



United Nations Environment Programme



UNEP(OCA)/MED WG.1/Inf.10
15 April 1988

Original: ENGLISH

MEDITERRANEAN ACTION PLAN

First Meeting of the Scientific
and Technical Committee

Athens, 23-27 May 1988

REPORT NO. 33 - PRELIMINARY REPORT
ON THE INTERCALIBRATION EXERCISE OF ORGANOCHLORINE
COMPOUND MEASUREMENTS ON SHRIMP HOMOGENATE MA-A-3/OC AND MA(S)-MED-86/OC
AND FISH HOMOGENATE MA-B-3/OC AND MA(F)-MED-86/OC
May 1987

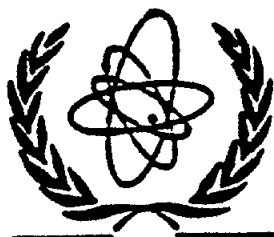
In co-operation with :



IAEA

UNEP

Athens, 1988



International Atomic Energy Agency

IAEA/RL/
(MONACO/33)

REPORT No. 33

INTERCALIBRATION OF ANALYTICAL METHODS
ON MARINE ENVIRONMENTAL SAMPLES

Preliminary Report on the Intercalibration Exercise of Organochlorine
Compound Measurements on Shrimp Homogenate MA-A-3/OC and MA(S)-MED-86/OC
and Fish Homogenate MA-B-3/OC and MA(F)-MED-86/OC .

May 1987

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Prepared in co-operation with UNEP



INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS ENVIRONMENTAL PROGRAMME
INTERNATIONAL LABORATORY OF MARINE RADIOACTIVITY/MEDPOL

PRELIMINARY EVALUATION OF THE INTERCALIBRATION EXERCISE ON CHLORINATED
HYDROCARBONS IN SHRIMP HOMOGENATE, MA-A-3/OC AND MA(S)-MED-86/OC,
AND FISH HOMOGENATE, MA-B-3/OC AND MA(F)-MED-86/OC

From September 1985, the Monaco Laboratory has distributed intercalibration samples of shrimp homogenate (MA-A-3/OC or MA(S)-MED-86/OC) to 26 laboratories and of fish homogenate (MA-B-3/OC or MA(F)-MED-86/OC) to 37 laboratories.

Samples labelled MA-A-3/OC and MA(S)-MED-86/OC are identical but used for different exercises. The same is valid for MA-B-3/OC and MA(F)-MED-86/OC. To obtain a basis for statistical treatment of data, which is as broad as possible, both exercises are included in this report.

To date, 10 laboratories have reported their results on the shrimp sample and 14 laboratories on the fish sample. These results enable us to do a very preliminary evaluation only.

The reporting laboratories are listed in Annex 1. Results obtained are listed in Table 1 for the shrimp homogenate and Table 2 for the fish homogenate.

From the results obtained after rejection of outliers (Tables 3 and 4) it appears that for both samples, the determinations of Lindane (γ -HCH)

are very scattered, and for the shrimp sample the same is valid for pp'DDD and pp'DDT. For the other compounds determined, the range of reported values is rather large, relative standard deviations being 50% to 60%.

For both samples as much as about 40% of the results (44% for shrimp and 39% for fish) are either "not reported" or "less than ...". This fact reduces the possibility of estimating the best value of each determination.

Values obtained after the application of Chauvenet's and Dixon's tests are the best possible estimates of the organochlorine compound concentrations in the samples. However, in case the number of reported values for a compound was too small, the application of the non-parametric test for the rejection of outliers was not advisable. Instead, the Student's t-test was used, which gives results similar to those obtained after Chauvenet's test.

A comparison was made of the dispersion (relative standard deviations) of results in this intercalibration exercise with earlier exercises on similar matrixes and with similar levels of pollution. As a criterium for the choice of exercises, the concentration level of Aroclor 1254 was chosen. The worldwide exercises in 1976 (W.W.76) on oyster, in 1980 (W.W.80) on copepod and in 1986 (W.W.86) on mussel tissues are all in the range of 200-600 ng/g Aroclor 1254, and is compared to the results on the fish sample in this exercise with its 500 ng/g mean value for Aroclor 1254. In Table 5, including all data reported, an improvement appears regarding pp'DDE and pp'DDT, while data on Aroclor 1254 in this exercise are more scattered. Table 6 presents the results after rejection of outliers. It appears that, except for Lindane, the dispersion of results is comparable to other exercises, even if it is still far away from the recommended 15%.

Table 1 : Organochlorine compound concentrations in Shrimp Homogenate (MA-A-3/OC)
Reported results in ng/g (ppb) dry weight .

Lab. Code N°	HCB	Lindane	pp' DDE	pp' DDD	pp' DDT	Ar.1254	Ar.1260
1	< 1	8.5	4.6	n.r.	< 1	< 10	n.r.
2	1	1	7	n.r.	< 1	75	n.r.
3	< 1	< 1	28.5	n.r.	< 1	35.5	n.r.
4	1	1	9	n.r.	< 1	54	n.r.
5	n.r.	10	5	n.r.	n.r.	n.r.	n.r.
6	0.4	0.2	9.7	< 0.2	0.35	4.9	4.55
12	0.131	0.213	0.916	n.d.	0.965	16.485	2.394
13	n.r.	n.r.	9.6	< 1.1	< 1.1	7	n.r.
14	n.r.	1.21	2.08	1.61	5.48	21.26	34.28
15	n.r.	n.r.	4.14	0.14	< 0.1	17.3	8.3
16	0.35	0.27	4.1	0.25	0.39	6	n.r.

n.r. : no reported results

n.d. : not detected

Table 2 : Organochlorine compound concentrations in Fish Homogenate (MA-B-3/OC)
Reported results in ng/g (ppb) dry weight .

Lab. Code N°	HCB	Lindane	pp' DDE	pp' DDD	pp' DDT	Ar.1254	Ar.1260
1	< 1	11	183	n.r.	12	7000	n.r.
2	< 1000	< 1000	< 1000	< 1000	< 1000	49000	n.r.
3	1.6	0.6	270	n.r.	94	297	465
5	< 5	9	211	n.r.	124	n.r.	n.r.
6	1.95	0.6	75.5	72.5	70	848	695
7	n.d.	0.22	217	n.r.	17	n.r.	n.r.
8	n.r.	n.r.	312	46	n.r.	2075	690
9	1.1	< 1.6	288	87.2	134	554	n.r.
10	n.r.	n.r.	128	45	42.5	13500	n.r.
11	0.85	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
12	0.483	n.d.	57.509	25.801	45.288	440.488	289.326
13	n.r.	n.r.	221	27	34	676	n.r.
14	n.r.	0.55	10.72	5.25	26.43	285.7	333.4
15	n.r.	n.r.	151.5	38.3	80.4	1282	617
16	2.4	1.6	267	62	107	406	259

n.r. : no reported results

n.d. : not detected

Table 3 : Organochlorine compound concentrations in Shrimp Homogenate (MA-A-3/OC)
Reported results in ng/g (ppb) dry weight .
Laboratories reporting " less than " values have been excluded .

	HCB	Lindane	pp' DDE	pp' DDD	pp' DDT	Ar.1254	Ar.1260
N ^o of particip. laborat.	5	8	11	3	4	9	4
Min.Val.	0.131	0.2	0.916	0.14	0.35	4.9	2.394
Max.Val.	1	10	28.5	1.61	5.48	75	34.28
mean	0.58	2.8	7.7	0.67	1.8	26	12
stand.dev.	±0.4	±4	±7.5	±0.82	±2.5	±24	±15
(%)	(69 %)	(140 %)	(97 %)	(120 %)	(140 %)	(92 %)	(130 %)
N ^o of res. after Chauvenet test	5	8	10	3	4	6	4
Chauvenet range	0.131- - 1	0.2- - 10	0.916- - 9.7	0.14- - 1.61	0.35- - 5.48	4.9- -21.26	2.394- - 34.28
mean	0.58	2.8	5.6	0.67	1.8	12	12
stand.dev.	±0.4	±4	±3.1	±0.82	±2.5	±7	±15
(%)	(69 %)	(140 %)	(55 %)	(120 %)	(140 %)	(58 %)	(130 %)
N ^o of res. after Dixon's test	3	8	10	3	4	9	3
Dixon's range	0.131- - 0.4	0.2- - 10	0.916- - 9.7	0.14- - 1.61	0.35- - 5.48	4.9- - 75	2.394- - 8.3
mean	0.3	2.8	5.6	0.67	1.8	26	5.1
stand.dev.	±0.14	±4	±3.1	±0.82	±2.5	±24	±3
(%)	(47 %)	(140 %)	(55 %)	(120 %)	(140 %)	(92 %)	(59 %)

Table 4 : Organochlorine compound concentrations in Fish Homogenate (MA-B-3/OC)
 Reported results in ng/g (ppb) dry weight
 Laboratories reporting " less than " values have been excluded .

	HCB	Lindane	pp' DDE	pp' DDD	pp' DDT	Ar.1254	Ar.1260
N ^o of particip. laborat.	6	7	13	9	12	12	7
Min.Val.	0.483	0.22	10.72	5.25	12	285.7	259
Max.Val.	2.4	11	312	87.2	134	49000	695
mean	1.4	3.4	180	46	66	6360	480
stand.dev.	±0.72	±4.6	±94	±25	±42	±14000	±190
(%)	(51 %)	(135 %)	(52 %)	(54 %)	(64 %)	(220 %)	(40 %)
N ^o of res. after Chauvenet test	6	7	13	9	12	7	7
Chauvenet range	0.483- - 2.4	0.22- - 11	10.72- - 312	5.25- - 87.2	12- -134	285.7- - 848	259- -695
mean	1.4	3.4	180	46	66	500	480
stand.dev.	±0.72	±4.6	±94	±25	±42	±210	±190
(%)	(51 %)	(135 %)	(52 %)	(54 %)	(64 %)	(42 %)	(40 %)
N ^o of res. after Dixon's test	6	7	13	9	12	9	7
Dixon's range	0.483- - 2.4	0.22- - 11	10.72- - 312	5.25- -87.2	12- -134	285.7- -2075	259- -695
mean	1.4	3.4	180	46	66	760	480
stand.dev.	±0.72	±4.6	±94	±25	±42	±580	±190
(%)	(51 %)	(135 %)	(52 %)	(54 %)	(64 %)	(76 %)	(40 %)

Table 5 : Dispersion of results for different exercises, including all data.

	Lindane	pp' DDE	pp' DDD	pp' DDT	Ar. 1254
W.W.76 Oyster	140 %	130 %	63 %	59 %	55 %
W.W.80 Copepod	47 %	110 %	110 %	50 %	47 %
W.W.86 Mussel	260 %	310 %	140 %	120 %	100 %
mean	150 %	180 %	104 %	76 %	67 %
W.W.87 Fish	135 %	52 %	54 %	64 %	220 %

Table 6 : Dispersion of results for different exercises after rejection of outliers.

	Lindane	pp' DDE	pp' DDD	pp' DDT	Ar. 1254
W.W.76 Oyster	33 %	28 %	36 %	59 %	55 %
W.W.80 Copepod	47 %	50 %	35 %	50 %	47 %
W.W.86 Mussel	52 %	54 %	42 %	58 %	64 %
mean	44 %	44 %	38 %	56 %	55 %
W.W.87 Fish	135 %	52 %	54 %	64 %	40 %

LIST OF PARTICIPATING LABORATORIES IN THE INTERCALIBRATION
OF ORGANOCHLORINE COMPOUND MEASUREMENTS ON MA-A-3/OC
(SHRIMP HOMOGENATE) AND MA-B-3/OC (FISH HOMOGENATE) SAMPLES

<u>Laboratories which reported the results</u>	<u>Sample analysed</u>	<u>Investigators</u>
<u>Belgium</u>		
University of Liege Institute of Zoology Quai Van Benedan 22 B-4020 Liege	MA-B-3/OC	J.P. Thome
<u>Canada</u>		
Department of Fisheries and Oceans Freshwater Institute 501 University Crescent Winnipeg, Manitoba R3T 2N6	MA-A-3/OC MA-B-3/OC	M. Hendzel
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<u>Cyprus</u>		
Ministry of Agriculture and Natural Resources Department of Fisheries Nicosia	MA-A-3/OC MA-B-3/OC	P. Loizide
<u>France</u>		
Laboratoire Central d'Hygiene Alimentaire 43 rue de Dantzig 75015 Paris	MA-B-3/OC	G. Cumont
<u>Germany (Federal Republic of)</u>		
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