United Nations Environment Programme

UNEP(OCA)/MED WG.5/Inf.5
10 February 1989

Original: ENGLISH

MEDITERRANEAN ACTION PLAN

Meeting of responsible investigators
of monitoring programmes

Athens, 20-23 March 1989

EVALUATION OF MED POL - PHASE II MONITORING DATA

Part III - Heavy metals in coastal and reference areas

UNEP
Athens, 1989

The present document was prepared by Dr. R. Fukai in his capacity of UNEP/FAO consultant. The views expressed in the document are those of the author and do not necessarily represent the views of either UNEP or the MED POL Co-operating Agencies. The designations employed and the material in this document do not imply the expression of any opinion whatsoever on the part of UNEP or the MED POL Co-operating Agencies concerning the legal status of any state, territory, city or area, or of its authorities, or concerning the delimitation of their frontiers or boundaries.

EP

United Nations Environment Programme

UNEP(OCA)/MED WG.5/Inf.5
10 February 1989

Original: ENGLISH

MEDITERRANEAN ACTION PLAN

Meeting of responsible investigators
of monitoring programmes

Athens, 20-23 March 1989

EVALUATION OF MED POL - PHASE II MONITORING DATA

Part III - Heavy metals in coastal and reference areas

UNEP
Athens, 1989

TABLE OF CONTENTS

1. INTRODUCTION

Over the past few years, the monitoring component of the MED POL-Phase II Programme was launched and developed by the collaboration between the Co-ordinating Unit of the Mediterranean Action Plan (MED UNIT) and Governments of the Mediterranean Coastal States. Several monitoring agreements involving a number of national institutions were concluded between the MED UNIT and these Governments which specify the planning and execution of specific national monitoring programmes and require the National Co-ordinators for MED POL to submit the results from the monitoring performed in their countries to the MED UNIT. In addition, some countries undertook to submit results of their national monitoring programmes voluntarily to the MED UNIT without any formal agreement, in order to facilitate the task entrusted to the MED UNIT to review the pollution situation in the Mediterranean region. Thus, by the summer of 1988, a considerable amount of national monitoring data was made available to the MED UNIT. The quality of these data, however, has not yet been systematically reviewed.

The scope of the present report is to evaluate the quality of the available data submitted to the MED UNIT of heavy.metal measurements on marine environmental matrices, with a view to their possible use in reviewing the current pollution position of the Mediterranean marine environment and deducing possible future trends. These data may also be useful in assessing the effectiveness of preventive measures taken against developing marine pollution. Through evaluation of the data procedures it is intended to put forward some suggestions for improving monitoring programmes to meet the stated goals.

2. DESCRIPTION OF DATA RECEIVED

The results of heavy metal measurements on marine organisms were normally submitted to the MED UNIT in the standard log-form formulated by them in consultation with experts, but for other matrices, i.e. sea water and sediments, various tabulated forms were used in the presentation of results. Sediment measurements are mandatory, while sea water is an optional matrix under the monitoring agreements. Though most of the tables presenting sediment results were quite straightforward, it is nevertheless preferable to use a standard format in reporting results of sediment analyses in order to facilitate the evaluation of submitted data. The use of the standard log-form for reporting the results of sediment measurements should therefore be encouraged.

The forms and sizes of the national monitoring reports received at the MED UNIT varied from a few data sheets to sizeable booklets which included scientific analysis of the results obtained. In some cases, the data were submitted in the form of computer print-outs or diskettes. All these reports were thoroughly reviewed in the data quality evaluations. The information indicating the size and extent of the implementation of national monitoring programmes, such as year, matrices monitored, number of samples analyzed, number of data submitted, and elements analyzed are shown in Table I for each country. Although much of the data for heavy metal measurements on sewage and industrial effluents were included in some of these reports, Table I presents environmental measurements only, excluding the effluent data.

The information given in Table I is summarized by country in Table II. As shown in this table, by September 1988 more than 14,500 monitoring data had been submitted from 12 Mediterranean countries. Nevertheless, however, approximately 87% of the data was submitted from only 4 countries out of a total of 12 participating countries. This indicates that the availability of data is heavily biased towards certain limited areas. Only very limited numbers of data are available for southern parts of the Mediterranean in particular. In order to review heavy metal pollution over the whole Mediterranean region, it is essential to balance the availability of the monitoring data so that a reasonable coverage of the whole region is achieved.

In Table III, the same information contained in Table I is arranged by year, covering the period 1979-1987. The numbers given in Table III show that, although the data reported for the 1987 measurements has not yet been completed, the numbers of data submitted reached a peak in 1985 and then decreased and remained at a certain lower level. This seems reasonable, since the number of analyses should be higher in a period of trial-and-error, when appropriate stations and matrices to be monitored have to be chosen for specific areas, rather than those for a period when routine monitoring procedures are well established. However, numbers of data submitted annually are expected to increase again when adequate coverage of the whole region is achieved in the near future.

Table IV shows the number of data submitted for various environmental matrices. While the numbers of data available for sediments and marine organisms are balanced, considering their required sampling frequencies, there seems to be an excess of sea water data in comparison with others. Sea water being an optional monitoring matrix, the percentage of sea water data, approximately 34% of the total number, is considered to be too high. Although sea water monitoring data may be useful for detecting acute local pollution, they have limited value in identifying and predicting long-term trends in regional pollution situations. Those additional difficulties encountered in sea water measurements performed for environmental monitoring will be discussed below.

<u>Table I</u>

The number of monitoring results submitted to the MED UNIT of heavy metal measurements carried out by national institutions within the framework of the MEDPOL Phase II monitoring programme (Sept. 1988).

Country	Year	Matrix	No. of Samples Analysed		No. of Data		Elements Analysed
Algeria	1979	BI		8		31	Mu,Cu,Zn,Cd,Hg,Pb
	1980	"		9		54	"
	1985	"		27		125	"
	1986	"		33		195	Mn,Cu,Zn,As,Se,Cd Hg,Pb
	Total	BI		77		405	
Cyprus	1983	BI		5		10	Cu,Zn
	1986	"		5		10	"
	1987	"		5		10	"
	Total	BI		15		30	
France	1983	SW		145		357	Cd, Hg
	1984	"		93		186	"
	Total	SW		238		543	
Israel	1982	BI		53		58	Cd,Hg
	1983	"		56		146	Cu,Zn,Cd,Hg,Pb
	1984	SD	22	191	44	336	Cd,Hg
		BI	169		292		Cu,Zn,Cd,Hg,Pb
	1985	SD	24	245	46	760	Cd,Hg
		BI	221		714		Cu,Zn,Cd,Hg,Pb
	1986	"		48		218	Fe,Cu,Zu,Cd,Hg,Pb

Table I (continued)

Country	Year	Matrix	No. of Samples Analysed		No. of Data		Elements Analysed
Israel (cont'd)	1987	SD	26	246	52	1276	Cd,Hg
		BI	220		1224		Fe,Cu,Zn,Cd,Hg,Pb
	Total	SD	72	839	142	2794	
		BI	767		2652		
Italy	1987	BI		4		8	Zn, Cd
Lebanon	1984	BI		24		48	Cd,Hg
	1986	SD	1	13	1	25	Hg
		BI	12		24		Cd,Hg
	1987	SD	14	38	14	62	Hg
		BI	24		48		Cd,Hg
	Total	SD	15	75	15	135	
		BI	60		120		
Malta	1984	SW	59		373		Cu,Mn,Fe,Co,Ni,Cu, Zn,Cd,Hg,Pb
		SD	12	94	120	608	"
		BI	23		115		Cu,Zn,Cd,Hg,Pb
	1985	SW	72	84	720	780	Cr,Mn,Fe,Co,Ni,Cu, Zn,Cd,Hg,Pb
		BI	12		60		Cu,Zn,Cd,Hg,Pb
	1986	SW	22			220	Cr,Mn,Fe,Co,Ni,Cu, Zn,Cd,Hg,Pb
		SD	13	51	130	417	"
		BI	16		67		Cu,Zn,Cd,Hg,Pb
	1987	SW	10		100		Cr,Mn,Fe,Co,Ni,Cu, Zn,Cd,Hg,Pb
		SD	8	28	72	222	"
		BI	10		50		Cu,Zn,Cd,Hg,Pb

Table I (continued)

Country	Year	Matrix	No. of Samples Analysed		No. of Data		Elements Analysed
Malta (cont'd)	Total	SW	163		1413		
		SD	33	257	322	2027	
		BI	61		292		
Morocco	1984	BI		11		11	Cu
	1985	"		20		20	Hg
	Total	BI		31		31	
Spain	1981	SD		40		320	Cr,Mn,Ni,Cu,Zn,Cd, Hg,Pb
	1982	SW	42		126		Cd,Hg,Pb
		SD	110	222	571	977	Cr,Mn,Ni,Cu,Zn,Cd, Hg,Pb
		BI	70		280		Cr,Ni,Cd,Hg,Pb
	1983	SD	62	185	318	746	Cr,Mn,Ni,Cu,Zn,Cd, Hg,Pb
		BI	123		428		Cr,Ni,Cd,Hg,Pb
	1984	SD	70	270	385	1124	Cr,Mn,Ni,Cu,Zu,Cd, Hg,Pb
		BI	200		739		Cr,Ni,Cd,Hg,Pb
	1985	BI		188		704	"
	Total	SW	42		126		
		SD	282	905	1594	3871	
		BI	581		2151		
Syria	1986	SW		12		48	Cu,Zn,Cd,Pb
Turkey	1983	SW	47	64	95	118	Cd,Hg
		SD	17		23		"

Table I (continued)

Country	Year	Matrix	No. of Samples Analysed		No. of Data		Elements Analysed
Turkey (cont'd)	1984	SW	92		196		"
		SD	52	158	86	310	"
		BI	14		28		"
	1985	SW	91		183		"
		SD	57	151	108	297	"
		BI	3		6		"
	1986	SW		23		23	Hg
	Total	SW	253		497		
		SD	126	396	217	748	
		BI	17		34		
Yugoslavia	1983	SW	91		684		Cu,Zn,Cd,Hg,Pb
		SD	54	170	203	960	"
		BI	25		73		"
	1984	SW	94		537		"
		SD	63	251	232	1123	"
		BI	94		354		"
	1985	SW	162		680		Cu,Zn,Cd,Hg,Pb
		SD	56	308	170	1140	"
		BI	90		290		"
	1986	SW	115		357		"
		SD	38	250	72	696	"
		BI	97		267		"
	Total	SW	462		2258		
		SD	211	979	677	3819	
		BI	306		984		

Matrices: SW = sea water; SD = sediments; BI = biota.

Table II

Summary of the number of the submitted monitoring results by country (Sept. 1988).

Country	Matrices	No. of Samples Analysed	No. of Data
Algeria	BI	77	405
Cyprus	BI	15	30
France	SW	238	543
Israel	SD, BI	839	2794
Italy	BI	4	8
Lebanon	SD, BI	75	135
Malta	SW, SD, BI	257	2027
Morroco	BI	31	31
Spain	SW, SD, BI	905	3871
Syria	SW	12	48
Turkey	SW, SD, BI	396	748
Yugoslavia	SW, SD, BI	979	3919
Grand Total		3828	14559

Matrices: SW = sea water; SD = sediments; BI = biota.

3. SAMPLING AND ANALYTICAL METHODS EMPLOYED

In order to obtain reliable values for heavy metal measurements on environmental samples, the sampling phase is as critical as the analytical phase. This is particularly so as far as sea water samples are concerned, where concentrations of heavy metals are normally very low, and therefore the possibility of contaminating the samples during the sampling procedure is greatly enhanced, so much so that without a guaranteed non-contaminating sampling operation, it is very hard to evaluate the validity of the data obtained in these samples. Such a guarantee is obviously extremely difficult to obtain and for this reason, heavy metal data on sea water have a fairly limited value as monitoring data. Even for marine sediments and organisms, in which heavy metal concentrations are much higher than those in sea water, the risk of sample contamination during sampling always exists, so that extreme care in sampling constitutes one of the important keys in producing reliable data (UNEP/FAO/IOC/IAEA, 1984a).

Table III

Summary of the number of the submitted monitoring results by year (Sept. 1988).

Year	No. of Samples Analysed	No. of Data
1979	8	31
1980	9	54
1981	40	320
1982	275	1035
1983	625	2337
1984	1092	3746
1985	1023	3826
1986	435	1632
1987	321	1578
Grand Total	3828	14559

In the monitoring reports submitted by the National Coordinators, usually simple descriptions only of sampling operations were given. Under the circumstances, it was not possible to evaluate the errors introduced during sampling. It was therefore assumed that the sampling operations for various marine matrices had been performed correctly.

As to the analytical methods used in producing heavy metal data on sediment and organism samples, a majority of the laboratories engaged in the monitoring programmes referred to the Reference Methods for Marine Pollution Studies for respective matrices and elements - that is, atomic absorption spectrophotometry with flame or graphite furnace for the measurements of Cu, Zn, Cd, Pb, etc. and with the cold-vapour technique for Hg measurements after appropriate digestion procedures (UNEP/FAO/IOC/IAEA, 1984b,c, UNEP/IAEA 1985a-d, 1986). A few laboratories utilized neutron activation techniques for measuring Cu, Zn, Cd and Hg.

Table IV

Summary of the number of submitted monitoring results by matrix (Sept. 1988).

Matrix	No. of Samples Analysed	No. of Data
Sea water	1170	4885
Sediments	739	2967
Marine Organisms	1919	6707
Grand Total	3828	14559

As the present reference methods cited above for sediment measurements describe the analytical procedures used in measuring total quantities of heavy metals in sediments, the results thus obtained have, in many cases, a limited significance in considering the state of pollution in sediments. The total quantities of heavy metals in marine sediments mainly reflect the geochemical composition of the adjacent coasts rather than represent heavy metal fractions originating from pollution sources. In this context, the analytical methods used in describing heavy metal pollution in sediments should be seriously reconsidered and modified, as appropriate, in future monitoring programmes.

The measurements of heavy metals, Cu, Zn, Cd, Pb, etc. in sea water were performed mainly by anodic stripping voltammetry at different pH values. As the scientific significance of the data obtained through this technique, however, has not been clearly defined in relation to the heavy metal pollution in sea water, these data have to be looked at with caution, although they may be useful for deducing some local pollution trends.

4. ANALYTICAL DATA QUALITY CONTROL

In order to ensure the comparability of heavy metal measurements on marine environmental matrices within those Mediterranean laboratories engaged in the monitoring programmes, five intercalibration runs, one on sediment sample and four on marine organism samples, were organised by the International Laboratory of Marine Radioactivity, IAEA, at Monaco (ILMR) over the period 1979-1987 (IAEA, 1978, 1980, 1986, 1987, 1988). In parallel, these intercalibration exercises were run on a world-wide scale, in order to

Table V

Reference concentration values for intercalibration samples of heavy metal measurements relevant to MED POL-Phase II and the participation of the Mediterranean laboratories in the intercalibration exercises (Sept. 1988).

Matrix	Sample Code	Date of Issuance of the report	Reference Concentration Values ($\mu g\ g^{-1}$ of dry matter) Cu	Zn	Cd Med Labs*	Hg	Pb	No. of partici-pating
Fish Flesh	MA-A-2	April 1980	4.5±0.6	33±2	0.17±0.08	0.49±0.04	0.8±0.2	10
Sediment	SD-N-1/2	Dec. 1986	72±4	440±20	11±1	1.5±0.5	120±10	5
Mussel Tissue	MA-M-2/TM	Dec. 1986	8.0±0.5	160±10	1.3±0.2	0.95±0.10	1.9±0.6	13
Shrimp Homoge-nate	MA(S)MED-86/TM	June 1987	22.0±0.7	66±3	0.63±0.07	1.8±0.3	0.5±0.5	10
Fish Flesh	MA(F)MED-86/TM	April 1988	3.0±0.5	110±10	0.05±0.03	0.54±0.08	4±2	13

*Mediterranean laboratories which have been participating directly in MEDPOL-Phase II monitoring programmes.

obtain more reliable consensus concentration values by including a large number of participating laboratories. The results of these intercalibration exercises, taken from the reports issued by the ILMR, are summarized in Table V. This table includes the "reference concentration values" (µg g^{-1} of dry matter) for Cu, Zn, Cd, Hg and Pb, on which the intercalibration measurements as well as actual monitoring measurements were most frequently performed by many of the laboratories participating in the monitoring programmes. The "reference concentration values" do not necessarily represent the "certified concentrations", but they are the most probable concentrations estimated on the basis of the results of the intercalibration exercises and their associated ranges represent 2σ of the central values which, in turn, are considered acceptable ranges for the reported values.

The values reported in these intercalibration exercises by the participating Mediterranean laboratories were evaluated for their acceptability on the basis of the concentration values presented in Table V and allowing ± 10% ranges for the reported values. Tables VI and VII summarize the results of this evaluation on the measurements of the sediments and marine organisms, respectively.

Table VI shows that more than 75% of the submitted values for the measurements of Cu, Cd, Hg and Pb in sediments was within the acceptable ranges. The low percentage of the acceptable values for Zn measurements is hard to interpret, but it may be related to incomplete sample pretreatment or inappropriate sensitivity adjustment in atomic absorption spectrometry. In any case, participation in the intercalibration exercises should be further encouraged as the number of participating laboratories is rather low.

While the percentages of the accepted values in the submitted values for biota samples presented in Table VII exceed 69% for Cu, Zn and Hg measurements, the similar percentages for Cd and Pb are lower, indicating the relative difficulty of many laboratories in producing acceptable values of Cd and Pb. These difficulties are also indicated by the fact that the number of values lying outside the limits set up by the statistical tests employed (outliers) is noticeably higher for Cd, followed by that for Pb. Three values for Pb measurements could not be evaluated, as they indicated only that the concentrations are less than the detection limits of the methods employed. The analytical difficulties involved in the Cd and Pb measurements are considered to be related not only to their relatively low concentrations in the marine environmental matrices, but also to their complexity for background correction in atomic absorption spectrophotometry.

On the basis of the evaluation results given in Tables VI and VII for individual elements, an attempt was made to rate the performances of the individual Mediterranean laboratories in the intercalibration exercises. The results of the rating for the measurements on sediment and biota samples, based on the arbitrary criteria set up by taking the percentage of the acceptable values in the submitted values for each laboratory, are given in Table VIII. One of the laboratories could not be rated since it had reported only one value and it is therefore not

Table VI

Summary of the intercalibration performances for heavy metal measurements on the sediment sample (SD-N-1/2) by the Mediterranean laboratories (Sept. 1988).

Number of Values	Elements Analysed				
	Cu	Zn	Cd	Hg	Pb
Submitted	4	6	6	5	4
Accepted	4 (100%)	1 (17%)	5 (83%)	4 (80%)	3 (75%)
Lying outside the limits set up by the statistical tests	0	1	0	0	0

included in this Table. Thus Table VIII indicates that 4 laboratories out of 4 for sediment measurements and 13 laboratories out of 19 for the measurements on biota samples performed acceptably in the intercalibration runs. These figures are encouraging, for the performances of the individual laboratories, including those at present falling within the unacceptable category, are expected to improve as such exercises are systematically continued. It seems however that something is fundamentally wrong with the analyses deriving from those laboratories in the poor category. Active guidance and assistance may be necessary for these. In any case, the results given in Tables VI, VII and VIII indicate that continued and systematic organization of intercalibration exercises and a wider participation in these are an essential means towards improving and validating the results of the international efforts implemented within the framework of the MED POL-Phase II monitoring programme.

Apart from the participation in the intercalibration exercises, another very important step in analytical data quality control is intra-laboratory quality control. Not a single monitoring report submitted to the MED UNIT described how the quality of data was controlled and maintained within a laboratory performing routine monitoring measurements. Intra-laboratory data quality control could be achieved simply by analysing systematically and repeatedly reference materials with the analyses of actual monitoring samples. Since it is mandatory for a monitoring laboratory to participate in intercalibration exercises, the materials distributed for the purpose of intercalibration are available for each of those laboratories. The materials themselves then act as reference materials after the issuance of the intercalibration reports with the consensus values for various heavy metals estimated on the basis of intercalibration results. Thus, the reference materials are available at each monitoring laboratory. In order to validate monitoring results produced at any laboratory, it is important to insert the analyses of the reference materials within a series of routine analyses as frequently as possible and to report the results of these reference analyses with the monitoring data. This practice, when introduced, will greatly facilitate the evaluation of submitted data.

Table VII

Summary of the intercalibration performances for heavy metal measurements on the biological samples by the Mediterranean laboratories (Sept. 1988).

Number of Values	Elements Analysed				
	Cu	Zn	Cd	Hg	Pb
Submitted	35	35	40	41	32
Accepted	24 (69%)	26 (74%)	22 (55%)	29 (76%)	15 (52%)
Lying outside the limits set up by the statistical tests	2	3	6	2	4
Not evaluated	0	0	0	0	3

* The values not evaluated were excluded in the computation.

While going over the contents of the monitoring reports, it was observed that mistakes in reporting units, miscalculations, disregard of significant figures, etc. were rather frequent. This indicates a general tendency towards an increasing lack of critical examination on the data validity by the analysts; this in turn seems, curiously, to coincide with the increasing use of computer facilities.

5. GROUPING OF DATA SUBMITTED

The monitoring data received at the MED UNIT were grouped according to the following criteria:

Group I Data: those from laboratories participating in the intercalibration exercises and producing acceptable results;

Table VIII

Provisional rating based on the intercalibration performances of the Mediterranean laboratories for heavy metal measurements (Sept. 1988).

Rating		No. of Labs	
		Sediment Analyses	Biota Analyses
Excellent	(80%<)*	0	3
Good	(66% - 80%)*	2	2
Acceptable	(51% - 65%)*	2	8
Unacceptable	(31% - 50%)*	0	3
Poor	(<30%)*	0	3
Not rated		1	1
Total		5	20

* Percentages were calculated for a laboratory:
  Nos. of Acceptable Results/Nos. of Submitted Results.

Group II Data: those from laboratories participating in the intercalibration exercises, but reporting poor results;

Group III Data: Those not supported by data quality control practices.

The results of the above grouping are given in Table IX. As shown, nearly half of the submitted data (49%) was classed as Group III data. This is due to the fact that no intercalibration exercise was organised for heavy metal measurements in sea water within the framework of the Mediterranean monitoring programmes and that only a few laboratories have participated in the intercalibration exercise organised for measurements on the marine sediment. On the other hand, Group II Data comprise only 4% of the total submitted data.

Table IX

Grouping of the heavy metal results submitted by the national laboratories within the framework of the MEDPOL-Phase II monitoring programmes (1979-87) (Sept. 1988).

Group	Number of results submitted			
	SW*	SD*	BI*	Total
I	--	1437	5323	6760
II	--	--	630	630
III	4885	1530	754	7169
Total	4885	2967	6707	14559

* SW = sea water; SD = Sediments; BI = biota.

The above grouping of the data suggests that analytical efforts employed in the monitoring programmes should be concentrated in analysing more marine organisms which are usually supported by the intercalibration exercises rather than analysing sea water, in order to increase their data validity. The measurements on sea water unsupported by the intercalibration are difficult to validate and are considered to supply limited information, as these results are hard to interpret within the context of the regional monitoring.

6. DATA APPLICATION

In order to obtain some ideas as to how the application of the submitted data could be used to identify and predict systematic pollution trends in the Mediterranean marine environment, the data available were examined, visually at first and then statistically, if applicable, in order to detect noticeable differences between those collected in different localities, seasons, years, etc. So as not to waste effort these examinations concentrated on Group I data. In examining the data on marine organisms, it is important to take the species specificity in heavy metal content into consideration. In order to achieve useful comparisons, systematic data sets collected on the same species from different locations, seasons, years, etc. have to be at hand. Data sets satisfying these criteria are available, however, for only two species, <u>Mullus barbatus</u> (fish, red mullet) and <u>Mytilus galloprovincialis</u> (Mediterranean mussel).

In comparing the data sets against each other, minor local fluctuations in concentration levels are often ignored, since detailed analyses of data within local situations related to specific pollution sources are supposed to be the tasks within the framework of the national monitoring programmes. The purpose of the present comparisons is to deduce comprehensive tendencies which will enable us to describe states of regional pollution.

In Table X, average concentration values for various heavy metals are given for several species of Mediterranean fish, including Mullus barbatus on which several data sets from different locations are available. Since the comparisons between the data sets within one species as to seasons and years did not show, in general, evident differences, the selected data sets for one specific species were arithmetically averaged and presented in Table X. In averaging these data, the detection limit values indicated in the reports, were taken into the computations when the reports showed the concentrations to be below the detection limits. The ranges associated with these average values are standard deviations of the mean values (1σ) and the numbers in brackets represent the number of data averaged. For fish the average values for different Mediterranean areas could be presented only for Mullus barbatus. Taking into account the standard deviations associated with the average values, no significant difference was observed between the different data sets for Mullus barbatus, except for a possible lower level of Hg concentration in the Atlantic area. However, as the lower Hg average for the Atlantic in Table X is based on only a small number of data, confirmation will have to be made by means of systematic collection of data.

As to the species specificity of heavy metal concentrations in Mediterranean fish, it is reasonable to deduce higher levels of Hg and, possibly, Zn in Xiphias gladius (swordfish). Lower levels of Cd and slightly higher levels of Hg observed in Pagellus erythrinus compared with other similar-sized fish, need confirmation.

In Table X, the weight ranges of fish analysed are also given. Wherever systematic data sets are available for both fish weight and Hg concentration, obvious positive correlations can also be noted between these two parameters. The correlation factors between 0.68 and 0.96 have been obtained for a number of the data sets examined. As has already been pointed out (UNEP, 1987), the slopes of the regression lines may be better indices for expressing the species specificity than the concentration ranges, where the above correlation exists. However, since the average values for the data sets presented in Table X do not show any sign of wide deviation, these values may be considered to be close to the normal concentration levels of heavy metals prevailing in the Mediterranean region for these species.

Table X

Heavy metal concentrations in Mediterranean fish deduced from the MED POL-Phase II monitoring data (1982-1987).

Species & Area	Weight Range (g)	Heavy metal concentration (μg g^{-1} wet tissue) Cu**	Zn**	Cd**	Hg**
<u>Xiphias cladius</u>					
Ionian Sea	6.5 - 220*	0.7±0.3 (14)	8 ± 2 (14)	0.02±0.01(14)	0.9 ± 0.5 (16)
<u>Mullus barbatus</u>					
East Med.	14.7 - 112	0.7±0.2 (71)	4.8±0.5(50)	0.04±0.02(57)	0.10±0.05 (64)
Ionian Sea	42.2 - 142	0.4±0.1 (7)	3 ± 1 (12)	0.02±0.01(12)	0.19±0.08 (12)
N. West Med.	-	-	-	0.01±0.01(43)	0.2 ±0.1 (41)
Atlantic	36.7 - 67.2	-	-	-	0.03±0.01 (5)
<u>Trachurus</u> sp.					
Ionian Sea	28.1 - 135	0.3±0.2 (11)	3.4±0.6(13)	0.012±0.005(13)	0.18±0.08 (13)
<u>Pagellus erythrinus</u>					
Adriatic Sea	27.5 - 263	-	-	0.003±0.001(13)	0.4 ± 0.2 (16)
<u>Diplodus sargus</u>					
East Med.	45.0 - 250	0.4±0.2 (21)	4.5±0.9(21)	0.08 ± 0.03(17)	0.19+0.09 (58)
<u>Lithognatus mormyrus</u>					
East Med.	32.8 - 118	0.5±0.1 (28)	5 ± 1 (28)	0.06 ± 0.04(15)	0.09±0.05 (47)

* kg.
** Numbers in brackets indicate the number of data averaged.

In Table XI, the average values for heavy metal concentration levels in Mediterranean molluscs are presented. The procedures for averaging and the computations for the associated standard deviations are similar to those used for Mediterranean fish. As has been done for Mullus barbatus in Table X, the concentration levels in Mytilus galloprovincialis collected in various areas from the Adriatic Sea and the north- and southwestern Mediterranean were compared in Table XI. Some of the standard deviations associated with the average concentrations, especially for Hg, are large, indicating a wide range of individual results around the average values. The comparisons of these average values, however, do not reveal any significant differences between different areas studied.

The systematic collection of data on two different subspecies of a bivalve, Mactra corallina, inhabiting the same area, presented in Table XI, indicates that these two subspecies are chemically identical as far as their heavy metal levels are concerned. One species of gastropod, Arcularia gibbosula, seems to accumulate heavy metals at higher levels than those found in other bivalve species. It may be worthwhile to pursue the suitability of this and other similar species as indicator organisms for heavy metal accumulation.

Tables X and XI show that very little effective comparisons of heavy metal content in the Mediterranean scale can be achieved on the basis of the data for marine organisms at hand. In order to improve this situation measurements should be concentrated on a small number of selected species giving a better coverage of the whole Mediterranean region. In some cases, it may be worthwhile to consider the reduction of sampling frequency in order to facilitate the production of better quality data by slimming down the work load for sampling and measurements.

Although systematic comparisons have not been warranted for sediment measurements, due to a relatively limited number of validated data from different areas, it seems that the reduction of sampling stations and frequencies may also help the production of higher quality data. In this case, however, the task of selecting a smaller number of representative stations in reference areas assumes critical importance for subsequent interpretation of the data obtained.

7. REMARKS

Ensuing from a review and evaluation of the heavy metal monitoring data submitted to the MED UNIT by September 1988 the following remarks are pertinent:

(1) A standard log-form for reporting the results of sediment analyses was not utilized in the monitoring reports.

(2) More than 14,500 heavy metal monitoring data were submitted from 12 Mediterranean countries in the framework of the MEDPOL-Phase II monitoring programme by September 1988.

Table XI

Heavy metal concentrations in Mediterranean molluscs deduced from the MED POL-Phase II monitoring data (1983-1987).

Species & Area	Heavy metal concentrations (μg g⁻¹ wet tissue) Cu*	Zn*	Cd*	Hg*	Pb*
Mytilus galloprivincialis					
Adriatic - Piran Area	-	-	0.22±0.05(20)	0.03±0.01(20)	-
- Rovinj Area	-	-	0.12±0.07(38)	0.02±0.01(38)	-
- Pula Area	0.9 ± 0.4(17)	-	0.19±0.05(26)	0.05±0.04(25)	0.4±0.2(17)
- Rijeka Area	-	-	0.14±0.05 (8)	0.02±0.01 (8)	0.3±0.1 (8)
- Kornati & Sibenik	1.1 ± 0.6(24)	23 ± 6(25)	0.18±0.09(39)	0.05±0.04(41)	0.3±0.1(22)
- Split Area	-	-	0.17±0.04(28)	0.08±0.07(29)	-
- Dubrovnik Area	1.5 ± 0.8(31)	19 ± 7(31)	0.18±0.05(31)	0.03±0.01(31)	0.4±0.2(31)
N. West Med.	-	-	0.13±0.08(74)	0.07±0.07(79)	0.7±0.4(68)
S. West Med.	1.6 ± 0.5(10)	29 ± 6(11)	0.2 ±0.1 (12)	0.09±0.09(11)	0.9±0.6 (9)
Mactra corallina corallina					
East Med.	0.7 ± 0.1(82)	17 ± 4(82)	0.13±0.04(78)	0.05±0.03(74)	0.3±0.1(60)
Mactra corallina stultorum					
East Med.	0.7 ± 0.1(61)	15 ± 4(62)	0.11±0.04(48)	0.05±0.03(46)	0.3±0.2(25)
Arcularia gibbosula					
East Med.	8 ± 3 (17)	140 ±60(17)	1.2 ± 0.6(17)	0.4 ±0.4 (17)	1.5±0.7(12)

* Numbers in brackets indicate the number of data averaged.

(3) The availability of the data is heavily biased towards certain limited areas. Data are particularly sparse in respect of some southern parts of the Mediterranean.

(4) While the numbers of data available for sediments and marine organisms are fairly well balanced, there seems to be an excess of sea water data.

(5) Insufficient information to judge the quality of sampling operations was given in the monitoring reports submitted.

(6) As the present Reference Methods for heavy metal measurements on sediment samples describe those for total quantities of heavy metals, the data thus obtained have limited significance in studying pollution situations in marine sediments.

(7) On the basis of the results of several intercalibration exercises for heavy metal measurements, it was judged that 4 out of 4 and 13 out of 19 participating laboratories are performing acceptably in measurements of the sediment and biota samples, respectively.

(8) It seems that something is fundamentally wrong with the analytical methods of those laboratories which do not perform well in the intercalibration exercises.

(9) No monitoring report submitted described how the intra-laboratory analytical data quality control was carried out within a monitoring laboratory.

(10) The grouping of the data submitted on the basis of the results of the intercalibration exercises showed that nearly half of the data (49%) was not supported by appropriate data quality assurance practices.

(11) As to heavy metal measurements in marine organisms, systematic data sets allow comparisons in the Mediterranean regional scale with respect to locations, seasons, years, etc. are available only for two species, Mullus barbatus and Mytilus galloprovincialis.

8. RECOMMENDATIONS

In order to improve the on-going monitoring programmes within the framework of the MED POL-Phase II, the following recommendations are made:

(1) The availability of the monitoring data should be improved especially for southern parts of the Mediterranean to allow of a comprehensive review of the pollution situation.

(2) In a monitoring context the efforts should be concentrated on measurements on sediments and marine biota rather than those on sea water, in which the validation of data is difficult to achieve.

(3) The revision of the Reference Methods for heavy metal measurements on sediment samples should be considered with a view to obtaining a better reflection of pollution situations in the data obtained.

(4) Continued and systematic organisation of intercalibration exercises and wider participation of monitoring laboratories in these exercises are essential in the maintenance of data quality with a special emphasis on the sediment matrix.

(5) Those laboratories performing poorly in the intercalibration exercises, should be given active guidance and assistance to improve their analytical performance.

(6) The importance of intra-laboratory analytical data quality control within a monitoring laboratory should be emphasized.

(7) In planning national monitoring programmes the following points should be taken into consideration in order to allow a comprehensive regional review:

(i) to concentrate efforts on a small number of selected species distributed widely in the region;

(ii) to reduce sampling frequency to twice a year for marine biota samples collected from well-selected representative stations;

(iii) to reduce sampling frequency to once a year for marine sediment samples collected from a relatively small number of well-selected representative stations in reference areas.

9. REFERENCES

IAEA, 1978. Intercalibration of Analytical Methods on Marine Environmental Samples Progress Report No. 18.

IAEA, 1980. Ibid. Prog. Rep. No. 20.
IAEA, 1986. Ibid. Prog. Rep. No. 31.
IAEA, 1987. Ibid. Prog. Rep. No. 34.
IAEA, 1988. Ibid. Prog. Rep. No. 35.

UNEP, 1987. Assessment of the state of pollution of the Mediterranean Sea by mercury and mercury compounds and proposed measures. UNEP/WG. 160/8, Athens.

UNEP/FAO/IOC/IAEA, 1984a. Sampling of selected marine organisms and sample preparation for trace metal analysis. Ref. Meth. Mar. Pollut. Stud., No. 7.

UNEP/FAO/IOC/IAEa, 1984b. Determination of total mercury in selected marine organisms by cold vapour atomic absorption spectrophotometry. Ibid., No. 8.

UNEP/FAO/IOC/IAEA, 1984c. Determination of total cadmium, zinc, lead and copper in selected marine organisms by flameless atomic absorption spectrophotometry. Ibid., No. 11.

UNEP/IAEA, 1985a. Determination of total mercury in marine sediments and suspended solids by cold vapour atomic absorption spectrophotometry. Ibid. No. 26.

UNEP/IAEA, 1985b. Determination of total cadmium in marine sediments by flameless atomic absorption spectrophotometry. Ibid., No. 27.

UNEP/IAEA, 1985c. Determination of total copper in marine sediments by flameless atomic absorption spectrophotometry. Ibid., No. 33.

UNEP/IAEA, 1985d. Determination of total lead in marine sediments by flameless atomic absorption spectrophotometry. Ibid., No. 34.

UNEP/IAEA, 1986. Determination of total zinc in marine sediments by flame atomic absorption spectrophotometry. Ibid., No. 39.