United Nations Environment Programme

Distr.
RESTRICTED

UNEP/WG.91/Inf.3
18 October 1983

Original: ENGLISH

Second Meeting of the Working Group for Scientific and Technical Co-operation for MED POL

Athens, 21-25 November, 1983

Mediterranean action plan

Long-Term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL - PHASE II)

REPORT ON INTERCALIBRATION EXERCISES CARRIED OUT BY IAEA'S INTERNATIONAL LABORATORY FOR MARINE RADIOACTIVITY IN THE FRAMEWORK OF MED POL - PHASE I

In Co-operation with:

INTERNATIONAL ATOMIC ENERGY AGENCY

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INTRODUCTION

The establishment of pollution monitoring networks, whether at the global or regional level, has imposed the need for comparability of the analytical results obtained by the laboratories participating in these networks in order to overcome the diversity of analytical techniques in use. To ensure the comparability of such measurements, intercalibration analyses, using aliquots of homogeneous samples of reference materials must be made.

An intercalibration programme was started as early as 1975 in the framework of UNEP's Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MED POL - PHASE I), organized by the International Laboratory for Marine Radioactivity (ILMR) of the International Atomic Energy Agency (IAEA) at Monaco in close co-operation with FAO(GFCM) and IOC (UNEP 1983).

Samples of various marine organisms and sediments were prepared and distributed to research centres from the Mediterranean Region participating in MED POL, as well as to other laboratories willing to participate in the exercises (see Annex I).

The homogeneity of all the samples had been tested by ILMR with the assistance of the IAEA's Seibersdorf Laboratory (Vienna), as well as other national institutions. Their distribution would only take place after finding their homogeneity to be suitable for achieving the stated objectives.

In addition to the intercalibration samples, all participating laboratories received NBS reference materials for heavy metal analysis or primary standards of PCBs for chlorinated hydrocarbon analysis in order to check in advance their analytical procedures within the laboratories.

All participating laboratories were requested to analyse the distributed samples by applying the analytical methods currently in use for environmental studies, and to report the results with the description of the analytical procedures, methods of calibration, methods of calculation and quantification, etc.

The distribution of the intercalibration samples was made stepwise. In the course of the progress of MED POL - PHASE I, samples of different matrices were forwarded to participating research centres at varying intervals depending on the development of the various components of the programme and involvement of the research centres.

The results of the analyses reported from these intercalibration exercises were treated statistically in order to deduce "consensus values" for the concentrations of the interesting components. The results of the laboratories, selected on the basis of their analytical reputation and performance, were treated similarly to derive "probable concentrations" of the components in the distributed samples. Based on "probable concentrations", ranges of acceptable values were estimated for each component.

In general, the policy was that, until a laboratory sent in the results of measurements made on one sample it did not receive the next sample, and, as soon as results were reported by a sufficient number of participating laboratories, overall averages and consensus values of the components of interest were computed and made available to the laboratories having reported results. In this way, the participating laboratories were able to judge their performance for themselves, comparing their results with those of others.

SAMPLE DISTRIBUTION

Since the beginning of the MED POL - PHASE I in 1975, and until its end in early 1981, the samples listed in Tables 1 and 2 were prepared, tested for homogeneity, distributed and results reported.

Table 1: Reference materials prepared for the purpose of analysing trace metals (Cu, Zn, As, Se, Ag, Cd, Sb, Hg, Pb, Cr, Mn, Fe, Co and Ni) in marine biological samples

Sample Code	Description	Distribution	References
MA-M-1	Oyster homogenate	1975 - 78	IAEA/UNEP 1976, 1978
SP-M-1	Sea-plant homogenate	1977 - 80	IAEA/UNEP 1977, 1978b
MA-A-1	Copepod homogenate	1977 - 80	IAEA/UNEP 1977, 1978b
MA-A-2	Fish-flesh homogenate	1978 - 80	IAEA/UNEP 1978, 1980

Table 2: Reference materials prepared for the purpose of analysing chlorinated hydrocarbons in marine biological samples

Sample Code	Description	Distribution	References
MA-M-1	Oyster homogenate	1976 - 79	IAEA/UNEP 1980a, 1980b, 1983
MA-A-1	Copepod homogenate	1976 - 79	IAEA/UNEP 1980a, 1980b, 1983
MA-A-2	Fish-flesh homogenate	1976 - 79	IAEA/UNEP 1980a, 1980b, 1983

RESULTS

The comparison between the "consensus values" and the "probable concentrations" showed that, in general, these two sets of values were in agreement. Based on the uncertainties associated with the "probable concentrations" of the elements concerned, the two standard deviations (2σ) range and the one standard deviation (1σ) range were regarded respectively as "acceptable range" and "good range". Based on the "acceptable range" and "good range" estimated for each element in each sample, the results reported by the Mediterranean research centres were evaluated, and when found adequate, used for the assessments of the state of pollution in the Mediterranan Sea (UNEP 1983a).

Comparability of the measurements on the trace metals was, in general, found to be satisfactory. However, it became apparent that some laboratories continued to have difficulties in reporting the results as scheduled, and that the comparability of the measurements of low concentrations of Pb in some samples, was poor. Although participation in intercalibration exercises was mandatory for participants in MED POL, major difficulties were encountered in recovering the reports of the analytical results from some research centres.

While most of the participating laboratories reported their results punctually, within specified deadlines, the data reporting of some laboratories was much slower, delaying the statistical treatment of the results, as well as the feed-back processes of the result-survey to individual laboratories. From some laboratories the reports were not received, despite the fact that they had been equipped with the necessary instruments, and these instruments had been proved to be functioning.

Nevertheless, except for a limited number of laboratories, the intercalibration exercises proceeded effectively during MED POL - PHASE I, and the participating laboratories received the necessary feed-back for their analytical quality control.

With regard to the chlorinated hydrocarbon samples, a relatively small number of Mediterranean laboratories positively responded to the exercise and therefore, their results required different statistical treatment than was possible for the trace metals exercises.

Similar uncertainties existed in ascribing a "probable concentration" for the chlorinated hydrocarbons. The Chauvenet test for outlying values was applied to the entire data set for each compound in each sample. Means and standard deviations were then computed for the values remaining after excluding the outlying values. These mean concentrations for the seven chlorinated hydrocarbons reported were designated as "probable concentrations". An "acceptable" range of analytical results was defined as those falling with $\pm$ 1 standard deviation for individual measurements around the "probable concentration".

Of the three samples analysed, one showed relatively high concentrations of chlorinated hydrocarbons (fish tissue homogenate). For this sample the variability in the reported measurements was in general, much better than for

the other two samples. Evaluation of the results by the stated criteria showed that except for "aroclor 1254" and pp'DDT in the fish sample, 50% or more of the laboratories reporting results were within the $\pm 1\sigma$ range. Thus the results for this exercise were an improvement over previous intercalibration efforts. These reductions in analytical variability were ascribed to the application by UNEP of pre-agreed analytical procedures, the distribution of quantification standards with the intercalibration materials, participant training both within the Monaco Laboratory or at participating laboratories, and to a generally greater analytical experience gained by many of the laboratories.

Several problems remain before analytical precision can be significantly improved for the analysis of chlorinated hydrocarbons under monitoring programmes. These include the inherent uncertainties in the quantification of complex mixtures of chlorinated hydrocarbons such as the PCBs and contribution of other halogenated hydrocarbon contaminants difficult to separate, such as the Toxaphenes. The introduction of more precise sample preparation methods and high resolution capillary columns into the gas chromatographic analysis significantly improves the accuracy of quantifications for individual components, reduces the interference between various contaminants and expands the possible range of contaminants able to be quantified. Such efforts to increase analytical accuracy and precision should be considered in future intercalibration exercises. Since many of the participating laboratories were not able to complete the analysis for chlorinated hydrocarbons, there is an obvious need to improve expertise in the region.

CONCLUSIONS

Experience gained through the intercalibration exercises carried out during MED POL - PHASE I proved these kind of exercises to be extremely important, not just for a routine check on the quality of the analytical work carried out by the participating laboratories, but for the sorting out of problems faced by them in implementing an entire work programme after having obtained new instrumentation, methodology, training etc.

On the other hand, the results of the intercalibration exercises showed no basic difference between the quality of analytical data reported by Mediterranean laboratories, and that of non-Mediterranean laboratories.

Finally, the need to have common methods has become strengthened, particularly with respect to chlorinated hydrocarbons, as well as the obligatory character of the intercalibration exercises at the Mediterranean and global level.

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ANNEX I

List of participating laboratories in the intercalibration exercises during MED POL - PHASE I

Country and Institution	Investigator	Heavy metals in oyster	Heavy metals in seapl. & cop.	Heavy metals in fish	Chlor. hydroc.
ALGERIA					
Centre de Recherches Océanographiques et des Pêches Alger	R. Semroud	x	x	x	
	D. Siblot	x	x	x	
	A. Aissi		x	x	
	A. Asso			x	
CYPRUS					
Department of Fisheries Nicosia	A. Demetropoulos		x	x	
	L. Nicolaidou		x	x	
EEC					
Joint Nuclear Research Centre Euratom - CCR Ispra	C.J. Toussaint	x	x	x	
	G. Aina	x			
	L. Roncari		x		
EGYPT					
Centre for Post-Graduate Studies Alexandria University Alexandria	A.H. El-Sebae				x
FRANCE					
Institute Scientifique et Technique des Pêches Maritimes Nantes	C. Alzieu	x			x
	Y. Thibaud	x	x	x	
Département de Chimie Appliquée Centre d'Etudes Nucléaires SEAPC Grenoble	R. Bourguillot	x		x	
	A. Cornu	x			
	A. Huart			x	
	J. Laverlochère		x	x	
	A.M. Andréani			x	
	M. Disant			x	
	J. Diebolt		x		
	P. Gault		x		
Laboratoire d'Océanographie Physique Villefranche sur Mer	P. Courau	x			
	M. Roméo	x			

List of participating laboratories in the intercalibration exercises during MED POL - PHASE I (Cont'd ../2)

Country and Institution	Investigator	Heavy metals in oyster	Heavy metals in seapl. & cop.	Heavy metals in fish	Chlor. hydroc.
Laboratoire Municipal de Bordeaux Bordeaux	M. Faugère P. Hooquellet	x x			
Centre d'Etudes Nucléaires de Saclay Gif sur Yvette	S. May N. Lefol	x x			
Laboratoire de Radioactivité de l'Air Orsay	J.C. Philippot	x			
Laboratoire de Spectrographie de l'ORSTOM Bondy	M. Pinta	x	x		
Service d'Etudes Analytiques Commissariat à l'Energie Atomique Fontenay-aux-RoseS	G. Baudin		x		
Laboratoire de Surveillance des Nuisances de l'Homme et de son Environnement Pierrelatte	J. Ruiz M. Cardi M. Clavel M. Jalat	x x x x	x		
Laboratoire Solaigue Nîmes	J. Laporte M. Kovacsik	x x	x x	x x	
Laboratoire de Sédimentologie sous-marine Perpignan	A. Monaco J.P. Cambon	x x			
Laboratoire Central d'Hygiène Alimentaire Paris	G. Cumont M. Feinberg		x x	x x	
Laboratoire de Chimie appliquée à l'expertise Faculté de Pharmacie Université de Montpellier I Montpellier	R. Mestres				x

List of participating laboratories in the intercalibration exercises during MED POL - PHASE I (Cont'd ../3)

Country and Institution	Investigator	Heavy metals in oyster	Heavy metals in seapl. & cop.	Heavy metals in fish	Chlor. hydroc.
GREECE					
Nuclear Research Centre "Demokritos" Athens	A.P. Grimanis	x	x	x	
	C. Papadopoulou	x		x	
	M. Draina	x			
	D. Zafiropoulos			x	
General Chemical State Laboratories Division of Research Athens	D.G. Marketos	x	x	x	
	P. Mavrikos	x		x	
Institute of Oceanographic and Fisheries Research Athens	A. Stephanidis	x			
	F. Voutsinou	x	x	x	
	J. Satsmadjis				x
University of Thessaloniki Thessaloniki	A.G. Panetsos	x	x	x	x
	S.A. Georgakis	x	x	x	
	G. Vasilikiotis	x	x		
	M. Sofoniou	x			
	D. Themelis	x			
	N. Voulou-voutis	x	x		
	E. Christou		x		
	T. Edipides				x
Benaki Institute of Phytopathology Athens	N. Adam				x
ISRAEL					
Israel Oceanographic & Limnological Research Ltd. Haifa	O.H. Oren	x	x	x	
	H. Hornung		x	x	
	R. Ravid				x
ITALY					
Centro di Radiochimica e Analisi per Attivazione Istituto di Chimica Generale dell'Universitá Pavia	E. Orvini	x	x		
	P. Borroni	x			

List of participating laboratories in the intercalibration exercises during MED POL - PHASE I (Cont'd ../4)

Country and Institution	Investigator	Heavy metals in oyster	Heavy metals in seapl. & cop.	Heavy metals in fish	Chlor. hydroc.
Istituto di Anatomia Comparata Laboratorio di Idrobiologia Siena	A. Renzoni E. Bacci	x x	x x	x x	x
Istituto di Chimica Generale Universitá di Genova Genova	R. Capelli M. Franchi M. Zanicchi B. Fassone	x x x	x x x x	x x x	
Laboratorio Radioattivitá Ambientale CNEN-CSN della Casaccia Rome	A. Cigna G. Mastinu M.E. Belli A. Barocas F. Pompéi	x x x	 x x x	 x x	
Laboratorio per lo Studio della Contaminazione del Mare Fiascherino, La Spezia	M. Bernhard M. Stoeppler	x x			
Istituto e Museo di Zoologia e Anatomia Comparata Universitá di Messina Messina	A. Bolognari L. Mojo S. Martella G. Martino	x x x x	x x x x		
Institute of Marine Biology CNR Venice	V. Fossato				x
Departmental Institute of Chemistry and Industrial Chemistry University of Catania Catania	M. Piattelli				x
MALTA					
The University of Malta Chemistry Department Msida	A.P. Storace		x	x	

List of participating laboratories in the intercalibration exercises during MED POL - PHASE I (Cont'd ../5)

Country and Institution	Investigator	Heavy metals in oyster	Heavy metals in seapl. & cop.	Heavy metals in fish	Chlor. hydroc.
SPAIN					
Instituto de Investigaciones Pesqueras Barcelona	A. Ballester Ll. Cros	 x	 x	 x	x
Laboratorio Oceanografico del Mar Menor San Pedro del Pinatar	J. Ros J.G. Perez	x x	x		
Institute of Chemistry of Sarria Barcelona 17	M. Gassiot				x
TURKEY					
Hydrobiological Research Institute Istanbul	M.I. Artuz G. Yurder		x x	x x	x
Marine Sciences Department Middle-East Technical University Erdemli-Icel	T.I. Balkas G. Ramelow C. Saydam S. Tugrul M.A. Ozkam G. Tuncel I. Salihoglu	x x x x x x	x x x x x	x x x	 x
Faculty of Sciences Ege University Bornova-Izmir	H. Uysal M. Aksoylar			x	 x
YUGOSLAVIA					
Institute "Jozef Stefan" Ljubljana	L. Kosta	x	x	x	
University of Rijeka Physics Department Rijeka	A. Ljubicic V. Pecar D. Rendic	x x x			
Center for Marine Research "Ruder Boskovic" Institute Zagreb	M. Branica M. Picer			x	 x
Marine Biological Station Portoroz	J. Stirn R. Planinc			x x	x

List of participating laboratories in the intercalibration exercises during MED POL - PHASE I (Cont'd ../6)

Country and Institution	Investigator	Heavy metals in oyster	Heavy metals in seapl. & cop.	Heavy metals in fish	Chlor. hydroc.
INTERNATIONAL ATOMIC ENERGY AGENCY					
Seibersdorf Laboratory	O. Suschny	x	x	x	
	A. Veglia			x	
Monaco Laboratory	R. Fukai	x	x	x	
	B. Oregioni	x	x	x	
	L. Huynh Ngon	x	x	x	
	D. Vas			x	
	D. Elder				x
	K. Burns				x
	J.P. Villeneuve				x