatives; Worthing and Walker, 1983) are used as fungicides and acaricides. Bis(tributyltin) oxide is used as a wood preservative (Blunden and Chapman, 1982). A minor use, although rapidly increasing in recent years, is as an antifouling agent in water; microorganisms, plants and animals can settle on submerged parts of boats, ships, docks, and in water-cooling pipes of coastal power stations and of industrial plant. Marine fouling of this type represents a serious problem for the shipping industry and also for pleasure boat owners by increasing hull friction, thus reducing vessel speed and increasing fuel consumption. Also, sub-surface fouling accelerates corrosion and makes maintenance more expensive, blocks seawater pipes and ships' valves, and alters signals from immersed acoustic and electronic navigation devices. As reported by Simmonds (1986), in 1952 about 2,000 species of fouling organisms had been identified and the list is now probably much longer. Many antifouling systems have been used in the past to control these organisms, ranging from copper and lead sheeting to the introduction of antifouling paints containing copper, lead, arsenic and mercury (UK DOE, 1986). Because of the high toxic potential to man of arsenic, mercury and lead, and some corrosion problems caused by the use of copper (as cuprous oxide), triorganotin-based antifouling paints were introduced some 20 years ago. These paints have as active ingredients bis (tributyltin) oxide, tributyltin fluoride and other tributyl- and triphenyltin salts (Evans and Smith, 1975).

A schematic representation of the relative weight of the biocidal and nonbiocidal uses of organotin compounds is given in Fig. 2.

2.2 Routes of entry into the marine environment

In principle, contaminants can reach the marine environment both directly via air or water as a result of losses during production and processing, use and disposal, and indirectly as a consequence of biotic and abiotic transformations.

At present little information is available in the current scientific literature on amounts of organotin compounds released into the environment by way of production and processing operations. So far as the marine environment is concerned, taking into account the high toxicity of some organotin derivatives for aquatic organisms, the absence of information on pollution incidents from these sources (except as accidental spills) indicates that they may not be important. However, identification of the major production industries in the Mediterranean basin, and an evaluation of losses of these compounds into their surrounding environment, might be a subject for future research and investigation.

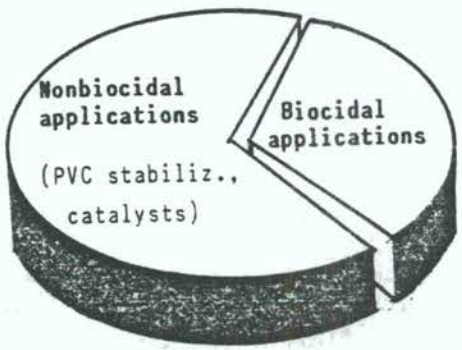

Fig. 2 Uses of organotin compounds (1980)

Non-biocidal uses

As the major use of organotin compounds is as a stabilizer in rigid PVC, the potential of this use as an environmental contamination source must be considered. Organotin compounds used for this purpose are essentially diorganotin (with a minor component of monoorganotin) derivatives (Blunden et al., 1984; Table I). The stabilized PVC is currently used for potable water piping, beverage bottles and food packaging. This indicates that the rate of release of these diorganotin derivatives into water should be very low, in order to avoid contamination of food and beverages for human consumption (Blunden et al., 1984).

Little is known about the environmental fate of diorganotin compounds arising from stabilized PVC, or other materials produced by means of catalysis by organotin derivatives (such as polyurethane foams and silicone elastomers). The incineration of waste containing such material is assumed to transform organotins into inorganic tin (Bock, 1981), but disposal by landfill could result in organotin compounds derived from plastics occurring in the leachate. However, leaching of dibutyltin compounds from PVC and other materials is likely to be minimal because of a low release rate from plastic matrices, and a relatively high affinity for the soil.

The key physico-chemical property regulating these phenomena is water solubility. For diorganotin compounds (excluding dimethyltin derivatives eg. Me_2SnCl_2), the solubility in water is of the order of 10 mg l^{-1} or less, and decreases with the length of the alkyl chains (Table II).

Considering that the locations of the majority of use and disposal sites of these chemicals are inland and relatively far from the marine environment, some time will be taken for them to reach the sea. Taking into account the present knowledge on degradation rates of diorganotin compounds, the actual loads of these contaminants reaching the Mediterranean from land-based sources by way of leaching, runoff and transportation via water, would appear to be negligible. Similar conclusions can be derived for the soil-air route, because of the low volatility and UV light instability of these chemicals.

Table II

Aqueous solubility of some diorganotin compounds (from Blunden et al., 1984).

compound	solubility in dist. water (mg l^{-1})
Me_2SnCl_2	20,000
Bu_2SnCl_2	4-50
$Bu_2Sn(OAc)$	6
$Bu_2Sn(O.C.Oct^i)_2$	6
Oct_2SnCl_2	<1

In conclusion, the load of diorganotin compounds likely to reach the marine environment, and the Mediterranean in particular, from nonbiocidal applications, by way of water and air transport appears at present to be of secondary importance.

Biocidal uses

Biocidal uses account for about 30% of total organotin manufacture. This is roughly divided equally between uses in agriculture as wood presevatives, and for antifouling treatments.

The compounds involved are mainly triorganotins; about 3-4,000 tonnes/annum are used for each of these categories of use.

Agricultural use is characterized by dispersive application to land, and by leaching into water they could generate many secondary pollution (nonpoint) sources. Because of the absence of accurate information on the actual usage and occurrence of these pesticides (mainly tricyclohexyltin and triphenyltin derivatives) in the Mediterranean area, predictions of their distribution in the environment have to be made by use of a model.

The predicted environmental distribution of fentin hydroxide (Ph_3SnOH, a non-systemic fungicide) applied at 250-450 g/ha (Worthing and Walker, 1983), into Mackay's 'Unit World' (Mackay 1979; Mackay and Paterson, 1981) is shown in Table III.

Table III

The equilibrium environmental distribution (20 ^{o}C) of fentin hydroxide, calculated from a fugacity model (Mackay, 1979). Input data: molecular weight 367; melting point 118 ^{o}C; water solubility 1 mg l^{-1}; vapour pressure 47 uPa (Worthing and Walker, 1983).

compartment	accessible volume (m^3)	% distribution
air	$6X10^9$	0.026
water	$7X10^6$	4.285
soil	$4.5X10^4$	49.147
aquatic biomass	7	0.015
susp. solids	35	0.077
sediments	$2.1X10^4$	46.447

This Unit World represents about 1/500,000,000 of the biosphere but assuming no degradation occurs, the chemical should partition in this manner on a global scale at equilibrium. Although this is a very crude model, the calculations do show that fentin hydroxide has a high affinity for soils and sediments, little for water and very weak for air. From these predictions it seems reasonable to conclude that only a very small percentage of this pesticide, when used in inland areas, will reach the sea. Similar conclusions can be reached for other triorganotin pesticides, all of which are characterized by similar high affinities for soil.

An evaluation of the pollution potential for triorganotin compounds in the Mediterranean can be made on the assumption that they are at equilibrium in the total biosphere, so that 5% of the total load is in the water. In a "worst possible case" scenario, if the annual global production for biocidal applications in agriculture and as a wood preservative (ca. 7,000 tonnes) was used in the Mediterranean area, and 5% was transported to the sea (volume 3.5 million km^3) then this input would result in an average concentration of 0.1 ng l^{-1} in the water.

This value is at least one order of magnitude below the "no-observed-effect level", NOEL, for triorganotin compounds (see Section 6.2) and, as it does not take into account degradation rates, it represents an over-estimation of several orders of magnitude over the level which might be obtained from these sources. Although estuaries will contain higher concentrations, these are unlikely to reach the NOEL.

In contrast, the input of organotins into marine environments from the use of antifouling treatments (3-4,000 tonnes per year worldwide, at present) differs from the other biocidal compounds in that their use is in the aquatic environment itself. Therefore, the load from this source will be more important that those from all other uses because although the possibility of large scale effects (eg. throughout the Mediterranean) is extremely remote, there is little doubt that severe contamination problems could occur on a local scale.

In conclusion, an analysis of the properties and uses of organotin compounds indicates that those used in antifoulants represent the priority problem in the marine environment.

3. SOURCES AND INPUTS INTO THE MEDITERRANEAN

At present there is no information on the theoretical or actual load of organotin compounds discharged into the Mediterranean. However, as shown above, it seems likely that the greatest pollution potential for the Mediterranean arises from biocidal use of triorganotin compounds in antifouling compounds, localised around areas where these substances are commonly used.

However, methyltin produced by the methylation of inorganic tin, both by biological and abiotic mechanisms should also be considered as a possible source of these chemicals in the marine ecosystem (Thompson et al., 1985). Such methyl-derivatives (which are much less toxic to aquatic organisms) are often detected in areas contaminated by the more toxic tributyl- and triphenyltin compounds and their presence is more likely to be the result of biodegradation of these substances.

3.1 Organotin compounds as antifouling agents

The main uses of antifouling agents are in cooling-water pipes for electric power plants and other industries such as chemical and steel factories, and in paints for boats, ships, and marine structures. The use of TBT coatings on structures used in mariculture may represent a minor input to the marine environment.

In considering the organotin compounds used as antifoulants for cooling system protection (mainly tributyltin derivatives), more information is needed about the number, location and the treatment programs of the industrial plants which use these chemicals. The potential load to the marine environment originating from this use may not be negligible. For example 7-10 ug l^{-1} (as active ingredient, eg. bis(tributyltin) oxide) is the effective concentration for protecting pipes against fouling organisms; the water flow in these pipes may range from 10,000 to 200,000 m^3 h^{-1}.

This means that from these treated pipes, between 1.7 and 48 kg d^{-1} of tributyltin compounds could be discharged into the sea. Such a load could be relatively significant as 15 kg d^{-1} represents the input of tributyltin from 100 large ships (ie. 100 metre in length) with 1,500 m^2 of painted surface each, assuming a constant release rate of 10 ug cm^{-2} d.

As stated above, organotin-based antifouling paints are replacing previous formulations such as those containing only cuprous oxide because they do not promote corrosion (particularly in aluminium vessels) and are said to give longer protection. Also, organotins can be degraded to inorganic tin (Sn IV), which is not considered to be of high toxicological importance.

The main triorganotin compounds used are bis(tributyltin) oxide, tributyltin fluoride, and, to a lesser extent, triphenyltin salts. These compounds may be incorporated into a polymer matrix in the so called "free-association" paints, or they can be directly attached to a polymer ("self-polishing" or "ablative" paints). The former type of paint is characterized by a shorter life-time (1-2 years) with the leaching of active ingredients following an exponential decay (Fig. 3). The leaching rate becomes more regular in the latter type (Fig. 3) because the active ingredients are released when the organotin-ester linkage is hydrolysed by seawater. The depleted ester layer, which is composed of hydrophilic free carboxylate groups has little integral strength and is eroded by water movement, so exposing a new layer of organotin-containing polymer (Stebbing, 1985).

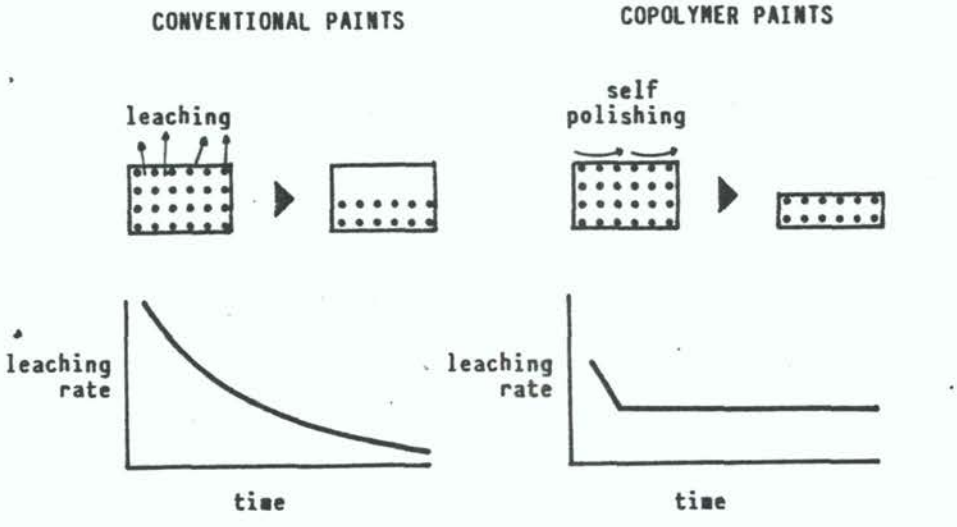

Fig. 3 Schematic representation of the organotin release rate in free association and copolymer paints (from Stebbing, 1985)

The leaching rate represents the input rate of these contaminants into the marine environment. Therefore, the results of quantitative leaching rate tests carried out by the UK Ministry of Agriculture, Fisheries and Food (MAFF) and from the Paintmakers' Association of Great Britain (UK DOE, 1986; Fig. 4) are of considerable relevance in this context.

It is important to note that the free association paints have to provide a leaching rate of 1-5 ug cm^{-2} d in order to give effective protection even after long periods of immersion. Because the leaching rate is an exponential decay, the initial rates are generally much higher at 15-50 ug cm^{-2} d (Fig. 4). According to the UK Paintmakers' Association, the release of tributyl tin from copolymer paints is less than one quarter of that from free association paints over a season (Fig. 4 A; UK DOE, 1986). As shown in Fig. 4, different results were obtained by the UK MAFF using a different experimental protocol; the total emission of organotin compounds from copolymer paints appears to be lower than the input from free association paint in winter, but very similar in summer.

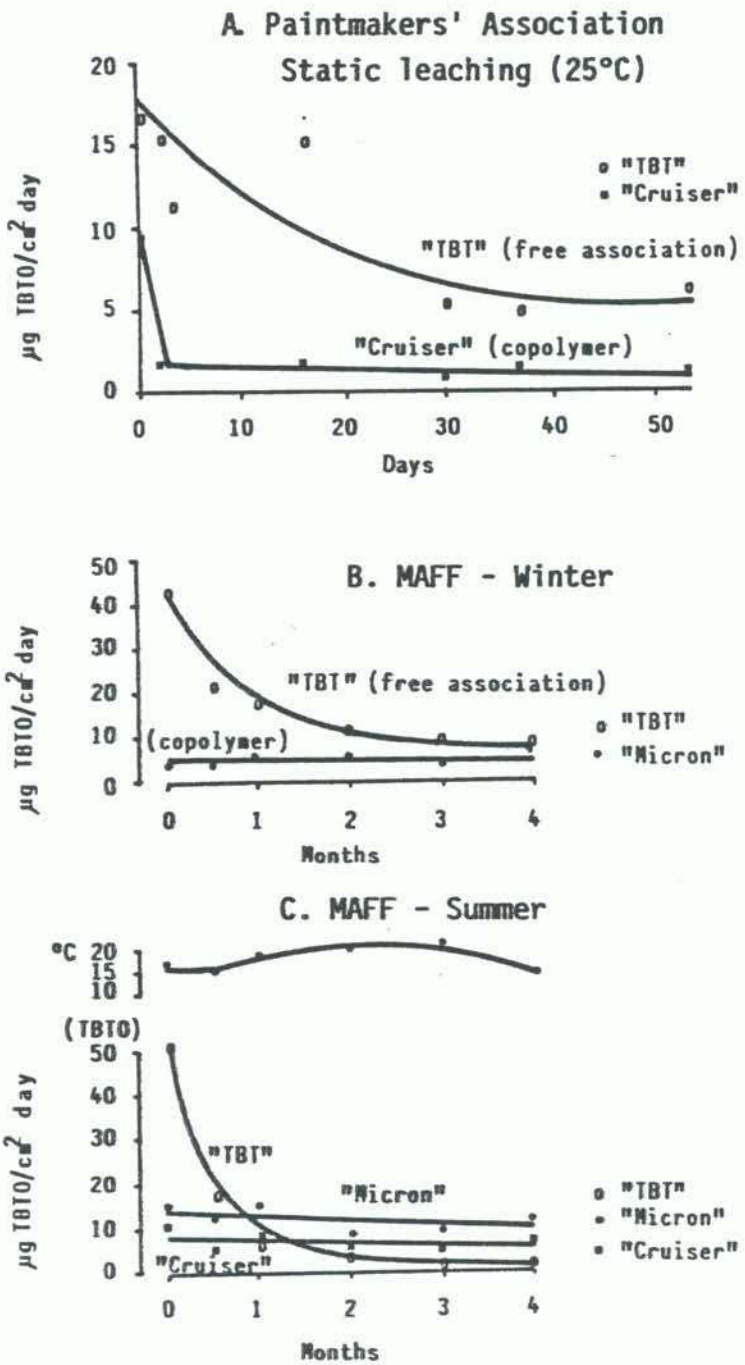

Fig. 4 Results of leaching rate tests (from UK DOE, 1986)

The present use of these paints on small boats and large ships leads to a generally diffuse load of TBT and to a lesser extent TPT, which could probably be assumed as negligible on a "total Mediterranean" basis. On the other hand, experience elsewhere in Europe and N. America indicates that high contamination levels can be expected in particular locations such as marinas, moorings and harbours where a large treated surface is immersed in shallow waters, and where the exchange of water is low. Also, localised inputs can occur from the disposal of unused or spilt paints, old containers in sites where boats are cleaned before repainting, and dry docks where old paint is removed in particulate form and discharged into the sea by wash-out or runoff.

4. ENVIRONMENTAL DISTRIBUTION OF ORGANOTIN COMPOUNDS

The environmental distribution, pathways and fate of contaminants are controlled by both environmental and intrinsic factors. Whilst the environmental factors (eg. temperature, pH, turbulence, advection...) fluctuate within a relatively large range as a function of location and time, intrinsic factors are strictly related to physico-chemical and partition properties of the pollutant. A schematic representation of transport and transformation processes for chemical compounds in environmental compartments is shown in Fig. 5.

4.1 Evaluative approaches

The main trends in transportation and distribution phenomena for chemicals can be calculated from their basic physico-chemical properties, such as water solubility (S) and vapour pressure (v.p.); with a high value of S, the chemical will show considerable affinity for the aqueous phase, whilst a low S value indicates a tendency to migrate away from water. Water solubility is also correlated with uptake by biota and with adsorption-desorption on solid substrates in the water.

The bioaffinity of a chemical substance can be expressed as its bioconcentration factor, BCF, which can be defined as the ratio between the concentration of a chemical in a test organism and the concentration of the same compound in the environmental compartment surrounding the organism, at equilibrium; in aquatic systems for example, it is the ratio between the concentration in a fish or a mollusc and that in the surrounding water.

4.2 Evaluating the environmental distribution of relevant organotin compounds

The main triphenyltin (TPT) compounds used as biocides are the chloride Ph_3SnCl, the acetate $Ph_3SnOCOCH_3$, and the hydroxide Ph_3SnOH, which are little used as antifoulants. The principal antifouling agents are the tributyltin compounds; the chloride (Bu_3SnCl; TBTCl), and the bis(tri-n-butyltin) oxide $(Bu_3Sn)_2O$ or TBTO).

There is little consensus in the literature on tributyltin speciation products in seawater: Eng and coworkers (1986) found that the two tributyltin compounds mentioned above were all converted in artificial seawater to the hydroxide analog (TBTOH). On the other hand Laughlin et al., (1986a) found that TBTO dissolved in seawater resulted in an equilibrium mixture of speciation products composed of TBTCl, TBTOH, the hydroxy complex ($TBTOH_2$), and a tributyltin carbonate species; the equilibrium species composition was dependent on the concentration of Cl ion, dissolved CO_2 and pH. At a pH ca. 8, which is typical of seawater, three butyltin products were found: TBTCl, TBTOH and the carbonate species, where TBTCl accounted for 60% of the tributyltin analogs.

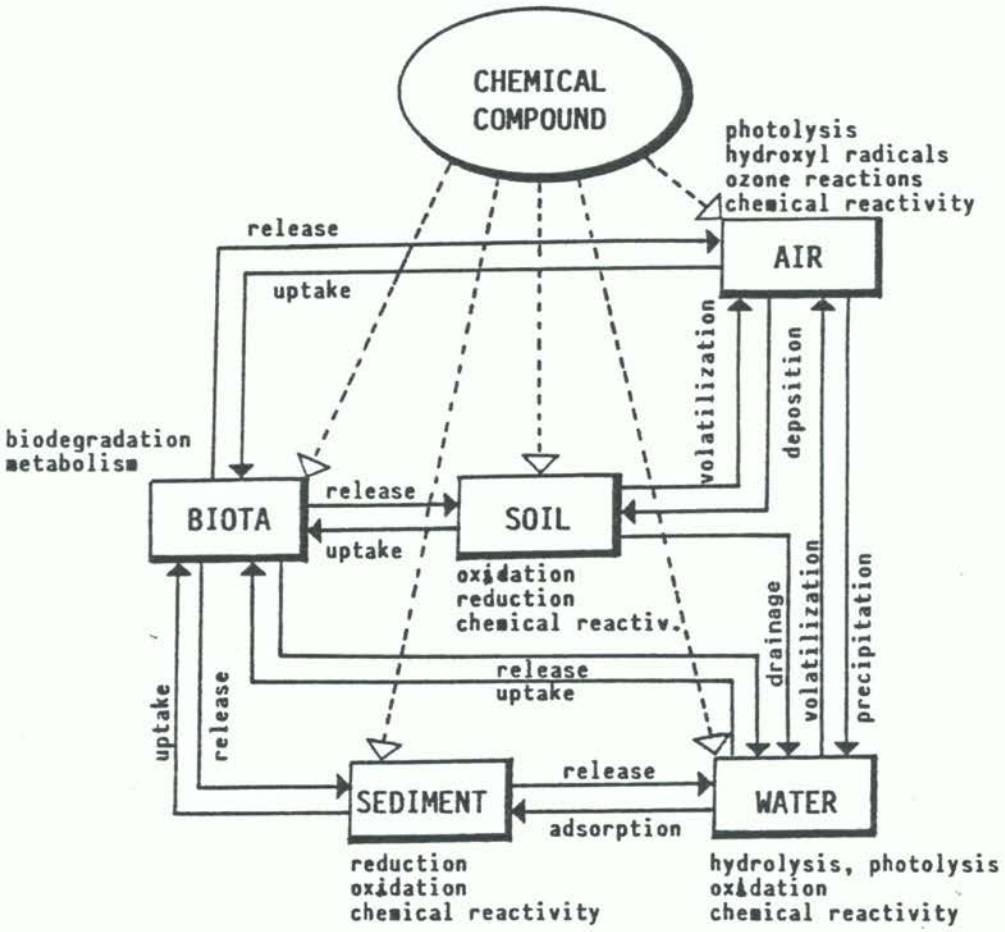

Fig. 5 Transport and transformation processes for chemical compounds in environmental compartments (from Calamari and Bacci, 1987)

As in the case of many other chemicals, information on the main physico-chemical properties is incomplete and sometimes contradictory; water solubilities may range within an order of magnitude and there is little information on vapour pressures. However, from the water solubility and the vapour pressure values of both TPT and TBT analogs, they generally appear to be relatively lipophilic chemicals of low volatility.

The solubility of the TBT compounds in seawater is of the order of 10 mg l^{-1}, while that for TPT derivatives is lower at 1 mg l^{-1} or less (Table IV). However, while TPT analogs are solid, with a m.p. of the order of 100 ^{o}C (Table IV), TBT analogs are liquids. Nevertheless, the two groups have similar octanol-water partition coefficient (K_{OW}) values; Yalkowsky et al. (1983) found that the crystal interaction energy of solids has a significant effect on solubility, but has no effect on partitioning.

Octanol-water partition coefficients for TPTCl and TBTO are given in Table V. These K_{OW} values for TPTCl and TBTO are more similar than their water solubilities (Table IV); a factor of 2 compared with an order of magnitude.

Table IV

Solubilities in water and seawater and vapour pressures of principal TPT and TBT compounds.

compound	solubility ($mg\ l^{-1}$) water	seawater	m.p. (°C)	v.p. (mmHg)
TPTCl	40 (20°C)*	<1 (ca. 20°C)*	105-107*	$5X10^{-4}$ (150-200°C)*
	78 (30°C)*			0.5 (185°C)*
TPTOH	8 (20°C)*	<1 (ca. 20°C)*	118-120*	$4X10^{-7}$ (20°C)+
TPTOAc	<3.3-28 (20°C)*	<1 (20°C)*	120-124.5*	$1,3\ 10^{-6}$ (30°C)i
TBTCl	17**	5.4-50**	liquid	no data
TBTO	18-19.5**	1.4-10**	liquid	$6.4X10^{-7}$ (20°C)**
				$\sim 5X10^{-6}$ ii
				$1.2X10^{-4}$ (20°C)**

*Bock, 1981; +Worthing and Walker, 1983; iWHO, 1976; **Blunden et al., 1984; iiSchweinfurth and Günzel, 1987.

Table V

Octanol-water partition coefficients (K_{OW}) for two organotin compounds.

compound	Log K_{OW}	reference
TPTCl	4.1	Wulf and Byington (1975)
TBTO	3.74-3.85	Laughlin et al. (1986a)

The K_{OW} was shown to be related to salinity, with a minimum value of 5500, at 25°/oo and increasing at higher or lower salinities, to a maximum value of 7000 in deionized water (Fig. 6).

According to Laughlin et al. (1986a), the effect of salinity on K_{OW} is negligible within the range 15-32°/oo (Fig. 6).

It can be predicted that for a marine sediment containing 4% of organic carbon and a density of 1.5 g cm^{-3}, the sediment/water partition coefficient expected for TBTO and TPTCl will be in the order of 10^2, and the expected BCF value will range from 300 and 600. Higher BCF values for sediments have been obtained from laboratory experiments (Laughlin et al., 1986b).

Concluding this subsection, TBT and TBT derivatives are chemicals which, in marine ecosystems, will tend to accumulate in sediments. Whether this will occur in practice will depend on rates of degradation in water and sediment. (Section 4.5.2).

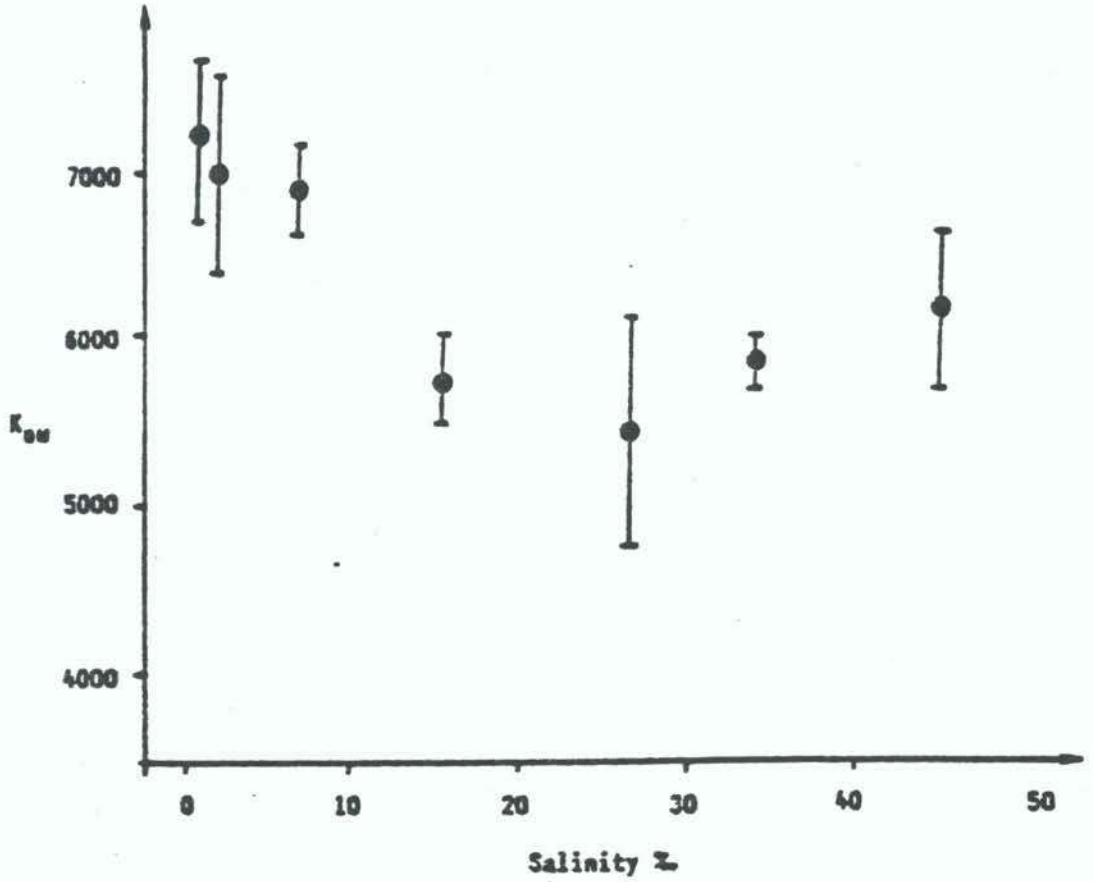

Fig. 6 Trend of the octanol-water partition coefficient, K_{OW}, of TBTO as a function of salinity (from Laughlin et al., 1986a)

4.3 Analytical techniques

Several analytical approaches have been used for the quantitative determination of organotin compounds in environmental matrices. These include spectrophotometry and spectrofluorimetry, electrochemical techniques, atomic absorption spectrometry, liquid chromatography and gas chromatography. Other techniques such as infrared spectrometry, nuclear magnetic resonance and Mossbauer spectrometry can be used to characterise tin compounds and to investigate on their molecular structures (Crompton, 1974), but these have received little attention from environmental chemists because of their low sensitivity.

4.3.1 Spectrophotometry, spectrofluorimetry and electrochemistry

As recently reported by Thompson et al. (1985), the earliest method for the analysis of organotins by spectrophotometry was that of Aldridge and Cremer (1957) for the colorimetric determination of diethyltin and triethyltin compounds. This method is based on the reaction of diethyltin and triethyltin chlorides with dithizone, resulting in coloured complexes; the method differentiates between the dialkyltin and trialkyltin species, without determining the identity of the alkyl groups. Other colorimetric reagents,

such as diphenylcarbazone, dithiol, phenylfluorone and pyrocatechol violet, have been used (Sherman and Carlson, 1980; Omar and Bowen, 1982). The limitation of these methods is that all these reagents form complexes with inorganic tin as well as with many other metals. Therefore, for organotin determinations, the sample must be mineralised to obtain inorganic tin, thus requiring an efficient pretreatment to separate out the different organotin compounds.

Fluorimetric techniques are generally more sensitive. Vernon (1974) used 3-hydroxyflavone in the determination of triphynyltin species in potatoes; a similar technique was used for water samples by Blunden and Chapman (1978). Concentrations as low as 0.004 mg l^{-1} of triphenyltin species can be readily determined.

Electrochemical techniques, such as polarography, anodic stripping voltametry (ASV) and potentiometric titrations, have been used to analyse organotin compounds both in aqueous and nonaqueous media. The ASV technique is generally more sensitive than other electrochemical methods, with detection limits of about 10 nmol l^{-1}.

In natural water samples the expected levels of organotin compounds are of the order of picomols per litre, so that electrochemical methods cannot be considered suitable for environmental analysis.

4.3.2 Atomic absorption spectrometry

Atomic absorption spectrometry (AAS) techniques are, in general, sufficiently sensitive for environmental purposes (part-per-10^{12} level), particularly when the flame standard atomizer (air-acetylene) is replaced by an electrothermal atomizer (eg graphite furnace, Short, 1987; quartz-tube furnace, Hodge et al., 1979), or provided with a hydride generation system (Hodge et al., 1979). However, this technique in principle is not able to distinguish between the various organotin compounds, but measures only inorganic tin after mineralization of the sample.

To overcome this lack of specificity of AAS methods based on the detection of total (inorganic) tin, a combination of tin hydride generation (by $NaBH_4$) and cryogenic trap was developed for the separation and determination of inorganic tin and organotin compounds (Braman and Tompkins, 1979; Hodge et al., 1979). According to Hodge et al. (1979), stannane (SnH_4) and organotin hydrides (produced by the reaction of $NaBH_4$ with the corresponding organotin halides present in aqueous solution) can be separated on the basis of their boiling points (-52 ^{o}C for SnH_4, and ranging from 1.4 to about 280 ^{o}C for organotin compounds), by means of a cold trap. By this technique, nanogram or subnanogram amounts of Sn(IV), and the halides of methyl-, dimethyl- and trimethyltin, diethyl- and triethyltin, n-butyl-, di-n-butyl- and tri-n-butyltin, as well as phenyltin can be determined.

4.3.3 Liquid chromatography

This technique is limited at present by the lack of sufficiently sensitive detectors. However, liquid chromatography can provide the means to separate different organotin compounds, without the need to derivatize the chemicals present in the original sample. For this reason, several attempts have been made in recent years to couple liquid chromatography specificity with AAS sensitivity. Thompson et al. (1985), describe the two main approaches in combining an atomic absorption spectrophotometer equipped with a graphite furnace, with a liquid chromatograph:-

(i) installing a sampling device between the liquid chromatograph and the furnace, to collect the eflluent and inject it into the atomizer;

(ii) converting the analytes on-line to volatile derivatives for continuous feeding to the furnace.

Jewett and Brinckman (1981) used the first method and connected a high-performance liquid chromatograph (HPLC) with a graphite-furnace atomic absorption spectrophotometer (GFAA), in order to study the speciation of di- and triorganotins in water. On-line hydride generation technique has been used by Burns et al. (1981) to determine tin tetraalkyls and alkyltin chlorides with a sensitivity suitable for environmental samples.

4.3.4 Gas chromatography

The main requirement for the determination of chemicals by gas chromatography (GC) is that they should be sufficiently volatile to be separated in the chromatographic column. To achieve this, hydrated alkyltin ions and polar congeners are now derivatized to more volatile species.

One of the most used derivatization techniques is alkylation by means of a Grignard reagent (MgRX, where R is an alkyl- or arylgroup and X a halogen). In this way, the mono-, di-, and triorganotin compounds are transformed to the more volatile tetraorganotins by adding new organic radicals (eg. the n-pentyl-, Unger et al., 1986). Generally, there is no rearrangement of the original chemical species, which can then be easily recognised.

Another derivatization technique is hydridization with sodium borohydride ($NaBH_4$), as for AAS. Organotin hydrides (R_nSnH_{4-n}) are collected in traps, such as cold traps or "purge and trap" systems (Jackson et al., 1982; Olson et al., 1983), or extracted into an organic solvent (eg. dichloromethane; Matthias et al., 1986).

In conventional GC analysis, mass spectrometers (MS), electron capture (EC) and flame photometric (FP) detectors have been used successfully. Butyltin compounds, in the 1-100 ng Sn l^{-1} range have been detected by GC-MS in estuarine water samples (Unger et al., 1986). A solid-phase extraction method, followed by GC-ECD has recently been proposed by Junk and Richard (1987) for determining tributyltin chloride in seawater.

At present, the most promising detector for gas chromatographic analysis of organotin compounds in environmental samples seems to be the flame photometric detector (FPD), as modified by Aue and Flinn (1980). Sub-picogram quantities of organotin compounds can be determined by the GC-FPD technique (Aue and Flinn, 1977; 1980). Matthias et al. (1986) have recently described a comprehensive method for the determination of methyl- and butyltin species in water samples using a simultaneous hydridization/extraction procedure, followed by GC-FPD. A similar procedure was used for the determination of butyltin species in water from UK estuaries (Waldock, Thain and Waite, 1987). However, Maguire and Tkacz (1983) found that residues of SnO_2 produced by the detector flame may cause a decrease in sensitivity; also, this detector can easily be contaminated by tropolone, a complexing agent used in some procedures for the extraction of butyltin species from water and sediments.

Atomic absorption spectrophotometry has been used as a detector for the gas chromatographic analysis of several organometallic compounds. Chau et al. (1982) coupled GC with AAS for the determination of organotin compounds in water. Maguire et al. (1986) studied the occurrence of organotin compounds in water and sediment samples from Canada, using packed column gas chromatography coupled with quartz tube furnace atomic absorption spectrophotometry.

In concluding this section, it should be pointed out that analytical techniques for organotin compounds in environmental samples are rapidly evolving, reflecting the growing concern about the environmental fate and toxicology of these chemicals. At present there are analytical methods available which have a sufficient sensitivity and capability to separate and determine the principal chemical species in water samples. In the past, the lack of suitable and reliable methods for organotin species in matrices other than water has prevented a corresponding data base being established. Nevertheless, the techniques for the determination of organotin compounds in sediments and biota are rapidly improving: an international intercalibration exercise has recently been carried out by 7 different laboratories to analyse butyltins in mussel tissue and sediment sample (Stephenson et al., 1987). Most of the results, although obtained with different pretreatments and detection apparatus (GC-FPD, graphite furnace AAS, and GC-AAS), agreed within a factor of 2 to 3. This indicates that several techniques are now available for analysing environmental samples other than water, with a degree of accuracy which can be considered satisfactory for monitoring purposes.

In order to improve the accuracy of available analytical methods, the US National Bureau of Standards (NBS) distributed an aqueous solution of tributyltin (ca. 1 ug ml^{-1}, as Sn) to an international group of laboratories (Blair et al., 1987) in 1984. Subsequently, an intercomparison program on organotin measurement methods has been established (Blair et al., 1987).

4.4 Levels of organotin compounds in the environment

4.4.1 Inorganic tin in crustal rocks and soils

Crustal rocks and soils contain low concentrations of inorganic tin as shown in Table VI.

4.4.2 Dissolved inorganic tin in waters

Because of the low solubility in water of inorganic Sn(IV) compounds, levels of dissolved inorganic tin in seawater are at the ultra-trace level. As with other trace elements, the concentration of dissolved total inorganic tin in seawater has shown a decreasing trend during the last decades, reflecting an increased accuracy in the analytical methods used (Bruland, 1983). The background level for dissolved inorganic tin is probably within the range 0.1-1 ng l^{-1}.

4.4.3 Inorganic tin and organotin compounds; measured levels in aquatic ecosystems

During the last ten years a considerable research effort has been directed towards evaluating the extent to which freshwater and marine ecosystems are contaminated by tin and organotin compounds.

Table VI

Concentration of tin in crustal rocks and soils.

rock type	Concentration (mg kg^{-1})	Reference
Silicic rock	2.5	Smith and Burton (1972)
Basalts	1.7	"
Ultramorphic rocks	0.8	"
Red clays	3.4	"
Shales	6	Iverson and Brinckman (1978)
Soils	5.8	Ure and Berrow (1982)

Table VII shows the order of magnitude and the range of tin and organotin levels found in various components of the aquatic ecosystem. The main data obtained through the MED POL FAO/UNEP/IAEA/WHO pilot survey on organotins in selected Mediterranean areas are shown at the end of the table. This survey was organised to provide data on existing levels of organotins in the Mediterranean which were missing; it concentrated on locations where "hot spots" were likely to be present such as marinas, harbours etc. A detailed report on the survey appears as Annex to this document. Inorganic tin may be present in rainwater, freshwater and seawater at around 1 ng l^{-1}. Methyltin concentration are more varied at $<$0.01-1090 ng l^{-1} (as Sn) in water samples, with the higher values at sites heavily contaminated by TBT and its derivatives (Maguire et al., 1982). In estuarine and marine waters no other organic species of tin such as phenyl or cyclohexyl derivatives have been reported (Thomspon et al., 1985).

Different objectives, rather than different analytical techniques, have led to heterogeneous sets of data. In some of these the main aim was to explore the possibility of methylation of inorganic tin, analogous to the methylation of mercury. Tugrul et al. (1983) occasionally found methyltins in some natural waters. They assumed that the methylation in waters was related to seasonal changes in the microorganism population and induced by some physical environmental parameter such as temperature and salinity. The limitation of this hypothesis is that information on the levels of butyltin species in these samples is missing. Most sediment samples collected from the Alexandria coastal area and analysed by Aboul Dahab (1988) contained monomethyltin (31 of 35 samples) and dimethyltin (29 of 35 samples) while trimethyltin was absent from most samples (detected in 6 out of 35 samples). Methyltin compounds may be derived from anthropogenic inputs, from methylation of inorganic tin, or from transformation of other organotin compounds, such as the TBT analogs (Maguire et al., 1986).

In locations where surfaces have been treated with TBT based antifoulants, the levels of TBT can exceed 1000 ng l^{-1} in water and 10,000 ng g^{-1} in sediments (Table VII). In a recent study, Waldock, Waite and Thain (1987) reported the concentrations of organotins in some UK rivers and estuaries, in a monitoring programme designed to verify the efficacy of control measures introduced in January 1986 by the UK Government. Fig. 7 shows the monthly variations of MBT, DBT, and TBT in estuarine water of the River Crouch (at the Burnham-on-Crouch sampling site) for the period January 1986-June 1987. The same figure shows the provisional environmental quality target (EQT) set by the UK Department of the Environment for TBT in water (20 ng l^{-1}). Generally TBT is the major component, followed by DBT and a small

Table VII

Inorganic tin and organotin compounds in aquatic ecosystems. Concentrations in water are as $ng_{Sn}\ l^{-1}$; sediments and biota are in $ng_{Sn}\ g^{-1}$, dry weight. Q indicates the corresponding anion.

Sample	Location	Inorg.tin	$MeSnQ_3$	Me_2SnQ_2	Me_3SnQ	$BuSnQ_3$	Bu_2SnQ_2	Bu_3SnQ	total tin	References
Seawater*	San Diego Bay, USA	6-38	1-4	8-24						Hodge et al., 1979
Rainwater,	Florida, USA	3-40	0.6-2.2	<0.01-7.4	<0.01-1.1				4-45	Braman and Tompkins, 1979
Rainwater	La Jolla, USA	1-3	nd-5							Tugrul et al., 1983
Freshwater	Lamas River, Turkey	5								"
Seawater	La Jolla, USA	3-6								"
Seawater	Lamas Harbour, Turkey	4-5	0.6-2.2	0.6						"
Seawater	Iskenderun Bay, Turkey	520-7700	13-21	11-22						"
Seawater	Iskenderun Bay, Turkey	7-110		nd-2.7						"
Sediments	Iskenderun Bay, Turkey	800-2100	0.03-0.4	0.1-2.4	0.04-0.4					"
Sediments	San Diego Bay, USA	3600	1-1.3	1.1-1.4	nd-0.12					"
Fish	NE Mediterranean, Turkey		0.4-13	1.4-1.6	7-8				86-260	"
Limpet, shell	NE Med., Turkey		0.2-1.4	0.1-0.7	0.4-1.6				13	"
Limpet, soft	NE Med., Turkey		0.6-2.4	1.0-10	0.5-38				50-75	"
Freshwater	Ontario, Canada	10-50100	54-1090	16-320	36	14-5730	5-285	4-1193		Maguire et al., 1982
Sediments (top 2 cm)	Ontario	114-5130				9.5-392	4.6-177	13-221		Maguire, 1984

Table VII (continued)

Sample	Location	Inorg.tin	$MeSnQ_3$	Me_2SnQ_2	Me_3SnQ	$BuSnQ_3$	Bu_2SnQ_2	Bu_3SnQ	total tin	References
Freshwater	Canada	nd-37200	nd-120	nd	nd-180	nd-1890	nd-1360	nd-2340		Maguire et al., 1986
Sediments	Canada	10-15500	nd-17190	nd-170	nd-750	nd-4730	nd-8510	nd-10780		"
Seawater	Chesapeake Bay, USA						nd-167	nd-432		Hall et al., 1987
Seawater	San Diego Bay, USA	1-10				nd-50	nd-148	nd-200		Valkirs et al., 1986
Seawater	California, USA					nd-155	nd-235	nd-180		Stallard et al., 1987
Sediments	California, USA					nd-40	nd-14	nd-9		"
Seawater	Turkey	14-319								Salihoglu et al., 1987
Fish	Turkey								160-1460[+]	"
Limpet, soft	Turkey		nd-12.4	nd-5.3	nd-5.5				19-450	Yemenicioglu et al., 1987
Seawater	SW England, UK							< 40-3180		Cleary and Stebbing, 1985
Seawater	Crouch, Holliwell Point, UK					nd-3	3.5-8	0.8-10		Waldock, Thain and Waite, 1987
Seawater	Plymouth, Sutton Marina, UK					nd-130	7-146	34-520		"
Dogwhelk	Loch Crinan, Scotland								1800-328000[+]	Davies et al., 1987
Seawater	Arcachon Bay, France								500-5050	Alzieu et al., 1986
Oyster	Arcachon Bay, France								min300-7000	Alzieu et al., 1986

Table VII (continued)

Sample	Location	Inorg.tin	$MeSnQ_3$	Me_2SnQ_2	Me_3SnQ	$BuSnQ_3$	Bu_2SnQ_2	Bu_3SnQ	total tin	References
Sediment	Alexandria coastal belt	310-5200	nd-1200	nd-135	nd-80	nd-450	nd-425	30-1375		Aboul Dahab (1988)
Seawater	Fossi Medicei, Italy					<100	65-385	1125-3180		Bacci and Gaggi (1989) and FAO/UNEP/IAEA/WHO (1988)
Seawater	Leghorn harbour, Italy					<100	<20-340	<20-810		"
Seawater	San Vincenzo marina, Italy					<100	45-170	260-570		"
Seawater	Cecina marina, Italy					<100	90-750	440-3930		"
Seawater	Punta Ala marina, Italy					<100	100-190	505-960		"
Seawater	Marseille harbour, France					20-98	38-141	41-201		FAO/UNEP/IAEA/WHO (1988)
Seawater	Cap d'Agde marina, France					16-56	16-36	34-536		"
Seawater	Bandol marina, France					<1-83	<1-161	10-390		"
Seawater	Thau mariculture area, France					<1-21	<1-38	<2-16		"
Seawater	Marmaris marina, Turkey					<0.5	121-742	11-353		"

* Seawater and freshwater values reported in this table are referring to subsurface samples (no microlayer)
+ To transform the results reported on fresh weight basis, a ratio fresh/dry of 4.5 was used

amount of MBT. The organotin levels are at a minimum in winter, and rise rapidly in April and May, due to the launching of newly painted yachts; levels below the EQT were reached only after the following October. A similar trend, but with levels one order of magnitude as high as those in Fig. 7 have been reported by the same authors for water samples collected at a marina in Sutton Harbour during 1986 (Fig. 8). However, the ratio of TBT:DBT is higher, probably reflecting the proximity to the source of TBT.

Organotin concentrations in seawater and freshwater reported so far are essentially those in subsurface samples. Higher levels of organotin compounds occur in the surface microlayer as shown in Table VIII.

The enhancement of organotin compound concentrations, particularly of TBT, in the surface microlayer is related to their lipophilic properties.

4.4.4 Bioconcentration potential of organotin compounds

The liphophilic nature of some organotin compounds, particularly tributyltin, can cause contamination problems in the marine fish farming industry. These chemicals have been applied to sea pens and marine cages to prevent biofouling; they are then slowly released and can be taken up by the cultivated species. Short and Thrower (1986a) have found 18-65 ng l^{-1} of TBT in seawater samples collected in sea pens for salmon farming. Muscle tissue of chinook salmon, Oncorhyncus tshawytscha, reared for 3 to 19 months in sea pens treated with TBT, contained organotin concentrations of 0.28-0.90 ug g^{-1} as TBT (Table IX).

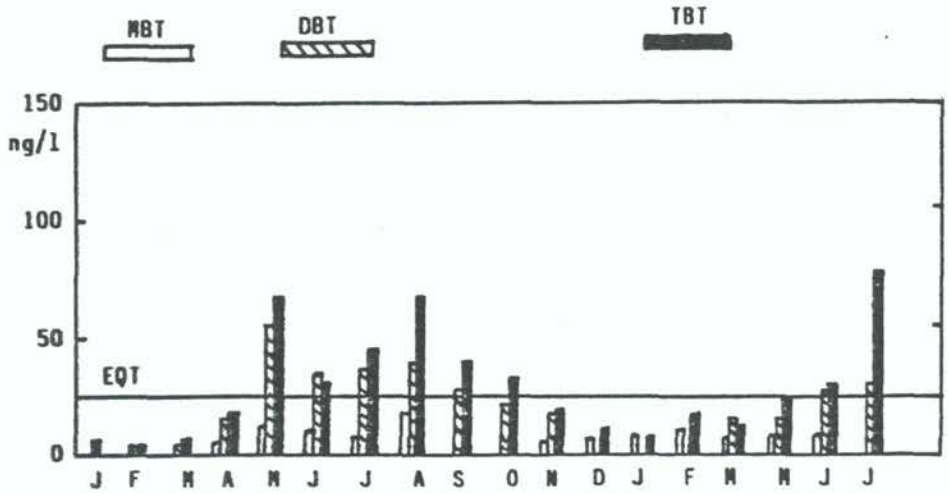

Fig. 7 Organotin compounds in water samples from the River Crouch (Burnham-on-Crouch, 1986-87; from Waldock, Waite and Thain, 1987)

Most of the common cooking practices (such as microwave, pan frying and boiling) were found to destroy or remove from 24 to 45% of butyltins from salmon flesh (Short and Thrower, 1986a).

Blue mussels, Mytilus edulis, accumulated bis (tributyltin) oxide (TBTO) when it was either dissolved in water or associated with phytoplankton Isochrysis galbana. Higher TBT burdens were found when accumulation occurred via the ingestion of treated phytoplankton (Laughlin et al., 1986b). TBT-exposed mussels returned to clean water, had a depuration half life of about 14 d (Laughlin et al., 1986b).

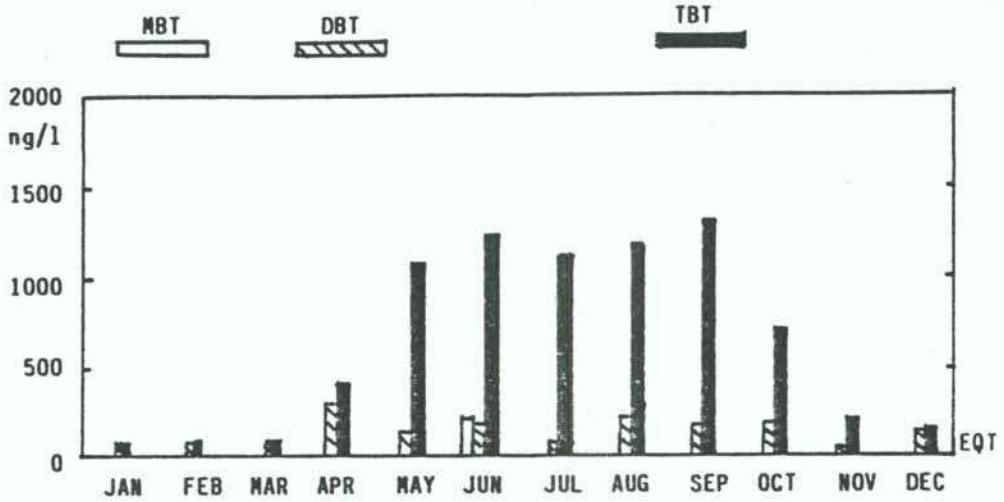

Fig. 8 Organotin compounds in water samples from Sutton Harbour; ns = not sampled. From Waldock, Waite and Thain, 1987).

Table VIII

Concentration of TBT and organotin compounds, ng Sn l^{-1}, in surface microlayer and subsurface water samples.

Sample location	Depth of microlayer (um)	surface microlayer	subsurface	reference
TBT				
Canada				
Great Lakes	-60	<4-24927	<4-1187	Maguire et al., 1982
USA				
Chesapeake Bay	-30	<8-186	<8-468	Hall et al., 1986
San Diego Bay		24-100	4-72	Valkirs et al., 1986
Great Bay estuary	-40-70	306	2	Donard et al., 1986
Organotin compounds				
UK				
Devon and Cornwall	-280-300	24-1069	<8-289	Cleary and Stebbing, 1987a
Devon and Cornwall	-40-70	119-3620	9-300	Cleary and Stebbing, 1987b
Essex	-280-300	17-91	11-41	"
Essex	-40-70	163-550	17-22	"
Norfolk	-280-300	89-552	8-396	"
Norfolk	-40-70	166-1600	8-396	"

Table IX

Concentrations of butyltins in the muscle tissue of 1981, 1982 and 1983 brood-year chinook salmon reared in TBT-treated and untreated sea pens at Little Port Walter, Alaska. n = number of salmon analysed (in triplicate); 95% C.L. = 95% confidence limits. From Short and Thrower (1986a).

Brood year	Residence time in TBT-treated sea pens (months)	Mean conc. of Butyltins (as TBT, ug g^{-1})	n	95% C.L.
1981	19	0.90	4	0.80-1.00
1982	13	0.82	8	0.77-0.87
1983	3	0.28	7	0.24-0.32
1983	0	<0.013	12	

Young stages of Pacific oyster, Crassostrea gigas, and the European flat oyster, Ostrea edulis, treated with 0.15 ug l^{-1} tributyltin in flow-through experiments, rapidly accumulated tributyltin in their tissues. Near equilibrium was reached within 5-10 d exposure, with BCF values of ca. 1000-1500 for the European flat oyster and ca. 6000 for the Pacific oyster (Waldock et al., 1983). Bioconcentration factors of 10000 and 2000 were obtained by Waldock and Miller (1983) for Crassostrea gigas and Ostrea edulis, respectively.

Waldock and colleagues (1983) found that depuration of TBT from oysters was rapid, with 50% of the body burden being lost in about 6 d; little change was found over a further 20-day elimination period (Fig. 9).

In a contaminated estuary, Pacific oysters (Crassostrea gigas) concentrated organotin compounds, and particularly TBT, up to 16,000-fold in respect to the seawater level. The ratio of organotin compounds in oysters was similar to those of the water, and in contaminated sites the animals show rapid increase in body burden in the spring, and a plateau in summer (Fig. 10). The depuration of these oysters seemed to take a longer time than the disappearance of organotin from water (cf. Figs 7 and 8).

A recent paper (Alzieu et al., 1986) reported that the total tin and the organotin concentrations in the Pacific oyster, Crassostrea gigas, from Arcachon Bay, France, fell rapidly in the period 1982-1984, after the French Government restricted the use of organotin based antifouling paints in January 1982. In this survey the organotins were not individually identified; however the results are relevant as an example of the likely recovery time of marine polluted areas. Some examples of these recovery trends in Pacific oysters from Arcachon Bay are reported in Table X (Alzieu et al., 1986).

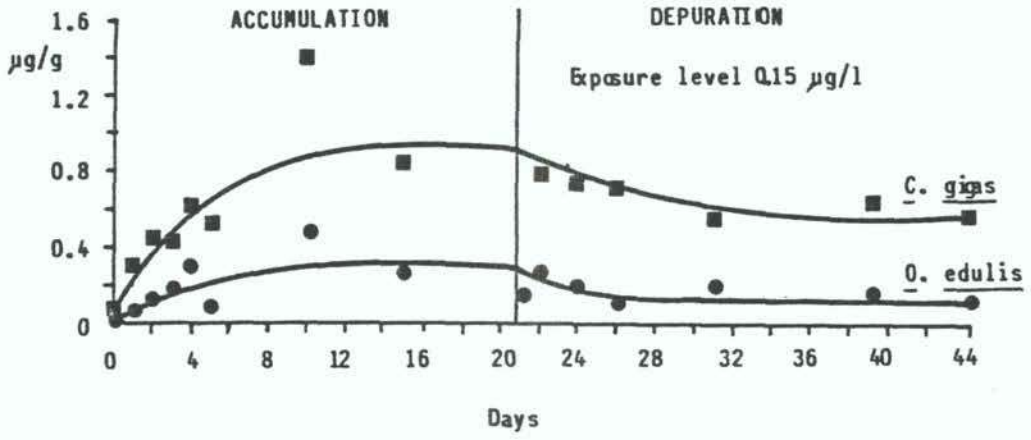

Fig. 9 Accumulation and depuration experiments with TBT in oysters (from Waldock et al., 1983)

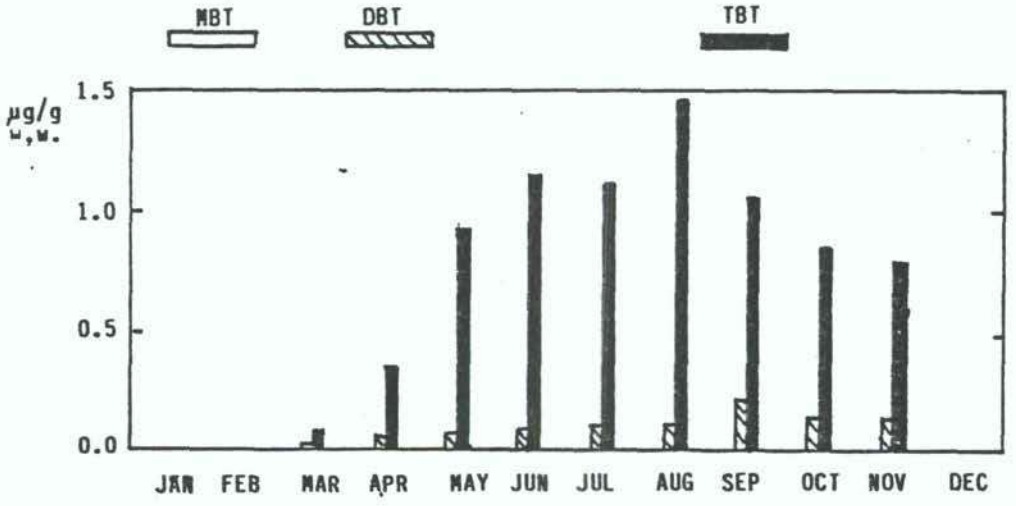

Fig. 10 Organotin residues in Crassostrea gigas from the River Crouch, Creeksea, 1986. From Waldock, Waite and Thain (1987)

From the data reported in Table X and elsewhere, it appears that organotin compounds and bioavailable inorganic tin are not very persistent chemicals under natural environmental conditions as in Arcachon Bay. By comparison, much higher persistence was reported for mercury released by a chloralkali plant and then biomethylated, in an open sea area (Northern Tyrrhenian, N.W. Mediterranean) where the water turnover is certainly much higher than in Arcachon Bay (Bacci et al., 1986). The difference in the behaviour between these chemicals essentially depends on their partitioning properties and their degree of resistance to degradation processes.

4.4.5 Measured distribution coefficients of TBT

In the previous sections it has been demonstrated that TBT is the principal organotin contaminant in the aquatic environment. The levels of DBT and MBT probably represent the primary degradation products. In order to define the basic trends of the environmental distribution and fate of TBT, some measurements have been made of relevant partition coefficients such as the sorption coefficient Kp and the BCF (Table XI).

The experimental Kp and BCF values appear to be about one order of magnitude higher than the corresponding calculated values. The main reason for this discrepancy is probably due to the fact that the calculations were based on sorption and bioconcentration phenomena controlled by hydrophobic mechanisms rather than by polar interactions.

Unger et al. (1987) found that in different natural sediments, Kp was related not only to the organic carbon (OC) content, but also to the % clay content and salinity. According to these authors the Kp (l kg^{-1}) values obtained ranged from $0.11X10^3$ to $8.2X10^3$ (Table XI), ie about 2 orders of magnitude. The corresponding Koc values, calculated from Kp and from the OC content (0.34-4.2%) range from $1.2X10^4$ to $2.0X10^5$, ie about 1 order of magnitude, indicating that the organic carbon content probably plays a role in TBT partitioning between sediment and water. However, the influence of clay and salinity on Kp indicates the presence of significant charge-charge and charge-dipole interactions between different dissolved TBT species in solution and the various sediment component surfaces.

As the experimental values of BCF were higher than predictions for TBT, based on a hypothesis of hydrophobic behaviour, it is possible that some mechanism other than lipid partitioning could be involved. As suggested by Laughlin et al. (1986b) the chemical conjugation of TBT to biological molecules could be one possible mechanism whereby these higher than predicted BCF values can be explained.

4.5 Environmental transformations of tin and organotin compounds

Previous sections have dealt with the partitioning properties of organotins, particularly TBT, in the environment. From these, estimates can be made of fluxes and environmental reservoirs (ie marine sediments), as well as bioaffinity. However, to calculate the main trends of the environmental behaviour of these chemicals, another relevant intrinsic factor is resistance to degradation and major transformation processes.

4.5.1 Inorganic tin

Inorganic tin can be easily converted from Sn^{2+} to Sn^{4+}, under 'environmental' conditions: the half-life for the oxidation of Sn^{2+} to Sn^{4+} is about 2 d in oxygenated water (Fanchiang and Wood, 1981). The Sn^{4+} species is thermodynamically more stable than the reduced form, so in most of the environmental compartments the inorganic tin can be expected to be present as Sn^{4+}.

In aquatic environments the species of inorganic tin most likely to be present are the hydroxide, $Sn(OH)_4$, and the hydroxyoxides $SnO(OH)_2$ and $SnO(OH)_3$. According to Amdurer et al. (1983), the neutral $SnO(OH)_2$ form should be predominant in seawater; Macchi and Pettine (1980) showed that this species was the major form in water, but at pH values lower than 7.

Table X

Recovery trends in Arcachon Bay: 1982-1985 levels of total tin and organotins (ng g^{-1}, dry weight) in Pacific oyster samples (from Alzieu et al., 1986).

Sampling site	Aug.'82	Sept.'82	Mar.'83	Apr.'84	Aug.'84	Oct.'84	Mar.'85	Aug.'85	Oct.'85
Cap Ferret									
total tin	3400	2200	2500	1100	500	<300	<300	<300	<300
organotin	170	160	420	<240	<220	<210	<200	<200	<200
La Vigne (Port)									
total tin	7000		4000	1700	500	500	530	910	780
organotin	1640		840	480		200	250	380	250
La Vigne (Parc)									
total tin	2000		2000	1300	<300	<300	<300	<300	<300
organotin	480		350	<230	<230	<220	<200	<200	<200
Les Jacquets									
total tin		3300	3400	1600	1500	1250	<300	<300	<300
organotin		310	350	230	<220	<220	<200	<200	<200
Comprian									
total tin		1300	1100	650		500	300	<300	<300
organotin		230	340	<240		<230	<200	<200	<200
Les Hosses									
total tin		2500	2700	800		700	<300	<300	<300
organotin		220	340	<240		<240	<200	<200	<200

Table XI

TBT: Kp, BCF and Koc (organic carbon sorption coefficient) experimental measurements.

partition coefficient and measured value	environmental compartment	references
BCF = ca. 16000	Pacific oyster	Waldock et al., 1983
BCF from 4100 to 22000	blue mussel	Laughlin et al., 1986b
Kp ($l\ kg^{-1}$)=0.11-8.2X10^3	Chesapeake Bay sediments*	Unger et al., 1987
Kp from 6250 to 55439**	Pearl Harbor sediments	Stang and Selingman, 1987
Koc from 1.2 10^4 to 2.0 10^5		Unger et al., 1987

* Organic carbon ranging from 0.34 to 4.2%

** Kp values have also been reported for DBT, 2069-26078 and MBT, 1758-28750 $l\ kg^{-1}$

The possibility that inorganic tin can be methylated is of great ecotoxicological importance; by this transformation the inorganic metal can produce more toxic and more mobile species. Byrd and Andreae (1982) found mono-, di- and trimethyltin to be ubiquitous in freshwater samples from Germany and from the southeastern USA; they have suggested that direct anthropogenic inputs may be implicated but nevertheless biomethylation is possibly the major cause.

The biomethylation of inorganic tin was investigated by some research teams using both mixed cultures of microorganisms similar to those in natural sediments, and pure cultures of microorganisms. Di- and trimethyltin compounds were identified in nutrient medium containing $SnCl_4$ inoculated with sediment from Chesapeake Bay, after 14 d of aerobic incubation; in the same series of experiments, no methyltin compounds were found in sterile or poisoned controls (Cooney et al., 1981; Hallas et al., 1982). Tugrul and colleagues (1983) found monomethyltin as a dominant species in partly anoxic-polluted marine sediments, whereas dimethyltin dominated in oxic-polluted marine sediments; trimethyltin was the main species in oxic-nonpolluted marine sediments.

Pure cultures of a Pseudomonas were able to transform Sn(IV) and to a lesser extent Sn(II) to trimethyltin species (Jackson et al., 1982). Transmethylation reactions involving methyl cobalamin can occur abiotically (Thayer 1979). $SnCl_2$ can react, under aerobic conditions, with methyl-B_{12} to yield methyltin trichloride (Fanchiang and Wood, 1981), but the reaction does not occur under anaerobic conditions, indicating that it would not occur in oxygen-deficient sediments. Due to the sensitivity of cobalamins to light, biological and abiotic methylation processes mediated by these compouns would be restricted in those environments which are exposed to bright sunlight.

Therefore, inorganic tin is probably methylated to different forms under various environmental conditions. Sequential mechanisms to yield mono-, di-, tri- and tetramethyltin compounds are possible in principle. However, Ridley et al. (1977) have shown that sequential mechanisms of demethylation of tin from tetramethyltin to tri-, di-, monomethyltin and eventually inorganic Sn(IV), can be activated by the mixed function oxidase system, as present in rat liver microsomes.

In summary, methylation and demethylation of tin can occur under natural conditions in aquatic ecosystems, by way of biological or abiotic processes. However, Thompson and colleagues (1985), suggest that the relative contributions made by the various mechanisms which control the environmental fate of tin and organotin compounds have yet to be determined.

4.5.2 Environmental degradation of TBT and other organotin compounds

The degradation of an organotin compound may be defined as the progressive removal of the organic groups attached to the tin atom (Blunden and Chapman, 1982).

$$R_4Sn \longrightarrow R_3SnX \longrightarrow R_2SNX_2 \longrightarrow RSnX_3 \longrightarrow SnX_4$$

The biological activity of organotin compounds is closely related to their structural properties, particularly the nature and the number of organic groups. Therefore, the stepwise loss of these groups causes a progressive lowering in the potential toxicity of the parent compound. The degradation processes require the breaking of Sn-C bonds. This can be achieved by several methods such as ultra-violet (U.V.) irradiation, biological cleavage, chemical cleavage, thermal cleavage, and gamma irradiation.

Under normal environmental conditions, gamma irradiation is of little importance because of its negligible intensity at the earth's surface. Thermal cleavage can play a significant role in reducing organotin inputs in the environment particularly in the incineration of waste materials containing PVC and other organotin treated materials; however thermal cleavage of organotin compounds seems unlikely in the natural environment because the Sn-C bond is stable at temperatures up to 200 ^{o}C (Blunden and Chapman, 1982). Chemical degradation also seems to play a minor role under normal environmental conditions.

In shallow and 'clean' waters a Sn-C bond cleavage due to photolysis appears to be possible. This is in agreement with the finding by Maguire et al. (1983), that tributyltin species do not lose butyl groups in the dark. The experimentally measured half-life of TBT under sunlight irradiation ranges from 18 to more than 89 d (Thomspon et al., 1985). Soderquist and Crosby (1980; cited by Blunden and Chapman, 1982) reported that UV light produced a diphenyltin species from triphenyltin hydroxide in water, under simulated environmental conditions; the diphenyltin form underwent further breakdown, probably to a polymeric monophenyltin derivative, but whether or not this species would degrade to inorganic tin was not demonstrated. Studies carried out with methyltin chlorides showed that these species can be degraded to hydrated tin(IV) oxide by means of UV irradiation (see Blunden and Chapman, 1982).

Photolysis is obviously less important as a degradative mechanism in situations where there is no exposure to intense light, such as in subsurface soils and marine sediments, and also in subsurface waters (ie more than 0.5-1 m deep; Maguire, 1986), because of the low penetration of UV light in water. Other degradation processes become of greater importance in such environmental conditions.

Barnes et al. (1973, cited by Blunden and Chapman, 1982) found that triphenyltin acetate is degraded to inorganic tin in soil, with evolution of CO_2; since the break-down did not occur in sterile soil, it was suggested that the degradation was caused by microorganisms. A similar result was reported for bis (tributyltin) oxide in soils (Blunden and Chapman, 1982). There are very few data on the degradation of organotin compounds in freshwater and marine sediments. Unpublished work in the UK suggests that TBT degrades very slowly in anaerobic marine sediments.

Thain et al. (1987) found that TBT in a naturally contaminated sample collected in a freshwater marina had a half-life of 6 d at 20 ^{o}C. TBT degradation rates were measured by Seligman and coworkers (1986) in microcosms using spiked ambient waters from San Diego Bay, California, and Skidaway Estuary, Georgia (USA). Half-lives ranging from 7 to 15 d were found for TBT, with DBT as the principal breakdown product and, to a lesser extent, MBT. Biodegradation of TBT by a common alga (Ankistrodesmus falcatus) and by oligochaete worms has been shown by Maguire (1986). Stang and Selingman (1986) obtained a TBT half-life of approximately 162 d in marine sediments collected in San Diego Bay and used in a laboratory tank experiment under aerobic conditions; the main degradation product was MBT, with a minor component of DBT.

In the present state of knowledge, it is difficult to assess the relative importance of photolytic and biological mechanisms for the degradation of TBT. However, these two pathways appear to represent the main routes for the environmental degradation of organotin compounds. A recent study by Lee and colleagues (1987) indicates that under sunlit conditions the TBT half-life was shorter than that in the dark (Table XII); but also, water with a higher phytoplankton population showed higher TBT degradation rates with half-lives in water with chlorophyll concentrations of 3 and 12 ug l^{-1} being 9 and 4 d respectively (Figs. 11 and 12). These authors conclude that microbial activity, and microalgae when present in high numbers, play a significant role in TBT degradation in estuarine waters.

Table XII

Degradation rates of TBT under light and dark conditions in estuarine water from Skidaway River, and James and Elizabeth Rivers. From Lee et al. (1987).

Site of water collection	treatment	TBT half-life (d)
Skidaway River	light	4-9
"	dark	9-13
James River	light	12
"	dark	14
Elizabeth River	light	6
"	dark	9

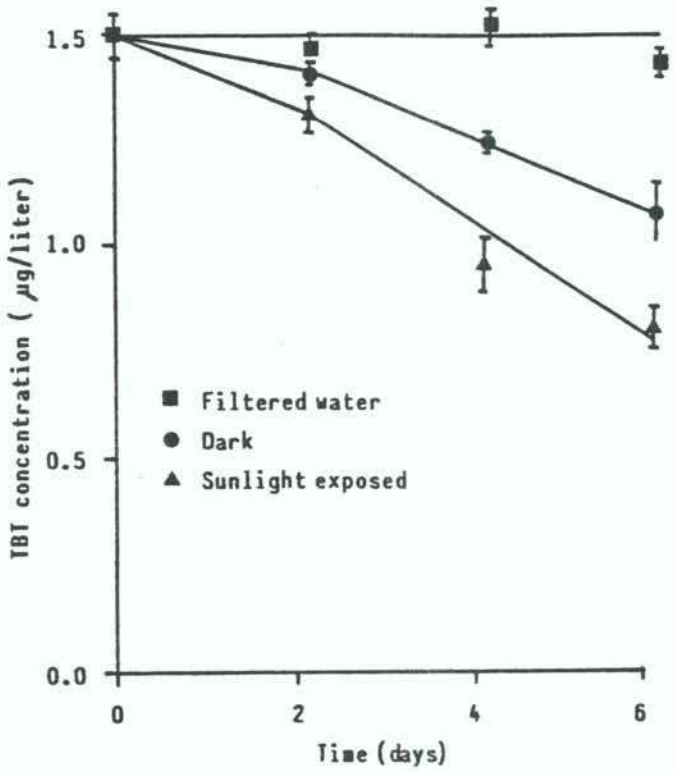

Fig. 11 Degradation of TBT added to river water under light and dark conditions. From Lee et al. (1987)

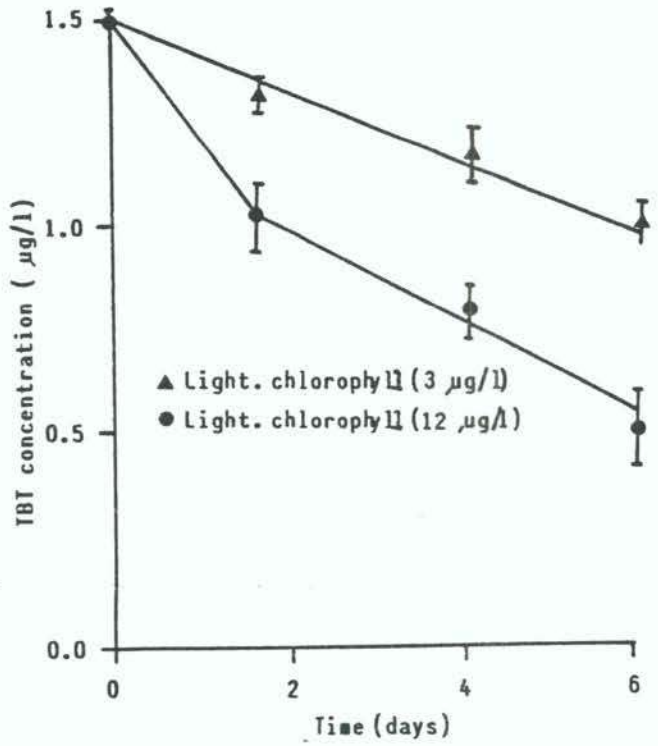

Fig. 12 Degradation of TBT added to river water with different chlorophyll concentrations. From Lee et al. (1987)

4.6 Conclusions

Although much of the information presented is recent and incomplete, some tentative conclusions can be reached on the environmental behaviour of TBT and TPT.

a) TBT and TPT compounds have a very low potential in principle for distribution in air, because of their low volatility;

b) TBT and TPT have a higher affinity for soils and sediments than for water; therefore in aquatic environments the sediments will be the main reservoir for these chemicals;

c) Because of their soil and sediment affinity, TBT and TPT have a low mobility in terrestrial ecosystems;

d) TBT and TPT are degraded, mainly by biological mechanisms and by photolysis, to di- and monophenyl- or monobutyltin, and then to inorganic tin, within a reasonably short timescale;

e) In principle TBT and TPT released in terrestrial environments should not seriously contaminate distant marine ecosystems because of their low mobility in air and in sediments, and because of their degradability;

f) In marine environments, the main organotin species found are tri-, di- and mono- butyltin; methyltins, which are less common, can be formed from the dealkylation of butyl derivatives and from methylation of inorganic tin;

g) At present, it seems that the major organotin contamination problem in marine ecosystems is from the use of TBT in antifoulants;

h) Marine organisms (eg fish, molluscs) are able to accumulate TBT to levels considerably greater than those in the surrounding water;

i) With a cessation of inputs, TBT contamination can be lost in a relatively short time (ie within one year), even in semi-enclosed marine environments. However, there is very little information on the degradation of TBT in anaerobic marine sediments.

5. HUMAN EXPOSURE TO TRIBUTYLTIN AND TRIPHENYLTIN, AND HAZARD ASSESSMENT

5.1 Toxic potential to mammals and man

5.1.1 General considerations

The toxic potential of organotin compounds received considerable attention in the 1950's, and particularly after 1954 when a large scale incident occurred in France (IRPTC, 1978), caused by an oral medication containing diethyltin diiodide ("Stalinon"). There were 210 reported cases of intoxication with 98 deaths (NIOSH, 1976, in IRPTC). Triethyltin derivatives were found to be more toxic than the diethyltins, and were extremely neurotoxic, causing severe edema and destruction of the myelin sheaths (Chang et al., 1983). Human exposure to trimethyltin produced symptoms of headaches, memory defects, loss of vigilance, seizures and disorientation (Fortemps et al., 1978).

The introduction of organic groups to the inorganic tin to obtain R_nSnX_{4-n} derivatives increases the biological activity and the toxic potential, reaching a maximum for n=3 for all types of living organisms tested (Evans and Smith, 1975; Laughlin and Linden, 1985). The anionic radical X seems to have little effect on the toxic potential (Maguire and Tkacz, 1985; Schweinfurth and Günzel, 1987).

Within a given series of tri-n-alkyltin derivatives, the biological activity for mammals initially increases with the length of the carbon chain, to a maximum with R=ethyl group, falling off quickly with further lenghtening of the R chain: the tri-n-octyltin compounds are almost non-toxic (Evans and Smith, 1975). The tributyltin salts are, in terms of toxicity, located between the two extremes of the highly toxic trimethyl- and triethyltin compounds and the relatively harmless octyl-derivatives.

A schematic representation of the biological activity of a series of tri-n-alkyltin compounds as a function of the length of the alkyl chain and of the type of organism, is given in Fig. 13. There is a striking difference between the toxic potential of tributyltin salts for mammals and insects and for aquatic organisms; it is this that probably led to the development of those compounds as bacteriocides, molluscicides and antifoulants.

Triorganotin compounds can enter the human body directly at the workplace where these chemicals are manufactured or formulated, and where formulations are used or removed after use (as with the removal of old paint). These compounds can also enter the human body indirectly, through residues contained in treated vegetarian food (TPT, Cyhexatin) or in contaminated seafood (TBT). Therefore, a toxicological evaluation is needed both for exposed workers and for the general population.

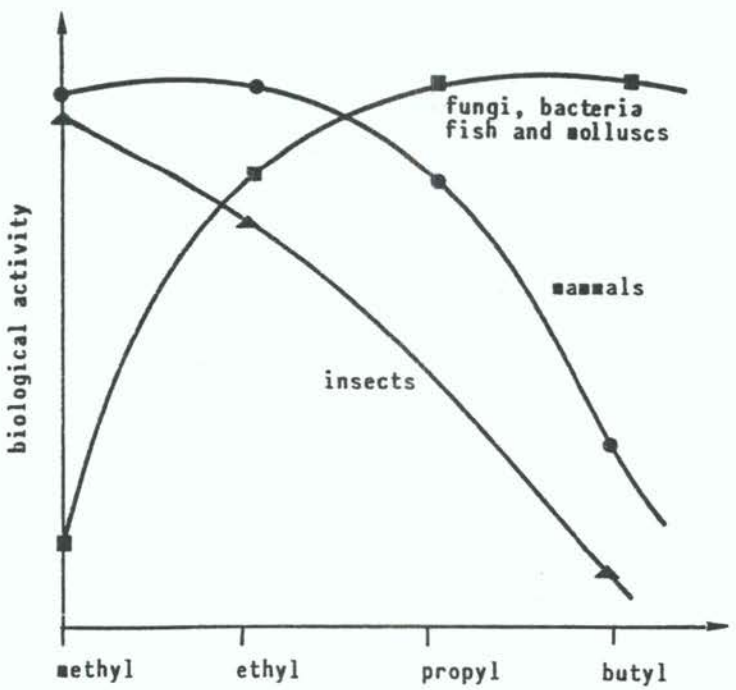

Fig. 13 Schematic representation of the biological activity of the tri-n-alkyltin compounds in relation to the carbon chain length. From Evans and Smith (1975), modified

5.1.2 Acute toxicity of triorganotin compounds

Single dose experiments

Several results of single-dose studies carried out to simulate accidental high doses of these chemicals (from oral ingestion, inhalation or skin contact) have been reported in the literature; LD_{50} values obtained from single oral doses are shown in Table XIII.

The acute toxicity of TBT and TPT compounds is very similar; in the rat, for example, the LD_{50} value for an oral single dose is of the order of 100 mg of compound per kg of body weight for TPT and TBT derivatives.

The inhalation route of organotin compounds may be important in those work places where the operational practices (eg pesticide treatments in agriculture, application or removal of antifouling paints) lead to production of aerosols and particles containing these chemicals. Short exposures to TPTOAc contained in technical fungicide formulations were shown to cause headache, nausea, vomiting and unconsciousness in some farmers (Guardascione and Di Bosco, 1967).

Table XIII

Acute toxicity of TPT and TBT compounds to mammals. Route: oral, single dose. LD_{50} values are expressed as mg of TBTX or TPTX per kg of body weight.

Compound	tested species	LD_{50}	Reference
TPTOAc	mice	81-93	Bock, 1981
TPTCl	"	80-90	"
TPTOH	"	80-510	"
TPTOAc	rat	136-491	"
TPTCl	"	125-135	"
TPTOH	"	110-360	"
TPTOAc	Guinea pig	10-41	"
TBTOAc	mice	46	Pelikan & Cerny, 1968
TBTCl	"	117	Schweinfurth & Günzel, 1987
TBTF	rat	94	"
TBTCl	"	122	"
TBTO	"	127	"

The acute toxic potential of sprayed TBTO was investigated by Schweinfurth (1985): an LC_{50} (4h) or 77 mg m^{-3} (total particles) or 65 mg m^{-3} (particles with diameter lower than 10 um) was found for rat. Because of the relatively low vapour pressure of TBTO (ca. $5X10^{-6}$ mmHg, room temperature), more than 99% of the compounds was associated with particulates in these experiments; saturated air at 20 ^{o}C contains less than 0.2 mg of TBTO per m^3. In an experiment where rats were exposed to air saturated with TBTO vapour (without particles) only minor effects were observed after single 7-hour exposures (Schweinfurth, 1985).

Results from acute dermal toxicity tests in rats indicated LD_{50} values of 605 and 505 mg kg^{-1} body wt for TBTO and TBT-benzoate respectively (Klimmer, 1969). A dermal LD_{50} of ca. 450 mg kg^{-1} body wt has been reported for TPTOAc in rats (see Bock, 1981).

Repeated dose experiments

Long term toxicity cannot be predicted from information on acute, single dose, experiments. In order to simulate the intake of low doses over long periods, repeated dosing toxicity tests are carried out to obtain an estimation of the "no-observed-effect levels" (NOEL). This represents the concentration which does not cause noxious effects under specific conditions.

Bock (1981), reports an experiment in which groups of 20 rats were supplied with TPTOAc-fortified feed for 4 months. At 100 mg TPTOAc per kg of feed or less, no abnormalities were found in rats, whilst at high loads, growth rate was reduced and at 600 mg kg^{-1} 30% of the animals died. Gaines and Kimbrough (1968) found that with 400 mg kg^{-1} in the diet, all rats (10) died; at 200 and 100 mg kg^{-1} all survived for 14 wk; rats receiving the 100 mg kg^{-1} dose showed normal behaviour, except for a lower food intake. Guinea pigs showed higher sensitivity; with 12 mg of TPTOAc per kg of food, 5 out of 6 treated animals died within 1 yr. In another experiment, groups of guinea pigs treated with feed containing 1.0 and 5.0 mg of TPTOAc per kg had a mortality rate not significantly higher than the controls over a period of 392 d, although food intake was reduced even when it contained only 1 mg kg^{-1}. The typical damage to the central nervous system caused by triethyltin compounds (ie increased water content, histological damage (Chang et al., 1983) was not found with TPT compounds.

Further studies showed that TBT compounds did not cause damage to the central nervous system as was found for the trimethyl- and triethyltins; the main target for TBT seems to be the lymphatic system. Schweinfurth (1985) found that 100 mg of TBTO per kg of diet was sufficient to reduce thymus weight in juvenile rats after 4- and 13-week treatments; other authors obtained similar effects with 20 mg of TBTO per kg of diet in a 4-week experiment with juvenile rats (Krajnc et al., 1984). A suppression of thymus dependent immune response and of nonspecific resistance was found in rats supplied with 20 mg TBTO per kg of diet and above (see Schweinfurth and Günzel, 1987). Measurements of TBTO toxicity with repeated inhalation exposure have been made by Schweinfurth and Günzel (1987): groups of 20 rats were exposed in "nose-only" chambers over 4 h period a day, 5 times a week, for 29-32 days (ie 21-24 treatments, 4 h each), at concentrations of 0, 0.03 (vapour), 0.16 (vapour) and 2.8 (aerosol) mg m^{-3} TBTO. The concentration of 0.16 mg m^{-3} is, at a first approximation, the equilibrium vapour pressure at room temperature; no effects were noted at this air contamination level. However, with 2.8 mg m^{-3} of aerosol containing TBT, 11 rats died and the remainder showed inflammatory reactions throughout the respiratory tract, and also lymphotoxic effects, apathy, and respiratory distress.

5.1.3 Chronic effects in mammals

Embryotoxic and teratogenic potential

In a recent study with an organ culture system using mouse limb buds, Krowke et al. (1986), levels of 0.03 ug l^{-1} TBTO and above interfered with morphogenetic differentiation processes. An increase in cleft palates occurred in mouse fetuses after TBTO oral doses of 11.7 mg kg^{-1} and above. Cleft palates were obtained also in rats treated with TBTO at a rate of 18 mg kg^{-1} (Schweinfurth and Günzel, 1987).

Carcinogenic and mutagenic potential

Studies on these aspects of toxic potential of triorganotin compounds, and particularly TBTO, are in progress.

From preliminary results obtained with 2 yr-treatment periods, TBTO at 50 mg kg^{-1} in the diet caused an increase in the frequency of those benign tumors with a high background level in rats, such as pituitary adenoma, adrenal medullary adenoma, and, in males only, parathyroid adenoma (Wester et al., 1986). These carcinogenic effects of TBTO may be caused by an interference with the endocrine system, by an enhanced aging process or by immunomodulation; a genotoxic mechanism seems unlikely.

However, Schweinfurth and Günzel (1987) report that there is no evidence of a mutagenic potential for TBTO in that it failed to induce point mutations in Salmonella typhimurium in the Ames test and genetic alterations in the yeast Saccharomyces cerevisiae. In the human lymphocyte test in vitro, no evidence of chromosome mutations was found.

5.1.4 Proposed provisional Acceptable Daily Intake (ADI) of Tributyltin oxide for humans

An Acceptable Daily Intake (ADI) for man was proposed by FAO/WHO in 1971 for TPTOAc, TPTOH and TPTCl at 0.5 ug kg^{-1} body weight. Although the setting of an ADI is usually difficult because it requires quantification of the maximum dose considered to be safe when taken in by man over a lifetime, a recent attempt has been made to estimate the ADI for TBTO and man; a Committee of the Japanese Ministry of Health and Welfare has proposed an ADI for man of 1.6 ug of TBTO kg^{-1} body wt and Schweinfurth and Günzel (1987) have calculated a provisional ADI for man of 3.2 ug TBTO kg^{-1} body wt.

5.2 Levels of TBT in seafood; potential loads and hazard assessment for humans

Assuming an acceptable ADI of 1.6 ug TBT kg^{-1} body wt, a person with a body weight of 60 kg could ingest 96 ug of TBT per day. Assuming a consumption of 100 g (wet weight) of seafood per day, this ADI corresponds to an "acceptable" contamination level of TBT in fish and shellfish of about 1 mg TBT kg^{-1} of wet sea food.

The main types of organotin compounds found in fish and shellfish from contaminated environments are the tri-, di- and monobutyltin compounds. TPT contamination of seafood samples has not been reported in the literature and methyltin derivatives are found occasionally and only at relatively low levels (Tugrul et al., 1983). However, levels of TBT in oysters and fish can exceed 1,000 ug (of TBT) kg^{-1} wet weight (Alzieu et al., 1986; Short and Thrower, 1986) either in highly polluted water or in aquaculture, for example salmon reared in cages of TBT-treated netting. Davies and McKie (1987) found that cultivated Atlantic salmon (Salmo salar) of commercial size from farms using TBT-treated nets normally contained 0.5-1.0 mg TBT kg^{-1} wet muscle tissue. Short and Thrower (1986a) found that the TBT levels in water from sea cages where salmon had been held for 19 months and accumulated around 1 mg TBT kg^{-1} wet weight ranged from 18 to 65 ng l^{-1}. These data indicate that a provisional 'safe' level of about 10 ng TBT l^{-1} in seawater may be appropriate for the protection of seafood consumers.

6. EFFECTS OF TRIALKYLTIN COMPOUNDS ON MARINE BIOTA

Concern about the effect of tributyltin on marine organisms arose when severe shell thickening of the Pacific oyster, Crassostrea gigas, was noted in the vicinity of yacht harbours (Alzieu et al., 1982; Alzieu, 1986). Partial evidence for a causal relationship was found at Arcachon Bay, France, and more fully confirmed subsequently by work in the UK and North America. This led to a rapid upsurge of research into the effects of TBT on a wide range of organisms, utilizing short-term acute toxicity tests and also long-term tests to detect sub-lethal effects.

6.1 Acute toxicity

Acute toxicity tests are carried out in order to determine the median lethal concentration (LC_{50}). This value is the concentration of toxicant in the water required to kill 50% of treated organisms in a given time. The exposure time in acute toxicity tests is generally short (eg 1 to 7 days). As discussed previously (section 5.1.1), tributyltin compounds are highly toxic to aquatic life which is why they are good antifoulants but they are similarly toxic to other, nontarget, organisms. Within the tri-n-alkyltin series, the toxicity exponentially increases from trimethyl- to tributyltin compounds (Fig. 13); in Fig. 14 the acute toxicity data (reciprocal of the 24-h LC_{50}) for Daphnia magna are plotted against the length of the alkyl chain.

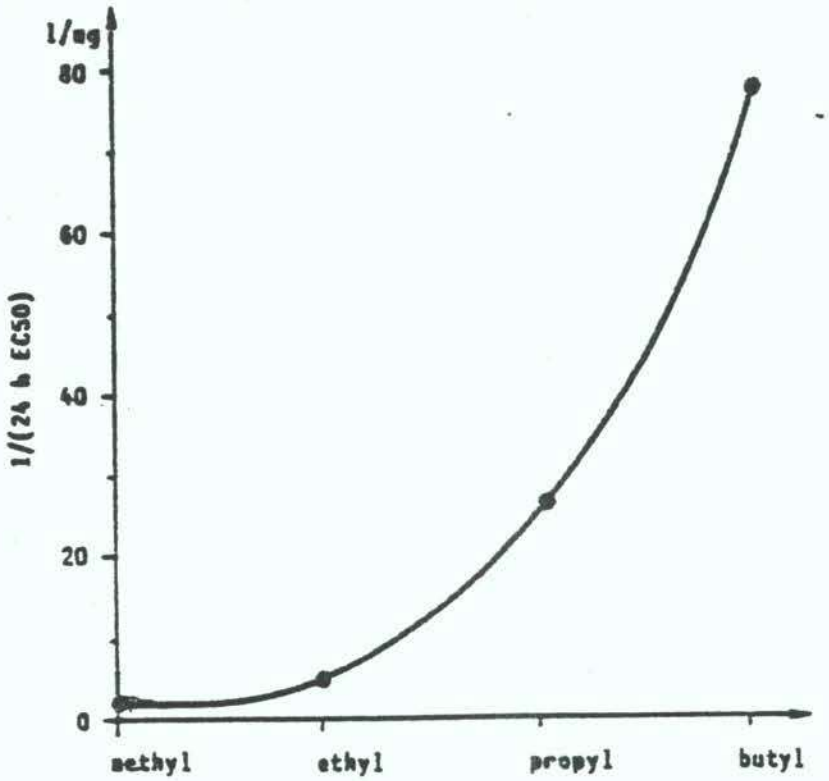

Fig. 14 Toxicity of a tri-n-alkyltin series to Daphnia magna (from Vighi and Calamari, 1985)

The toxic activity of a chemical is strictly related, under given environmental conditions, to its structural, physico-chemical and partitioning properties. Recent studies have shown that lethal concentrations may be quantitatively related to the structure of the toxicant (quantitative structure activity relationship, QSAR). Using larvae of the crab Rhithropanopeus harrisii exposed to 8 different organotin compounds, Laughlin et al., (1984), found that the LC_{50}s obtained for a 10-12 d exposure (corresponding to the duration of the zoeal development) were related to the Hansch parameter, to the Leo fragment constant, and to the total surface area of the molecule. The toxicity increased from trimethyl- to tricyclohexyltin compounds. Results obtained by Laughlin and Linden (1985) for some di- and triorganotin homologues are shown in Fig. 15.

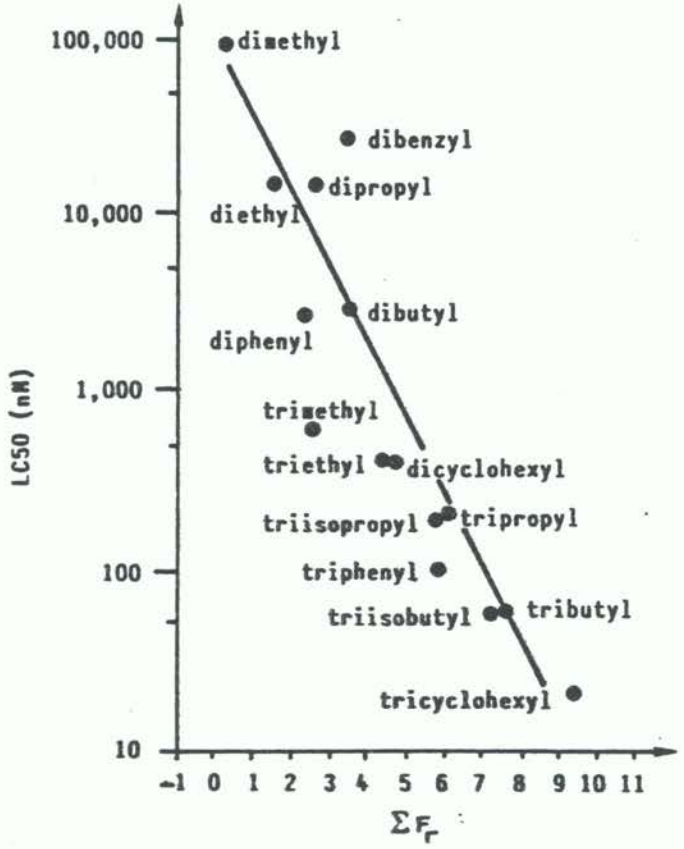

Fig. 15 Correlation between the LC_{50} values from larvae of the crab Rhithropanopeus harrisii (10-12 d exposure time) and the Leo Fragment constant (an index of the hydrophobic behaviour) for some di- and triorganotin homologues. From Laughlin and Linden (1985)

Vighi and Calamari (1985) calculated the 24-h LC_{50} (mg l^{-1}) of organotin compounds for Daphnia magna from the n-octanol/water partition coefficient, Kow, and the cologorithm of the acid dissociation constant, pKa, from the equation.

$$\text{Log } 1/\text{24-h } LC_{50} = 0.412 \text{ Log Kow} + 0.523 \text{ pKa} + 0.099$$

where the 24-h LC_{50} is expressed as the reciprocal. In Fig. 16 the relationship between experimental and calculated toxicity data for Daphnia magna with some mono-, di- and triorganotin compounds is shown.

QSARs have recently been obtained for several classes of chemicals and have been proved accurate for strictly homologous series of molecules as well as for relatively non-homologous compounds. At present this approach is not yet a substitute for laboratory and field experiments; however, with continuing improvement in their predictive potential, QSARs may greatly help environmental toxicology by reducing (but probably not replacing) the number of experiments carried out.

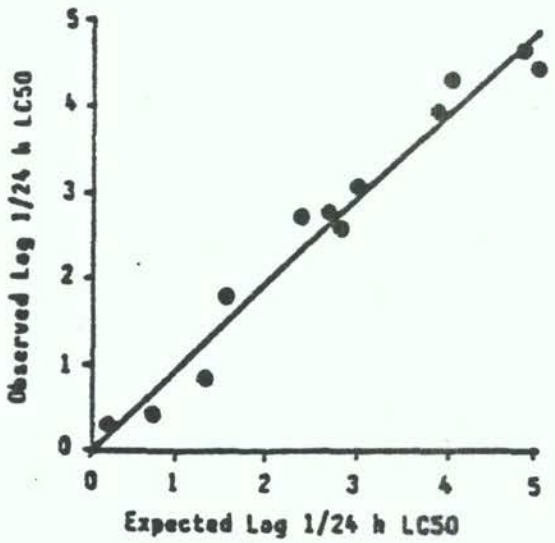

Fig. 16 Relationship between observed and calculated acute toxicity data in Daphnia magna (Vighi and Calamari, 1985). LC_{50} values in mg l^{-1}

Nevertheless, this combined experimental/theoretical approach confirms that TBT and TPT are among the most toxic of the organotins to aquatic organisms. Table XIV is a compilation of experimentally derived acute toxicity data for triorganotin compounds and nontarget aquatic organisms.

In general, larvae and juveniles are more sensitive than adults to the toxic action of organotin compounds. To illustrate this point, results of parallel toxicity tests on four species (Thain, 1983) are shown in Table XV. These data show clearly that sensitivity of the larvae may not be related to sensitivity in the adult. For example, the adult Pacific oyster is the most resistant to TBTO with a 48-h LC_{50} value of 1800 ug TBT l^{-1} whereas the larvae are the most sensitive of the 4 species listed in the Table.

In the context of this report, data on acute toxicity are of value in assessing the comparative sensitivity of a wide range of organisms and their various life stages. They also give an indication of the harmful effects of a chemical spill, or the concentrations required to achieve a total kill of certain pests, such as aquatic snails which are the intermediate hosts of the schistosomiasis parasite. Such data are of limited value in the prediction of the effects of low concentrations which may occur in the aquatic environment over a long period of time.

Table XIV

Acute toxicity values of triorganotin compounds for nontarget aquatic organisms.

Test Organism	Compound	Concentration in water (ug l^{-1})	Effect	Reference
FISH, fresh-water				
Carassius auratus (goldfish)	TBTO	75	24-h LC_{100}	Floch et al. (1964)
Salmo gairdneri (rainbow trout)	TBTO	28	24-h LC_{50}	Alabaster (1969)
Salmo gairdneri (rainbow trout)	TBTO	21	48-h LC_{50}	Alabaster (1969)
Lebistes reticulatus (guppy)	TBTO	75	24-h LC_{100}	Floch et al. (1964)
Lebistes reticulatus (guppy)	TBTO	39	7-d LC_{50}	Polster and Halacka (1971)
Tilapia mossambica (Mozamb. mouthbrooder)	TBTO	28	24-h LC_{50}	Matthiessen (1974)
Ictalurus punctatus (channel catfish)	TBTO	12	96-h LC_{50}	M&T Chemical Co. (1976a)
Lepomis macrochirus (bluegill)	TBTO	7.6	96-h LC_{50}	M&T Chemical Co. (1976b)
Fundulus heteroclitus (mummichog)	TBTO	24	96-h LC_{50}	M&T Chemical Co. (1976c)
Lebistes reticulatus (guppy) fry	TBTO	10-20	24-h LC_{50}	Schatzberg & Harris (1978)
Salmo gairdneri (rainbow trout)	TBTO	6.9	96-h LC_{50}	M&T Chemical Co. (1978)
Lebistes reticulatus (guppy)	TBTCl	21	7-d LC_{50}	Polster and Halacka (1971)
Lebistes reticulatus (guppy)	TBTOAc	28	7-d LC_{50}	Polster and Halacka (1971)
Cyprinus carpio (carp)	TPTOAc	521	24-h LC_{50}	Bock (1981)
Cyprinus carpio (carp)	TPTOAc	320	48-h LC_{50}	Bock (1981)
Carassius auratus (goldfish)	TPTOAc	75	24-h LC_{100}	Floch et al. (1964)

Table XIV (continued)

Test Organism	Compound	Concentration in water (ug l^{-1})	Effect	Reference
Gambusia affinis (mosquitofish)	TPTOAc	400	24-h LC_{100}	Gras and Rioux (1965)
Anguilla anguilla (eel)	TPTOAc	400	24-h LC_{100}	Gras and Rioux (1965)
Carassius auratus (goldfish)	TPTCl	250	24-h LC_{100}	Floch and Deschiens (1962)
Salmo gairdneri (rainbow trout)	TPTOH	78	24-h LC_{50}	Tooby et al. (1975)
FISH, salt-water				
Alburnus alburnus (bleak)	TBTO	13-17	96-h LC_{50}	Lindén et al. (1979)
Cyprinodon variegatus (sheepshead minnow)	TBTO	18	7-d LC_{50}	Ward et al. (1981)
Cyprinodon variegatus (sheepshead minnow)	TBTO	1	14-d LC_{50}	Ward et al. (1981)
Cyprinodon variegatus (sheepshead minnow)	TBTO	0.96	21-d LC_{50}	Ward et al. (1981)
Solea solea (sole), adult	TBTO	88	48-h LC_{50}	Thain (1983)
Solea solea (sole), larvae	TBTO	8.5	48-h LC_{50}	Thain (1983)
Solea solea (sole), adult	TBTO	36	96-h LC_{50}	Thain (1983)
Solea solea (sole), larvae	TBTO	2.1	96-H LC_{50}	Thain (1983)
Oncorhyncus tshawytscha (chinook salmon)	TBTO	1.5	96-h LC_{50}	Short and Thrower (1986b)
MOLLUSCS				
Crassostrea gigas (Pacific oyster), adult	TBTO	1800	48-h LC_{50}	Thain (1983)
Mytilus edulis (blue mussel), adult	TBTO	300	48-h LC_{50}	Thain (1983)

Table XIV (continued)

Test Organism	Compound	Concentration in water (ug l^{-1})	Effect	Reference
CRUSTACEANS				
Daphnia magna (water flea)	TBTO	1.7	48-h LC_{50}	M&T Chemical Co. (1976d)
Crangon crangon (brown shrimp)	TBTO	41	96-h LC_{50}	Thain (1983)
Crangon crangon (brown shrimp), larvae	TBTO	1.5	96-h LC_{50}	Thain (1983)
Acartia tonsa (copepod)	TBTO	1.0	96-h LC_{50}	U'ren (1983)
Daphnia magna (water flea)	TBTCl	13	24-h LC_{50}	Vighi and Calamari (1985)
Acartia tonsa (copepod)	TBTCl	1.1	48-h LC_{50}	Bushong et al. (1987)
Eurytemora affinis (copepod)	TBTCl	0.6	72-h LC_{50}	Bushong et al. (1987)
Acanthomysis sculpta (mysid shrimp), juveniles	TBT leachate	0.42	96-h LC_{50}	Davidson et al. (1986)
ALGAE				
Skeletonema costatum (marine diatom)	TBTO	1-18	algistatic within 5 d	Thain (1983)
Skeletonema costatum (marine diatom)	TBTO magg	18	algicidal within 5 d	Thain (1983)
Skeletonema costatum (marine diatom)	TBTO	0.1	no growth	Beaumont and Newman (198

6.2 Chronic and sublethal toxicity

Because the effect of tributyl tin in estuaries was first seen as a shell-thickening of oysters, considerable research has been carried out on sub-lethal effects on these species. At the same time, sub-lethal effects of tributyl tin were also looked for in other species or life stages which are known to be sensitive to pollution. Much of the data has been summarised by Waldock, Thain and Waite (1987) and a selection of the data is presented in this Section.

Table XV

Acute toxic concentrations of bis-(tributyltin) oxide, TBTO, for adults and larvae of four species (Thain, 1983).

Species	48-h LC_{50} (ug TBTO l^{-1}) adult	larvae
Crassostrea gigas (Pacific oyster)	1800	1.6
Mytilus edulis (mussel)	300	2.3
Crangon crangon (brown shrimp)	73	6.5
Solea solea (sole)	88	8.5

Molluscs; bivalves

Alzieu et al. (1980; 1982; 1986) and Alzieu and Portmann (1984) found anomalies in the shell calcification of the Pacific oyster, Crassostrea gigas, caused by tributyl tin released from marine antifouling paints. Alzieu et al. (1982) recorded shell malformation at 0.2 ug l^{-1} of TBTF leachate (measured as total tin) after 100 d exposure. Waldock and Thain (1983) found that the Pacific oyster grew poorly and showed significant anomalies in shell growth at tributyl tin concentrations of 0.15 ug l^{-1}, under laboratory conditions. Similarly, tributyl tin concentrations of the order of 1 ug l^{-1} caused significant decreases in oyster body weight (Valkirs et al., 1987); Gendron (1985) found anomalies in shell calcification of the Pacific oyster exposed to 0.05 ug l^{-1} tributyl tin.

The effects of exposure to TBT acetate on Pacific oyster spat are shown in Table XVI.

Lawler and Aldrich (1987) exposed spat of the Pacific oyster, Crassostrea gigas, to low levels of TBTO and examined the effects on oxygen consumption, feeding rate, compensation for hypoxia and growth rate. Significant effects were observed at levels of 0.05 ug TBTO l^{-1} for oxygen consumption and feeding rate, at 0.02 ug l^{-1} for growth and as low as 0.01 ug l^{-1} for compensation for hypoxia.

Long-term flow-through microcosm experiments showed that a decreased density of several marine species occurred with exposure to 0.5 to 1.8 ug TBT l^{-1}. Tributyl tin concentrations of 0.1 ug l^{-1} and higher reduced the condition index of oyster, Crassostrea virginica, caused significant reduction in the number of species and species diversity of organisms that settled on virgin panel surfaces (Henderson, 1986).

Table XVI

Effects of TBT acetate exposure on Pacific oyster spat (His and Roberts, 1983).

TBT acetate (ug l^{-1})	Effect
1.0	abnormal veligers, malformation of trocophores
0.5	larval anomalies, total mortality in 8 d
0.2	perturbation in food assimilation, total mortality after 12 d
0.1	slow growth, total mortality after 12 d
0.05	slow growth, high mortality after 10 d
0.02	NOEL

Veligers of the clam Mercenaria mercenaria showed a change in growth rate after exposure to 0.05 ug l^{-1} and above of TBT (Laughlin et al., 1987).

Stromgren and Bongard (1987) found reduction of the growth of juvenile mussel Mytilus edulis at exposure levels of 0.4 ug TBTO l^{-1}.

Tributyl tin was found not to be genotoxic to the larvae of mussel Mytilus edulis, from analyses of sister chromatid exchange and chromosomal aberrations (Dixon and Prosser, 1986).

Molluscs: Gasteropods

Organotin compounds have been shown to cause the development of male characteristics (imposex) in the female mud snail, Nassarius obsoletus, and in the female dog-whelk, Nucella lapillus (Smith, 1981; Bryan et al., 1986; Gibbs and Bryan, 1986) at concentrations close to 1 ng l^{-1}. This is the most sensitive effect recorded for TBT and for this reason it has been used as a field bioassay to measure concentration related effects in estuarine and coastal waters. For example, Davies et al. (1987) used the degree of imposex in the dogwhelk as an indicator of tributyl tin pollution in Scottish Sea Lochs originating from small boats and salmon cage farms.

Crustacea

Davidson et al. (1986) observed a reduction in the release of viable juveniles after reproduction of the mysid Acanthomysis sculpta exposed to 0.14 ug l^{-1} of TBT leached from panels coated with antifouling paint.

Weis et al. (1987) exposed the fiddler crab, Uca pugilator, to TBTO and found that at 0.5 ug l^{-1} the limb regenerative processes were retarded and deformities occurred.

Echinoderms

Walsh et al. (1986) observed an inibition in the regeneration of arms in the brittle star, Ophioderma brevispina, after exposure to 0.1 ug l^{-1} of TBTO and TPTO.

Fish

Rainbow trout, Salmo gairdneri, exposed to 0.2 and 1.0 ug l^{-1} of TBTCl for 110 d showed a dose-related decrease in growth rate. The NOEL was found to be less than 0.2 ug l^{-1} (Seinen et al., 1981).

7. HAZARD ASSESSMENT TO MARINE BIOTA

7.1 Effect concentrations

The previous section summarised a selection of data on the acute lethal and chronic sublethal effects of triorganotin in antifouling paints and coatings. Most of the data relate to TBT; other triorganotins have received much less attention. However, data presented in previous sections of this Report indicate that tributyl tin is probably the most toxic compounds so that effects of triorganic tin on aquatic organisms would probably not occur at concentrations at which TBT has little or no effect.

The most sensitive effect found for TBT is the development of imposex in certain gasteropod molluscs at concentrations greater than 1 ng l^{-1}. Effects on other molluscs occur at concentrations of 10 ng l^{-1} and above, and for fish and crustacea at 100 ng l^{-1} and above (Waldock, Thain and Waite, 1987).

7.2 Environmental concentrations

There are no data published on concentrations of triorganotin in Mediterranean waters, although some laboratories have begun to obtain such information. Therefore, concentrations which are likely to be present at predictable 'hot spots' - yacht harbours, marinas - have to be obtained either from calculations based on known usage and physico-chemical properties of tributyl tin compounds, or from monitoring data from countries outside the Mediterranean area.

Predicted concentrations in marinas

If it is assumed that TBTCl is found in marine waters in the undissociated form (Junk and Richard, 1987), the equilibrum partitioning in a model environment, can be calculated by using the fugacity approach (Mackay and Paterson, 1981).

A 10,000 m^2 harbour with a mean depth of 3 m (30,000 m^3 water volume), with 0.3 m^3 of aquatic organisms and 0.45 m^3 of suspended solids, with a 10 cm depth of accessible sediment (1,000 m^3) is assumed to receive 100 boats with 1,000 m^2 of painted surfaces, emitting 50 mg m^{-2} d^{-1} (UK DOE, 1986); this corresponds to a daily emission of about 0.15 mol of TBT derivatives. As a first approximation, no allowance is made for dilution by water turnover, degradation or chemical speciation and the exposure period of the marine waters to TBT emissions was assumed to be 20 d. Because TBTCl is a 'low volatile' chemical (Maguire and Tkacz, 1985), a vapour pressure value of 10^{-5} mmHg has been arbitrarily chosen because values of 10^{-3} mmHg or less have very little influence on the partitioning in an aqueous environment (Holysh et al., 1986). Sediment/water (Kp) and organism/water (BCF) partition coefficients have been calculated from the n-octanol/water partition coefficient (Kow), following Karickhoff et al. (1979) and Veith et al. (1979); the Kow was calculated from water solubility, using the equation proposed by Yalkowsky et al. (1983). A water solubility of 50 mg l^{-1} was selected from the literature (Blunden et al., 1984). The results of this simulation are shown in Table XVII.

This highly simplified simulation shows that concentrations higher than 1 ug l^{-1} of TBTCl may be present in "hot spots". Actual values will be lower where significant water exchange or degradation occurs.

Measured environmental concentrations

Concentrations of triorganotin found in seawater have been given in Section 4.4.3. Concentrations in areas of high yacht density can exceed 1 ug l^{-1}, as predicted by the above model. Dilution and degradation will reduce these levels to 10 ng l^{-1} and less in more open waters.

Table XVII

Equilibrium distribution of TBTCl in a model environment, with no water turnover or chemical transformations, with an input of 3 mol of TBTCl in 20 d derived from 1,000 m^2 painted surface emitting 50 mg m^{-2} d^{-1}.

environmental compartment	accessible vol	% distrib.	mol m^{-3}	mg kg^{-1}
water	30,000	5.82	$5.8\ 10^{-6}$	$1.9\ 10^{-3}$
aquatic biota	0.3	0.04	$3.7\ 10^{-3}$	1.2
suspended sed.*	0.45	0.04	$2.8\ 10^{-3}$	0.6
sediments*	1,000	94.10	$2.8\ 10^{-3}$	0.6

* Sediment density = 1.5 kg dm^{-3}

7.3 Hazard to marine biota

It is clear that the concentrations found in "hot spots" (> 1 ug l^{-1} TBTO) are likely to have an acute toxic effect on sensitive organisms and chronic effects on those with a greater resistance to TBT. These effects will become associated with fewer species as the concentrations reduce, and it is possible that very few effects will occur at concentrations less than 1 ng l^{-1} TBTO. However, this thousand-fold reduction may not readily be achieved in enclosed waters, so it is clear that there will be places where the impact of triorganotin on the local marine biota will be unacceptable. The extent to which protection will need to be given will vary from place to place, but appropriate water quality standards will be in the range of 1 to 20 ng l^{-1} TBTO.

Data presented in Section 5.2 suggest that the ADI for TBT in sea food of 1.6 ug TBT kg^{-1} body weight would be associated with an ambient water quality standard of 10 ng TBT l^{-1}. Even allowing for errors in some of the assumptions, it is likely that measures taken to protect aquatic life will protect human health also.

8. EXISTING NATIONAL AND INTERNATIONAL PROVISIONS FOR THE PREVENTION OF MARINE POLLUTION

The use of antifouling paints containing organotin compounds was first brought under control by the French Government (January 1982), which banned the use of paints containing more than 3% in weight of these compounds for the protection of hulls of boats less than 25 tons (Alzieu, 1986). This initial action applied to the Atlantic French coast and to the English Channel. A second decree (16 September 1982) extended the ban to the whole French coastal area and to all organotin paints. Present regulations, in force from February 1987, ban the use of antifouling paints containing organotin compounds for all boats and marine craft less than 25 m in length, with the exception of hulls made of alloy.

In January 1986 the United Kingdom prohibited the retail sale and supply of antifouling paints containing organotin compounds at levels exceeding 7.5% by weight of total tin in the dried paint for copolymer paints, and 2.5% of total tin in free association paints (UK DOE, 1986). A new regulation reducing the maximum allowable tin concentration in copolymer paints from 7.5 to 5.5% was introduced in January 1987 (Abel et al., 1987). These regulations were designed to apply to small pleasure craft which can be concentrated in areas of low water exchange, and thereby cause high local contamination. At the same time an upper limit was set for the content of organotin in copolymer paints, and the retail sale of free-association paints containing high concentrations of organotin compounds was banned. The effectiveness of these controls was measured by environmental monitoring, the aim being to reduce concentrations to below a provisional water quality standard of 20 ng l^{-1} TBT. Results approved the total ban of the use of triorganotin compounds on vessels of less than 25 m overall length and on structures used in fish and shellfish farms (Abel et al., 1987).

Switzerland and Germany banned the use of TBT in antifouling paints in fresh waters (Champ and Pugh, 1987). In Italy, organotin biocides were forbidden from May 1985 for use in industrial cooling waters discharged to shellfish farming areas. In other European countries the control of organotin pollution is at present under review.

Canada and USA are considering the registration of antifouling paints. The US EPA, in initiating its Special Review for TBT, identified significant gaps in the information supporting the registration of TBT for antifouling paints. In order to complete the data requirements the EPA has planned the issue of a series of Data-Call-In Notices to the registrants (Champ and Pugh, 1987). At the same time some individual States in the US have approved, or are considering, restrictions and regulations for the use of organotin compounds similar to those recently adopted by the UK government.

At the European Community level, a proposal for a ban on the sale to the general public of paints containing organotins and the use of these paints on boats under 25 m and in fish farm nets and cages is under consideration by member states.

The Commission of the Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention) has recently adopted (February, 1988) the following recommendantion:

"RECOMMENDS that the Governments of the Contracting Parties to the Helsinki Convention:

a) take, as soon as possible, but not later than 1991, effective measures to eliminate such pollution;

b) include in the measures taken, as a first step, a ban on the retail sale or use of organotin paints for pleasure boats or fish net cages;

c) consider the need for restrictions on other uses of organotin compounds in anti-fouling paints, for example on sea-going vessels and underwater structures;

RECOMMENDS FURTHER that the Contracting Parties report on measures taken in accordance with this Recommendation, and on organic tin concentrations in the marine environment in areas where organic tin compounds may still be entering the marine environment of the Baltic Sea Area, one year after the adoption of this Recommendation and thereafter every five years."

9. RATIONALE FOR ESTABLISHING CONTROL MEASURES IN THE MEDITERRANEAN REGION

From the information and calculations made in the previous sections of this Report, a number of conclusions emerge. It is clear that, on the basis of organotin production, usage and toxicity, the triorganotins are the most likely to cause environmental harm. Also, it is clear that those uses which introduce significant quantities of organotin compounds into the marine environment are the prime candidates for control measures. In effect, therefore, the first priority is to control the use of triorganotin in antifouling paints and coatings, and secondly to investigate the use of triorganotin as an antifoulant in the cooling water systems of coastal power stations and other industries.

There is a considerable amount of information on the environmental hazards arising from the use of triorganotin antifouling paints (in practice tributyltin and to a much lesser extent triphenyl tin) on boats and mariculture structures. However, although scientifically based water quality standards can be set for different levels of environmental and human protection (Section 7), this information can only be used to define the scale

of the problem which may exist in the Mediterranean. This is because a collection of boats represents a diffuse source of inputs and there is little scope for controlling the emission from each vessel so that the local water quality standard is not exceeded. In theory it might be possible to limit the number of boats in any one area in order to achieve the appropriate water quality standard but in practice this would probably present considerable difficulties. These problems become greater when considering the emission of triorganotins from antifouling paint on large ships, such as naval vessels and freight ships engaged in international trade.

In these circumstances, effective control of triorganotin inputs from these sources can be achieved only by restrictions on the use of products containing such compounds. This is the rationale behind the national control measures outlined in Section 8. As a first step the controls have been applied to boats less than 25 m in length, because this is a sector where the usage of paint can be separately regulated and where some of the more severe environmental problems arise. A ban on the use of triorganotin in antifouling paints for this market will do much to reduce the level of triorganotin in the marine environment. Similarly, a ban on use of triorganotin in antifouling coatings used in mariculture will reduce both the environmental hazard to marine life and seafood consumers. The paint industry is urgently investigating the use of environmentally acceptable biocides for incorporating into paint and coatings.

It is recognised that these controls may leave a residual problem. Environmental monitoring may reveal that larger ships coated with triorganotin antifouling paints leach sufficient TBT into the water to exceed the water quality standard. A recent calculation showed that recreational boats accounted for 66% of the TBT input from all vessels in the US State of Virginia (Schatzberg, 1987), although the larger ships would be located mainly in areas where the water exchange and dilution of inputs is greater than that for small boats. Also, any place where boat hulls are stripped of oil paint and then repainted could be a source of triorganotin pollution. Environmental monitoring should be carried out to determine the extent of this contamination, but immediate advice should be given for the proper disposal of water containing old paint, and of spillages of new paint. A code of practice for this purpose has been published by the UK Dept of the Environment (1986).

It is not known to what extent triorganotin biocides are used as antifoulants in water cooling systems. Data presented in Section 3 of this Report indicates that a treatment of 10 ug l^{-1} TBT would constitute a considerable load on the marine environment, especially where flows of 200,000 m^3 h^{-1} are used as this would lead to discharges of 48 kg TBT d^{-1}. However, such discharges are point sources and as such are more readily controllable in order to achieve the required water quality standard in the receiving water.

Environmental monitoring for triorganotin is clearly a key element in assessing the scale of the problem and the success of control measures. Water concentrations of 1 ng TBT l^{-1} can be measured by present analytical techniques, but further development is required to improve the sensitivity and reliability of the methods. Also, little is known about the environmental significance of triorganotin sinks in sediments; more work is required on the development of appropriate analytical techniques, and measuring the effects of such contamination on sediment-dwelling organisms, before a decision can be made on the need for further controls and the most appropriate type of regulation.

ANNEX

FAO/UNEP/IAEA/WHO Pilot Survey of Organotins
in Selected Mediterranean Areas

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1. INTRODUCTION

The FAO/UNEP/IAEA/WHO Ad-hoc Meeting on Organotin Compounds (Athens, 5-7 October 1987) reviewed the existing information on organotins in the Mediterranean and agreed that a primary requirement would be the provision of data on existing levels of triorganotin compounds in Mediterranean locations where "hot spots" were likely to be present, such as marinas, harbours, etc. It was therefore recommended that, as a first step, two or more laboratories chosen for their geographical location and known analytical competence should undertake a survey of tributyltin and possibly triphenyltin in selected locations of the region.

The pilot survey was undertaken during 1988 and the results are presented in this annex.

2. SELECTED AREAS

The four selected areas are shown in Fig. 1 and they are the Mediterranean coast of France, the North Tyrrhenian coast (Italy), the Southern coast of Turkey and the Alexandria coastal area (Egypt).

2.1 French Mediterranean Coast

The survey in this area was conducted by IFREMER, Nantes, (principal investigator C. ALZIEU) in the following five locations (Figs. 2,3,4,5 and 6).

Marseille

Twelve stations were sampled in the harbour and the adjacent marina. Ten stations were located within the commercial harbour in the vicinity of mooring areas for large ships, i.e. ferries (station 2), cargoships (station 3 to 8), tugboats (station 9). Station 1 (avant-port de la Joliette) and 10 (Passe d'entrée nord du Port de Commerce) represent points of inflowing and outflowing waters. At stations 2 to 9 the water exchange with the open sea is very low. Stations 11 and 12 are located in the Vieux Port marina which has a capacity for 3200 boats. The water is also highly contaminated by various organic inputs.

Bandol marina, near Toulon:

Five stations were sampled in this marina, which has a capacity for 1350 boats. A high density of boats is present throughout the year, and some moored boats are up to 25 m long.

Cap d'Agde marina:

Eight stations were sited in this marina, located on the western part of the French Mediterranean coast. It has a capacity for 1700 boats; station 5 corresponds to the "mixing zone".

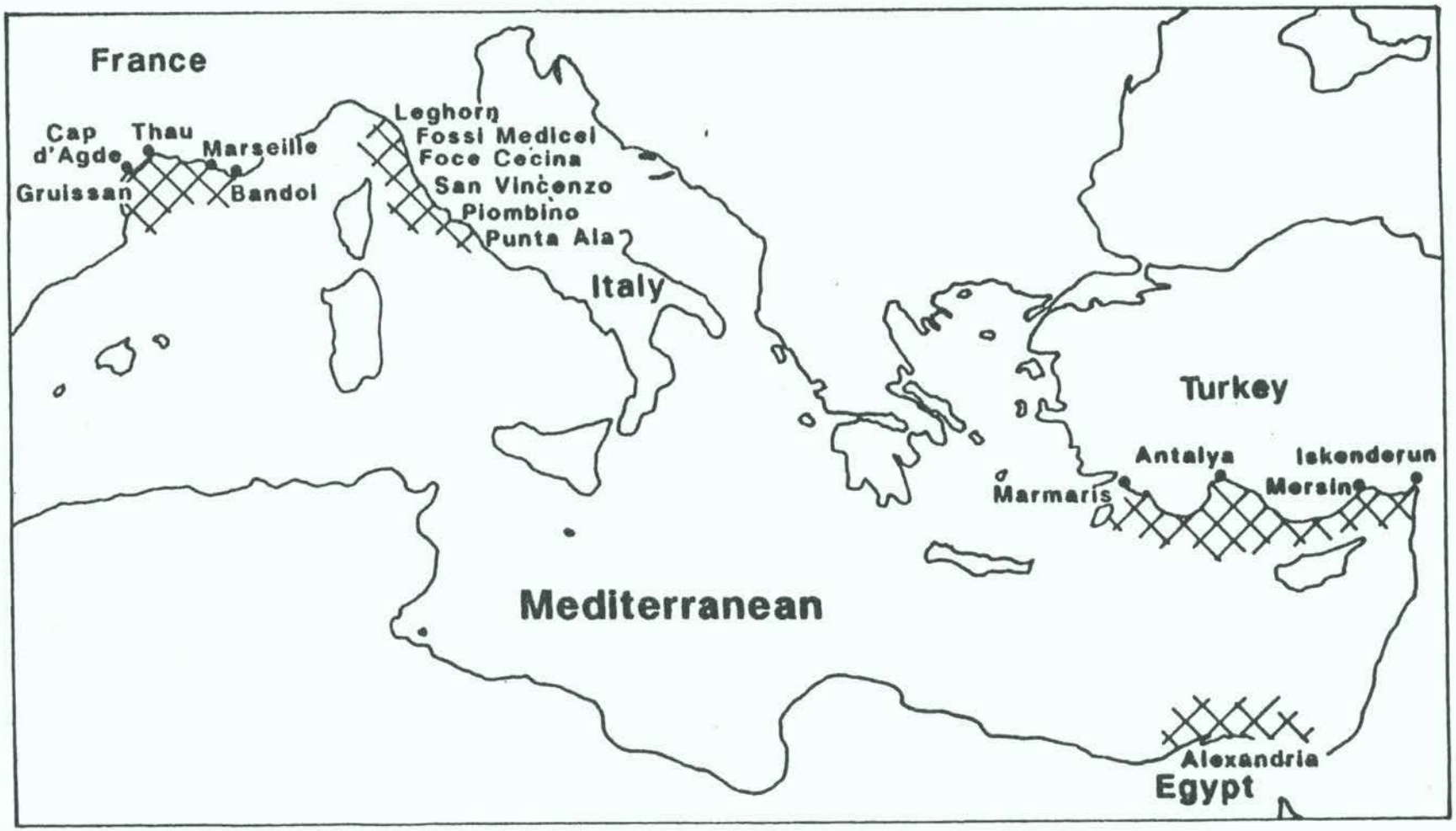

Fig. 1 Mediterranean areas investigated by the organotin pilot survey. Coastlines sampled are shaded by cress-hatching and individual sites are named.

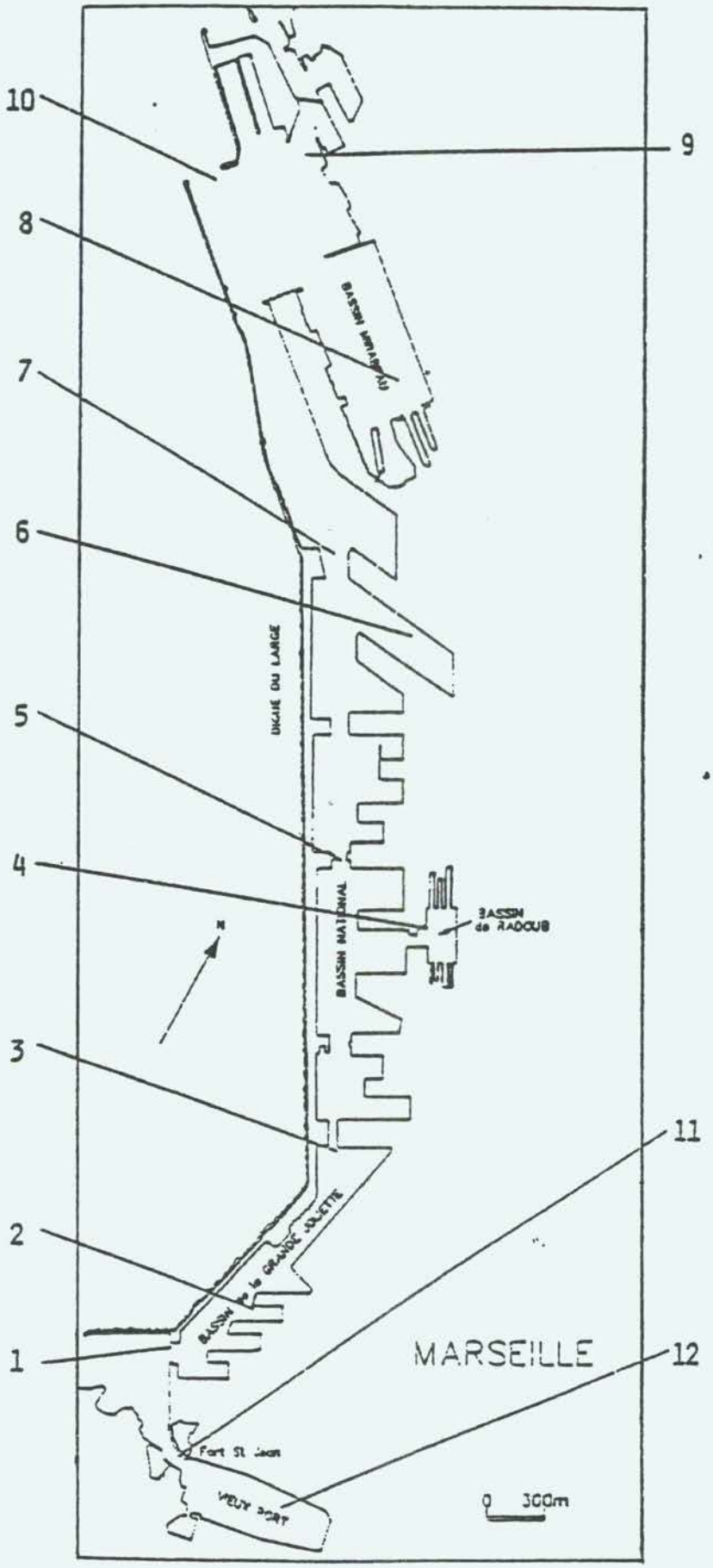

Fig. 2 Stations in Marseille area

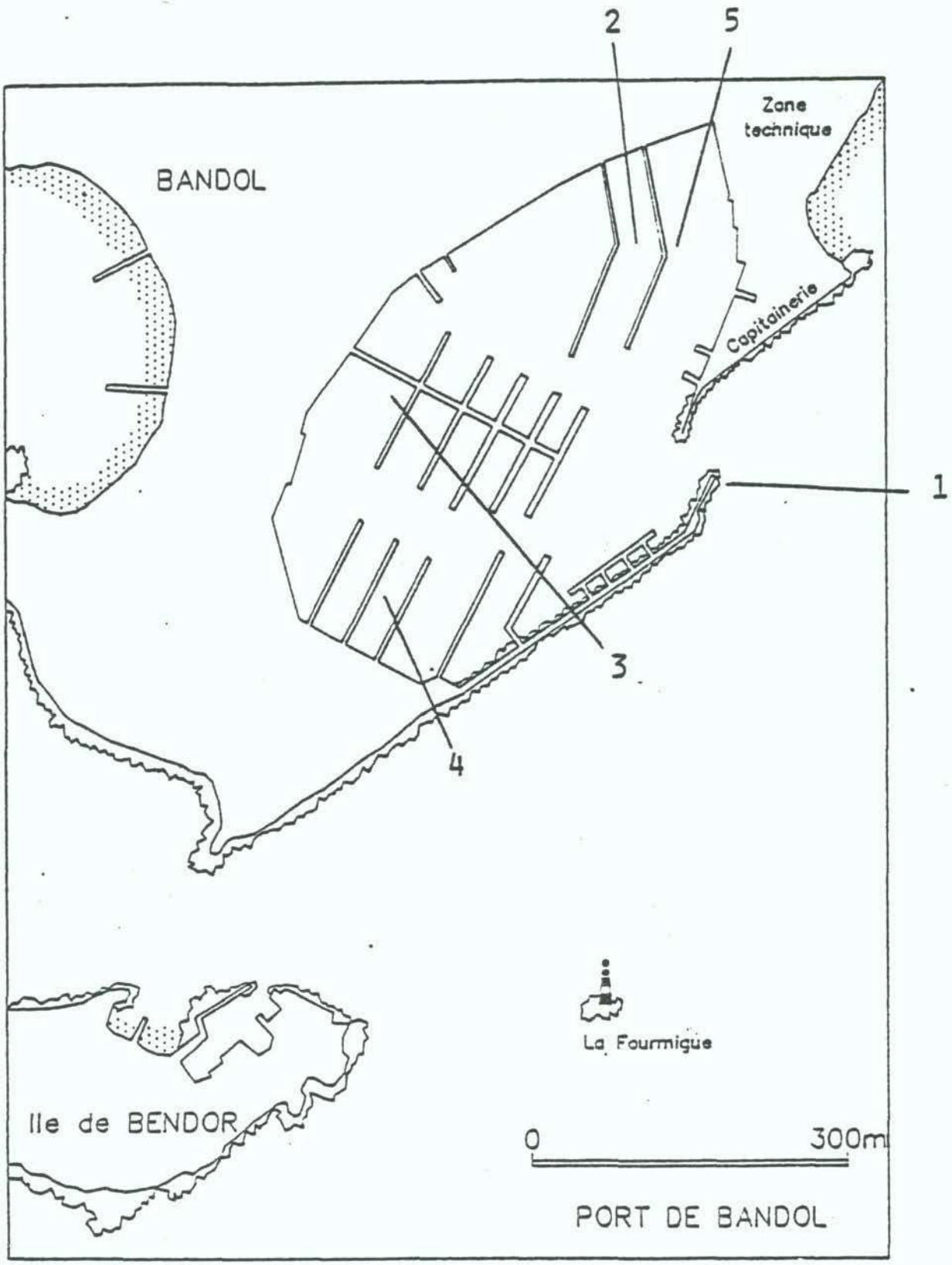

Fig. 3 Stations in the Bandol marina

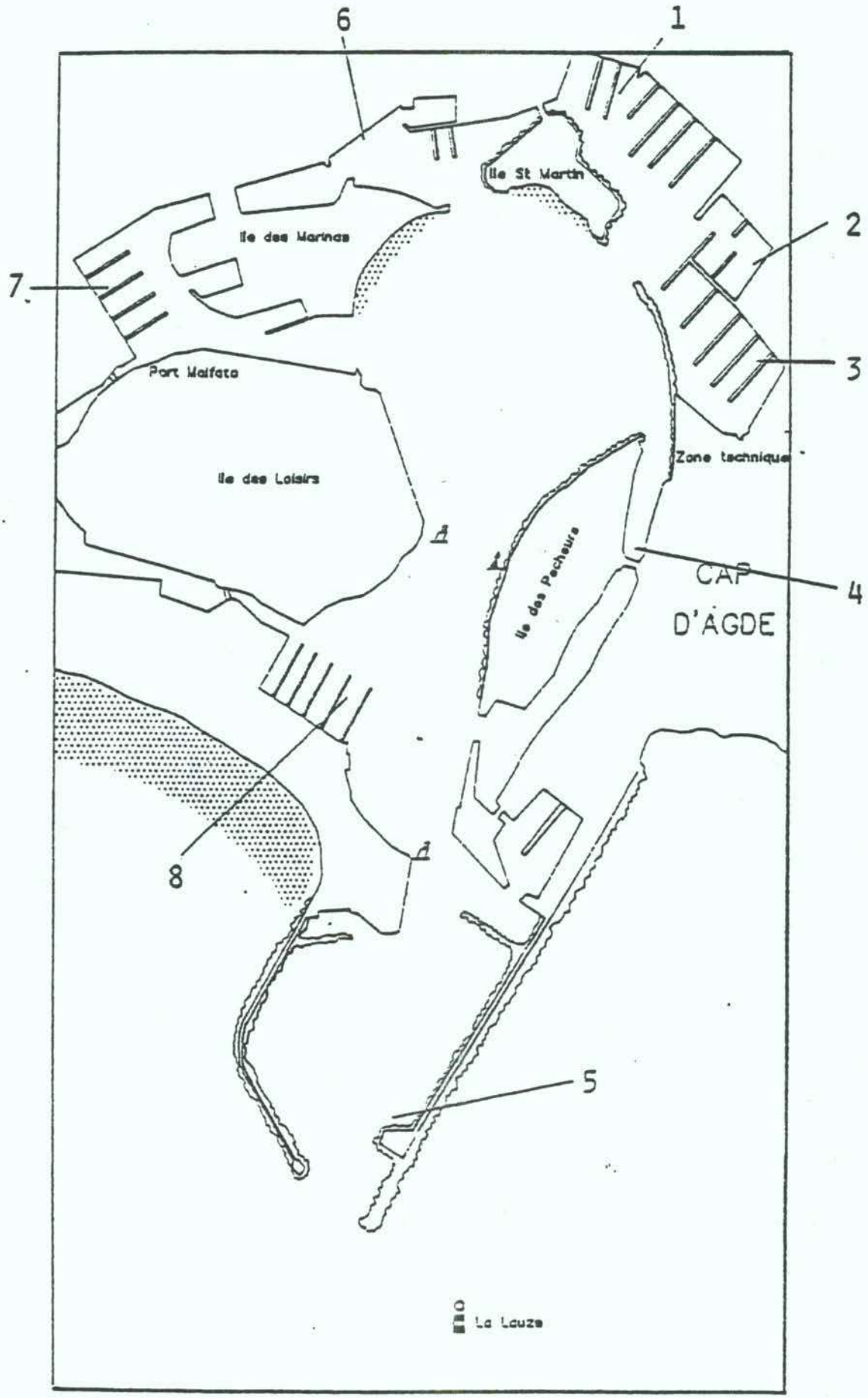

Fig. 4 Stations in the Cap d'Agde

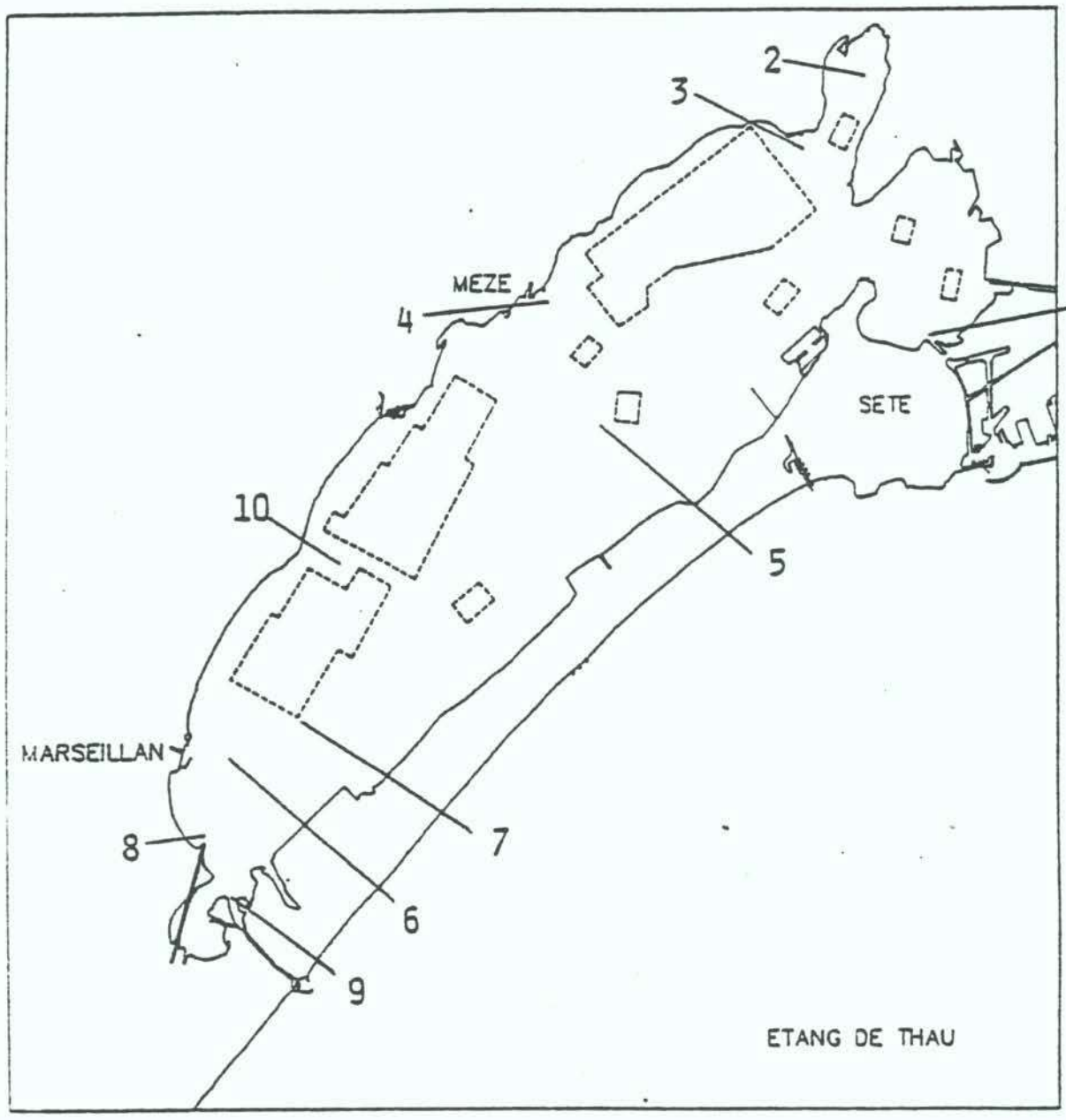

Fig. 5 Stations in the Etang de Thau

Etang de Thau:

This is the largest shellfish culture area on the French Mediterranean coast; the production is in the range of 10000 t/year of mussels and 5000 t/year of oysters. It is a saltwater pond of 20 km long, 5 km wide and 7 m mean depth. Ten stations were sampled. There is only one outlet with the open sea (station 9). At the Northern part there is a link with Séte harbour (station 1). There are about 700 local boats operated by shellfish farmers, and 300 pleasure boats. In 1980, before the ban on organotins in antifouling paints the TBT input in Etang de Thau was estimated at 80 kg/year. Station 3(Bouzigues), 4(Meze) and 7(Marseillan) represent marinas.

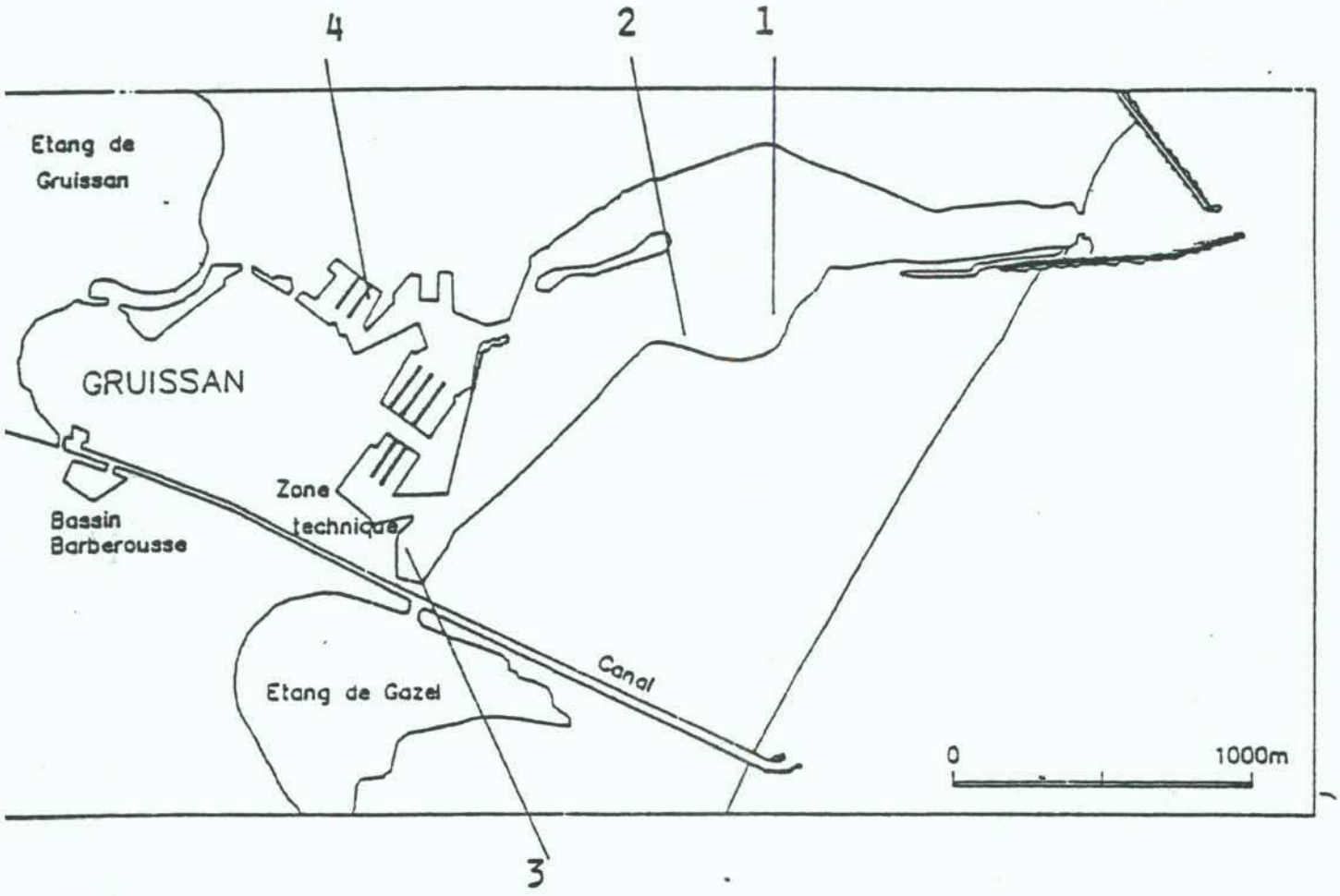

Fig. 6 Stations in the Gruissan

Gruissan:

Four stations were located in this bay where there is a marina for pleasure boats (station 4) and a fishing port (station 3). The shellfish farmers use the mouth of the bay for storing oysters and mussels during winter season.

Bandol marina was sampled in April (station 1 and 2) and September (station 1 to 5). All other samples were taken during April 1988. All seawater samples were analysed for TBT, DBT, MBT and salinity. The temperature of water surface was determined at the time of sampling.

2.2 Northern Tyrrhenian coast

The survey in this area was conducted by the University of SIENA, Dept. of Environmental Biology (principal investigator E. BACCI) in the following five locations (Fig. 7).

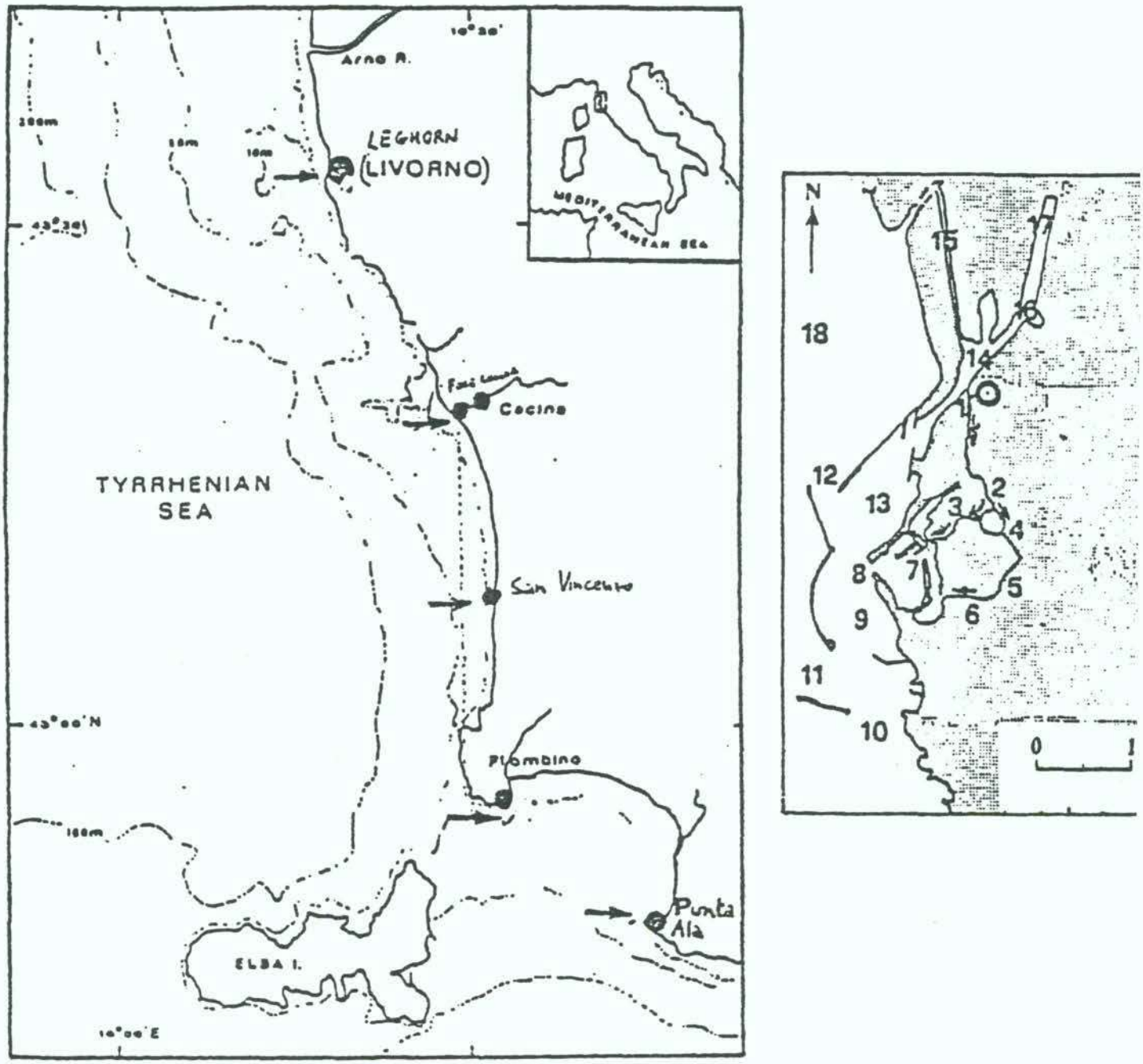

Fig. 7 Sampling locations in the North Tyrrhenian Sea with a detailed plan showing sampling sites in the Leghorn harbour area and in the "Fossi Medicei" (stations 2-6). ⊙ Power plant

Leghorn:

This is one of the most important Italian commercial harbours. A local thermoelectric power plant is using a TBT- based antifoulant in its cooling water at a concentration of 7-8 ug l^{-1}. The flow of contaminated waters reaching the harbour through the Fossi Medicei is about 40,000 m^3 h^{-1} corresponding to a TBT input in the range of 7 kg per day. The 18 stations of this area were sampled in April, May, June, July and August.

Piombino:

This is minor commercial harbour with a small marina and receives inputs of industrial effluents (TBT free). Sampling was carried out in June and August.

Foce Cecina:

A small harbour for pleasure craft (up to 650), at the mouth of the River Cecina, the majority of boats being 5-7 m long. Sampling was carried out in April, May, June, July and August.

San Vincenzo Marina:

This has a capacity for 520 small pleasure boats; it was sampled in May, June, July and August.

Punta Ala Marina:

This has a capacity for 900 boats of 10-12 m long; sampling was carried out in May, June, July and August.

In Leghorn harbour, sampling was carried out 3 to 6 h after low tide. In other sites samples were collected in the middle of the marina after high tide. Samples were analysed for TBT, DBT and MBT.

2.3 Southern coast of Turkey

The survey of the southern coast of Turkey was conducted by the Middle East Technical University, Institute of Marine Sciences (principal investigator I. SALIHOGLU) in the following five locations (Fig. 8).

Iskenderun harbour:

This is located in a semiclosed bay which receives discharges form industry (agrochemical, petrochemical, textile, food, iron and steel). Next to the harbour there are several small shipyards specialized in the maintenance of boats from throughout the region, with a busy season from April till mid August. The harbour itself receives some domestic and industrial discharges, and is usually occupied by commercial ships.

Mersin harbour:

This is located in a bay with a good water exchange. The bay receives domestic and industrial discharges; dry docks are also a possible source of TBT. The harbour is busy and used by commercial ships including oil tankers, fishing boats and pleasure craft.

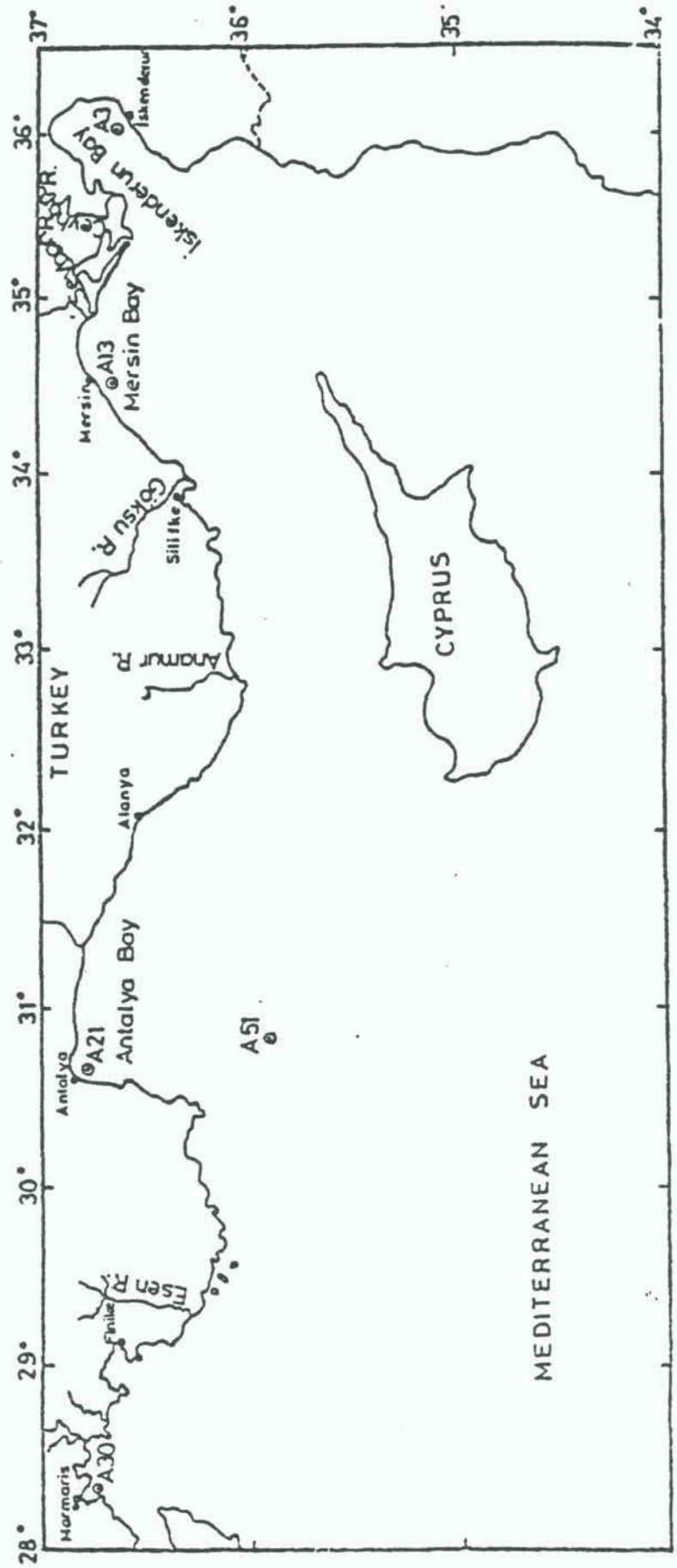

Fig. 8 Sampling locations in the Southern coast of Turkey

Antalya marina:

This small marina is usually occupied by pleasure boats and small fishing boats (excluding trawlers).

Marmaris marina:

This marina is in an enclosed estuary, and is occupied almost completely by pleasure boats. Maintenance of boats is carried out within the marina.

Open sea: subsurface sample

In each location there was only one station which was sampled during May and July except Mersin Harbour which was sampled only in May 1988. Samples were analysed for TBT, DBT and MBT. Additional data were obtained for temperature, salinity, chlorophyll a, total suspended solids and humid material.

2.4 Alexandria coastal area

The survey of sediments in the Alexandria coastal belt was carried out by the University of Alexandria, Department of Oceanography (Principal investigator O. ABOUL DAHAB).

The sampling area extended more than 45 km along the coast from Agamy (West of Alexandria) to Abu Kir Bay (East of Alexandria) and in a seaward direction to a depth of 35 m. The coastal belt includes the major Egyptian commercial harbour (Western harbour), a small fishing harbour (Eastern harbour) and two ecologically important bays, Mex Bay to the west and Abu Kir Bay (another fishing harbour) to the east. Both are used as fishing grounds. Thirty-five sampling stations were selected to evenly cover the area under investigation (Fig. 9).

Surface sediments were sampled in 1986 and analysed for inorganic tin, methyltins and butyltins content. In addition data on granulometry and organic carbon content were obtained.

3. METHODOLOGY

3.1 Sampling techniques

3.1.1 Sea water

Sampling and storage vessels (either glass or teflon bottles) were precleaned by soaking in dilute hydrochloric acid solution (10%) followed by rinsing with distilled water. Sampling/extraction bottles used for cGC-FPD protocols were additionally solvent rinsed using high grade dichloromethane.

Sub-surface water samples were collected either on-shore or from non-TBT treated boats. Sampling bottles were immersed prior to opening and retrieved closed to prevent potential contamination from the surface micro-layer.

Samples collected for AAS analyses were then preserved using glacial acetic acid (>1% final concentration). Those samples collected for cGC-FPD analyses were stored at <4°C in darkness and were analysed within 2 days of collection.

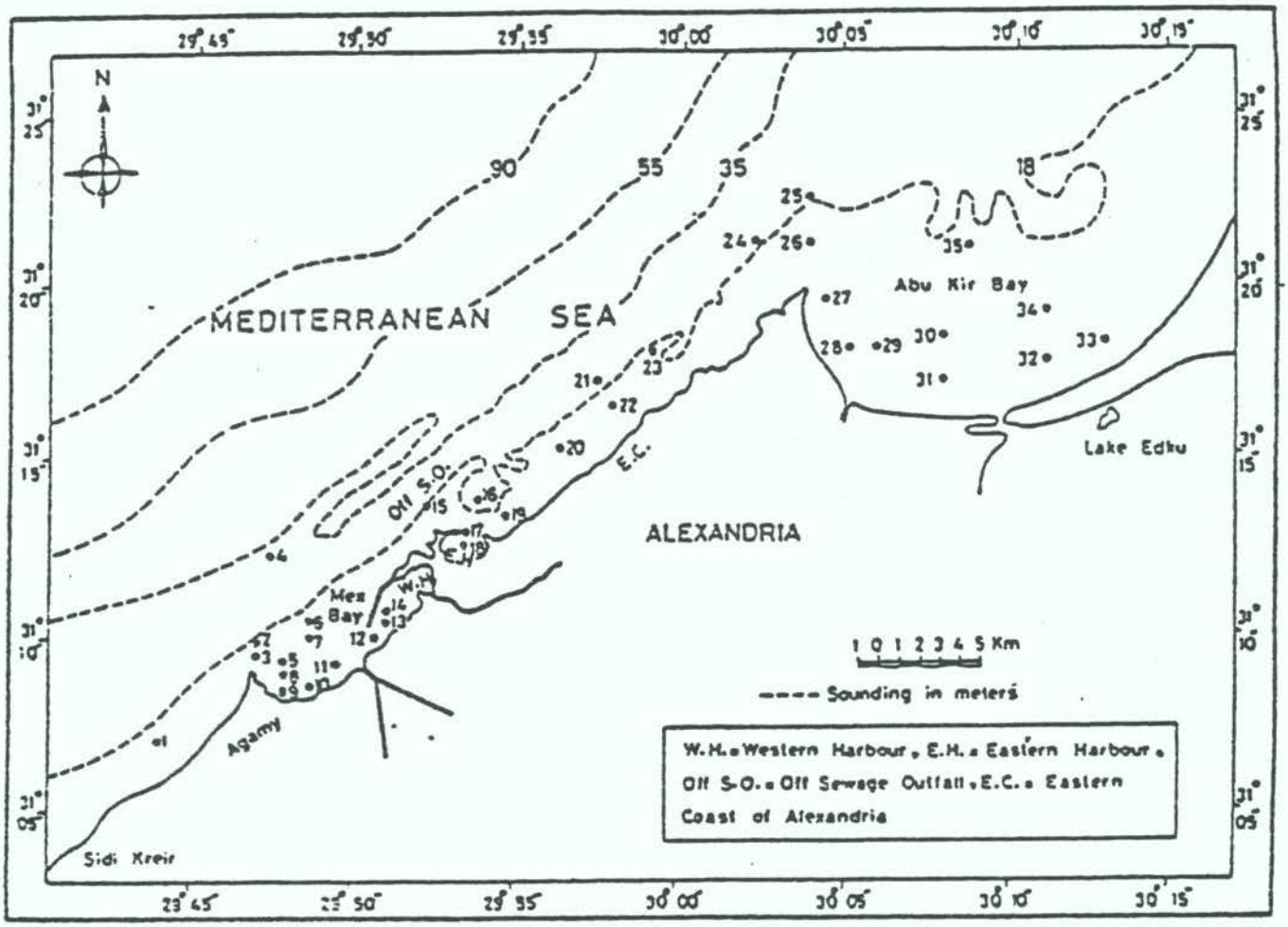

Fig. 9 Area of study and sampling stations (from O. Aboul Dahab, 1988 in press)

3.1.2 Sediments

Samples of surface sediment were collected using a Van Veen Grab. The surface layer (approximately <2 cm depth) of the sediment was then removed using a teflon spatula. Samples were stored frozen in acid pre-cleaned/distilled water rinsed polypropylene bags. After air- drying on a clean laminar flow bench, each sample was ground and sieved (63 um stainless steel mesh) prior to organotin analysis.

3.2 Analytical techniques

3.2.1 Sea water

The following techniques were used to determine butyltins in sea water:

3.2.1.1 Hydride Generation - Atomic Absorption Spectrophotometry (HG- AAS)

HG-AAS techniques used to quantify butyltin species in this pilot survey are derived from the methods described by Braman and Thompkins (1979) and Hodge et al. (1979). The technique involves generation of hydrides from acidified sea water samples using sodium borohydride. The butyltin hydrides are then purged and trapped in a liquid nitrogen cooled coil. As the coil is warmed the species are liberated from the trap according to their volatility, and are then quantified by Atomic Absorption Spectrophotometry. This technique was used to quantify butyltins in samples from the Southern coast of Turkey and the French Mediterranean coast, the latter using the automated analytical protocol described by Michel (1987). Each reported French Mediterranean coast concentration was determined from 5 replicate analyses.

Detection limits for the HG-AAS techniques are approximately 1 ng l^{-1} for DBT and MBT and 2 ng l^{-1} for TBT using the automated technique (10 ng l^{-1} for TBT using the manual technique).

3.2.1.2 Capillary Gas Chromatography-Flame Photometric Detection (cGC- FPD)

The samples from the North Tyrrhenian coast were analysed by cGC- FPD using an application of the simultaneous hydridization and extraction procedure introduced by Matthias et al. (1986) with minor modifications according to Waldock et al. (1987). Glass separating funnels (1.5 l) with teflon stopcocks and glass stoppers were used to simultaneously hydridize (using one pellet of approximately 300 mg of sodium borohydride) and extract (into 25 ml dichloromethane) the butyltins. The apparatus with sample and added reagents was shaken manually for 15 minutes to facilitate the derivatization/extraction. Following phase separation (20 min standing) the dichloromethane layer was collected. The procedure was then repeated using a further 15 ml of dichloromethane. Any water present in the recovered dichloromethane phase was removed by centrifugation. The solvent was then concentrated using a micro-Kuderna-Danish followed by passing a gentle stream of nitrogen over the surface to produce a final sample volume of 100 to 200 ul. Individual butyltins were then separated by capillary gas chromatography and quantified using a flame photometric detector. The system was calibrated by analysing replicate distilled water samples spiked with known amounts of butyltins and by standard addition analyses of environmental samples. Detection limits of the technique are approximately 20 ng l^{-1} for tri- and di- butyltins and 100 ng l^{-1} for monobutyltins.

3.2.2 Sediments

Extraction of sediments was achieved by shaking (15h) sediment (1g), calcium chloride solution (final concentration 2.5M) and HCl (final concentration 2.5M, total volume 10 ml) in a sealed centrifuge tube. Following centrifugation (1500rpm; 10min) the supernatant was filtered (0.4 um Nucleorope R polycarbonate filter). The filtrate was diluted to 10.0 ml with double-distilled water, aliquots (0.5 ml) of which were analysed using hydride generation -AAS as described in Section 3.2.1.1. Appropriate reagent and sediment blanks were analysed simultaneously. Detection limits for individual alkyltins were approximately 1 ngSn g^{-1} dry sediment and 2 ng g^{-1} (as Sn) dry sediment for inorganic tin. Recovery experiments (8 replicates) demonstrated 79 to 105% recovery of spiked alkyltin species. Triethyltin was used as an internal standard.

3.3 Intercalibration of techniques

The various techniques employed to quantify individual butyltins were intercalibrated through analyses of bulk samples prepared during the IAEA/FAO/UNEP Workshop on the methodology and intercalibration of organotin compounds in the Mediterranean marine environment (Monaco, 18-20 April 1988). Selection of samples suspected of containing negligible contamination, the same sample "spiked" with tributyltin and finally a polluted sample from a marina, were distributed for analysis. Results have indicated that all the laboratories participating in this pilot survey can adequately differentiate "polluted" areas from uncontaminated regions and reasonable agreement was achieved for analyses of the "spiked" sample.

4. RESULTS AND DISCUSSION

The data obtained through this pilot survey represent the first information on butyltin levels in seawater and sediment from different Mediterranean areas.

The survey includes 17 areas from which 113 seawater samples were analysed and one area where 35 sediment samples were analysed. Additional parameters mentioned in Section 2 are not discussed further in this report.

4.1 Seawater samples

Seawater samples were collected at sites selected according to potential inputs of TBT (and relevant compounds) as well as according to differing environmental conditions.

Two shellfish-culture areas (where Pacific oysters and mussels are grown and stored) which are located near marinas in enclosed sites, were included.

Results from this pilot survey can be considered, as a first approximation, representative of the various contaminated sites occurring in the Mediterranean region. Typical TBT contaminated sites can be grouped as follows:

- those receiving industrial discharges, mainly related to the use of TBT as an antifoulant in cooling pipes;
- harbours, where commercial shipping activities and marinas occur, often together with ship maintenance operations, and which receive large quantities of industrial and other effluents;
- marinas, occupied by pleasure boats;
- mariculture areas.

As shown in Table I, extremely high and relatively constant levels of TBT were found in water samples collected at the Leghorn power plant outlet, selected as an example of TBT load from antifouling treatments in cooling pipes. In the same samples DBT and MBT appear as minor components. The TBT contamination in the Fossi Medicei, essentially originated by the power plant outlet, is 4-10 times less, due to dilution, and to a lesser extent, to degradation processes, as some relatively high value of the DBT concentration seems to indicate. From these findings, the TBT contamination of the Leghorn harbour waters, receiving those of Fossi Medicei, appears greatly influenced by the contribution (about 7 kg d^{-1}) from the power plant outlet.

Table I

Range* of butyltins (ng l^{-1}) in seawater samples from the survey areas.

SITE	TBT	DBT	MBT
INDUSTRIAL DISCHARGES			
LEGHORN (I)			
Power Plant outlet Fossi Medicei	11930;12150	70;95	<100
Stations 2 to 6	1125-3180	65-385	<100
HARBOURS			
MARSEILLE (F)			
Stations 1 to 10	41-201	38-141	20-98
LEGHORN (I)			
Stations 7 to 17	<20-810	<20-340	<100
PIOMBINO (I)	<20	<20	<100
ISKENDERUN (T)			
Station A.3	<10;83	56;484	8;2774
MERSIN (T)			
Station A.13	936	266	30
MARINAS			
GRUISSAN (F)			
Stations 3 and 4	16;102	17;26	4;9
THAU (F)			
Stations 4 and 6	54;59	23;25	8;38
CAP D'AGDE (F)			
Stations 1 to 8	34;536	16-36	16-56
BANDOL (F)			
Stations 1 to 5	10-390	<1-161	<1-83
MARSEILLE (F)			
Vieux Port (11;12)	410;736	119;190	78;98
CECINA (I)	440-3930	90-750	<100
SAN VINCENZO (I)	260-570	45-170	<100
PUNTA ALA (I)	505-960	100-190	<100
MARMARIS (T)			
Station A.30	11-353	121-742	<0.5
ANTALYA (T)			
Station A.21	154;184	121;677	<0.5
MARICULTURE			
GRUISSAN (F)			
Stations 1 and 2	13;17	16;16	10;10.5
THAU (F)			
Stations 1 to 10 except 4 and 6	<2-16	<1-38	<1-26

* A single number represents the result from a single sample. Two numbers separated by a semicolon represent the results from two samples. Two numbers separated by a dash represent a range of results of more than 2 samples taken from one or more stations.

As far as harbours are concerned, LEGHORN and MERSIN (936 ng l^{-1}) represent the most contaminated sites; others ranged between 83 ng l^{-1} (ISKENDERUN) to 210 ng l^{-1} of TBT (MARSEILLE). At ISKENDERUN the high concentration of MBT (2774 ng l^{-1}) might be explained by degradation. Further research is in progress.

Of the marinas, the highest level of TBT was recorded at CECINA (3930 ng l^{-1}) but the majority of values range between 100 and 1000 ng l^{-1} of TBT. In some marinas with low capacity for boats or well exchanged water, the level can be less than 100 ng l^{-1}. DBT level was generally lower than 200 ng l^{-1}, with the exception of CECINA. The particularly high TBT and DBT concentrations found at the Foce Cecina marina, probably relate to the high density of boats, the shallow depth (1-2 m), and restricted water exchange.

The mariculture areas, sampled on the French coast exhibited less contamination by TBT with concentrations ranging from <2 to 17 ng l^{-1}. With respect to TBT effects on mollusc larval development the highest concentration approached the No Observed Effect Level (NOEL) of 20 ng l^{-1}.

A few water samples were also collected away from directly impacted areas: about one Km away from the Leghorn harbour and also the open coastal Turkish waters. Concentrations in both samples were below the detection limits of the adopted analytical techniques (10 ng l^{-1}). Although concentrations within the range 1 to 10 ng l^{-1} are known to be harmful to highly sensitive marine organisms, it is clear that the areas of significant environmental impact will be confined to inshore waters.

The data presented in Table I show that for each type of area sampled, the concentrations of the butyltins vary within a wide range; examples are shown in Figs. 10 and 11 for concentrations of tributyltin in harbours and marinas. Such variations can be caused in part by the location of specific sampling sites, the density of boats present, and the water turnover. It is inappropriate, therefore, to aggregate the data and provide average values for each type of site.

However, the concentrations of the butyltins found are comparable with those found in similar situations outside the Mediterranean area, and therefore there is no evidence that the areas covered by this plot survey present a uniquely different problem to that encountered elsewhere.

4.2 Sediment samples

The spatial concentrations of tin species are given in Table II.

All samples contained inorganic Sn concentrations ranging from 310 to 5200 ng g^{-1}. Monomethyltin was detected in 31 out of 35 samples and the concentrations ranged from undetectable to 1200 ng g^{-1}. Dimethyltin was detected in 29 of 35 samples with concentrations ranging from undetectable to 135 ng g^{-1}. Trimethyltin was present in 6 of 35 samples, ranging from undetectable to 80 ng g^{-1}. Monobutyltin was detected in all samples and ranged from undetectable to 450 ng g^{-1}. Dibutyltin was absent from 6 samples and ranged between undetectable and 425 ng g^{-1}. All samples contained tributyltin with concentrations ranging from 30 to 1375 ng g^{-1}.

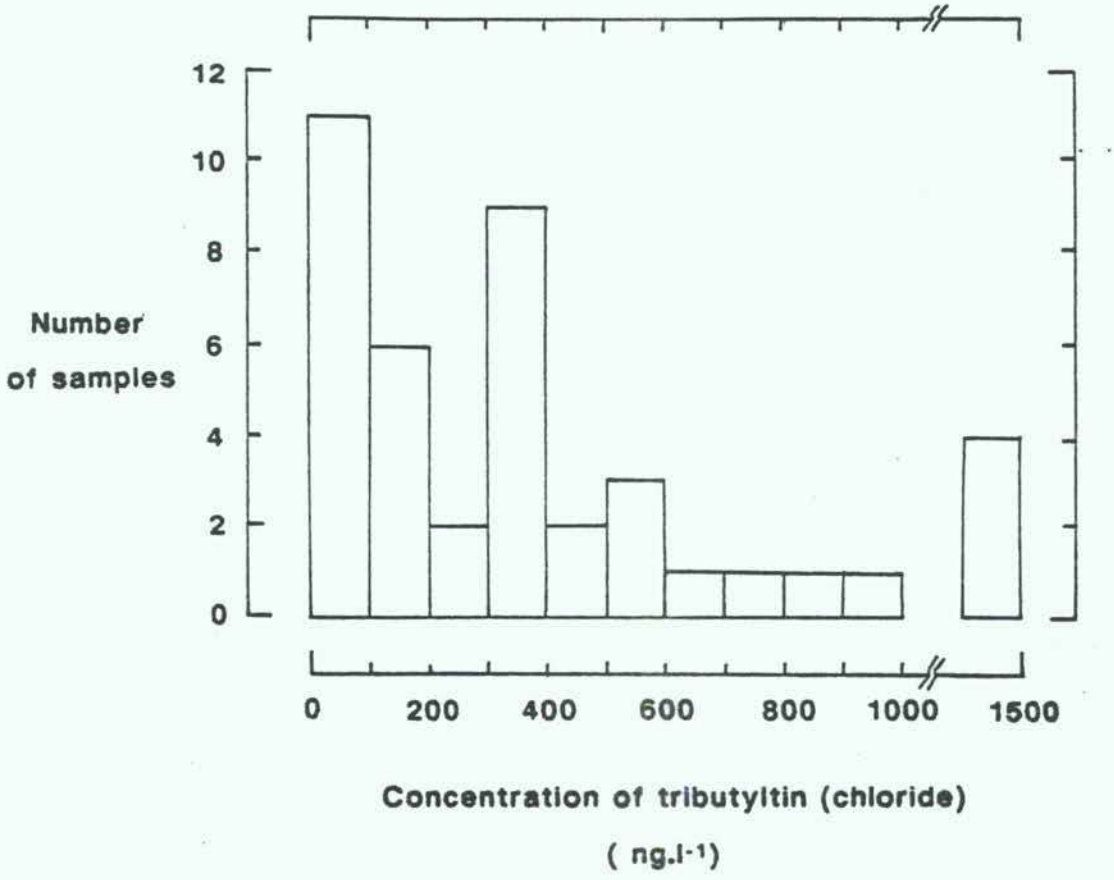

Fig. 10 Frequency histogram of TBT concentrations in water samples from marinas

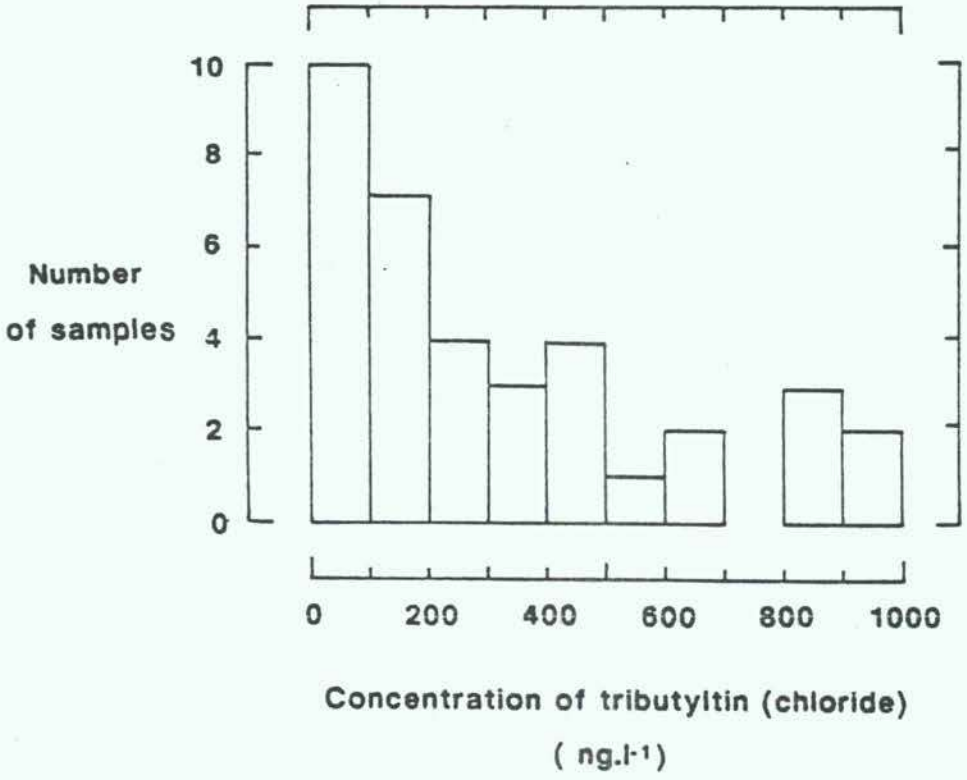

Fig. 11 Frequency histogram of TBT concentrations in water samples from harbours

Table II

Spatial concentrations of tin species in Alexandria coastal belt sediments (ng (as Sn) g^{-1}) (from O. Aboul Dahab, in press).

	I Ref. St	II Agamy	III Mex Bay	IV Western Harbour	V Off Sewage outfall	VI Off Eastern	VII Eastern Harbour	VIII Eastern coast	IX Abu Kir
Station No.	4	1-3	5-11	12-14	15	16	17-18	19-26	27-35
No. of samples	1	3	7	3	1	1	2	8	9
Inorg.Sn	310	488	2147	4720	2430	1080	3645	1075	2252
MMT	0	20	69	1000	85	0	500	41	127
DMT	15	12	35	77	70	45	23	23	43
TMT	0	0	0	60	0	0	23	0	3
Total MT	15	32	104	1136	155	45	545	64	173
% MMT/Total MT	0	63	68	88	0	0	91	68	70
% DMT/Total MT	100	37	32	7	45	100	4	32	30
% TMT/Total MT	0	0	0	5	0	0	4	0	0
MBT	0	41	57	330	45	55	138	60	83
DBT	10	17	49	305	65	60	120	63	67
TBT	35	40	187	975	185	160	260	63	252
Total BT	45	97	294	1610	295	275	518	186	401
% MBT/Total BT	0	38	19	22	15	20	27	32	20
% DBT/Total BT	22	15	16	19	22	22	23	34	15
% TBT/Total BT	78	47	65	59	63	58	50	34	65

The highest levels for all Sn species in any sediment sample from the investigated area, were found in the Western Harbour, the main commercial harbour of Egypt, followed by the Eastern harbour, a small fishing harbour and the lowest at the reference station followed by the adjacent "Agamy" stations. The trend reveals a gradual increase in Sn species concentrations in sediments from the Eastern Alexandria coast to the area off the Eastern harbour to Mex Bay. Abu Kir Bay sediments showed rather higher concentrations of tin species than those of Mex Bay.

Significant variations in tributyltin levels were observed between stations. Tributyltin concentrations in sediments of the Western Harbour was 28 times higher than that of the background station (975 as compared to 35 ng g^{-1}), 7 times greater in Eastern Harbour (260 as compared to 35 ng g^{-1}) and about 7 times greater in Abu Kir Bay (252 as compared to 35 ng g^{-1}). This could indicate that tributyltin release to the coastal area of Alexandria is mainly from the Western Harbour followed to a limited extent by the two fishing harbours, Eastern Harbour and Abu Kir Bay.

This is consistent with its use as an antifouling agent for ships. Tributyltin composed the greater percentage, more than 55% of the total butyltin in sediments of the 28 stations located out of the two main harbours. The overall relative proportions of mono- and dibutyltins to total butyltin were 24 and 21% respectively. This provides an indication that tributyltin is the anthropogenic form and that both mono- and dibutyltins are derivatives. Most sediment samples contained monomethyltin (31 of 35 samples), and dimethyltin (29 of 35 samples) while trimethyltin was absent from most samples (detected in 6 out of 35 samples). It was detected in traces where relative anomalies of tin existed (Western Harbour, Eastern Harbour and Abu Kir Bay).

Finally, there was a large difference in the sediment contamination between harbour (Western) and fishing ground (Abu Kir); Values were in the following ranges ($ng_{Sn}\ g^{-1}$).

	HARBOUR	FISHING GROUND
MMT	700 - 1200	45 - 600
DMT	35 - 85	<1 - 135
TMT	30 - 70	<1 - 25
MBT	140 - 400	45 - 150
DBT	120 - 425	<1 - 150
TBT	275 - 1375	<1 - 150

5. CONCLUSIONS

The regulatory action recommended in the Report UNEP(OCA)/MED WG. 1/7 was based in part on the assumption that the use of organotin antifouling products in the Mediterranean would cause the same type of environmental problems known to occur elsewhere in the world. This pilot survey has shown conclusively that there are high concentrations of tributyltin in the vicinity of harbours and marinas where there are high densities of ships and pleasure craft. The range of concentrations found are comparable with those known to be present in similar situations outside the Mediterranean region.

In addition to the well-known source of tributyltin from antifouling paints, its use in industrial cooling water systems has been shown to result in very high concentrations in the locality of the discharge.

Also, this survey has shown that the ratios of tributyltin to the breakdown products di- and monobutyltin found in the Mediterranean are not dissimilar to those found elsewhere. There is no evidence, therefore, that the breakdown of tributyltin occurs at a significantly different rate in the Mediterranean.

Therefore, the environmental effects caused by the use of tributyltin in the Mediterranean are likely to be similar to those known to occur elsewhere. Recent laboratory and field investigations have provided further confirmation that tributyltin is harmful to marine organisms at extremely low concentrations. While there may be differences of opinion about the concentrations which may be regarded as "safe", there is a general consensus that concentrations as low as 20 ng l^{-1} are harmful to a number of sensitive marine organisms, and some may be affected by concentrations as low as 1 ng l^{-1}. It is clear, therefore, that the results of this pilot survey have reinforced the need for the regulatory action outlined in the document UNEP(OCA)/MED WG. 1/7 "Assessment of organotin compounds as marine pollutants and proposed measures for the Mediterranean".

In contrast to the large amount of information on the harmful effects of tributyltin in the water phase, much less is known about contaminated sediments. Such sinks may form a continuing source of pollution after the use of tributyltin has been regulated, especially as the degradation rates in sediments may be very slow. Also, in areas close to shipyards, the tributyltin may be attached to persistent paint fragments. There is a need for continuing research to identify the importance of this potential problem, including studies on the mechanisms of adsorption and desorption, alkylation and de-alkylation and the bio-availability of tributyltin to sediment dwelling organisms, so that appropriate predictive models can be constructed.

The analytical techniques used in this pilot survey were more than adequate to identify areas of high, medium and low contamination by tributyltin. However, as environmental concentrations fall as a result of control and modification of antifouling products, there will be a greater need for accuracy and precision where these levels fall within the range 1-50 ng l^{-1}. This will be necessary not only for trend analysis but also to allow proper comparisons between data from different areas of the Mediterranean. Co-operative action should continue in order to achieve this aim, and linked with inter-laboratory comparisons carried out by other international organizations.

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