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Role of Sedimentation in the Pollution of the Mediterranean Sea

The attached document, which was prepared by the United Nations Educational, Scientific and Cultural Organization, is distributed to participants for their information.

Rôle de la sédimentation dans la pollution de la mer Méditerranée

Le présent document, préparé par l'Organisation des Nations Unies pour l'Education, la Science et la Culture, est distribué aux participants pour information.

UNESCO/UNEP Project MED IX
Role of Sedimentation in the Pollution of the Mediterranean

FINAL REPORT (August 1977)

I. BACKGROUND OF THE PROJECT

The Intergovernmental Meeting on the Protection of the Mediterranean, convened by UNEP in Barcelona (28 January - 4 February 1975) approved an Action Plan which consists of three major components: legal, scientific, integrated planning.

Among others, the Action Plan states in Section I-4:

"It would be appropriate, in particular to develop programmes of activities or to amplify those which are already being implemented, for example
a) the development and application of national techniques from the point of view of economy, ecology and health in various fields such as
i) treatment, use and safe disposal of organic and industrial wastes resulting from various human activities.

In view of these objectives UNEP has initiated a project on the "Role of Sedimentation in the Pollution of the Mediterranean".

2. OBJECTIVES

The long-term aim of this project was to provide the Governments of the Mediterranean Coastal States with an assessment of the quantity of pollutants entering the Mediterranean Sea through the particulate load carried by the rivers.

The following tasks were identified as the immediate objectives of Project MED IX.

i) to review the role of river sediments in pollutant transfer.

ii) to review the present knowledge on the quantity and quality of river particulate load discharged into the Mediterranean.

iii) to coordinate the actions of the Mediterranean countries and help them to survey the pollutant load carried by suspended particles in rivers.

3. IMPLEMENTATION

3.1. Preliminary report: "Assessment of knowledge and development of guidelines for environmental assessment".

This report has been recommended by the first meeting of experts from the different Mediterranean countries, held in Paris, 17-21 May 1976, to develop common methodology to ensure a uniform approach for the collection of a first set of water pollution data relevant to river discharge into the Mediterranean, within the framework of MED X. This report has been subsequently prepared by the Secretariat of the

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Division of Water Sciences,in order to review: (i) the role of sediments in pollution studies (ii) the sediment-pollutant interactions (iii) the particulate pollutant distribution and the sampling procedures and (iv) references for analytical procedures. The report also proposed a list of pollutants to be monitored in the Mediterranean rivers. Finally a complete list of all major and secondary rivers in the Mediterranean was given with their water discharge, drainage area, average turbidity and information on the quality of the suspended load, if there was any such load.

3.2. Meeting of Experts of Mediterranean Countries, Rome(December 1976)

The above-mentioned report was extensively discussed by the experts which met in Rome for discussion on Projects MED IX and MED X. The major conclusions are summarized hereafter (4.1)

The Meeting recognized the importance of pollutants carried by suspended particles for the assessment of the total pollutant contribution by rivers, especially as far as heavy metals and organochlorinated compounds are concerned.

Taking into account the short time available for the assessment and the present lack of data on the Mediterranean rivers, the Meeting recommended a phase of action for obtaining a general picture of the order of magnitude of the present level of pollutants based on a limited number of selected rivers and a very restricted number of samples (at least one between January and June 1977).

The Meeting agreed on a list of pollutants and on a suitable frequency of sampling (Tables 1, 2 and 3).

The IAEA Representative in Rome proposed that the IAEA Marine Laboratory in Monaco could take a restricted number of samples for analysis. In view of the difficulties in sampling and pretreatment, the Meeting asked Unesco to prepare a document on these procedures.

3.3. Report on "Recommended sampling and pretreatment procedures for articulat pollutants analysis".

After consultation and advice from the staff of the International Laboratory for Marine Radioactivity (IAEA), this report was sent in February 1977 to all UNEP focal points and to the experts who attended the Rome Meeting. This Report included: (i) suspended load measurements, (ii) sample collection and pretreatment,(iii) analytical procedures and (iv) standard format to report analysis. Heavy metals and pesticides were treated separately.

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TABLE 1. LIST OF POLLUTANTS FOR THE INVENTORY OF PARTICULATE POLLUTANTS

1. Extremely hazardous pollutants (black list)

   Arsenic
   Mercury
   Lead
   Cadmium
   PCB
   Other chlorinated organic compounds

2. Certain other significant pollutants (grey list)

   Copper
   Chromium
   Nickel
   Zinc

TABLE 2. <u>MAJOR RIVERS TO BE SURVEYED FOR PARTICULATE POLLUTANTS</u>

ALBANIA	:	to be determined later
ALGERIA	:	Cheliff, Seybouse
EGYPT	:	Nile and coastal lakes
FRANCE	:	Aude, Hérault, Rhône (to be confirmed)
GREECE	:	Evros
ISRAEL	:	nil
ITALY	:	Adige, Arno, Pescara, Po, Tevere
LEBANON	:	to be determined later
MOROCCO	:	Moulouya (to be confirmed)
SPAIN	:	Ebro, Llobregat
TUNISIA	:	Medjerda
TURKEY *	:	Seyhan, Ceyhan, Buyak Menderes.
YUGOSLAVIA	:	Neretva.

* Rivers suggested by the Secretariat.

Table 3. Proposed Sampling Frequency for Particulate Pollutants

Type of parameters	Sampling Frequency	
	Large rivers Q > 100 m3/s	Small rivers Q < 100 m3/s
Black list	Monthly during the 1st. year Monthly or 4-6 times during the subsequent 4 years	4 times each year (occasionally)
Grey List	Same as above	One year every 5 years (4 times in that year)
Environmental parameters	To be measured at the time of each sampling	

TABLE 4. Percentage of trace elements carried in the particulate form relative to the total load of some world rivers.

Place	Co	Ag	Pb	Cr	Cu	As	Hg	Cd	Zn	Ni
Rhine (The Netherlands)(°)	-	-	72	70	64	56	56	44	37	23
Rhine (Germany) (1)	17	-	83	80	50	-	61	28	44	24
North Sea (2)	-	57	64	-	83	-	-	18	44	50
Thames (3)	-	-	-	-	-	-	92	-	-	-
La Have (4)	-	-	-	-	-	-	20	-	-	-
Southeastern rivers (U.S.A.) (5)	45	-	-	92	53	-	-	-	87	82
Amazon (6)	98	-	-	90	93	-	-	-	-	97
Yukon (6)	98	-	-	87	97	-	-	-	-	98
Columbia (7)	-	-	-	-	-	-	52	-	-	-
Mississipi (8)	-	-	99.2	98.5	91.6	70.2	-	88.9	90.1	94.7
Saar (9)	-	-	97	60	70	-	64	78	36	25

(°) De Groot, Allersma and Van Driel (1973)
(1) Förstner and Müller (1974);(2) Preston et al.(1972);(3) Smith et al.(1971);
(4) Cranston and Buckley(1972); (5)Windom et al.(1971);(6) Gibbs(1973);(7)
Bothner and Carpenter (1973);(8) Trefry, Presley(1976);(9) Meisch, Reinle, Bielig(1977).

4. RESULTS

4.1. Importance of sediments in pollution studies

4.1.1. Relative importance of particulate pollutants

The possibility of quantifying the flux of pollutants through the aquatic ecosystem depends upon the identification of the various phases that act as reservoirs of chemical substances. There are basically three major reservoirs: i.e. dissolved reservoir (water and dissolved load), particulat reservoir (suspended and bottom sediment) and biological reservoir (plankton, benthos, nekton...)

The assessment of pollutant behaviour within these reservoirs, as well as the flux of material from one to the other, and the boundary conditions of the system are the prerequisites of a holistic knowledge of pollutant pathways in the aquatic environment. Moreover, this will help to implement a monitoring programme and to provide a basis for prevention and eventual control of pollution.

In this connection, the particulate reservoir is one of the major sub-systems of the aquatic environment, and requires special attention. The comparison between dissolved and particulate elemental concentrations shows that most heavy metals and organic pollutants are enriched in the solid phase by two or three orders of magnitude. When the relative amount of pollutants transported in river waters and in the suspended sediments are compared, the importance of sediment is clearly seen.

4.1.2. Principal interaction processes between pollutants and particulates

(1) Particle size

Decrease in grain size of natural suspended particles (sand → silt → clay → colloids) is accompanied by mineralogical variations, i.e. an increase of the clay mineral content, and by physical property changes, the greater importance of surface processes (ion exchange capacities, specific surface) with decreasing grain size.

According to these variation in size and/or mineral nature, smaller particles generally exhibit the highest pollutant concentrations. This is the general case for heavy metals and radionuclides, and also for pesticide residues that are adsorbed on clay particles.

(2) Types of association processes

As a first approximation, association processes between pollutants and particulates can be classified as follows:

- chemical and physical sorption on smallest particles (clays, colloids, hydroxides) and on particulate organic matter...

- coprecipitation with oxides and/or hydrous oxides, hydroxides, especially with iron and manganese, causing coatings on sands grains.

- insoluble organic compound formation

- incorporation in mineral lattice

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(3) Stability of the association processes

Any change in the chemical composition or in the physical parameters of a water body may cause a pollutant to be released from the particles. Among the variations of chemical parameters able to affect the pollutant-particle association, pH variation plays a significant role. Diagrams of the solubility of metals as a function of pH indicate that, in acid waters, hydroxides, carbonates and sulphides become unstable and metals may pass into ionic form. Such pH variations can be caused by bacterial decomposition of organic matter or by release in the rivers of industrial acid effluents.

Disposal of certain organic effluents, especially complexing agents and detergents can also result in solubilisation of metals in dissolved comple form, the toxicity of which is sometimes higher than the ionic dissolved form (e.g. mercury, cadmium).

4.1.3. Problems of particulate pollutant load assessment

(1) Separation of particulate and dissolved phases

The most popular method of separation currently in use is the microfiltration on cellulose filter (such as Millipore, Nucleopore...). The phase passing through the filter is the so-called dissolved fraction while the fraction retained upon the filter is regarded as suspended sediment.

This criterion of separation is still an open question. In fact, the separation between various particle sizes is arbitrary, and colloidal or macromolecular material will pass through the filter (usually a 0.45 micron/pore size). If we consider the various specific forms of metals in natural waters, there is obviously a continuous range of metallic species between soluble and particulate phases (e.g. colloidal ferric hydroxide which is able to pass through a 0.45μ filter will be retained by a 0.01μ filter). The importance of particulate ferric hydroxide as a scavenger of many heavy metals could then be under-estimated by using a 0.45 μ pore-size filter. On the other hand, the so-called supersaturation of water with respect to many trace metals is possibly an artefact due to inadequacy in filtration procedure in many cases.

Geochemists are very much aware of this problem but there is still no consensus in how to solve it. Intercomparison of data with those obtained in most of the world hydrological and chemical laboratories will require the use of 0.45μ pore-size filter in the Mediterranean project although there is now evidence that this limit is rather arbitrary and sometimes misleading.

(2) Background value estimates of heavy metals

For determining quantitatively the amount of heavy metals introduced by human activities it is necessary to have some idea of the natural background concentrations of these elements, i.e. if a rough estimate of heavy metal supplied to the Mediterranean Sea were to be achieved through analyse of bulk sediment, it must be kept in mind that natural particulates contain an appreciable amount of heavy metals. Various solutions to this problem have been proposed:

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(a) Use of a world standard of reference: Mean values of metal concentrations in fine sediments excluding anthropogenic contamination have been estimated by TUREKIAN and WEDEPOHL (1961) for clay minerals. This composition may be assumed to approximate those of suspended sediments in streams.

These values must be substracted from the measured concentrations, assuming the difference is related to pollution, but such a procedure does not account either for local natural geochemical variations which can be important or for possible natural enrichment of river suspended materials.

(b) Comparison with old unpolluted river sediments: In this case, difficulties may arise from different quaternary depositional environments (not comparable with present situation), secondary contamination by polluted groundwaters and unknown post-depositional mobilisation processes occurring in sediments.

(c) Reference to present sediments in non-industrialized areas: It is difficult to find virgin aquatic systems free of industrial pollution. Vanadium,lead and cadmium contamination of atmospheric dust is well-known especially in the northern hemisphere, etc. Moreover, regional geochemical anomalies may again result in a false estimate of the natural level existing in the polluted systems to be compared.

(3) Preferential leaching of heavy metals

Preferential leaching of heavy metals by various chemical reagents is often used to estimate the amount of particulate-bound metals that are potentially released to the environment and/or available to aquatic organisms.

This preferential leaching method is probably adequate for pollutant flux studies, but one must be aware that heavy metals in adsorption sites and natural coatings will be also dissolved. Moreover, it is difficult to be sure that none of the metallic species incorporated within the mineral lattice is unleached. Finally, the amount of metallic elements leached from the suspended sediment is largely dependent upon their mineralogical and chemical composition.

(4) Post-depositional mobilisation

Once the suspended particles are deposited, several mechanisms may alter the water and sediment quality. Various metallic elements can be trapped as insoluble sulphide compounds, while there is often an increase of dissolved concentrations in interstitial waters, caused by solubilization processes, which generate an upward diffusive flux of pollutants through the benthic boundary layer.

An important increase of pollutant concentrations in the water body is more likely to occur through recycling of bottom deposits either by natural phenomena, e.g. floods or bioturbation, or by anthropogenic action e.g. dredging activities. Ingestion of polluted particles by benthic organisms can change their chemical speciation and cause a new availability of the pollutant

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(5) The estuarine problem

The estuary is the meeting place of river waters (salinity usually ranging from 50 to 500 mg/l) with sea water of much higher ionic strength (salinity close to 36 g/l). In this zone pollutants are subject to new physicochemical, dynamical, sedimentological and hydrological conditions which may alter their speciation and modify their flux to the ocean. Furthermore, as industrial settlements are often found in the estuarine zone of rivers, additional sources of pollutants are likely to occur. From these observations we can see that any balance based on upstream data could not represent the actual flux of pollutants entering the ocean.

4.2.Particulate pollutant load in Mediterranean rivers

4.2.1. Results

Owing to great technical difficulties in sampling, pretreatment and analysis and to the short time available to collect new data, very few results on river particulate matter composition are presently available. At the present time, we have some information on the heavy-metal composition of bulk suspended sediment of the Adige, Po, Rhône and Aude rivers (table 4).

For comparison, the global average heavy-metal concentrations in river sediment suspended and the composition of the heavily polluted Rhine river are given. All these data refer to the bulk composition of suspended sediment.

Moreover,and following the recommendations of the Rome meeting and the recommended sampling and pretreatment procedures for particulate pollutant analysis prepared jointly by the International Laboratory of Marine Radioactivity (IAEA, Monaco) and the Division of Water Sciences of Unesco, some rivers were sampled and their sediment analyzed. They include the Ebro and Llobregat (Spain). Rivers A and B (country no identified) were analyzed by the IAEA.

Tunisia also sent a sample to IAEA but the data are not yet available. For comparison, literature data from Israel rivers have been included.

The following remarks can be made on these preliminary results.

If we consider Table 5, the four Mediterranean rivers do not appear as heavily polluted in comparison to the Rhine river. However, there is good evidence of contamination for the following rivers: Adige (Zinc), Po (Zinc) Rhône (Zinc, Lead), locally Copper, Chromium, Mercury, Aude (Chromium).

From Table 5, it is obvious that the listed rivers are subjected to some degree of pollution with the consequent liability of contamination by trace metals. The Ebro, Llobregat, river A, Ayyalon, Gadura and Qishon carry sediments exhibiting pollution effects.

It is interesting to compare the relative importance of the dissolved and suspended pollutant loads in these rivers. On the basis of the average contents in the dissolved and particulate phases, and of the average long-term turbidity, we have computed the ratio of dissolved transport over total river transport (i.e. dissolved + particulate) (Table 6). Data from the Rhine and Mississippi rivers are given for comparison.

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For the more turbid rivers (Adige, Po) and to a lesser extent the Rhône, the suspended phase plays a major role.

This importance of the particulate phase is a worldwide phenomenon that is observed in highly polluted rivers such as the Rhine or in very turbid rivers such as the Mississippi. On a world scale the following proportions of trace metals carried by rivers are in the dissolved form: the Chromium 2,5%; Copper 19%; Nickel 5%; Lead 7%; and Zinc 17%. It is most likely that for the Mediterranean rivers which are generally highly turbid, the suspended phase has a similar importance.

however, in the Llobregat and Ebro rivers, the dissolved phase appears as the major phase of transport; this is most likely attributable to the analytical method used, i.e. "preferential leaching" instead of "total content"; and in the case of the Ebro river it is also attributable to the existence of upstream dams which trap a large percentage of the river sediment.

Table 5. Total pollutants content in some river suspended sediment from Mediterranean countries ($10^{-6} g.g^{-1}$)

River / pollutant	Adige (a)	Po (a)	Rhône (b)	Aude (c)	World average(d)	Rhine(1970) (e)
Arsenic	-	-	-	-	5	220
Mercury	-	-	0,5 - 1,5	1,2	-	23
Lead	203	185	270	-	150	800
Cadmium	-	-	-	-	1	45
Copper	93	112	50 - 250	-	100	600
Chromium	76	112	70 - 200	173	100	1240
Nickel	-	-	60	-	90	100
Zinc	1310	2100	760	318	350	2900
P.C.B.	-	-	15	-	-	-
D.D.T.	-	-	-	-	-	-

(a) C.N.R., Italy, average of 3 and 6 analyses.
(b) MARTIN, J.M. (1971), VERNET and al. (1977)
(c) MONACO A. (1977)
(d) MARTIN J.M., MEYBECK, M. (in press)
(e) DE GROOT, A.J., ALLERSMA E. (1973).

Table 6. Leachable contents of heavy metals in suspended and deposited sediments from mediterranean countries.

River / pollutant	SPAIN		IAEA		ISRAEL (3) (b)						
	Llobregat (1) (a)	Ebro. (1) (a)	river A (2) (a)	river B (2) (a)	YARGON	AYYALON	ALEXANDER	MADERA	QISHON	GADURA	NA'AMAN
Arsenic	1.1	4.1	-	-	-	-	-	-	-	-	-
Mercury	0.4	1.6	-	-	n.d	p.d	.15(.07-.30)	.56	(0-0.1)	(0 - 0.3)	(0 - 0.3
Lead	53	159	74	11	28(20-48)	81(12-266)	13(7-22)	14(5-25)	2[illegible](9-72)	158(93-275)	12(10-16)
Cadmium	7	5	2.6	0.45	N.d.	7.9(.1-16)	n.d.	n.d.	(0-4)	55(7-123)	n.d.
Copper	43	16	59	20	2.8(1.6-3.3)	6.7(2.3-16)	1.7(2.1-3.0)	7(3-13)	14(3-48)	17(6-43)	4(3-6)
Chromium	55	16	37	8.5	2.8(1.9)	35(12-124)	13(11-17)	14(12-17)	18(3-56)	294(62-610)	[illegible]5(4-26)
Nickel	-	-	30	11	1.0(1-4)	17(8-60)	6,3(6-7)	9(6-12)	15(11-19)	22(17-31)	[illegible]7(4-14)
Zinc	787	174	204	67	52(12-83)	196(49-323)	45(48-72)	87(42-176)	130(20-325)	931(365-1500)	46(9-136)

(1) Centro de Estudios Hidrográficos, Spain, 1977 (one analysis)
(2) I.A.E.A. Monaco Laboratory, average of 2 analysis, Northwestern Mediterranean Rivers.
(3) KRONFELD J. and NAVROT J. (1975) average of 3-9 analysis.
(a) suspended sediment, leaching with diluted Hcl acid
(b) deposited bank sediment ($<$ .17 mm, leaching with hydroxylamine-hydrochloride in 25% acetic acid.

Table 7

TRACE METAL TRANSPORT BY MEDITERRANEAN RIVERS

Ratio of dissolved transport over total transport (in %)

	Adige	Po	Rhône	Llobregat	Ebro	Rhine	Mississippi
Turbidity mg/l	220	245	84	165	20	32	530
Arsenic	–	–		94	93	44	–
Mercury	–	–	–	–	–	0	–
Lead	10	17	30	57	56	13	0.8
Cadmium	–	–		76	96	72	11
Copper	14	53	32	93	99	50	8.4
Chromium	20	–	39	87	97	20	1.5
Zinc	–	9	36	85	96	56	10

5. CONCLUSIONS

i. With regards to the first objective (review of contribution of suspended material transported by rivers to the pollution of the Mediterranean sea), a review of scientific publications and reports from countries surrounding the Mediterranean Sea, clearly showed that at that moment, no data on particulate pollutants were being collected on a routine basis. The preliminary analyses which have been performed do not permit a mass balance statement of particulate pollutants discharge by rivers into the Mediterranean Sea. This gap is mainly due to the technical difficulties in pre-treatment i.e. the separation of a sufficient amount of suspended sediment, and to the fact that sediments are usually considered as a trap for pollutants which increase the river water quality. If their self-purification capacity is well known, they could be important sources of contaminants to marine organisms (i.e. filter feeders). Moreover, there is a complex equilibrium governed by various chemical and physical and biological factors between the sediments and the surrounding water, the result being possibly the desorption of an important amount of pollutants, this is likely to occur at the benthic boundary layer and within the estuarine system.

The preliminary results obtained in a restricted number of rivers do not point to contamination as being as important as in some highly polluted rivers like the Rhine. However, some metals, e.g. cadmium and zinc, are already present at a high level compared to the natural values.

ii. The second objective (to identify research and information needs on critical pathways and methodology), has been achieved in a paper prepared by the Secretariat. This paper was extensively discussed at the expert meeting held in Rome. The paper includes a review on the role of sediments in pollution studies, sediment-pollutant interactions, pollutants to be monitored, particulate pollutants sampling and analytical procedures, and finally a catalogue of Mediterranean rivers to be monitored. This paper clearly emphasized that most heavy metals and organic pollutants are carried in the suspended matter, e.g. 75-99% of heavy metals are carried by rivers in the particulate form.

Further, a paper on "Recommended sampling and pretreatment procedures for particulate pollutant analyses" was prepared by the Secretariat after consultation and advice from the Staff of the International Laboratory on Marine Radioactivity (IAEA). However, it should be clearly understood that this paper describes methods which may not be the best scientifically; they were chosen for their simplicity in order to obtain the necessary data. If a long-term project is to be carried out, these methods should be reviewed and more satisfactory methods adopted or developed.

iii. The third objective (evaluation of the possible role of IAHS and IHP in this project) is being achieved in collaboration with the IHP and IAHS.

Of special interest are the IHP 3.8.5. and IHP 6.1 projects. Project 3.8.5 deals with the relation between water quality and sediment transport whereas project 6.1 reviews the state of knowledge on processes affecting water quality in rivers, lakes and estuaries. The reports of these projects are now in preparation.

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6. FOLLOW-UP

Taking into consideration both the status of implementation of the MED IX project, its progress, failures and successes, and the recommendations made by the various IHP and IAHS Working Groups, it seems worthwhile to prepare a long term project on this subject.

The following section gives a preliminary outline of the action foreseen in such activities:

PHASE I

Sampling and analytical procedures

i) A prerequisite to any long-term project is to develop a technical manual of sampling, pretreatment, and analytical procedures for particulate matter in rivers, which does not exist at the present time.

ii) In this first phase it is essential to proceed to an intercalibration exercise between the laboratories of the riparian countries which will be concerned with the regular river survey and/or by the pilot survey. It is proposed that the intercalibration exercise be conducted in collaboration with the IAEA International Laboratory for Marine Radioactivity (Monaco).

PHASE II

Assessment of particulate pollutants discharge through rivers to the Mediterranean Sea.

The preliminary assessment must be completed by an intensive survey (12 samples a year, minimum) completed during at least one hydrological year on a larger number of rivers chosen according to their water discharge, sediment discharge and potential pollution load. This assessment must be conducted jointly with the dissolved pollutant inventory in order to establish a relation between these two forms of transport.

The minimum list of pollutants to be monitored has been adopted at the Rome meeting. It includes extremely hazardous pollutants (Arsenic Mercury, Lead, Cadmium, PCB and other chlorinated organic compounds) and certain other significant pollutants (Copper, Zinc, Nickel,. Chromium). Other pollutant such as asbestos and red mud, should also be included according to local conditions.

Finally, environmental parameters (Temperature, pH,dissolved oxygen) and pertinent hydrological parameters (solid and water discharges) should be measured to facilitate the interpretation of the data.

This project must be included by the riparian countries in their regular water-quality surveys. The UNESCO Division of Water Sciences will continue to act as a coordinator of the project and will provide financial and technical assistance (Technical Guidebook, consultant for selection of stations...) to the countries. The IAEA Laboratory in Monaco should provide analytical assistance for intercalibration as mentioned above, and also for some special analyses.

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Pilot project: Distribution and behaviour of dissolved and particulate pollutants with regards to the pollution of the Mediterranean Sea.

The implementation of a pilot project in a polluted watershed which would include both the river and its estuary should greatly benefit the knowledge of particulate pollutent fates and behaviour in the aquatic environment.

This project would examine in great detail the chemical, biological and hydrological processes which affect the distribution of pollutants between particulate and dissolved phases both in the river and the estuary.

i) River Zone: among these processes are those which improve the water quality such as sorption reactions versus the different sources of pollutants (natural anthropogenic, point and non-point sources). The nature of the particulate phase (mineralogy, granulometry, chemical composition both organic and inorganic, and the composition of the dissolved phase (acid water, higly mineralized...).

   Other processes such as remobilization at the benthic boundary layer (diffusion bioturbation, chelation, may conversely, increase the river-water toxicity).

   Speciation of particulate pollutants will be thoroughly studied in order to determine those readily available. It will also be necessary to examine the impact of particulate pollutants on the river ecosystem. This phase of the project will be conducted by the Unesco Division of Water Sciences.

ii) The Estuarine Zone: We should bear in mind that in the estuarine and deltaic areas, which are the meeting place of river and sea water, pollutants are subject to new physicochemical, dynamical, sedimentological and hydrological conditions which may alter their speciation or concentration, and finally the flux of pollutants to the Mediterranean Sea. Thus, taking into account the recommendations of the SCOR/Unesco Workshop on the biogeochemistry of estuarine sediments held in Melreux (Belgium), 29 November - 3 December 1976, and those of the SCOR Working Group-46 ("River Input to Ocean Systems"), the estuarine processes must be studied in great detail within this pilot project. This could be conducted by the Division of Marine Sciences of Unesco in close cooperation with the Division of Water Sciences.

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