MEDITERRANEAN ACTION PLAN
MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME

INTERNATIONAL ATOMIC ENERGY AGENCY

TRANSPORT OF POLLUTANTS BY SEDIMENTATION

COLLECTED PAPERS FROM THE FIRST MEDITERRANEAN WORKSHOP

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This series contains selected reports resulting from the various activities performed within the framework of the components of the Mediterranean Action Plan: Pollution Monitoring and Research Programme (MED POL), Blue Plan (BP), Priority Actions Programme (PAP), Specially Protected Areas (SPA) and Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea (REMPEC).

This collection of papers, represents the scientific contributions made at the First Mediterranean Workshop on the Transport of Pollutants by Sedimentation which took place from 10-12 December 1987 in Villefranche-sur-Mer, France. The meeting was co-sponsored by The International Laboratory of Marine Radioactivity, IAEA, the Coordinating Unit for the UNEP Mediterranean Action Plan and the Intergovernmental Oceanographic Commission as part of their joint contribution to the MEDPOL programme of UNEP's Mediterranean Action Plan.

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Introduction

The association of aquatic contaminants with suspended particles plays a critical role in their transport, fate and bioavailability. It is perhaps paradoxical that many chemists concerned with water quality filter their samples and discard the all-important solid material in order to turn their attentions to the dissolved fraction, unaware that they have thrown away the key to the problem they are studying!

As an illustration of this, one could consider a static experiment of equilibrating a litre of seawater with 100mg of fine coastal sediments and a small spike of a heavy metal. If the metal has a distribution coefficient, under the experimental conditions, of 10^5 (not atypical), only 0.01% of it would remain in the dissolved fraction! Of course, this may not emulate the process in the marine environment where kinetic factors may dominate and a true equilibrium may never be attained, but nevertheless it illustrates an important point.

In the Mediterranean environment, sediments undoubtedly play a key role in determining the transport and ultimate fate of contaminants. The three major sources of particulate material are from rivers, atmospheric deposition and the marine food chain. Riverborne fluxes are dominated by four major rivers, the Nile (of lessening importance since the construction of the Aswan high dam), the Po (dominating particle flux to the Adriatic), the Rhone and the Ebro (to the north west Mediterranean basin). Fresh water inflow to the Mediterranean is however, exceeded by evaporation giving it a characteristic slight hypersalinity. Sedimentary evidence suggests that the particulate loading to many parts of the Mediterranean may be dominated by airborne dust deposition, often arriving in pulses during southerly storms. Biogenic material is of particular importance in areas where seasonal mixing or upwelling events fertilize the water column (causing, for example, spring blooms in the north western Mediterranean basin). Most of the Mediterranean however, is rather oligotrophic compared with the adjacent eastern Atlantic. The northern Adriatic (as well as some lagoons and semi-enclosed bays) receive large quantities of nutrients as a direct or indirect consequence of human activities (domestic sewage, agricultural runoff) and are becoming increasingly eutrophic to the detriment of the environment.

These processes provide the basic framework for our knowledge of the transport of contaminants by sedimentation. Each of the three basic sources of particulate material exercise a distinct control mechanism on contaminant distribution. Riverborne sediments often reach the marine environment by the same pathway as land based sources of pollution and a large fraction of the contaminant load is already associated with particulate material when it is discharged to the sea. Following discharge a given contaminant may remain associated with particles or be released by physico-chemical action (change in ionic strength of the medium, re-equilibration between phases), chemical transformation (such as degradation), or biological action (bacterial attack and/or incorporation into the food-chain).

Airborne particulates, principally Saharan dusts, do not normally represent a major source of contaminants. However they can serve to purge contaminants from the atmosphere present as aerosols (eg. the phenomenon of nuclear fallout as evidenced following the Chernobyl accident in 1986, or globally distributed atmospheric DDT). During their passage through the water column, they may release the atmospherically-derived contaminants and adsorb and remove additional trace constituents.

The biological accumulation and transport of contaminants is one of the most interesting and complex facets of this issue and one which has received an enormous amount of attention from researchers. Of particular interest to scientists have been those contaminants which become progressively more concentrated along the food chain - eventually revealing themselves as "pollutants" (i.e. associated with a measurable adverse biological effect). Contaminants which are excreted from animals (eg. in zooplankton faecal pellets or crustacean moults) may be rapidly transported to the sea floor and this process often dominates the entire transport mechanism. It is interesting to observe that, as in the case of riverborne sediments, this process should also be enhanced in the vicinity of river discharges, or those of domestic sewage, where primary productivity is stimulated.

In each of these basic processes, a variety of chemical mechanisms prevails. Polar charged contaminants, such as heavy metals, are often adsorbed to clay particles. The degree of adsorption depends on the number and concentration of active surface sites as well as the chemical nature of the sites and the contaminant, the ionic strength of the medium and the adsorption kinetics. Some highly polar molecules and highly-charged ions may become irreversibly bound to the particles whereas lesser-charged ions may be readily exchanged (and hence more bioavailable). In the case of non-polar contaminants, partition occurs into biogenic organic material (usually lipids). Distribution coefficients of individual contaminants differ considerably and are often of similar magnitude to those measured experimentally between octanol and water.

From the above discussion, it is evident that in order to model the transport of contaminants by sedimentation, detailed knowledge is required of aquatic chemical processes, all sources of contaminants and particulate material, physical oceanographic processes (current regimes, mixing, dispersion, etc.), biological productivity and trophic dynamics as well as the settling rate and composition of marine particulates. To complicate matters further, once trapped in the sediments, the fate of contaminants may not be finally sealed! They may still be bioavailable to benthic organisms or can be released to the water column by diverse diagenetic mechanisms. It is important to measure the size of the sedimentary reservoir of any contaminant in order to understand its potential as a pollutant of the marine environment.

Clearly, not all of these points can be addressed in a single study. One of the basic purposes of this Workshop was to review the current state of knowledge on this subject in the Mediterranean region. The nineteen papers collected in this volume reflect, for the most part, research studies conducted as part of the research component of the MEDPOL programme. They cover a wide spectrum of research activities from physical and biological oceanography to physical chemistry. The scientific papers presented herein, are divided into general process-related papers (section 1), case studies (section 2) and shorter contributions and abstracts (section 3).

Section 1 commences with two studies of particulate matter distribution, a large-scale study by Nyffler (using optical techniques) and a very detailed study focussing on the north western basin (DYFAMED studies) by Monaco. Pravdic et al. then discuss physico-chemical techniques for characterizing particulate matter as carriers of sediments in the light of the concept of assimilative capacity. Nolan and Fowler describe research on the incorporation of sedimentary pollutants into biota. The study by Koutsoukos and Giannimares is an illustration of Mediterranean research into fundamental aquatic chemistry and shows how divalent cations in seawater play a major role in regulating trace metal adsorption. Zutic and Legovic's paper illustrates the importance of estuarine microstructure in determining the distribution of particulate-borne contaminants. Two papers give practical methods for investigating pollutant transport by sediments. Krom et al. demonstrate a method for interpreting field data on trace metals, and Caillot applies a radioactive tracer technique to study dispersion from a point source. Finally, a physical oceanographic study by Salusti and Zambianchi demonstrates how the entire bottom water formation in the eastern Mediterranean depends on processes at the surface of the northern Adriatic.

Section 2 presents case studies commencing with three studies of the northern Adriatic. The first, by Orio and Pavoni, examines the release of nutrients from the sedimentary reservoir of contaminants in the Venice Lagoon. Guerzoni then presents a study of the transport of trace metals by sedimentation in the open northern Adriatic. The third study, by Faganeli et al., analyses the sources and distribution pathways of suspended organic matter in the Gulf of Trieste by examining the content of stable carbon and nitrogen (given sources of detritus have characteristic stable C and N isotopic ratios). Fabiano et al. demonstrate the manner in which Ligurian submarine canyons channel trace metal rich particulates to the deep sea. In contrast, Vasilikiotis et al. focus their attention on the mobility of heavy metals in a contaminated and a relatively pristine river in Greece. Koutsoukos et al. and Koliadima et al. examine the trace metal distribution in sediments and suspended material in two Greek lagoons (the latter study characterizes the suspended material using a novel optical technique).

Finally, three abstracts examine trace metal sediment/water partition, airborne contaminants, and organic contaminants respectively.

The excellent summary discussions of the working groups at the meeting are presented as a verbatim report at the end of this collection. The reader is strongly recommended to read this report as it provides background information for the formulation of future MEDPOL research projects in this field.

This collection of research papers makes a modest but significant contribution to our knowledge of the Mediterranean environment. By consolidating and further developing this work in the future, the MEDPOL programme will provide a scientific basis for making rational decisions on the management of the marine environment.

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STUDIES OF GENERAL PROCESSES IN THE MEDITERRANEAN

PARTICULATE TRANSPORT ON TWO CONTINENTAL MARGINS OF THE MEDITERRANEAN SEA

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ABSTRACT

The suspended particles play a major role in the transfer of pollutants from landbased sources towards the open sea. Although they are prone to settling, their dispersion on the continental margins is governed by active hydrodynamical processes which contribute to their spreading and also to the remobilisation of the surficial sediment. The nepheloid structures observed on two typical continental margins of the Mediterranean sea show an influence of the morphology of the margin and of the basin on the vertical distribution of the suspended matter. This study was conducted within the framework of the ECOMARGE program.

INTRODUCTION

By definition, the pollution of the sea is originating from landbased sources. Some of the pollutants are injected as solid small particles, or tend to aggregate onto particles already present in the sea water. The study of the processes governing the dispersion of the discharged material on the continental margin and its subsequent transport towards the deep sea is presently adressed on a multidisciplinary basis within the framework of an international programme ECOMARGE, (Ecosystèmes des Marges Continentales).

Instruments

Although the marine particles shall not be considered as a pollutant strictly speaking, the suspended matter remains a nice and cheap natural tracer. The optical methods provide for instance a simple tool to track the movements of highly loaded landbased sources, to localize areas of active remobilization of the sediment, or to help insuring a relevant sampling. In the ECOMARGE program, the nephelometric measurements are used in association with the classical hydrological parameters, mainly to investigate the structural features of the water column in order to highlight some key processes of the particle dymanics.

The instrumental system comprises a prototype deep-sea nephelometer coupled with a NEIL BROWN Mk III CTD probe and a BENTHOS sonar altimeter. This last apparatus provides high accuracy depth soundings over the last hundred meters of the profiles thus allowing continuous measurements to within about one meter of the bottom (Nyffeler F. and Godet CH.H., 1986).

Methodology

Two typical margins of the Mediterranean sea; e.g. the Gulf of Lion margin and the Thermaïkos margin have been studied in 1986-1987 during three cruises with the N.O. Noroit and the N.O. Aegaio. The strategies adopted for surveying both areas were based on previous knowledges of the regional hydrodynamics and of the key processes governing the spreading of the suspended material.

Gulf of Lion:

This region is under the influence of the Liguro-Provencal current flowing westward along the steep continental slope. The Rhône river is a relevant source of suspended matter. Previous studies have shown that the numerous canyons cutting the slope act as active link between the shelf area and the deep water (Monaco et al., 1987).
The aims of the survey were:

-- to evaluate the extention seawards of the nepheloid structures detached from the bottom at the shelf-break
-- to localize areas of strong resuspension of the sediment (on the shelf and on the slope)
-- to describe the changes in the nepheloid structure along the axes of the canyons.

The Thermaïkos margin

The Thermaïkos margin is located in the Sporades basin (North Western Aegean sea). It separates a vast northern shallow shelf and the deep southern area of the basin. High loads of suspended material are injected by the city of Thessaloniki and the river Axios on the Northern coast, and by the rivers Aliakmon and Pinios on the western coast.
The aims of the survey were:

-- to describe and to quantify the distribution of the suspended matter over the whole basin.
-- to evaluate the renewal of the water in the basin.
-- to compare the remobilization processes on the margin with those observed in the Rhône river area.

RESULTS

Preliminary results have been reported in Monaco A. et al. (1987), Nyffeler F. et Godet Ch.H. (1987), Bapst A. et Beck C. (1987) for the Golf of Lion and in Chronis G. et al. (1987) for the Sporades basin. They can be summarized as follows:

In the Gulf of Lion, high concentrations of particles have been observed near bottom in the shelf area, partly as a consequence of the Rhône river input but also due to active resuspension processes. However, the transfer of suspended material from the shelf towards the open sea is controled by the Liguro-Provencal current, which tend to hold the light brackish water on its right side. The extention towards the high sea of the nepheloid layers detached at the shelf-break level is therefore limited.

High concentrations of particles have been measured in the head of the canyons, confirming thus their ability to be a path to the abyssal area. The rapid decrease of the concentrations along the canyons indicates however that the transfert of material is not continuous and should occur mainly as strong episodic slumping events.

The increased mean concentration observed in the western canyons of the Gulf of Lion (Aude canyon, Rech Lacaze-Duthiers) is ascribable to the narrowing of the shelf and to the orientation of their axis with respect to the Liguro-Provencal current.

In the Sporades basin, the spreading of the suspended material is governed by the general circulation, which is clearly reproduced by the nepheloid pattern.

The bottom nepheloid layers detached from the Thermaïkos margin were tracked as intermediate nepheloid layers over the entire deep area, suggesting the existence of a secondary circulation cell.

CONCLUSIONS

During the last two decades, a considerable effort has been dedicated to establish an inventory of the discharges in terms of chemical compounds and fluxes. Simultaneously, countless studies were undertaken in areas surrounding the discharges to undestand the behaviour of specific pollutants in the marine environment and to assess their potential impact on the ecosystem. It is however increasingly being recognized that the hazards are not restricted to such coastal areas. The results obtained in the Aegean sea illustrate how particles (and their potential pollutant load) are transported far away from the sources by the currents. The complexity of the pattern observed at a regional scale also confirms that such intensive surveys are of great help (if not a basic requirement) for the design of realistic and representative monitoring networks.

This brings up a new set of questions, which need to be addressed not only by means of field surveys but also including the development of suitable models:

- where does a pollutant come from and where does it go to?
- how long does it remain in the system and what is its dilution rate?.

Such questions are a direct concern of geochemists, physical oceanographers and modelists and remain a challange for the near future, because the dynamics of pollutants and its modelling is of prime importance in a long time/large scale concept of the pollution problem.

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PARTICLE TRANSPORT AND SEDIMENTATION ON THE MEDITERRANEAN MARGINS

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ABSTRACT

The southwestern part of the Golfe du Lion has been selected as the first ECOMARGE sampling site for studying processes governing particle flux and deposition at different time scales: influence of hydrological and hydrodynamical factors, impact on benthic ecosystems and biogeochemical processes at sediment-water interface. Quantitative results were obtained especially by using sediment traps moored at various depths. Complementary nephelometric and radioisotopic studies were carried out in the same area. The Golfe du Lion appears to be an advective system associated with benthic and intermediate nepheloid layers. The system is shown to fluctuate rapidly. Its behavior depends on seasonal input variations. Such studies will be extended to various Mediterranean margins in the EURECOMARGE program.

INTRODUCTION

Metallic compounds resulting from human activity are known to be transported and deposited together with fine particulate matter in the marine environment. For several years, a multidisciplinary approach (including biological, physical and chemical investigations) has been chosen to study the characteristics of a system from its source to its deposition place. An emphasis has been given on the influence of hydrological factors and hydrodynamics on sedimentation, on the impact of particle flux on benthic ecosystems and on biogeochemical processes at sediment-water interface. Such studies cover different time scale: sediment traps dealing with seasonal variations, instantaneous nephelometric and hydrological measurements with present time. Historical and geological records are obtained from the sediment column.

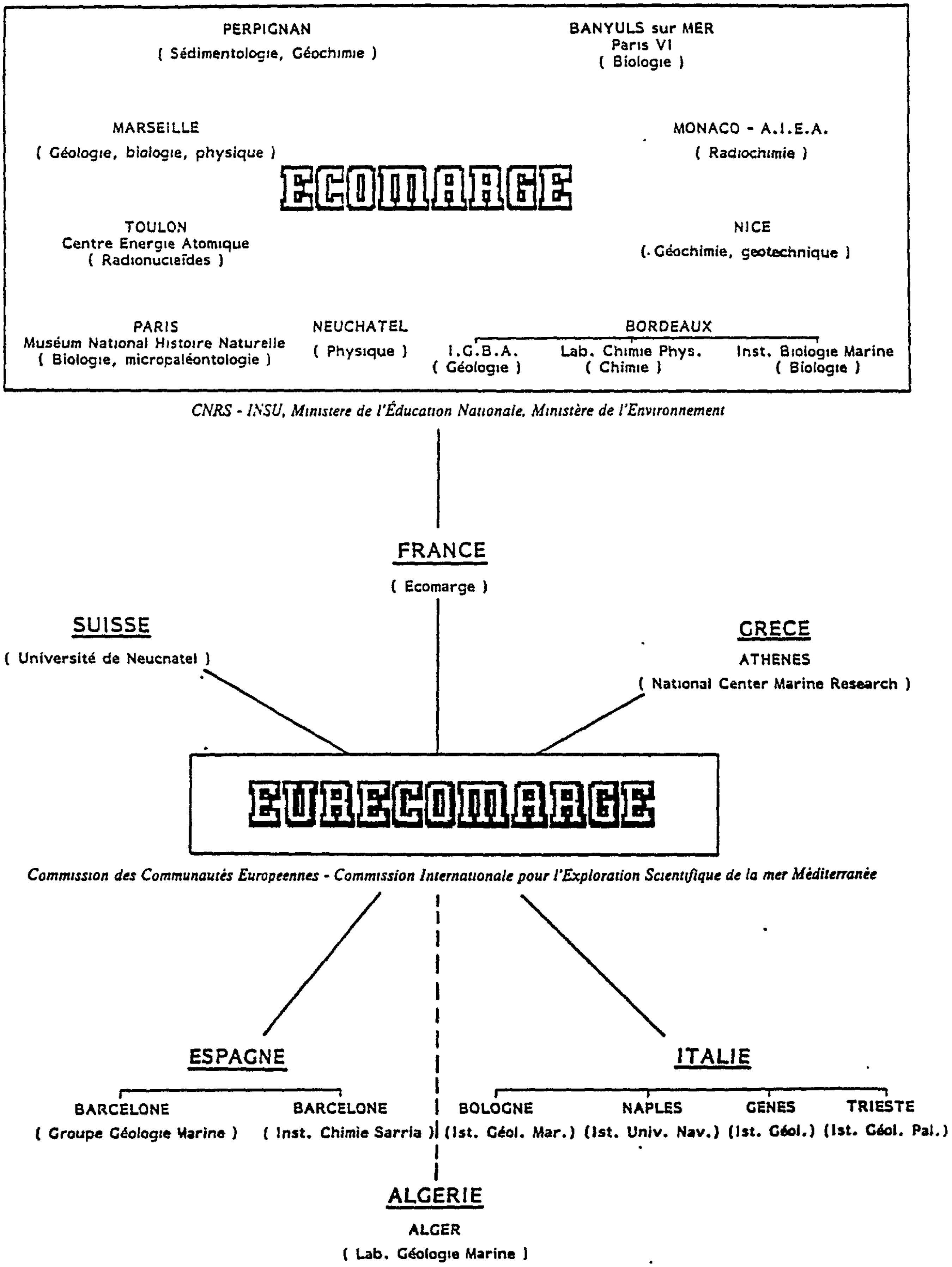
ECOMARGE has been the first French national program on particle fluxes. It began in 1983 studying the ecosystem of the continental margin of the Golfe du Lion (northwestern Mediterranean Sea). ECOMARGE is a joint program which brings together investigators from the Laboratoire de Sedimentologie et Geochimie Marines of Perpignan , the Laboratoire Arago of Banyuls sur Mer (biology), the International Laboratory of Marine Radioactivity, IAEA, Monaco (radioisotopy), The Centre Oceanologique of Marseille (biology, geology, chemistry), the University of Bordeaux (geology, chemistry, biology), the Museum National d'Histoire Naturelle of Paris (biology, microbiology), the University of Nice (geochemistry), the Commissariat à l'Energie Atomique of Toulon (radiochemistry) and various other participants.

The project has been extended to European investigators from Switzerland (OCEANE Group of the University of Neuchâtel), Spain (Universitat de Barcelona: Grup de Geologia Marina and Instituto Quimico de Sarria), Italy (Istituto Universitario Navale of Napoli, Istituto di Geologia of Genova, Istituto di Geologia of Trieste and Istituto di Geologia Marina of Bologna) and Greece (National Center For Marine Research of Athens). Financial support has been provided by EEC since 1986 to promote an EURECOMARGE project.

Algeria is associated to the scientific program through a collaborative agreement with the University of Perpignan and an EEC contract. (Fig. 1)

The joint project has had the advantage of covering a wide scope of physiographically different continental margins in the Mediterranean: carbonated margin of the Baleares, Ligurian, Campanian, Adriatic, Ionian and Aegean margins further east. The data acquired will be incorporated to a hydrosedimentological model, necessary step toward a predective scheme for pollution prevention.

Fig. 1: Structure of the French National ECOMARGE Program and of the International EURECOMARGE Program.



Previous studies including both particle budget and quantitative evaluation of particle fluxes are few. Studies have been carried out on the Pacific (Baker and Hickey, 1986 ; Thorbjarnarson et al., 1986) and Atlantic (Biscaye, 1987). In the Mediterranean, qualitative data on suspended particulate matter were obtained by Emylianov (1972) and Aloisi et al. (1982). They proposed a model of multilayer transfer for the northern mediterranean platform. The association of artificial radionuclides with large biogenic particles and their transfer to sediment have been studied by Fowler and Knauer (1986). The results presented in this paper were obtained on the Golfe du Lion margin subjected to strong continental inputs. Some partial results have been published already.

METHODS

A geophysical survey was carried out first in the area: high resolution sismic reflection, 9 to 1 kj sparker, boomer, uniboom, surfboom, 3.5 kHz probe. Such a preliminary survey is essential for a good recognition of mass and diffuse sedimentation zones, areas without deposition and erosion sites at the historical scale. Kullenberg and box corers provided records of the sediment column and water-sediment interface samples for mineralogical, geochemical, biogeochemical and geological studies.

Since 1984, automatic and hand-operated particle traps (Technicap PPS3) were used for sampling prodeltas (at 30m depth) of the Têt and Rhône rivers and canyons (800m depth). The Lacaze-Duthiers Canyon which is located at the southwestern end of the Golfe du Lion is presented in this paper (Buscail and Monaco, 1987; Heussner et al., 1987 and 1988; Monaco et al., 1987). A fifteen day mooring period was chosen for each experiment. Mooring periods were defined to follow the seasonal hydrological variations associated with temperature and salinity stratification and homogenization. Current meters and acoustic pingers were moored together with the traps.

Nephelometric instantaneous measurements were performed seasonally with the OCEANE group's instruments (Neil-Brown MkIII C.T.D. and nephelometer). More than 150 measurements were made on the inner and outer shelf and slope, in the basins and on special morphological features such as canyons, channels and levees (this volume) (Fig. 2).

This paper will focus especially on the hydrosedimentological characteristics of the Mediterranean system which are responsible for particulate pollutant dymanics, transport and deposition.

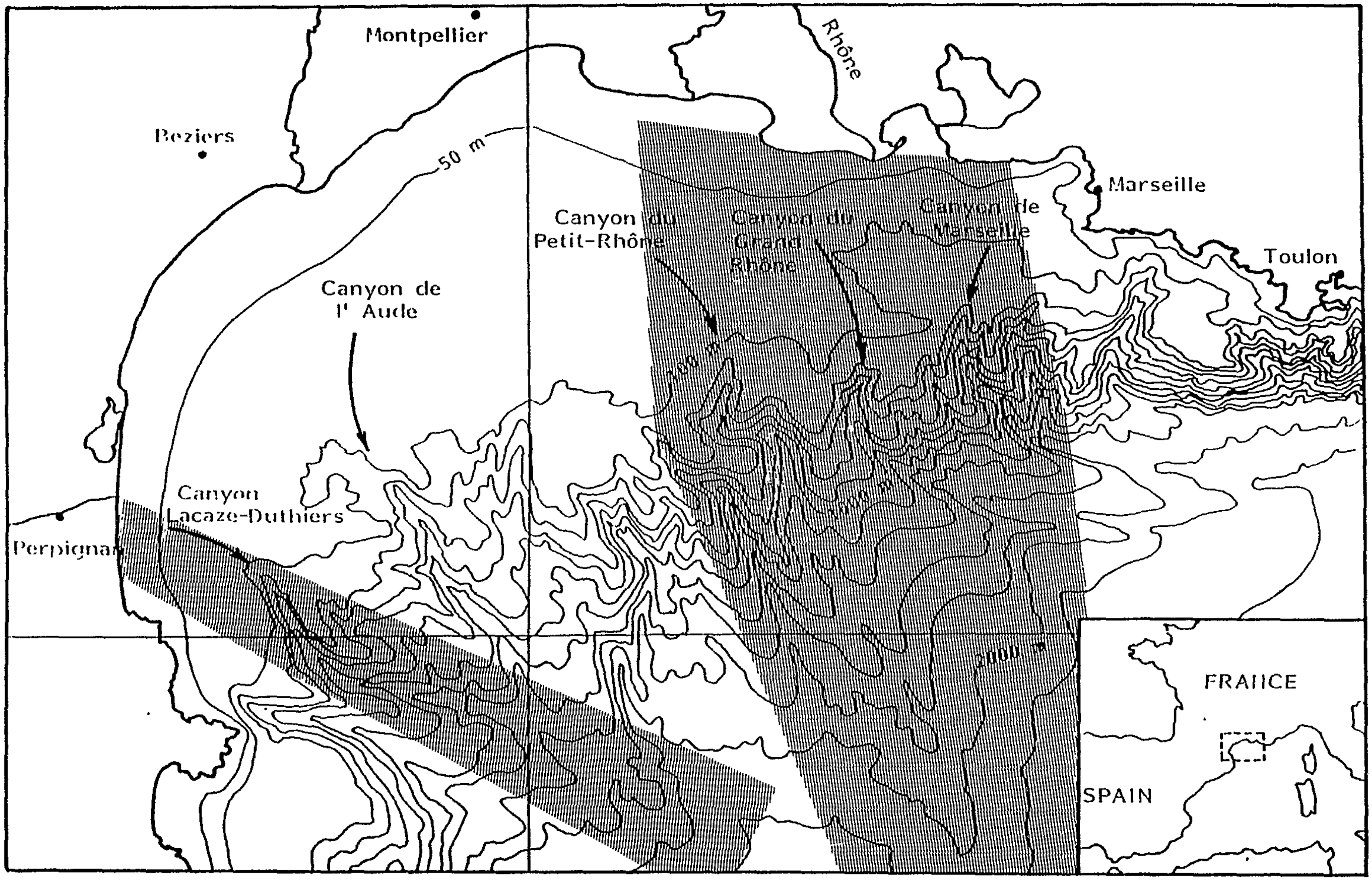


Fig. 2: First selected site: The Golfe du Lion (Northwestern Mediterranean). The location of sampling areas is indicated in hachured grey.

RESULTS

Prodelta is a fine particle deposition area which is commonly found in front of all natural and artificial water flows on the Mediterranean margins. This sedimentary unit has a prismatic geometry. Its volume and extention depends both on river discharge and ambient turbulence. The surface shape of the mud blanket reflects ambient dynamics. Prodeltas of major Mediterranean rivers are oriented as the general circulation of the basins, i.e. west for the Rhône and Nile rivers, south for the Ebro and southwest for the Pô.

These fine particle early deposits are due to the salinity front at continental/marine water interface. They contain terrigeous particles, marine sediments resulting from phytoplancton production and pollutants from human activity they have trapped. Prodeltas are preferred areas for metallic and organic pollution trapping and environment dystrophy assessment. The distribution of stable and radioactive elements follow that of fine particles, especially those clays which show either strong adsorbing properties or large specific surfaces (smectites and illites) and that of organic carbon. 137Cs can be considered as a good example of a tracer for deposition process study and modelling. It has been previously studied in the Rhône (Got and Pauc, 1970; Fernandez et al., 1987) and Pô rivers (Frignani et al., 1987).

As far as hydrosedimentology is concerned, previous results obtained off the Rhône river and other main Golfe du Lion rivers (Aloïsi et al., 1979/1982) have been confirmed by recent measurements carried out on the Rhône delta and continental platform (Bapts and Beck, 1987). A multilayer pattern is found to be oriented by salinity and temperature gradients. Its major component appears to be a benthic nepholoid layer (BNL) well developed even at the river mouth. The origin of this nepheloid layer varies depending on the season and on hydrological and hydrodynamical conditions. It can be due either to floculation which traps fine mineral and organic particles or to reworking resulting from swell and residual currents. Particle transfer from prodeltas to muddy deposits of the inner and outer shelf, slope and basins takes place inside the BNL. The virtual resulting particle dislocation has been estimated to 1.5 km/day (Aloïsi et al., 1979).

Hand-operated particle traps moored in the prodelta of the Têt river have provided quantified data of fluxes and evidences of great seasonal variability. Fluxes vary from $2.7 g.m^{-2}d^{-1}$ to $23 g.m^{-2}d^{-1}$ at the surface level and from 8 to $66 g.m^{-2}d^{-1}$ at a 25m depth (3m above the sediment) (Courp et al., 1987). Measurements of the Rhône prodelta have been carried out only for short periods of time under conditions of relative climatic and hydrodynamical stability. Fluxes vary in the range of 14 to $65 g.m^{-2}d^{-1}$.

On the Golfe du Lion outer shelf and at the shelf break (80-100m), there is a well known strip of relic carbonate sediments dated 12000 to 16000 B.P.. Such sand outcrops are the evidence of rather high energetic conditions which prevent recent fine sediments from deposition. This phenomenon of reworking or "rebound fluff" (Dymond, 1984) is common to all Mediterranean platforms. It can be more or less developed and associated with carbonate sedimentation. Fine sediments appear again at a depth of about 200m on the slope. Their distribution pattern is complex due to the existence of submarine canyons.

Hydrometrical and sedimentological measurements were carried out in the open sea during several cruises at various periods of the year. They have shown complex nepheloid structures subjected to salinity and temperature gradients in the water column and to slope gradients at the sea-bottom (Nyffeler and Godet, 1987; Nyffeler et al., this volume; Monaco et al., 1987). During the summer stratification when there is a thermocline, particles belonging to the shelf BNL are transferred to the open sea water column through the shelf break. They are maintained at the thermal barrier level and form a large intermediate nepheloid layer (INL). In deep water benthic nepheloids develop mainly in the canyon axes. Turbidity peaks at the surface layer (SNL) are due to phytoplancton (Fig. 3).

When the water column is homogenized and during the rainy winter season, terrigeneous particles are predominent in the water load. Intermediate nepheloids are less developped. Benthic nepheloid layers characterize deep water masses. In fact, open ocean sedimentation can be considered as the result of particle transport from the shelf either directly or indirectly after weakly cohesive deposits are reworked (rebound fluff of Dymond). The structures responsible for the transfer, such as hydrological structures and bottom morphology, are complex. Shelf break and canyons appear to play an important part.

The mechanisms of these processes have been confirmed and quantitative results were obtained by deploying sediment traps down to 650m in the Lacaze-Duthiers Canyon (Fig. 2), southernmost canyon of the Golfe du Lion (Monaco, 1984; Monaco et al., 1987; Heussner et al., 1987). The two annual climatic and hydrological situations described above were distinguished. The period of stratification is characterized by a surface flux of biogenic material $1.5 g.m^{-2}d^{-1}$ at 50m and a terrigenous flux in the water column at a 300-600m depth which can reach $4 g.m^{-2}d^{-1}$ at the most. A minimum flux value is always observed at about 100m. From November, the homogenization period is characterized by a flux gradient which increases with depth. In January-February, particle flux can reach $20 g.m^{-2}d^{-1}$, one of the highest values even measured. Alumino-silicates represent 70% of that flux.

In all cases, the highest fluxes are observed at depth and related to advective transfers. In summertime, when rivers are not operative, fluxes are subjected to general circulation and supplied by sediment reworking either from the shelf or from the slope. During the fall, advective fluxes seem to be related to rain falls. Since thermocline is still effective, a time lag of about twenty days is necessary to observe a flux increase at a 300-600m depth in the canyon. In wintertime, the reaction of advective flux to rain fall needs only a few days at the same depth.

Predominant advective fluxes, rapid transfer and seasonal variability are shown to be the main characteristics of the prodeltaic margin. Hydrological and climatic fluctuations control the equilibrium between biogenic and terrigenous components.

In summertime, primary and secondary organic fractions are strictly associated with the euphotic layer. In winter and spring, primary organic matter can penetrate deeper layers (floculation) due to water column homogenization. This explains biological and biogeochemical activity at sediment-water interface at depth. Canyons act as natural sediment traps for organic and mineral particles transported by fluxes along the continental shelf and slope. Benthic activity is thus greater in the upper part of submarine canyons (100-200m) than in either side.

DISCUSSION

The Golfe du Lion advective system is much like those described by McCave (1972) and Baker and Hickey (1986). It is associated with turbidic structures, benthic and intermediate nepheloid layers. It is responsible fot the transfer of stable and radioactive metallic compounds and organic matter (Fig. 3).

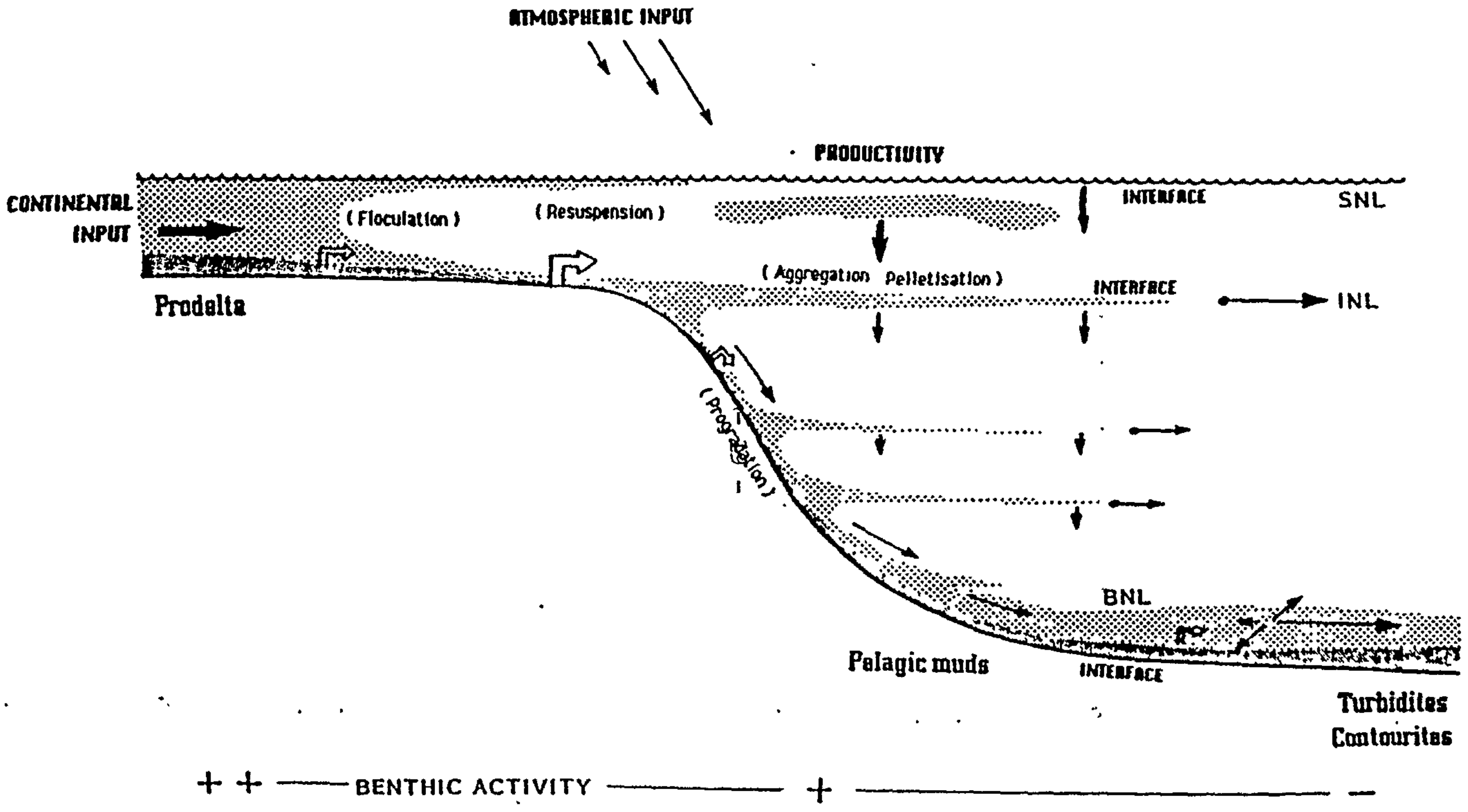


Fig. 3: Schematic pattern of transfer mechanisms on the Mediterranean margins where ecosystems are subjected to continental inputs.

These processes are confirmed by chemical analysis carried out on samples recovered from automatic sediment traps: extractible metals such as Cu and Mn (Monaco, 1987), artificial radionuclides and chlorinated hydrocarbons (Fowler et al., 1987), natural radioisotopes ^{210}Pb, ^{210}Po (Heussner et al., 1987). These compounds are originated either from the reworking of platform fine deposits, especially prodeltas, or more or less directly from continental fluxes related to rain falls. Transfer to depth can vary from several weeks to a few days and such a short time lag is characteristic of Mediterranean dynamics.

Two main processes control particle sedimentation on the shelf and slope environments: hydrological and hydrodynamical factors (advection) on one hand, organic production (convection) on the other. The limit of prodeltaic deposits is associated with the bathymetric limit of swell penetration, about 25m deep. Inner shelf muddly sediments at 50-80m represent only a late dispersion of the shallow deposits. Hemipelagic and pelagic clays are found off the 200m energetical limit of the shelf break. They cover the slope and rise, the sides and the bottom of canyons. Fine particle sedimentation is controlled by organomineral floculation. It takes place in the euphotic zone of prodeltas, at the saline front of river mouths and even at the salted edge of fluvial channels (Zutic et al., 1987).

At greater depths, particle aggregation and pellet formation are the only mechanisms which can explain particle sinking toward sediment-water interface. Fowler and Knauer (1986) have shown the prominent part played by fecal pellets in transferring to sea bottom compounds resulting from human activity. The content of our last trap experiments confirms that marine snow is made of fine particles aggregated with debris and mucus.

The answer of benthic ecosystem to this energetic material is rather quick. Organic matter input maintains a rather high biological activity (meiobenthos, microflora) at great depth. This activity fluctuates as advective fluxes vary (De Bovee, 1987; Soyer et al., 1987; Buscail et al., 1987). Biogeochemical activity at water-sediment interface is also controlled by the same mechanisms (Buscail, 1987).

Below 1500m biological and biogeochemical activity is reduced. It is due to both sediment reworking by deep contour and turbidity currents (Millot and Monaco, 1984) and degradion of organic matter transported to bassins.

CONCLUSION

The cascading model proposed for the input/sedimentation in the Mediterranean margins is a succession of transport and deposition episodes. This succession is controlled by the input volume and by the environment energy. Two major deposition zones were recognized: prodeltas which are close to the continental input sources and continental rise beyond the reworking zone of the shelf break. As particle fluxes proceed away from continental sources, they can be barred by a succession of interfaces or ergoclines: picnoclines, thermoclines, sedimentary interfaces, margin fronts and morphological discontinuities. The major biochemical processes influencing the cycle of natural and human compounds occur at interface leval (Fig. 3).

These results suggest some comments and can help to propose strategies for future research on continental margins, especially in areas similar to the Mediterranean environment.

The major characteristics of this type of environment is its lack of homogeneity due to the numerous interfaces which control terrigenous and organic deposition and to nepheloid structures. These features often fluctuate and disappear easily. Special attention should be given to the "boundary layer". The measurements carried out without control by instruments such as either nephelometer or transmissometer should be interpreted extremely carrefully (Nyffeler, this volume).

It needs a short period of time for the material to be advected to the basin through the slope and canyons. Investigations on deep environments should begin as soon as possible, especially to follow pollutant transfer on the margins along which urban and industrial activity is high.

In shallow environments, previous mineralogical and sedimentological investigation is necessary to better focussing chemical analysis. Prodeltaic deposits should be mapped precisely. They represent the historical record of fine particle deposition. A systematic study of the pollutant content of sedimentary units could represent a good basis for a general inventory of pollution in the Mediterranean.

It is recommended to develop multidisciplinary investigation which focusses on a given system rather than local studies. A good knowledge of the hydrosedimentary characteristics of the system has to be obtained first.

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THE PHYSICO-CHEMICAL PARAMETERS CHARACTERIZING SEDIMENTS AND PARTICULATE MATTER AS CARRIERS OF CONTAMINANTS

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ABSTRACT

The physico-chemical mechanisms of the association of contaminants with suspended matter and sediment particles are a key in understanding the solid/liquid partition and its contribution to the total receiving capacity of the marine environment. This is specifically important in estuarine regions, and in semi-enclosed marine areas dominated by riverine terrestrial inputs.

The mineralogical identity and origin of an inorganic particle, along with the grain size, will influence the available surface for adsorption. The adsorption of contaminants is a complex surface process, involving hydration, surface alteration either by hydrophilic carbohydrates, amphipatic proteinaceous substances and animoacids, or by hydrophobic substances like hydrocarbons, lipids, and their derivatives. The influence can be identified by surface area measurements, energetics (heats) of adsorption, ion exchange capacity and colloidal stability. The oxidation/reduction processes (depending on local Eh in each transition and adsorption event) modify both the ionic form of the contaminant and the state of the surface of the mineral particle.

The paper reviews the physico-chemical parameters used in recent research in the Adriatic region, with examples of case studies of the Krka and Adige estuaries. The use of environmental and chemical modelling is described and critically reviewed in its relevance for the assessment of the total environmental capacity of the investigated areas.

INTRODUCTORY REMARKS

1. The purpose of this paper

The presentation is based primarily on the knowledge of the importance of particulate matter in the transport of contaminants in the estuaries in the Adriatic sea, our area of research. The terminology used is the one recommended by GESAMP (1986): a toxic substance present for a determinable time, in space elements at concentrations in excess of the natural background is called a **contaminant.** If it causes damage either to a species or to the ecosystem, then, according to GESAMP's definition of marine pollution, it becomes a **pollutant.** It also aims at critically reviewing the available knowledge, test the currently established cliches, this particularly with respect to the interpretation of interrelated parameters on the basis of models.

It is the prime purpose of the paper to illustrate the role of suspended matter in shallow areas for the determination of the **environmental capacity,** a concept considered crucial in understanding the principles needed for the sound management of marine and coastal areas. The concept of environmental capacity has been long known under various terms, such as absorptive, receiving or assimilative.

This paper describes the approach to characterize suspended matter from the physico-chemical point-of-view, as used in recent studies of the present authors, particularly in the Krka (Yugoslav (eastern) Mid-Adriatic) estuary (1979-1986), and in the Adige (Italian (western) North-Adriatic) estuary (1984 - 1985), but reference is also made to other authors who have studied either some critical Adriatic region, or have made studies of the world oceans.

The paper also aims at pointing deficiencies in the conventional approach to studies of the suspended matter, sediments and the process of sedimentation, and the need for additional, or refined, information. However, it is the aim to illustrate a rational expenditure of means, time, and manpower in the light of the information obtained.

The presentation also includes a description of the use of model substances for some measurements, capable of providing simplified conditions, with a reduced number of variables, and thus help in devising methods of extrapolation. In this sense the presentation draws heavily on the fundamental knowledge developed in a preceding and concurrent time span and effort of the same Laboratory in developing and understanding the scope of techniques, methodologies and interpretation.

The parameters reviewed are needed, if the role of suspended matter as vehicle of transport of contaminants, and of sediments as either the ultimate, or the time-dependent depository of contaminants is understood as a significant component of the **environmental (assimilative) capacity** of an estuarine region.

1.1 The concept of the environmental capacity:

The general framework of our work has been the development of the scientific basis for a rational management of coastal areas of the Adriatic Sea. At present the most frequently applied pollution combating strategy, if applied at all, is the one of the uniform emission standards. It belongs to a category beloved by administrators, since it offers a clearcut possibility of enforcement. It has usually been applied with a focus on industries, by arbitrarily judging their capability to deal with technology and its waste product. In some regions it works, although it has failed to produce the expected results in heavily populated and industrialized areas. But in a multi-national Europe, it has long been favored on the basis of the assumption that similar industries in various parts of the continent would work under the same economic conditions (EEC, 1976).

GESAMP has defined the environmental (=assimilative) capacity as a possible basis of a management strategy based on probabilistic assessment. The definition reads (GESAMP, 1986):

"The Environmental Capacity is a property of the environment and can be defined as its ability to accommodate an activity, or a rate of activity (e.g., volume of discharge per unit time, quantity of dredgings dumped per unit time, quantity of minerals extracted per unit time) without unacceptable impact".

It is this last term which defines the end points of tolerable activity or state, that determines the usability of the approach. Many warnings have been sounded on the danger of misuse of this concept (Portmann & Lloyd, 1986; Pravdic & Juracic, 1988).

Pollution is primarily unacceptable. However, putting the whole concept into the frame of a probabilistic statement, that is managing an environment in a way that even remotely possible detrimental effects would be avoided, one encounters difficulties. First of all, one should consider whether the part of the environment is an open or a (semi) enclosed system (such is the Adriatic region). For a semi-enclosed system it is easier to assume a steady - state condition, than applying the same concepts to an open system (the Mediterranean, or e.g., the Atlantic Ocean).

1.2 What data are needed?:

It would go beyond the scope of this paper to discuss all the aspects of the environmental capacity concept. Let us' define it as. a dynamic concept, requiring a substantial amount of scientific knowledge and data on hydrodynamics and delineation of the impacted area, concentrations and biogeochemical fate of pollutants, biological activity particularly on the micro-scale, transport of particulates and the distribution of active species between water and particulate matter. In addition, one does not have to emphasize that the marine environment can only, and then with considerable difficulty, be approximated by equilibrium considerations, molecular level included. It is a living system. Atkins (1987) has recently emphasized that much of physical chemistry has been taught at the university level using equilibrium concepts. These were long ago understood as being crude approximations, rarely if ever representing the state of nature, or simply life. However, the simplicity of calculation in equilibrium concepts has led to onesidedness in thinking. With the advent of computers and numerical analysis, there is no reasonable need for any oversimplifications. Thus the approximation of the segment of the marine or coastal environment can be understood in terms of steady-state rather than equilibrium. The chemical or biochemical reactor theory and its accompanying models, such as the receptor model, have been more and more frequently used as approximations. It is exactly in the chemical reactor theory that most, if not all, of the principles have been included, which one would need in the determination of the steady-state approximation of a segment of the environment (Hopke, 1985; Ruzicka & Hansen, 1981; Franks, 1972; NAS, 1975).

2. Environmental Modeling: myths and realities, advice and precautions

It is necessary at the present stage and before entering the presentation of data to illustrate our fragmentary knowledge, yet interesting observations, on the road to understand the environmental capacity of the Adriatic sea, or more precisely of some of its semi-enclosed or estuarine areas.

Most of physical science is based on models: from the structure of matter and the existence of elementary particles in atomic nuclei, through the structure and conformation of proteins and nucleic acids in an attempt to understand their function, to meteorology, as possibly the most important and yet elusive field.

Consequently, marine scientists have not invented modelling and the model approach: they have only raised it to the level of a powerful tool in dealing with complex, multiparameter natural ecosystems. In the process it has become one of the untouchable myths, a panacea of all evils in dealing with a body of scarce, uncertain or inaccessible data. Even in many cases, if no model is mentioned explicitly in discussing some collective events in marine areas, any in-depth analysis would soon recognize one or another level of a model.

An estuarine ecosystem is often considered in terms of a simple model, one that makes the estuaries hydrodynamically tractable, and thus provides the transport component of the steady-state approximation. This is the reason why estuaries have been the first attempt at defining the environmental capacity, with research emphasis limited to transport of suspended material and sedimentation as a major contribution to the retention of contaminants within the studied region. An embayment, a semi-enclosed area, a zone of mixing between freshwater and seawater, particularly if it is highly stratified like the Krka river's Prokljan basin, is particularly inducive to modelling attempts.

Coping on one side with the usual tendency of modellers to make their models dangerously complex, a warning should be sounded on the other on oversimplifications and hastily reached conclusions (including recommendations on the environmental capacity!). Usually there is an abundance of data on contaminant concentrations, particularly on metals, but data on incorporation of these into the biota, as well as data on chemical and microbiological degradation are often scarce. For practical purposes the following 4 levels of complexity of models are defined (Pravdic & Juracic, 1988):

Level 1. Hydrodynamic transport only. It is used when there is large uncertainty of all other parameters in well flushed areas.

Level 2. Hydrodynamic transport combined with particulate transport and sedimentation. It requires detailed studies of the rate of transport of particulates, rate of sedimentation, adsorption capacities, ion exchange properties and the distribution of contaminants between the organic coating and the (sea) water. It is useful in areas in which at least seasonally there is substantial particulate load, thus a significant contribution to the hydrodynamic transport mode.

Level 3; Sub-Level 3a. If data are available on the bacterial flora and the phyto- and zoo-plankton blooms, including the production of fecal pellets, the model of level 2 is refined in this sense. The result would be an increase in the apparent mean life of a contaminant in the area, whether or not it will be also undergoing microbial degradation.

Level 3; Sublevel 3b. If instead of microbial and planktonic data information has been obtained on the chemical and photochemical degradation and/or transformation of contaminants, the assumption is made that this is the major path modifying hydrodynamic and particulate transport data, as used in Level 2.

Level 4. This level is a comprehensive model incorporating Levels 3a and 3b. Very few models of this Level will be possible, mostly because in each advanced level one has to recognize or gather information on mutual interactions, the cross-paramaters of a complex matrix.

An example of a Level 2. model is given in Section 4.

Instead of criteria based on complexity, one can subdivide models according to their general applicability, following the recommendations of GESAMP (1987).

A transportable model is the very desirable condition, when a model verified as usable in one area can be transposed to another, in which the same generic processes are known to be operative. It is indeed an idealized situation, rarely if ever found in nature; however, such a model can be used with a precision within an order of magnitude in most cases. This sounds poor on the first glance, it is however as good as any in many cases of estuaries, semi-enclosed bays, and regions where seasonal events are quite distinct.

A robust model is one which obtained for an average set of data would yield approximately the same level of accuracy if some parameters are forced to the very extremes. Such a model, e.g., of the Chesapeake Bay in the Eastern United States (Atlantic Coast) should be tested against such once-in-a-century events like the flooding and flushing produced by hurricane Agnes in the mid 1970's. It would also be useful to have such a model ready for events like major oil spills in coastal regions.

Tuned models are what theoreticians like most. Such models are usually complex, however, they contain forcing functions with a large number of parameters. These parameters are then adjusted to give a fit to field observations. Such a model would defy description of being a "good model" (GESAMP, 1987), since it can be adjusted to fit almost any set of data, and it is one with little, if any predicting capabilities. Furthermore, one has to verify that a good model does not contradict the physics, the chemistry, and the biology of the particular environment, neither directly, nor implicitly. A good model has to recognize mutual interactions, even those of multiple steps, but should not neglect processes, which simpler models have shown to be important.

3. Review of Physico-chemical parameters

Usually, in the literature there are many parameters describing the interaction of particulate matter with seawater and its role in the cycling of matter in a segment of the environment.

The parameters describing the solid/liquid interface interaction in the transport of contaminants are subdivided into: (i) those measured in the seawater, including the interstitial water in sediments, and (ii) those pertaining to the particulate matter. It should be immediately said that the following discussion does not describe all hydrographic parameters usually considered in marine science.

TABLE I
REVIEW OF PHYSICO-CHEMICAL PARAMETERS

Parameter	Interpretative importance
1. SEAWATER	
Hydrological parameters	
Salinity	Salting-out of organics coagulation of colloidal and humic matter.
Oxygen concn.	E_h, redox couples, ionic forms
Temperature	Seasonal variations - limits.
Concentrations of contaminants	
Inorganic	Ionic and molecular species as adsorbates;
Organic	identification of preferential adsorbates: lipids, proteins, proteinaceous matter, hydrocarbons and halogenated hydrocarbons.
Microbial activity (considered here only as a reactivity parameter)	Probable mean life of hydrocarbons, aromatics, halogenated hydrocarbons.
Chemical reactivity parameters	Oxidative degradation rates, anoxic degradation rates, photochemistry, surface catalyzed reactions.
2. PARTICULATES	
Origin	Geological, biogenic or anthropogenic; stability, sedimentation rates;
Chemical and mineralogical composition	Core and coating of particles;
Specific surface area	Surface available for adsorption and interaction.
Particle size and shape	Size and size distribution as stability measure.
Adsorption on particulates	Polarity of the surface and its ion exchange capacity; adsorbability of organics as function of polar or nonpolar functional groups; adsorption energy as a measure of binding forces; adsorption isotherms.

3.1 Focus on particulate matter:

In the context of Table I, there is a need of some clarification of the interpretative importance of some of the above parameters.

The specific surface areas are an important factor in addition to measures of shape and size distribution. It shows the potential for the particulate matter to bind contaminants, if the basic prerequisites of ionic (polar) or nonpolar interaction of the surface with the contaminant are present. The inherent difficulty is that most of the reliable techniques for surface area determination require the particulate sample to be dehydrated, evacuated, heated and then exposed to a test vapor (nitrogen or argon at temperatures of liquid nitrogen). Such data do not necessarily reflect the same conditions as in the medium of seawater, but are the best reproducible and reference values available.

The charge of the particles, most often calculated from the data on electrokinetics (electrophoretic charge distribution for small stable particles, or the streaming potential for large particles) relates closely to the ionic exchange capacity and stability factors. The ionic exchange capacity can, of course, be measured directly using several different techniques (ion exchange columns and selective ion electrodes, titration or radioactivity counting if using radiotracers), however the charge density is a general measure of polar forces.

Finally, in adsorption experiments in addition to measuring the adsorption isotherms and calculating the maximum adsorbable amount on a particle, one usually needs the binding energy for the adsorbate. Thus, in determining the reversibility or irreversibility of binding of hydrocarbons on particulates, microcalorimetric measurements of adsorption equilibria have been used (Juracic & Pravdic, 1983). The information obtained is the enthalpy of adsorption, and if such measurements of reversible adsorption are made at different temperatures (usually one can measure at 15, 25 and 40°C), one can calculate the free energy and the entropy of the adsorption process. The last value is of particular interest in the adsorption of macromolecular substances, polysaccharides or proteins.

3.2 Accessibility of data and their interpretative value:

Most of the parameters characterizing particulates must be obtained by sampling and laboratory measurements; this merits mentioning only in the sense that they have to undergo some treatment prior to measurement which is capable of changing the surface properties. Thus standardization of the methodology is essential. One aspect of the measurements of the specific surface areas and the adsorption on particulate matter is the preparation of the surface: usually there is a need to strip the organic coating from the surface of a mineral particle, and evacuate the sample and adsorb gas at liquid nitrogen temperatures. If the particles are of organic matter without the mineral core, or if the interest is entirely confined to the properties of the (organic) coating, then appropriate techniques have to be developed which would ensure minimum interference with the original chemistry of such matter (Hunt, 1983). Determination of specific surface areas in such cases may become difficult to interpret.

Another problem associated with measurements of parameters described above is sampling and the preparation of a small amount of the representative sample. All laboratory techniques of specific surface area determination, of microcalorimetric adsorption measurements, and of the measurement of electrokinetic properties are, by virtue, microscale. Unless careful standardization of sampling techniques is established, the pitfalls of misinterpretation are many.

4. The Adriatic Region

The presentation to follow does not intend to be a compendium of research done in this region. It focuses only on some recent research, partly from this laboratory, and partly referring to recently published work.

The Adriatic region receives a large contaminant loading from land-based sources. In this sense the particulates are carriers of a large proportion of heavy metals, chlorinated organics, and hydrocarbons which would without this transport vehicle remain in other zones, determined by hydrodynamic transport only.

The input of contaminants from the atmosphere is assessed at present by rough estimates. There is evidence that the input of mercury into the Mediterranean is largely atmospheric (Pacyna, 1983; Buat-Menard, 1983; Arnold et al., 1984); the same is claimed for low molecular weight hydrocarbons. The total fraction of atmospheric particular load into the Adriatic region, including the Saharan dust, is still open for assessment. Any calculations of the fraction of atmospheric input of contaminants carried by particulates is hampered by the lack of reliable data and its associated uncertainty. Therefore the planned programmes of monitoring of the atmospheric input, planned within the MEDPOL programme under the auspices of WMO, and the continental exercise within the framework of EUREKA programmes, the EUROTRAC, are important components in the overall assessment. Before this missing link is established our knowledge on the pathways of contaminants, carried by particulates into the Adriatic region, will remain wanting.

4.1 The Krka River Estuary:

This eastern river in the Yugoslav middle Adriatic (Fig. 1) is a dwarf in its total load contribution, but a giant as an information source as one of the rare Karstic estuaries. Part of the studies on sediments, obtained in three locations, marked in the map (Fig. 1) as stations 1, 2, and 3 are given in Table II.

Tables II and III indicate an interesting pattern: The grain sizes of the sediments, expressed as medians, differ significantly from station to station. The Guduca Creek mouth, which supplies most of the fine grain suspended material to the Prokljan basin has higher values, than the sample taken from the bottom of the Prokljan basin. The Vrulje sampling point (Station 2), close to the land in the Prokljan basin, shows coarse sediments, mostly sand washed out from the fine particles. The sediments are poorly sorted, a consequence of bimodal size distribution indicating two different sources of sedimented material. The large size particles are mostly biogenic in origin (foraminfera, shell fragments), the small size particles are clayey and silty material with an increasing fraction of large surface area clays.

The specific surface area of native and organic free particulates (Table III) is a parameter characteristically different for fresh and seawater sediments. The former always shows an increase in the specific surface area per unit weight when stripped from organics by mild oxidative treatment; the seawater, or brackish water sediments show the reverse. The heat-of-wetting by water of freshwater sediments is less for the organic-free surface than for the native, organic coated, indicating a highly hydrophilic nature of the freshwater organic material. The physico-chemical interpretation of the influence of seawater is an increase in salt concentration, primarily of chloride and sulfate which causes salting-out effects (a decrease in solubility of organics) and changes in the conformation of the adsorbed species. Inspecting the data it seems obvious that the seawater organic coating is primarily hydrophobic (Jednacak-Biscan & Juracic, 1987).

The interpretative value of these considerations and the associated measurements of physico-chemical parameters, is the variety of phenomena and extreme caution is advised in using some average values for the adsorption of some contaminant species. Particular attention is always needed when considering estuarine phenomena in the transition from freshwater to seawater.

The model of the Prokljan basin in the Krka River estuary (Fig. 2) has been used to show limitations imposed by releases of Cu on two competing activities: mariculture of salmonides, and mooring of pleasure boats in the adjacent marina. Using crude approximations and a reasonable safety factor, it has been shown that the number of boats allowed to enter and remain moored must be limited in the area, where intensive mariculture is going on.

Fig. 1. Map of the Krka River Estuary. Stations: (1) Prokljan: (2) Vrulje: (3) Guduca Creek mouth.

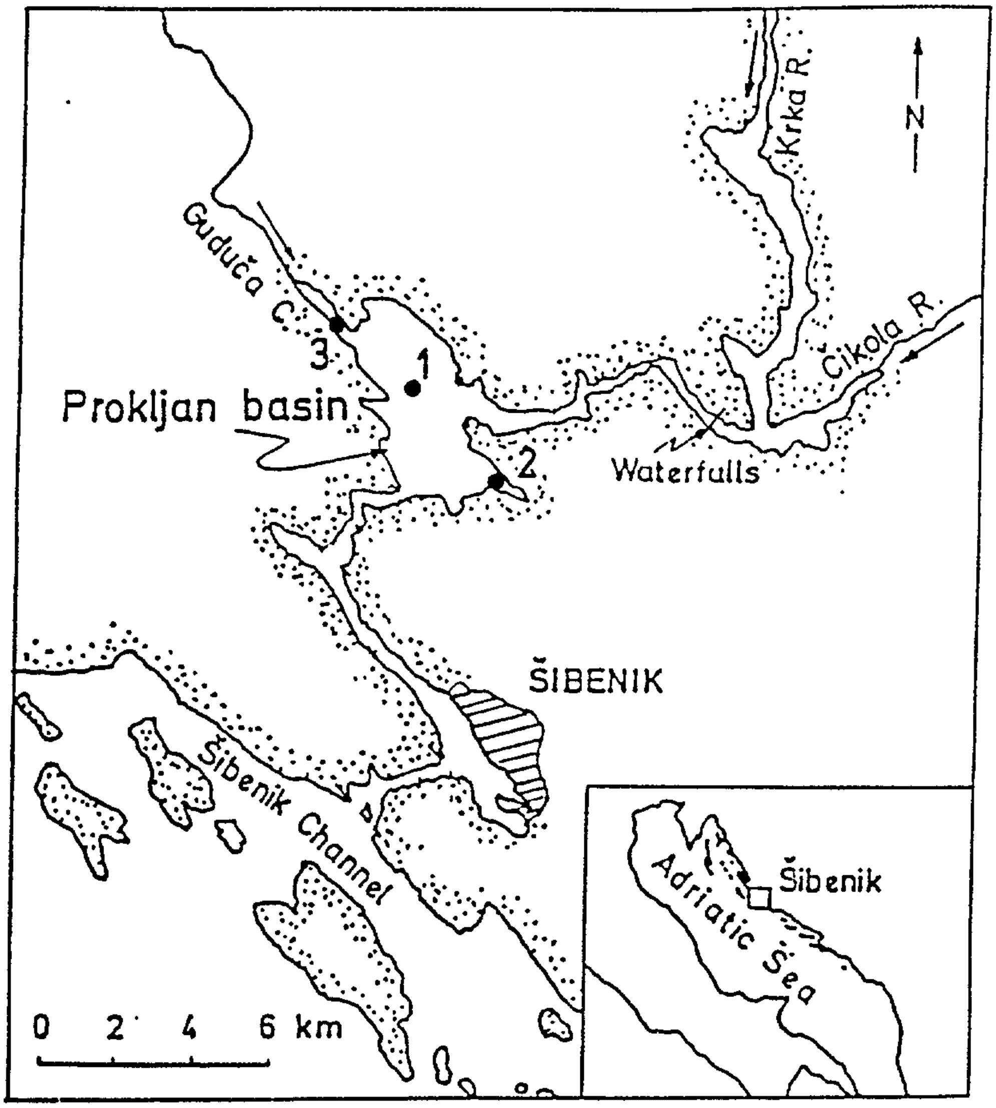


TABLE II

Krka River Estuary Sediments
Location

Parameter	(1) Prokljan	(2) Vrulje	(3) Guduca Creek mouth
Median grain size, micrometers	6.6	126	8.9
Sorting, So	1.39	2.77	2.19
Organic matter, % w/w	9.0	10.9	8.7
Carbohydrates, % w/w of total organic bound	5.6	9.0	-
Major fraction:	glucose, galactose, xylose		
Medium fraction:	mannose, glucosamine, glucuronic acid		-
Mineral composition, w/w			
$CaCo_3/SiO_2$	3.1	2.4	(37)
$MgCO_3$/SiO2	0.30	0.24	(0.1)
Specific Surface Area, m^2/g			
Native sediment	30	12	39
Organic free	28.5	-	41
Sediment/water partitioning for some metals			
Pb	2.4×10^5	-	2.7×10^5
Cu	1.9×10^5	-	1.5×10^5
Zn	5.8×10^4	-	6.8×10^4

Source: Juracic (1987): Hadzija et al. (1985).

Krka River Estuary Sediments
Specific Surface Areas and Heats-of-Wetting

	Specific Surface Area m^2/g		Heat of Wetting uJ/cm^2	
Sample	Native	Organics free	Native	Organics free
Krka River	14.4	16.4	102	69
Water falls	4.3	8.5	367	77
Zlarin (Sea)	3.2	1.1	73	130

Source: Jednacak-Biscan & Juracic (1987)

The mass balance of Cu in the Prokljan basin includes three measured throughputs: river input, $55 m^3/s$ at $0.5 ug/dm^3$, equalling 27.5 mg/s; saline (bottom) water input, $5.5 m^3/s$ at $0.25 ug/dm^3$, equalling 1.4 mg/s; and the surface outflow, $60.5 m^3/s$ at $0.44 ug/dm^3$, equalling 28.6 mg/s. The surplus of 0.3 mg/s is a part of the input to the lower compartment.

The adsorption of Cu at the suspended matter surface in the upper layer, and its subsequent partial release following the sinking into the lower saline compartment, is taken as the only vertical transport mode of Cu. This assumption has the weakness of the unknown variability of the amount of suspended matter supplied by the Guduca creek, and of the concentration of Cu in it. The measured ion exchange capacity of the suspended matter is 0.1 meg/g or 3.2 mg/g for Cu^{2-} (=3200 ppm) (Musani-Marazovic et al., 1984). At the concentration of 125 ppm Cu in the suspended matter, the exchange capacity is used only at 4% thus, the suspended matter is acting as a (fast) adsorption/desorption buffer.

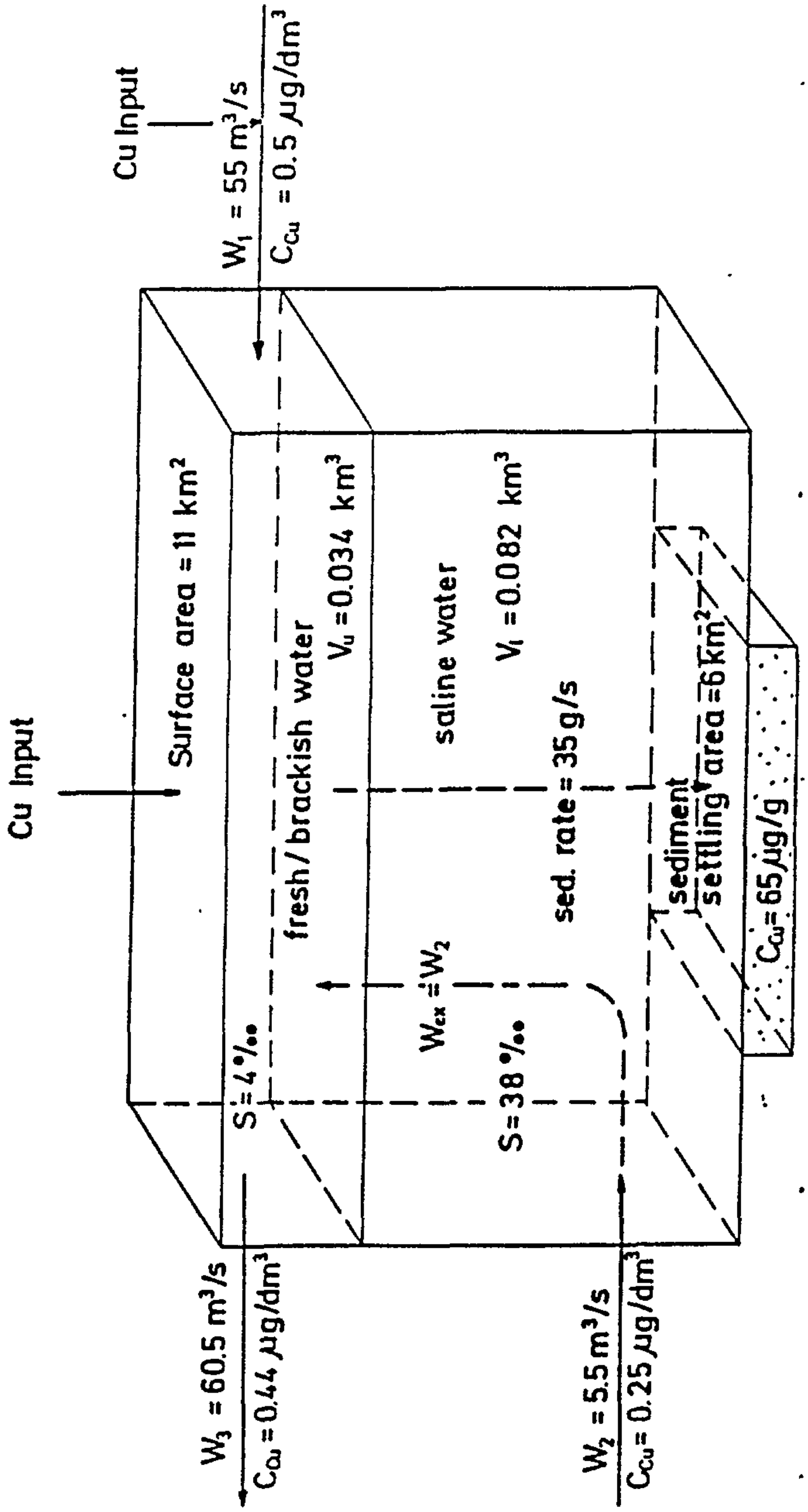
Following these data, the assumptions made and the model used, the compartment under investigation should be in a steady state with respect to existing sources of Cu. Choosing the mean residence time of water $t_{mr} = 174$ days, the cumulative suspended matter mean load of Cu is 30 kg (i.e., = 0.172 kg/day), and the mean, steady-state concentration in the compartment of $0.082 km^3$ will be increased by $0.37 ug/dm^3$, yielding a total of $0.37 + 0.25 = 0.62 ug/dm^3$.

The calculation is based on the assumption that the additional anthropogenic Cu will be adsorbed onto the suspended matter in the upper water layer, and subsequently released into the lower compartment. This assumption is corroborated by recent research on the sedimentation of terrigenous particles in the estuary (Juracic, 1987).

The ultimate usable environmental capacity was assessed using as the end point of $0.01 mg/dm^3$, the volume of $0.082 km^3$, and a mean residence time of water of 174 days. The conclusion reached was that only 190 "average" boats can be accomodated in the same time in the Prokljan basin (Pravdic & Juracic, 1988).

Environmental modeling is a fairly advanced art, and a useful tool in environmental studies. If the precautions mentioned in Ch. 2 are heeded, models are the best framework to combine data into a coherent system. Their greatest potential is in their predictive capabilities: in this category, there is much to be desired yet.

Fig. 2: A mass-balance model of the Prokljan basin. It is an example of modeling level 2. Source: Pravdic & Juracić (1988).



4.2 The Piran Bay: The E_h problem:

The foregoing discussion of the parameters should be coroborated by oxidation state measurements. In the absence of a coordinated study within our own work in the estuarine areas of the Krka or Adige river estuaries, reference is made of the work by Ranke (1976). In Fig. 3 the profiles of E_h are shown: in the left hand side of the Figure the potential in 5 cm depths of sediment; in the right hand side the depth for $E_h=0$. In such a small bay, characteristic of the highly indented coast of the Adriatic sea, particularly of its eastern seaboard, the large variations are strongly dependent, upon seasonality. The seasonal variations of E_h for the major areas of the Adriatic, known to sustain a large terrestrial contaminant load have yet to be studied in this manner.

Consequently, the residence time of a contaminant is an important parameter in the coastal areas in zones of such widely differing oxidation state with data on reactivity of organic contaminants. Associated data on microbiological activity, would yield useful indication on the fate of contaminants. Averaging, as seen from the above discussion, carries dangers of wide errors.

4.3 The Adige River Estuary:

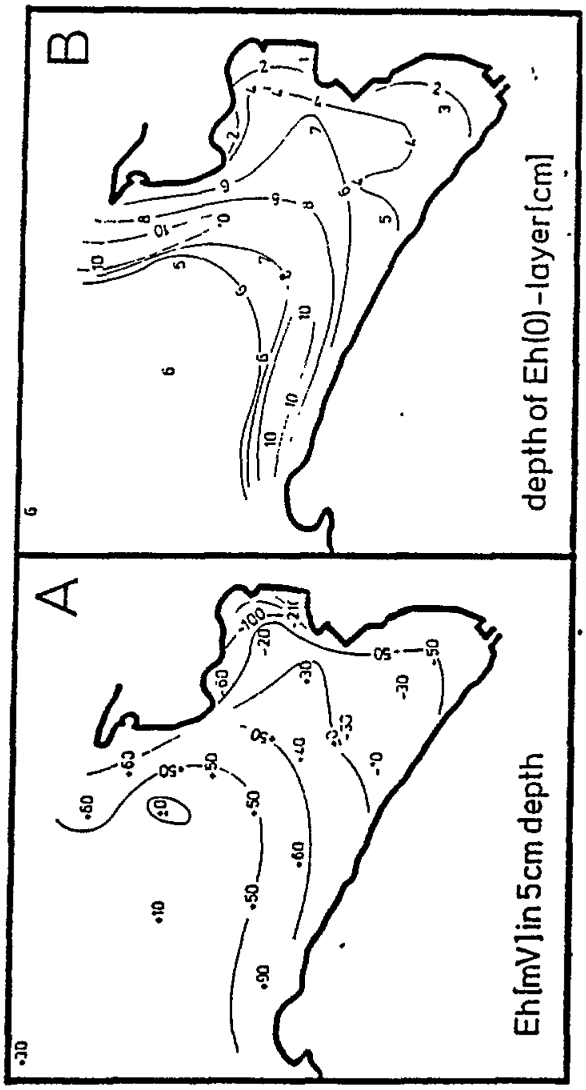
Similar parameters are presented, as for the Krka river estuary, where available. A review of some characteristic parameters is given in Table IV.

The information available on the Adige River estuary is much more limited than that on the Krka river. The river sediments are well sorted sands, while the marine sediments are poorly sorted clayey silts. The pattern of specific surface areas is the same as described above for the Krka river, except for considerably lower values. Indeed, in spite of the predominant clay component in the sediments, the specific surface areas are considerably smaller as compared to the Krka river sediments. Once again the parameters indicate the need for specific information in each area, and the dangers of averaging.

4.4 Comparisons with some other Adriatic areas:

Studies of similar scope have been made before for the Rijeka Bay and West Istrian coast sediments (Juracic et al., 1981; Juracic & Pravdic, 1983). The major problem in oil spills in the marine environment is the final deposition of nondegradable or slowly degradable hydrocarbons. In table V data are shown on the microcalorimetric adsorption of water and a hydrocarbon, n-hexadecane, on two samples of sediments. Hexadecane has been chosen to represent a typical nonvolatile and moderately soluble hydrocarbon, however, one, which is still liquid at temperatures of the ambient, and which because of its aliphatic character does not polymerize into tar.

Fig. 3: Redox potential patterns in the surface sediments of Piran Bay (N. Adriatic, tip of the Istrian peninsula). Type of coast: flysch; sediment mean grain sizes in the Bay: 3 to 5 um. Source: Ranke (1976).



The information from data in Table V is that the organic coating is decreasing the energy of adsorption for seawater and relatively increasing that for the hydrocarbon. This observation holds in spite of the fact that the values for seawater are from 3 to 10 times as high as those for hexadecane. It is therefore highly probable that hydrocarbon would be desorbed from the surface of such sediments. Thus, microcalorimetric data give characteristic information on the interaction of contaminants with particulates. The main drawback for the general applicability of this technique is that the effects for adsorption of heavy metals at concentrations prevalent in seawater and interstitial water are unmeasurable. Thus the above evidence has to be interpreted as circumstantial in adsorption studies.

5. Chemical Modelling

In studying the interaction of solid surfaces with solutes, or in the context of the present discussion of mineral particulates with dissolved contaminants, the properties of the particles can be modelled by some pure minerals, mixture of well-known minerals, and glass, representing a silicate mineral of amorphous structure. Most of the physico-chemical techniques for surface studies, or for probing into solid surfaces, are amenable to interpretation only if the surface structure and solid particle composition is exceedingly well understood. Thus using models, and trying to extrapolate to real field conditions is another form of modeling and model interpretation.

5.1 The influence of organics:

Chemical modeling of mineral particle surfaces is most needed to understand the role of the organic coating. There are two directions of research done in this laboratory highlighted. The first is the modification of the mineral surface by some organic agent, which can be covalently coupled to the surface: then, measurements are done of some characteristic parameters, such as microcalorimetric heats-of-wetting, amounts and heats of adsorption, electrokinetic experiments in well defined media. The alternative approach is to modify the surface and expose it to the marine environment and analyze the changes produced by such surface modification.

5.2 Models of surface modification:

The most suitable and experimentally easiest model to use for surface modification are silicates, and particularly amorphous materials like silicate glasses. Figure 4 taken from Jednacak-Biscan & Pravdic (1982) shows the currently accepted though simplified model of a silica glass surface in contact with water (left hand side of the Figure 4).

TABLE IV

Adige River Estuary Sediments

Parameter	Portesine	Station Busiola	Open sea
Salinity at sampling point	0.1	1	34.7
Mean grain size, milimeters	1.34	1.5	0.53
Organic matter, %w/w	0.5	0.7	6.2
Mineral composition, w/w			
$CaCO_3/SiO_2$	(0.2)	(0.2)	0.4
$Dolomite/SiO_2$	0.25	(0.3)	(0.33)
Total carbonates	16.7	12.6	23.0
Specific Surface Areas, m^2/g			
Native sediment	1.6	1.9	4.8
Organics free	1.3	2.1	7.1

Source: Juracic *et al.* (1987).

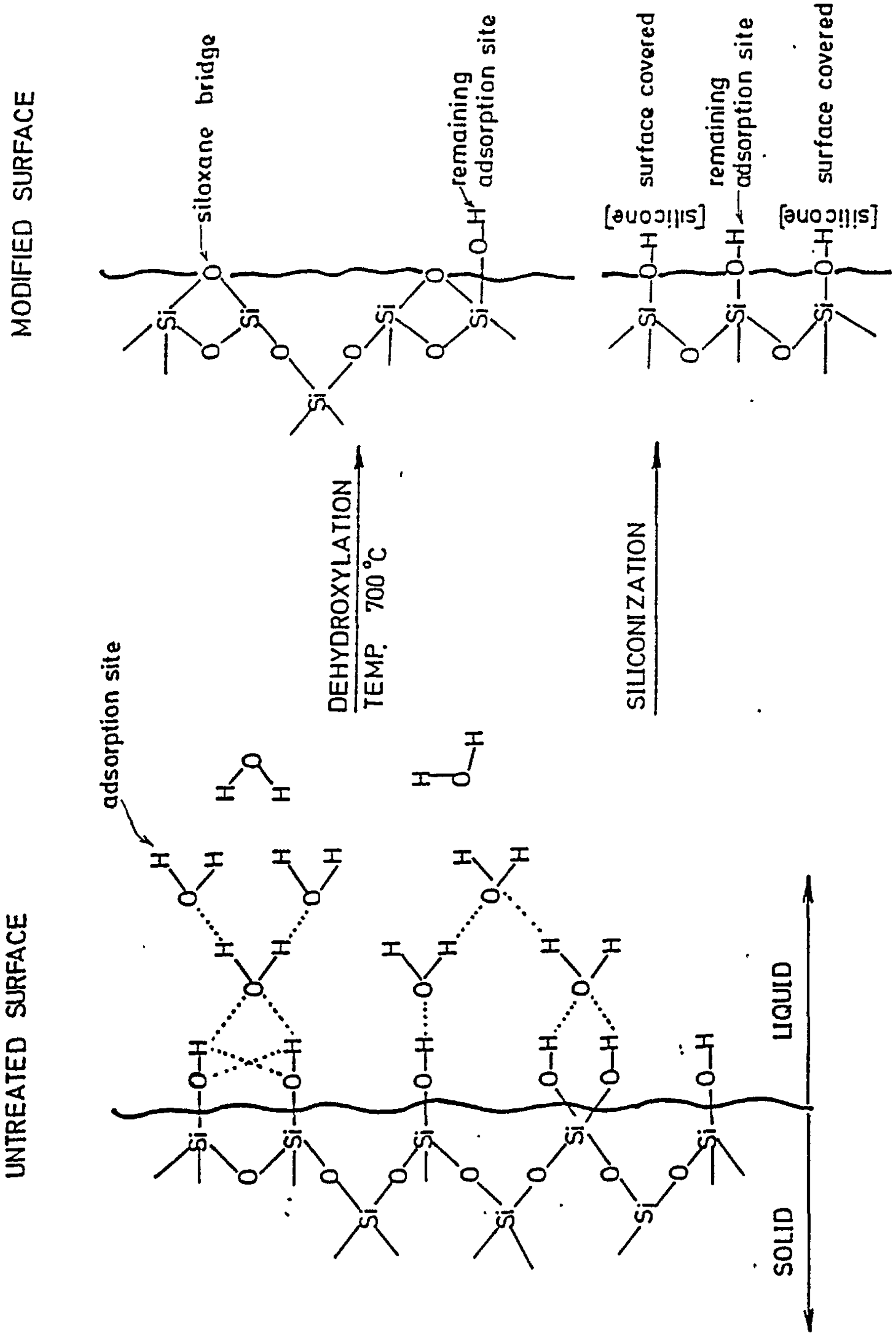
TABLE V

Heats-of-immersion of Northern Adriatic Sediments into Seawater and n - Hexadecane, in uJ/cm^2

Sample	Seawater	Hexadecane
Rijeka Bay		
Native	125 +/- 28	36 +/- 12
Organics free	298 +/-111	29 +/- 9
West Istrian Coast		
Organics free	181 +/- 77	51 +/- 19

Source: Juracic *et al.* (1981).

Fig. 4: The model of the silica/water interface and the modification of silicate surfaces. Left: native surface; right upper surface after thermal treatment at 700°C; right lower part: adsorption of silicone. Source: Jednacak-Biscan & Pravdic (1982).



The most simple modification of the surface is by heating, producing a dehydrated surface, as shown in the upper right hand part. Such surfaces are produced by burning of coal and are present in the silicate part of the fly ash. Treating the surface by a highly adsorbable material, like silicone oil, a blockade of the surface is effected. Such parts of the surface are highly organophyllic and increase the surface affinity for various organic contaminants. Instead of simply adsorbing layer upon layer, chemical models of silicate glass surfaces can be prepared by covalently binding silanes (e.g., tri-chloro alkyl, or aryl, silane, or triethoxy alkyl-amino silane), producing surfaces which can be predominantly acid or alkaline, or have some specific surface active group. A model of such a surface is shown in Fig. 5.

Samples of silicate glass beads and pure minerals, such as calcite, have been exposed to the water in the Krka estuary, and measurements were made of the effects on the specific surface area, and on the heat-of-wetting. Data are shown in Table VI.

A close inspection of the data in Table VI reveals large data dispersion involved in such experiments, due mostly to the characteristics of the model solids used. The observed small variations in values for the same solid material between native and organics free, and between the two water samples of different salinity, are dwarfed by the large differences observed by the two materials, glass and calcite. The main advantage of the approach suggested here is that many basic parameters, from the amount adsorbed, to binding energies can be quantitatively interpreted and stereochemically understood.

6. Conclusions

Where hence? The answer seems obvious. Suspended particulate matter and sediments hold the key to understanding the fate of contaminants in enclosed or semi-enclosed marine areas and estuaries. The physico-chemical parameters described above are the mechanistic component of our understanding of the biogeochemical fate particularly of some trace elements and persistent organics. Thus, a monitoring programme should always be coupled with such studies to gain significance for the ultimate aim: how to manage an ecosystem in the face of increasing loads from urban and industrial development.

What data are needed for management action? The verbal answer is simple: we need to know the biogeochemical fate of each contaminant, and have to make a decision on which species or what part of the total ecosystem needs to be declared as the target in need of protection. The answer is much more involved and requires a wide variety of scientific research. Simple monitoring exercises, such as those in effect at present both in the Mediterranean and in most other coastal areas around the world, do not provide the answers; these are but the essential, basic and necessary steps toward adaptive management. And adaptive management in our terminology signals the need for the assessment of the environmental capacity.

Fig. 5: Surface modification of silicate surfaces by organics. Left: basic surface = anion adsorption; right: acidic surface = cation adsorption.

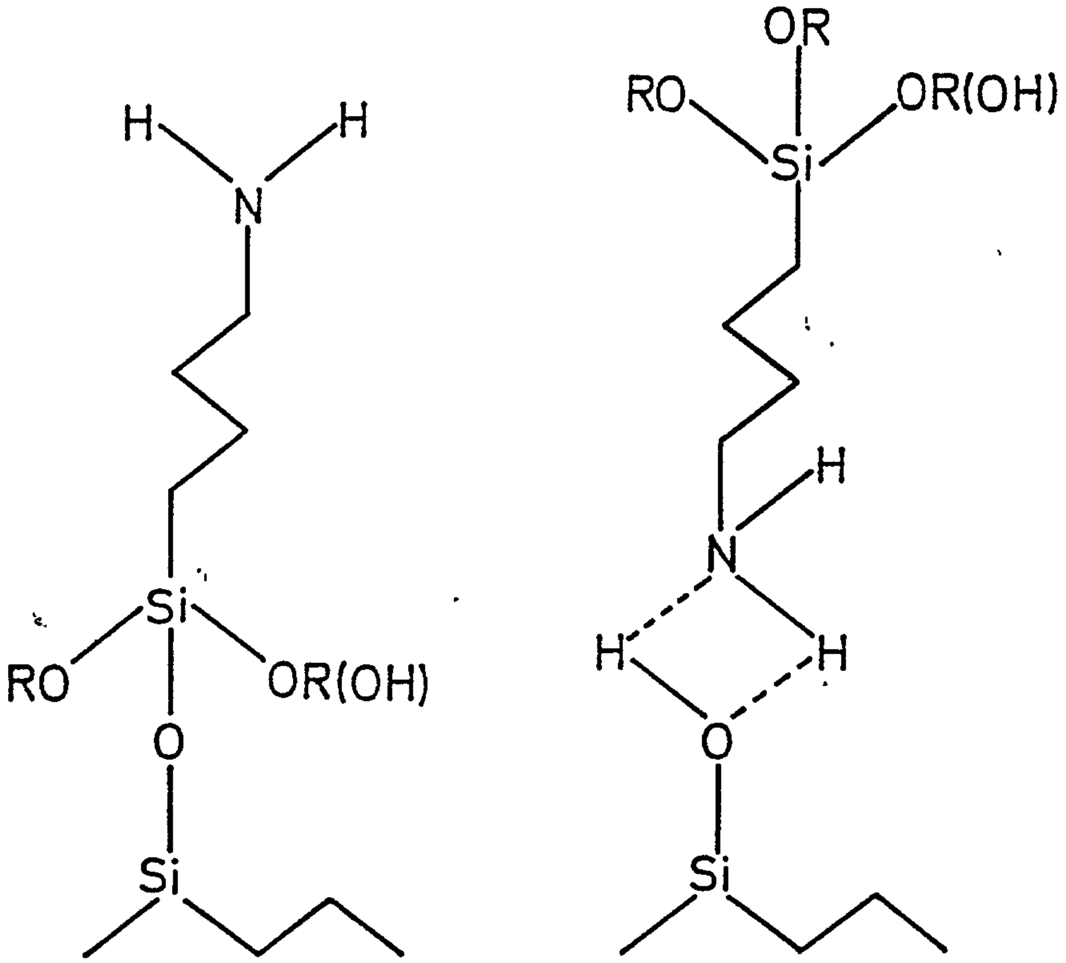


TABLE VI

Adsorption Experiments with Model Solids
Powdered Silicate Glass and Calcite Mineral Samples

	Specific surface area m^2/g		Heat-of-Wetting uJ/cm^2	
Sample	native	organics free	native	organics free
CPG	34.4	-	23	-
CPG-S1	34.4	30.9	31.5	20.4
CPG-S4	28.2	24.1	52.6	23.6
CPG-ODS	25.0	-	16.3	-
CPG-ODS-S1	26.2	29.1	14.1	34.1
CPG-ODS-S4	25.0	33.5	30.9	22.2
Calcite	1.9	-	28.0	-
Calcite-S1	1.2	1.4	50.7	4.6
Calcite-S4	1.0	1.5	105.5	29.9

Legend: CPG = controlled pore glass; ODS = octadecylsilane derivatized; S1 = Krka river water; S4 = Adriatic seawater, salinity 38 o/oo.

Source: Jednacak-Biscan & Rhebergen (1988): unpublished results.

Acknowledgement

This review paper is a highlighting of the most instructive components of many years of research of marine pollution in the coastal areas of the Adriatic sea. Much of this work has been supported by the Authority for Scientific Research of the Republic of Croatia, Yugoslavia. Support from the UNEP MEDPOL programme both Phase I and II has not only provided instrumentation and supplies, but enabled frequent exchange of ideas: specific acknowledgement is due to WHO (Grant CIP/CEH 039-YUG 63 (C). Support from the US EPA, (Grant No. JFP 717) for the same work is gratefully acknowledged. Part of the work on fundamental research into the surfaces of silica glass, including supplies of controlled pore glass samples, has come through a long term cooperative programme with the National Bureau of Standards, Washington, D.C. USA (Grant JFP 690), both Grants are within the Programme of the US - Yugoslav Joint Board for Scientific Research.

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INTERACTION OF SEDIMENTARY POLLUTANTS WITH BIOTA

- RESEARCH AT ILMR -

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ABSTRACT

The interaction of three classes of pollutants - chlorinated hydrocarbons, radionuclides and heavy metals - with sediment-dwelling biota is reviewed. Their accumulation from sediments by benthic infauna is contrasted with that from seawater and the relative importance of each pathway is examined using, as examples, results from the sediment-exchange research programme of the IAEA International laboratory of Marine Radioactivity (ILMR). It is concluded that pollutants which are present in bulk sediments are practically unavailable to biota and that of the small measurable uptake which can occur, the sediment is a more important route of uptake than the interstitial water largely because of the large sediment: water distribution coefficient of most contaminants.

INTRODUCTION

The fate of almost all contaminants entering the marine environment is an inexorable gravitation to the sedimentary sink. Interaction of potential pollutants with biota during and after this process can occur at the surface, throughout the water column and in the sediment itself. Although it is generally the case that contaminants are introduced to the marine environment at the surface, there are cases when they may be introduced directly to the bottom (so-called dumping) as with, e.g., seabed disposal of radioactive waste and of sewage sludge and dredge spoils. In this regard, concern has often been expressed as to whether the sediment acts as a sink for the pollutants or whether it may become a source of pollution at a later date long after the original source has disappeared. Sediments are often neglected during discussions of water quality even though monitoring of sediment pollutant content and of the community structure can yield useful information (Phillips, 1979; Bilyard, 1987). Bioavailability of contaminants from sediments is discussed in a useful compilation of Campbell et al. (1988).

In this review, bioavailability of three classes of contaminants - chlorinated hydrocarbons, radionuclides and trace metals - is discussed along with the research effort being expended at ILMR relevant to this subject.

In the upper reaches of the water column, biota can accumulate and perhaps be adversely affected by contaminants both in soluble and particulate form. Mediation of the vertical flux of contaminants by biological activity has been reviewed by Fowler (1982). Radionuclides and heavy metals can be concentrated many thousand-fold by phytoplankton - a process which can introduce them into the food-web (IAEA, 1985). These contaminants subsequently can be packaged into particulates such as fecal pellets by zooplankton and be transported rapidly to the sediments (Fowler, 1982). This was recently demonstrated by Fowler et al. (1987) for Chernobyl radionuclides entering the surface waters of the Mediterranean. A significant part of the research effort at ILMR is concerned with the role of biota in facilitating the vertical flux of radionuclides in the marine environment within the framework of both national and international research programmes such as DYFAMED, ECOMARGE, VERTEX and JGOFS (IAEA, 1987). An interest in the biological fate of sedimenting particulate contaminants and a concern for the potential contamination of benthic infauna by these and other contaminants introduced directly to the benthos has resulted in the examination of their relative bioavailability through controlled laboratory experiments.

The sediment-exchange programme at ILMR has included experiments on sediments from Bikini Atoll in the Marshall Islands, Thule in Greenland and the Baltic, Black, Irish and Mediterranean Seas (Table 1). In some cases sediments were used which were naturally labelled through fallout from weapons testing, from nuclear accidents including Chernobyl and Thule and from nuclear power-plant and reprocessing-plant wastes. In other studies conducted, we have utilised sediments which were obtained from the Mediterranean Sea and from prospective OECD dumpsites in the Atlantic and Pacific Oceans. These sediments were then labelled in the laboratory.

Elements and organic compounds studied have included chlorinated hydrocarbons (PCBs), transuranics (Pu, Am) and other radionuclides, and essential (Co, Cu, Fe, Zn) and non-essential (Cs, Tc, Ag) trace metals.

Table 1.

Sources of sediments used at ILMR and their pollutant content

Origin	Labelled with	Source of Label
Monaco	PCB	Industrial
Monaco	PCB, 99m-TC	Laboratory
Monaco	134/137-Cs, 110m-Ag, 106-Ru	Chernobyl fallout
Bikini Atoll	238/239-Pu, 241-Am, 55-Fe	Nuclear-device tests
Thule, Greenland	238/239-Pu, 241-Am	Nuclear weapons (plane crash)
Sellafield, U.K.	238/239-Pu, 241-AM	Reprocessing waste
North Atlantic	241-Am	Laboratory
Pacific	241-Am	Laboratory
Black Sea	134/137-Cs, 106-Ru	Chernobyl fallout
Baltic Sea	134/137-Cs, 106-Ru	Chernobyl fallout
Baltic Sea	134/137-Cs, 106-Ru, 65-Zn, 60-Co	Chernobyl fallout and nuclear power plant waste

Research With Nereis

To understand better the interactions of potential contaminants with sediment biota, we have chosen to study the accumulation and loss of chlorinated hydrocarbons, radionuclides and trace metals in the sediment-dwelling polychaete Nereis diversicolor. The potential of using this species as an indicator of sediment contamination has been reviewed by Phillips (1980).

Nereis is particularly suitable for laboratory studies (Goerke, 1984). It is a small animal (about 1 g) which is relatively common and accessible. It is easily transported, can be maintained without problems in laboratory aquaria and commonly lives for two to three years which is ideal for long term uptake and loss studies. For this reason, coupled with the facts that it is (a) an ubiquitous sediment-dweller, (b) an important food-web link to fish and other predators and (c) widely-used in other laboratories, we have decided to utilise it as the test organism of choice in our studies. By using just one species, it is hoped to minimise the biological variability which so often confounds comparisons between experiments and thus to identify differences in the behaviour not only of individual contaminants but also between different classes of contaminants such as radionuclides and organic compounds.

Relative uptake and accumulation of contaminants from sediments and water is best described using transfer factors (TF) and concentration factors (CF), respectively. TF is defined as the concentration of a substance in an organism relative to that in the bulk sediment. CF is defined as the concentration of a substance in an organism relative to that in the water. The derivation of these and related terms, their use in ecological modelling and the effects of biotic factors upon them is discussed by IAEA (1985), Harrison (1986) and Gomez et al. (1988). A related term, the distribution coefficient (Kd), is defined as the concentration of a substance in sediment relative to that in water (IAEA, 1985).

Chlorinated Hydrocarbons

Chlorinated hydrocarbons which enter the marine environment rapidly become associated with the sediments (Larsson & Sodergren, 1987). Research with chlorinated hydrocarbons include experiments conducted where Nereis diversicolor has been exposed for periods of up to several months to both unspiked (0.1 ug PCB/g dry) and spiked (ranging from 0.65 to 80 ug PCB/g dry) sediments and seawater (0.57 ng PCB/l) (Fowler et al., 1978; Elder et al., 1979). Worms living in the unspiked sediments showed little change in their PCB concentrations whereas those living in the spiked sediments readily accumulated the pollutants, reaching equilibrium conditions after about two months. Uptake increased with dose and the higher concentrations used proved to be toxic.

Equilibrium TFs were approximately 3-4. On the other hand, worms exposed to the PCB in the water rapidly accumulated the contaminant and reached equilibrium conditions in 10-15 days. CFs at this time were about 800. CFs calculated for the mucus secreted by the worms were about the same as those calculated for the worms themselves. The results indicated that both sediments and seawater can serve as sources of contamination of Nereis by PCB, and on the basis of the CF data one would expect that uptake from the water would predominate. Yet, as discussed by Fowler et al. (1978) and Polikarpov et al. (1979), this is not the case. Since the unspiked sediments contained 0.05 ug/g (wet) PCB, one would expect to find 0.175 ug/g sediment-derived PCB in the worms. Overlying water PCB concentrations at Monaco, found to be 1.5 ng/l would result in water-derived PCB levels of only 1.2 ng/g in the worms. It was therefore suggested that about 99% of the body burden of PCB in the worms was derived from the sediments. On the basis of the PCB Kd of 2 x 10^5, it was demonstrated that the interstitial water could account for only 0.2% of the PCB burden in the animals. This concurs with the reports of Young et al. (1976, 1977) that for mussels, sediments are a major source of contamination by organochlorines.

In Table 2 are shown CF and TF data for several organic contaminants. Generally, CF values are orders of magnitude greater than those for TF. It was recently reported by Oliver (1987) that where oligochaete worms and Lake Ontario sediments were used, the concentration of the chlorinated hydrocarbons in the interstitial water of the sediment was the driving force behind accumulation. The author noted that of the 37 compounds tested, only 17 were detectable in the pore-water. His argument for the relative importance of the pore-water relative to the sediment is based on the fact that the collected fecal pellets had the same concentrations of test compound as did the sediments. These results are in contrast with those discussed below for trace metals and radionuclides and indicate the relatively high bioavailability of PCBs which are supposedly locked in the sedimentary sink.

Table 2. Laboratory-derived TFs and CFs (in parentheses) for organic pollutants (after Fowler, 1982)

Organism	Exposure (days)	Phenanthrene	Chrysene	Dimethyl-benzan-anthracene	Benzopyrene	Naphthalene	Alkyl-naphthalene	PCB (DP-5)	Reference
Nereis diversicolor	125 (14)							3-4 (800)	Fowler et al., 1978 Elder et al., 1979
Arenicola marina	0.2 (0.4)					0.1-4 (20-300)			Lyes, 1979
Macoma inquinata	7 (7)	0.2 (10)	0.04 (694)	0.06 (1349)	0.09 (861)				Roesijadi et al., 1978
Anonyx laticoxae	4 (4)						2-4 (10-1000)		Anderson et al., 1979

a in situ at Cap La Hague, France
b in situ at Thule, Greenland

Radionuclides and Trace Metals

Radionuclides and trace metals will be grouped together for two reasons: (i) their similar behaviour and (ii) radiotracers were used in the trace metal studies.

(a) Transuranic Radionuclides - As with chlorinated hydrocarbons, it is well-known that the transuranic elements Pu and Am accumulate in the sediments (Noshkin, 1972; Noshkin & Bowen, 1973). Both of these elements are present in fallout from weapons testing and nuclear accidents as well as in nuclear power-and reprocessing-plant wastes. The chemical form of the radionuclides in the sediment is probably highly dependent on the source-term since fallout from weapons testing has been subjected to extremely harsh physical conditions and nuclear wastes are routinely treated with a battery of chemical reagents prior to discharge. In addition, sediment contamination by wastes tends to be a coastal phenomenon whereas fallout is global in scope. In cases where prolonged dumping occurs of relatively soluble radionuclides such as caesium and technetium, the potential hazards may be of regional concern.

Sediments were collected from the coast near Sellafield in the Irish Sea (5.0 Bq total Pu/g dry and 8.3 Bq ^{241}Am/g dry) and from the vicinity of Bikini Atoll in the Marshall Islands (3.3 Bq total Pu/g dry and 1.8 Bq ^{241} Am/g dry). Nereis were exposed to these sediments for 225 and for 40 days respectively (Beasley & Fowler, 1976). In both cases the uptake of Pu and Am was small (typically 5%) and there was a decidedly preferential uptake of the Pu relative to the Am. This is in contrast to other measurements in marine systems (Aarkrog et al., 1987). It was also found that the Am in the Sellafield sediment was more bioavailable than in the Bikini sediment and it was suggested that among other possibilities such as differences in the physico-chemical form of the radionuclides, the reason may be that the Sellafield sediment contained both "free" and "ingrown" Am whereas the Bikini sediment contained only "ingrown" Am (Beasley & Fowler, 1976). The importance of characterising the source of contamination is illustrated in this case.

TFs in the worms exposed to the Sellafield and Bikini sediments were 0.0012 and 0.0015 for Pu and 0.0006 and 0.0003 for Am respectively. It was concluded that the worms were receiving most of their body burden of radionuclides from a source other than the sediments - possibly from the water. In a previous study, it has been shown that the CF in Nereis for Pu in water was greater than or equal to 200 (Fowler et al., 1975). Applying this value and the Kd of Pu to the Sellafield sediment and water data, the authors concluded that 83% of the body burden of Pu in these animals could come from the water alone (Beasely & Fowler, 1976). This result could explain the preferential uptake of Pu over Am noted by these authors since others have generally found that only about 10% of the Pu uptake could be accounted for by water (Table 3). In this experiment the contribution of sediment to Am uptake is similar to that described elsewhere (Table 4).

Table 3. TFs and CFs for Plutonium

Organism	Exposure (days)	CF	TF	% Uptake due to sediment	Reference
Venerupis decussata	20-22	61-74	0.006	77.5	Aston & Fowler, 1984
Hermione hystrix	20-222	275-370	0.05	87.0	" " "
Arenicola marina	14-21	7	0.002	94	Miramand *et al.*, 1982
Corophium volutator	12-14	780	0.01	86	" " "
Scrobicularia plana	14-42	190	0.01	70	" " "
Cerastoderma edule	14-56	160	0.014	82.4	Miramand & Germain, 1985
Nereis diversicolor	400	-	0.00145	14.5	Beasley & Fowler, 1976
Nereis diversicolor	a	315	-		Fraizier & Guary, 1976
Arenicola marina	a	103	-		" " "
Shrimps	b	-	0.0002		Aarkrog, 1977
Brittlestars	b	-	0.0006		" "
Molluscs	b	-	0.004		" "
Shrimps	b	-	0.0005		Aarkrog *et al.*, 1987
Brittlestars	b	-	0.0000002		" " "
Macoma calcarea	b	-	0.027		" " "

a *in situ* at Cap La Hague, France
b *in situ* at Thule, Greenland

Table 4. TFs and CFs for Americium

Organism	Exposure (days)	CF	TF	% Uptake due to sediment	Reference
Scrobicularia plana	14	230	0.009	28	Miramand *et al.*, 1982
Corophium volutator	14	1200	0.12	66	Miramand *et al.*, 1982
Arenicola marina	14	16	0.003	79	Miramand *et al.*, 1982
Venerupis decussata	50	106	0.004	72	Vangenechten *et al.*, 1983
Venerupis decussata	50	780	0.02	66.0	Vangenechten *et al.*, 1983
Cirolana borealis	50	180	0.007	72	Vangenechten *et al.*, 1983
Cirolana borealis	50	1290	0.032	65	Vangenechten *et al.*, 1983
Hermione hystrix	50	1600	0.053	68	Vangenechten *et al.*, 1983
Hermione hystrix	50	4690	0.117	65	Vangenechten *et al.*, 1983
Hermione hystrix	22	1000	-	-	Grillo *et al.*, 1981
Nereis diversicolor	400	-	0.006	57.5	Beasley & Fowler, 1976
Nereis diversicolor	400	-	0.003	14.9	Beasley & Fowler, 1976
Nereis diversicolor	20	16-21	-	-	Murray *et al.*, 1978
Cerastoderma edule	14-56	340	0.008	39.7	Miramand & Germain, 198?

The importance of sediment characteristics, some effects of which were discussed above in relation to Sellafield vs. Bikini, were more clearly illustrated in a series of experiments performed with sediments obtained from prospective deep-sea dumping sites in the Northeast Altantic and the Pacific Oceans (Vangenechten et al., 1983). These sediments were artificially labelled with Am and the animals used were the polychaete Hermione hystrix, the isopod Cirolana borealis and the clam Venerupis decussata. In both cases, Kd values were about 1.5 x 10^5 and TFs, over a period of 50 days exposure of the animals, were always less than unity (though still increasing at the end of the experiment). In spite of the similar Kds of the sediments and the identical labelling techniques used, TFs were 2 to 5 times higher in the sediments from the Pacific than from the Atlantic.

In the Atlantic sediment, 62% of the Am was present in a form which was highly resistant to chemical leaching whereas in the Pacific sediment only 12% was resistant. Although pore water Am and known CFs from water could satisfactorily account for almost all of the Am in the Atlantic-exposed animals, this was not the case in those exposed to the Pacific sediments and it was concluded that some uptake occurred from the ingested, less refractory Am in Pacific sediments (Vangenechten et al., 1983).

These studies indicate not only the very low bioavailability of transuranics from sediments relative to water but also the importance of both the source of contamination and the physico-chemical characteristics of the sediment on uptake by the biota. The low TFs derived from the laboratory studies are in good agreement with those of Aarkrog and co-workers who measured TFs for Pu and Am in situ in the biota at Thule, Greenland (Aarkrog, 1977; Aarkrog et al., 1987). They obtained values of 10^{-4}-10^{-3} for Pu and approximately twice these values for Am.

An interesting aspect of the Pu in the sediments at Thule is that Aarkrog et al. (1984) detected contaminated animals at distances from the crash site where the radionuclides were not detected in the sediments, indicating that redistribution of the contaminants can take place by migration, etc. Half-distances from the site of impact for Pu in the sediments were about 3 km whereas for the biota they were 5-6 km.

(b) Other Radionuclides, including Trace Metals - The sediments from Sellafield and Bikini Atoll discussed above were not only contaminated with transuranic radionuclides but also with ^{55}Fe. Iron is an essential component of many biological processes and one would expect that there should be significant uptake of the radionuclide because of the metabolic requirements of the biota. In experiments where Nereis was exposed to these sediments for periods of up to 88 days, it was demonstrated that uptake of the iron was very low and was not significantly different between the two sediments (Jennings & Fowler, 1980). Equilibrium TFs of 0.063 and 0.066 respectively, were reached after about 30 days exposure. These TFs are about 10 to 30 and 25 to 90 times greater than those found for Pu and Am in the same sediments (Beasley & Fowler, 1976). It was concluded that for ^{55}Fe uptake is essentially independent of both the stable iron content of the sediment and of the sediment type. The single factor influencing uptake was the concentration of ^{55}Fe in the sediments (Jennings & Fowler, 1980).

Table 5. TFs and CFs for Cobalt

Organism	Exposure (days)	CF	TF	% Uptake due to sediment	Reference
Arenicola marina	14	*264	*1	-	Triquet, 1973
Nereis diversicolor	14-100	12	0.12	99	Nolan, 1989
Nereis japonica	11	6	0.05	99.9	Ueda *et al*., 1977
Macoma inquinata	390	244	0.48	95	Young *et al*., 1982
Neanthes virens	180-370	343	2.25	99.2	Young, 1982

* CFs are not given by the author. The CF value is relative to the TF value of 1.

Table 6. TFs and CFs for Caesium

Organism	Exposure (days)	CF	TF	% Uptake due to sediment	Reference
Nereis diversicolor	14-100	6	0.05	89	Nolan, 1989
Nereis diversicolor	58	6.3	-	-	Bryan, 1963
Nereis diversicolor	11	6	0.18	83.3	Ueda *et al*., 1977

The Atlantic and Pacific sediments discussed above which had been artificially-labelled with Am by Vangenechten et al. (1983) were also artificially labelled with ^{95m}Tc (Fowler et al., 1985). Technetium is very soluble in water and Kd values of 2 to 3 were obtained. During a period of 36 days exposure of a clam, Tapes decussatus, to these sediments, the radionuclide was repidly leached to the overlying water. Uptake in the clams was low (TF = 0.3) but because of the 120-day biological half-life of the Tc taken up by the animals, it was concluded that the clams would remain contaminated long after the radioactivity had disappeared from the sediment (Fowler et al., 1983).

The Chernobyl accident resulted in the fallout contamination of the Baltic, Black and Mediterranean Seas with a variety of radionuclides including ^{134}Cs, ^{137}Cs, ^{106}Ru, ^{110m}Ag, ^{144}Ce, ^{239}Pu, ^{241}Am and ^{244}Cm (C.E.A., 1988). Sediments were collected from each of these regions and experiments were conducted with Nereis to determine the relative bioavailabilities of the radionuclides. It was found that the sediments from the Black Sea, the Mediterranean Sea and the southern end of the Baltic Sea contained too little of each of the radionuclides to enable accurate determinations of the transfer coefficients to be made - even after up to six months of exposure. It was concluded that the TFs were considerably less than unity (Nolan, 1989).

In a sediment sample collected at the northern end of the Baltic sea near a nuclear power plant, in the region where Chernobyl fallout over the Baltic had been greatest, the radionuclides detected were ^{54}Mn, ^{60}Co, ^{65}Zn, ^{95}Zr/Nb, ^{106}Ru, ^{110m}Ag, ^{134}Cs, ^{137}Cs and ^{144}Ce. When Nereis was exposed to this sediment for up to 105 days, only ^{60}Co and ^{137}Cs were detected in the animals. TFs for these radionuclides were calculated to be 0.12 and 0.05 respectively and maximum possible TFs were calculated (Based on the detection limits of the apparatus) for the other radionuclides. These values were ^{54}Mn=0.36, ^{65}Zn-0.63, ^{95}Zr/Nb=1.8, ^{106}Ru=0.37, ^{110m}Ag=0.3, ^{134}Cs=0.0.15 and ^{144}Ce=0.20 (Nolan & Fowler, 1989). These values are all low but are still considerably greater than those derived for the transuranics Pu and Am. In contrast CFs of 12 and 6 were estimated for ^{60}Co and ^{137}Cs in Nereis when the animals were exposed to these two radionuclides in the water for 4 days (Nolan, 1989).

These results confirmed the previous results of Ueda et al. (1977) where, in laboratory experiments with artificially-labelled sediments, low TFs were found for ^{60}Co, ^{95}Zr/Nb, ^{106}Rh/Ru and ^{137}Cs. Ueda and co-workers calculated a "biological factor of the sediments" (which they defined as the relative importance of water- to sediment-based uptake of the radionuclides) for these isotopes as 120 for ^{60}Co, 440 for 95Zr/Nb, 1000 for 106Rh/Ru and 30 for ^{137}Cs - underscoring again the relatively higher bioavailability of these nuclides from water than from sediments (Ueda et al., 1977).

DISCUSSION AND CONCLUSIONS

Discussion of contaminant interactions with biota can conveniently be divided into two parts: (i) the effects of the biota on the behaviour of the contaminants and (ii) the effects of the contaminants on the biota. Research at ILMR over the last decade or so has been concentrated primarily on the former rather than on measuring effects on biota as it was felt that the accumulation of basic bioaccumulation and transfer data was a more sensible approach given the current paucity of our basic knowledge of bioaccumulation and transport processes. Furthermore, with toxic trace metals and chlorinated hydrocarbons it is often possible to measure effects on biota at levels which are so low as to be challenging to the analyst, whereas with radionuclides the reverse is normally the case and one can often easily measure radionuclides at levels where no obvious effects are occurring. A clear difference in the philosophies of pollution studies with radioactive and with other contaminants is that with trace metals and organics, one usually has a solid foundation of toxicity data with which to interpret results and to quickly determine whether there is a pollution problem or not, whereas with radionuclides this is clearly not the case. The perception among the general population is that any amount of radioactivity is dangerous, that there is no tolerance threshold and that the presumed effects increase with the dose. Although this may apply to the biota, there is as yet no evidence that there is any direct danger to man at the levels normally found in the environment (IAEA, 1976). Our food-web studies are designed to help estimate the likelihood of any potential threat to man of radionuclides in the sediment biota. The long half-lives of up to several hundred thousand years of some radioactive contaminants underscore the need to make assessments now in order to avoid suffering possible consequences later.

There is no standard sediment. Therefore experimental results which may be valid for one type are not necessarily applicable to another. Sediment type and characteristics are important factors governing the uptake process and operating variables include grain size, packing density, proportion of organic material as well as grain minerology. The oxidised upper layer and the reduced material beneath will have very different characteristics and cycling of material back and forth from one to the other either by turbulence or by biological activities such as feeding, burrowing and migration can slowly result in the release of refractory contaminants. Ingestion of considerable amounts of sediment is common in marine polychaetes and otherwise unavailable contaminants may also be released by the differing chemical regimes found along the length of their gastro-intestinal tracts. The roles of microbial microcosms on the sediment particles and of microbial food-webs on the degradation and release of contaminants are still poorly understood. Biological factors affecting radionuclide behaviour in sediments have been thoroughly discussed by Bowen et al. (1976), Lee & Swartz (1980), Swartz & Lee (1980) and Schulte (1986).

Uptake from water is potentially a far more important source of contamination for biota than that from sediments because the contaminants are already in a soluble and presumably more bioavailable form. It should be noted in this context, however, that contaminant concentrations in the water are generally up to orders of magnitude less than those in the sediment (IAEA, 1985). Estimation of the relative contributions of sediment and water to the body burdens of biota are very difficult to make. The results of field studies are often difficult to interpret because of the dynamic nature of the processes occurring there and the impossibility of determining the sources of the contaminants in the organisms studied (Lee & Swartz, 1980). The most common experimental approach to this problem is to expose the test animals to contaminated bulk sediments and to water separately. A criticism of this method is that with the former, the animals are also exposed to the contaminant in the interstitial water and the measured TF will actually be a composite valve from two sources of uptake. In spike of this, TFs from sediment are generally less than unity whereas CFs from water are up to hundreds of times greater than unity.

Laboratory and field-derived TFs and CFs for sediment-dwelling biota are listed in Tables 2-6 for organic contaminants, the transuranic radionuclides Pu and Am and the metals Co and Cs. The data include estimates of the relative importance of the sediment in total contaminant accumulation. The tables are not intended to be comprehensive since detailed information can be found in the compilations fo Noshkin (1985), IAEA (1985), Harrison (1986) and Gomez et al. (1987). In all cases, the CF values are orders of magnitude greater than the TF .values, implying that sediment-bound contaminants are generally very unavailable to the biota relative to those in water. Uncritical comparison of the data may lead one to assume that water is the major source of contaminants to the biota but when one considers the Kd values of these contaminants (IAEA, 1985), it becomes apparent that this is not the case. When, as for example with a Kd for Pu of 150,000 (Vangenechten et al. 1983), less than 0.0007% of the radionuclide is present in the aqueous phase, then even the low TF values can become significant.

In Tables 3-6 are presented estimates of the contribution of the sediment to the body burden of the contaminants tested for a variety of benthic invertebrates. These data were calculated as described by Nolan (1989) using, wherever possible, the original Kd and sediment wet/dry weight ratios. Where the original data were not available, substitute Kd values listed by the IAEA (1985) were used and it was assumed that the wet sediment water content was 35%. Where similar estimates were made by the original authors, they are in good agreement with the calculated values presented here.

It is clear that in almost every case, the sediments are the major source of contamination in the animals tested. This is in good agreement with the reports of Noshkin et al. (1971) and Ayling (1974). The former reported, from consideration of 238/239-Pu ratios in sediment-dwelling worms, water and sediments, that sediments were the predominant source of Pu contamination of the biota. Ayling (1974) showed that the correlations between trace metal content in oysters and sediments were so good that it would be preferable to use TF data rather than CF data when discussing pollutant uptake.

Too little is known of food-web transfer processes to accurately determine their importance in the overall bioaccumulation process. The same difficulties are encountered in its estimation as are those discussed above. Presumably, once a contaminant has entered the food-web, it is immediately more bioavailable than it would be from sediment or water because its association with vital nutrients such as polysaccharides and proteins would increase the chances of it being assimilated into the organism during digestion. To date, our knowledge of the fluxes involved in benthic food-webs are scanty.

There are no firm rules for predicting the bioavailability of pollutants from contaminated sediments. Bioavailability can be influenced by, e.g.

(a) Sediment type: Gross differences are seen between the Sellafield and Bikini Atoll sediments for Pu and Am. Such differences were not seen for the same two radionuclides between the Atlantic and Pacific dumpsites. The observed differences in the former cases were probably due to the different sources of the contamination.

(b) Pollutant type: Whereas radionuclides (Transuranics and others) show a low bioavailability, PCBs are relatively high. However, PCBs may be unusual even among organic contaminants since many others display a low bioavailability similar to that of radionuclides.

(c) Kd: Kd is a very insensitive indicator. It may help in predicting longevitity of contaminants in the sediments but not bioavailability. For example, the Kd of Tc is low whereas that of Pu is high yet both have a low bioavailability. The Kd can change with sediment/water ratios - as indeed can TF values (Ueda et al., 1977); alberts et al., 1986).

(d) Leachability: Whereas the octanol/water partition coefficient or even just the aqueous solubility may be useful indicators in studies with organics (Isnard and Lambert, 1988), there is as yet no efficiently formulated extraction method for radionuclides and trace metals. Luoma and Jenne (1976) considered a suite of extractants for estimating the bioavailability of trace metals in sediments but concluded that none gave suitable results for all metals.

We conclude that, for PCBs, transuranic radionuclides and non-essential trace metals, the sediment is an efficient sink since contaminants in the sediments are up to thousands of times less available for uptake by the infauna than they would be in the water. Some small, but significant transfer from the sediments to the biota does take place, however, this transfer can account for up to 99% of the body burdens of some contaminants by the benthic infauna.

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THE FORMATION OF CALCIUM PHOSPHATES AND CALCIUM CARBONATES IN THE PRESENCE OF CATIONIC AND ANIONIC SPECIES

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ABSTRACT

Precipitation and dissolution studies in natural waters are of importance in understanding the accumulation of minerals in the ocean floor and in the sediments of rivers and lakes. Information on the kinetics of precipitation is very limited, despite the fact that in several cases, kinetics rather than thermodynamics determine the nature of the precipitating solid phase. The solubilities of many inorganic solids decrease with increasing temperature, as is the case with the calcium carbonate polymorphs and the calcium phosphates. The former solids, form as a result of interaction of the atmospheric CO_2 with free calcium. The increase of phosphate concentrations in lakes and rivers on the other hand, renders the formation of calcium phosphates very likely. The adsorption of cations such as Mg^{2+}, Zn^{2+} or anions such as oxalate and phosphate on calcium phosphates and carbonates may serve as a mechanism of immobilization of these ions in natural waters. Thus, it was found that magnesium strongly adsorbs on hydroxyapatite surfaces, thus blocking the active growth sites and reducing the rate of precipitation, while at the same time the surface charge of hydroxyapatite becomes significantly more positive. The presence of low concentrations of Zn^{2+} resulted in reduction of the rate of crystallization of hydroxyapatite by adsorption onto the active growth sites. Phosphate, was found to strongly adsorb on calcite and the subsequent rates of crystallization were drastically reduced with increasing phosphate concentrations up to 1×10^{-6}M. In the presence of oxalate anions, the formation of calcium carbonate monohydrate was favoured.

INTRODUCTION

The precipitation and dissolution of sparingly soluble salts, such as calcium carbonates and calcium phosphates, are phenomena of great interest in a number of fields including limnology (Stumm and Morgan, 1981), sedimentology (Berner, 1971) and oceanography (Whitfield, 1975). The appearance and subsequent development of crystals in the aquatic environment, is a typical example of the selectivity shown in nature. Among a number of solutes, certain salts are forming while others dissolve, rendering situations in which the water composition is different from that expected by equilibrium considerations. This discrepancy, if often explained by the fact that kinetics factors are often prevailing over thermodynamics. Calcium carbonate has probably been the mineral on which most of the research interest in natural waters has been focused. During the precipitation process in water, in equilibrium with atmospheric carbon dioxide, a number of calcium carbonate polymorphs may be formed, in the order of decreasing solubilities: calcium carbonate monohydrate, vaterite, aragonite and calcite. The presence of magnesium in the aqueous media, may result either in the inhibition of calcium carbonate nucleation and growth (Pytkowitz, 1965) or in the formation of dolomites (Nancollas and Sawada 1982, Mucci and Morse, 1983, Kamiya et al, 1977). Moreover, the increase of phosphate concentrations in lakes and rivers, especially near heavily populated areas is an additional reason for stressing the importance and high priority of understanding the nature of the crystalline phases that may be forming (Lindsay, 1979, Brown, 1973). The adsorption of metal ions on the surface of the solid particles of calcium carbonates and calcium phosphates, formed by precipitation of the adsorption of anions may be an important factor regulating not only the nature of the phase forming but also the transport of these ions to the sediment. More specifically, it has been shown that very low concentrations of phosphate in calcium carbonate supersaturated solutions, may cause inhibition of calcium carbonate precipitation or even coprecipitation of calcium phosphate (Kazmierczak, 1978, House and Donaldson, 1986). On the other hand, the presence of carbonate is found to strongly inhibit the precipitation of calcium phosphate at low supersaturations, typical of environmental levels (Koutsoukos, 1980). Once a crystalline nucleus is formed, the growth process occurs by transport of the growth units on the surface of the crystal from the bulk solution, followed by surface diffusion of the units in the active growth sites (Nielsen 1964). The driving force, is the deviation of the ionic product of the solid phase forming from the value corresponding to equilibrium. Experimental studies aiming at investigating precipitation processes of calcium carbonates and phosphates and the influence of substances foreign with respect to their lattice constituent, have been done in the past employing either high solution supersaturations, (where spontaneous precipitation occurs and due to the rapid decrease of the ion activities in solution it was impossible to distinguish between the possibly forming intermediate phases), or at very low supersaturations, more pertinent to natural water conditions. In the latter studies, the small extent of the precipitation reaction often made the studies impossible and precluded the accurate assessment of the effect of the presence of cationic or anionic impurities. These problems were overcome by the possibility of studying the precipitation processes at constant, low supersaturation (Tomson and Nancollas, 1978, Koutsoukos et al 1980, Kazmierczak et al, 1982).

In the present work, we have employed this method in order to investigate quantitatively the effect of both cationic and anionic substances on the kinetics of precipitation of hydroxyapatite ($Ca_5(PO_4)_3OH$, HAP), the thermodynamically most stable calcium phosphate, and calcite, the most stable calcium carbonate polymorph. Cations of interest examined include Zn^{2+}, Cd^{2+} and Mg^{2+}. Moreover, the effect of oxalate and phosphate anions on the precipitation kinetics and surface charge characteristics of calcite were examined.

Experimental

a. HAP Crystal Growth Experiments: Crystal growth experiments were done at 37° ± 0.1°C, under nitrogen. HAP seed crystals were prepared from direct mixing of concentrated solutions of calcium nitrate and potassium dihydrogen phosphate (Nancollas and Mohan, 1970) and were characterized by specific surface area (SSA) measurements using a single point B.E.T. nitrogen adsorption method (Quantasorb II, Quantachrome), infrared spectroscopy (Perkin Elmer 467), powder x-ray diffraction (Phillips XRG-3000, Cu K radiation, Ni filter), scanning electron microscopy (SEM, ISI model II) and by chemical analysis for calcium and phosphate. The SSA was $21.5 m^2 g^{-1}$ and the molar ratio Ca:P = 1.64 ± 0.01. The powder XRD and IR sectra were identical to those for pure HAP. The supersaturated solutions employed were prepared in a double walled thermostatted pyrex vessel, volume totalling 0.200 dm^3, by mixing equal volumes of standard solutions of calcium nitrate and potassium dihydrogen phosphate. The pH was adjusted by the addition of standard potassium hydroxide (Merck, Titrisol). Following the verification of the stability of the supersaturated solutions, as indicated by the constancy of the pH or the solutions, a quantity of HAP seed crystals was introduced and as a consequence, crystallization started immediately. The proton release, following the onset of precipitation, triggered the addition of titrants of calcium nitrate, potassium phosphate and potassium hydroxide from two mechanically coupled burettes of a pH-stat (Radiometer, TT1b) appropriately modified (Zawacki et al, 1986). Samples were withdrawn randomly during the course of reaction, filtered through membrane filters (0.22 μm, Millipore, Bedford Mass.) and the filtrates were analyzed for calcium by atomic absorption spectrometry (Perkin Elmer 503, Varian 1200) and by photometric titrations at 504 nm, using murexide indicator. Phosphate analysis was done by a spectrophotometric method (Murphy and Riley 1962).

b. Calcite growth experiments: Experiments were made at 25.0± 0.1°C at pH 8.50. Supersaturated solutions were prepared by mixing equal volumes of calcium nitrate and sodium bicarbonate solutions, made from the solid reagents (Merck puriss.) using triply distilled water. Sodium bicarbonate solutions were made fresh for each experiment. The crystallization process was initiated by the addition of calcite seed crystals with SSA=3.26 $m^2 g^{-1}$ as detailed elsewhere (Giannimaras and Koutsoukos, 1987). The study of the effect of phosphate was done at constant pH, maintained by the addition of standard potassium hydroxide from an automatic titrator (Radiometer TT1b, SBR2c, PHM26). The effect of metal ions such as Zn^{2+}, Cd^{2+} and of the $C_2O_4^{2-}$ anions was studied by the constant supersaturation method in a manner analogous to that described for the growth of HAP.

c. Adsorption experiments: Adsorption experiments were done at the same temperatures as the crystal growth experiments. Quantities of HAP or calcite, sufficient to yield a total surface area of approximately 0.2 m^2, were equilibrated with 0.010 - 0.015 dm^3 of solutions of the ions studied. The suspensions were made in polyethylene vials, sealed and rotated end over end for 24 hours. Next, the suspensions were filtered and the filtrate was analyzed for the ion of interest. The oxalate anion analysis was done spectrophotometrically (Lee and Hwang, 1968).

D. Electrokinetic measurements: The electrophoretic mobility of the HAP and of the calcite particles, were measured in suspensions 0.1 or 0.01 mol dm^{-3} in potassium nitrate, both in the presence and in the absence of foreign ions. For the measurements, a Rank MK II microelectrophoresis apparatus equipped with a videocamera and a monitor (Phillips) using a four electrode, capillary cylindrical cell, was employed and the velocities of at least 20 particles (in both directions of the electric field) in each of the two stationary layers were measured. The difference in the velocities measured in the two layers was not greater than 7%. The electrophoretic mobility measurements of the HAP and calcite particles were performed following equlibration of the solid with potassium nitrate solutions for twelve hours.

RESULTS AND DISCUSSION

The concentration of the ionic species in the supersaturated solutions were calculated by taking into account all acid-base and ion-pair equilibria, mass balances and the electroneutrality condition making successive approximations for the ionic strength (Nancollas, 1966). For the estimate of the activity coefficients the Davies equation was used (Davies, 1962). For the calcium carbonate experiments, the system was considered to be closed. The assumption is valid because of the high pH value (8.50) and the minimization of the air above the liquid phase (Koutsoukos and Kontoyannis, 1984). The driving force for the formation of a crystalline phase $M_{\nu+}A_{\nu-}$ is the change in Gibbs free energy, AG, for going from the supersaturated solution to equilibrium:

$$\Delta G = - RT \ln \frac{(M^{m+})^{\nu_+}(A^{a-})^{\nu_-}}{K^{o}_{s,M_{\nu_+}A_{\nu_-}}}$$

$$= -RT \ln \Omega_{M_{\nu_+}A_{\nu_-}}$$

In equation (1), (M^{m+}) and $A^{a-})$ are the activities of the lattice ions in solution and $K^{o}{}_{s,m_{\nu+}A_{\nu-}}$ is the thermodynamic solubility product for the crystalline phase. $M_{\nu-}$ $A_{\nu-}$ is defined as the saturation ratio of the crystalline precipitate. The initial conditions of the experiments of crystallization of calcite are shown in Table 1:

TABLE I:Crystallization of calcite on calcite seed crystals; 25° C, pH 8.50.

Exp. #	Ca_t /10^{-4}M	C_t /10^{-4}M	ΔG KJ/mole^{-1}	Additive	Add.Conc. M	Rate /10^{-6}mole min^{-1}m^{-2}
70	20.19	20.19	-2.7	-	-	36.7
80	18.87	18.87	-2.6	-	-	35.1
90	16.01	16.01	-2.2	-	-	17.1
100	9.89	20.00	-2.0	-	-	12.9
110	8.67	8.67	-1.0	-	-	1.0
120	9.89	20.00	-2.0	KH_2PO_4	1E-08	7.8
130	9.89	20.0	-2.0	"	2.2E-08	5.7
140	9.89	20.0	-2.0	"	3.3E-08	4.9
150	9.89	20.0	-2.0	"	4.5E-08	4.7
160	9.89	20.0	-2.0	"	5.6E-08	3.3
170	9.89	20.0	-2.0	"	8.9E-08	0.3
180	20.00	20.0	-2.1	-	-	20.0
190	20.00	20.0	-2.1	Zn	1.0E-06	12.8
200	20.00	20.0	-2.1	"	3.0E-06	10.3
201	20.00	20.0	-2.1	"	5.0E-06	-
202	20.00	20.0	-2.1	Cd	1.0e-07	16.9

It can be seen that the rate of crystal growth is strongly dependent on the solution supersaturation. The kinetics of growth for a sparingly soluble salt $M_{v+}A_{v-}$ may be described by equation (2) (Koutsoukos et al 1980):

$$R = ks \left\{ \left[(M^{m+})^{v_+} (A^{a-})^{v_-} \right]^{1/v} - \left(K^{0}_{s, M_{v_+} A_{v_-}} \right)^{1/v} \right\}^{n} \qquad (2)$$

In equation (2), k is the precipitation rate constant, s is proportional to the total number of available active growth sites, $v = v_+ + v_-$ and n is the apparent order of the crystallization reaction. Kinetics analysis of the crystal growth of calcite both in the presence and in the absence of all additives, except for oxalate, gave an apparent order of n=2 as it may be seen in Fig. 1. The order resulting from the slope of the straight line, is typical for a number of sparingly soluble salts. The insensitivity of the rates of precipitation towards changes in the fluid dynamics of the system, point to surface controlled crystallization reaction. The presence of very low concentrations of phosphate, reduced drastically the rate of calcite crystallization. At the experimental conditions, the precipitation of HAP is not likely, although the driving force is negative, but not sufficiently large for the indiction of precipitation of this phase, even if HAP seed crystals were used to seed the solutions. Moreover, spectroscopic and morphological examination of the crystalline precipitates, did not show the formation of any calcium phosphate precipitate. Analysis of the kinetics data according to a Langmuir-type adsorption model (Christoffersen et al, 1983) yielded the straight line shown in Fig. 2. Further investigation of the adsorption of phosphate on calcite substrates, showed that this ion, strongly adsorbs on the mineral. Adsorption isotherms at 0.01M and 0.1 M KNO_3 are presented in Fig. 3. The adsorption was found to be almost irreversible. The significant ionic strength dependence, suggests that the predominant factors are electrostatic in nature. The adsorption of phosphate on the surface of calcite particles strongly affected both the magnitude and the sign of their electrokinetic charge as it may be seen in figure 4. Both Zn^{2+} and Cd^{2+} had a strong inhibitory effect on the seeded growth of calcite, as it is shown in figure 5, where the addition of titrants, reflecting directly the quantity of the solid precipitated, with time are plotted.

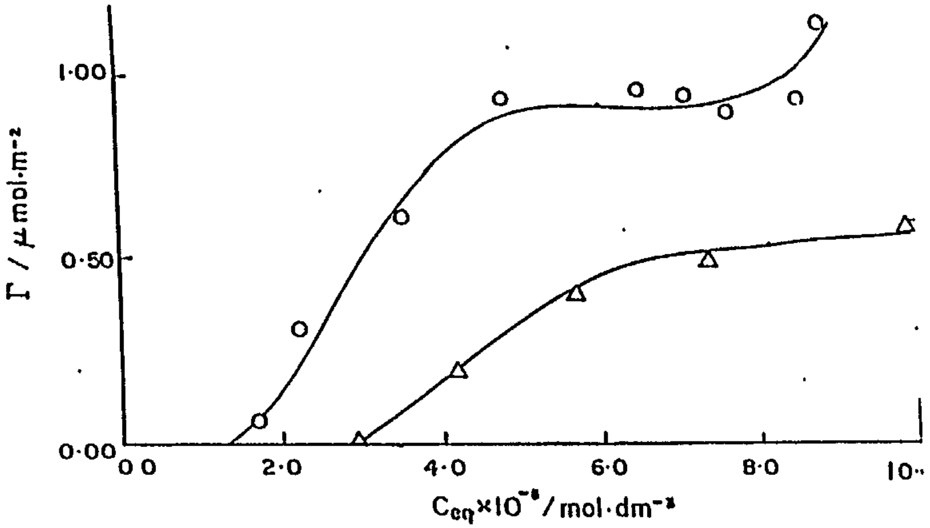

FIG.3. Adsorption isotherms of inorganic phosphate on calcite. (O) 0.01 M KNO_3; (Δ) 0.1 M KNO_3

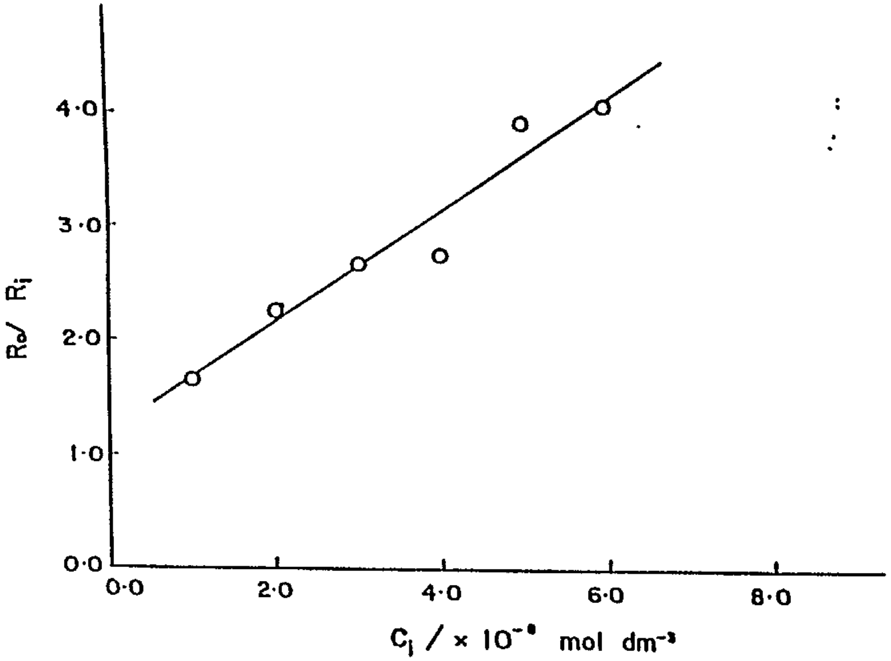

Fig.2. Kinetic model based on Langmuir type adsorption for the growth of calcite on calcite seed crystals in the presence of inorganic orthophosphate. R_o is the crystallization rate in the absence and R_i in the presence of C_i M of additive in the supersaturated solution.

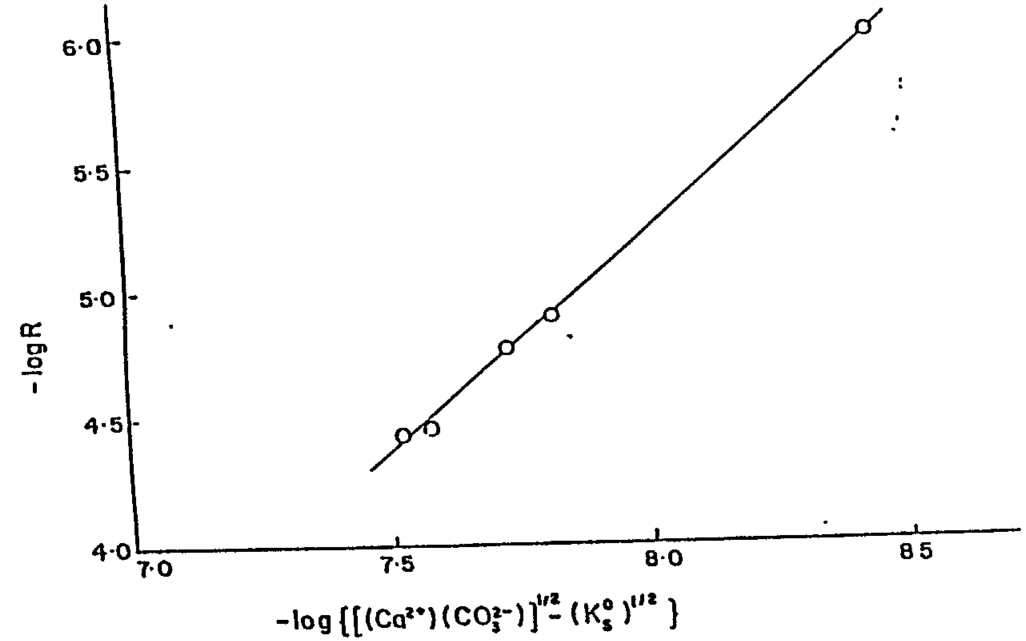

FIG.1. Crystal growth of calcite on calcite seed crystals; 25°C, pH 8.50

Most interesting is the effect of oxalate ions on the crystallization of calcite. As it may be seen in Table 1, the presence of oxalate ions had a strong inhibiting effect on the mineral forming. Kinetics plots however, according to equation (2), yielded an apparent order of $n=4$. Spectroscopic and thermogravimetric analysis of the solid precipitate, showed the existence of calcium carbonate monohydrate, which is apparently stabilized by the presence of oxalate ions in solution. In fig. 6 typical results of the thermogravimetric analysis and differential scanning calorimetry are shown. Powder XRD confirmed the existence of this phase in the precipitates. Further experiments showed that oxalate ions are strongly adsorbed onto calcite surfaces, rendering them negative, in a way similar to that of inorganic orthophosphate. The formation of the unstable calcium carbonate monohydrate, is not possible to be observed by conventional pH-stat techniques as this phase is a sensitive function of the solution supersaturation. Moreover, the initial precipitation rates may be measured with a precision hitherto unattainable.

The conditions of the experiments of HAP crystallization on HAP seed crystals are summarized in Table 2:

TABLE II. Crystallization of HAP on HAP seed crystals at constant supersaturation: pH 7.40, 0.1 M KNO$_3$, 37°

Exp. #	Ca_t /10^{-4} M	P_t /10^{-4}M	ΔG_{HAP} KJ/mole^{-1}	Zn /10^{-8} M	R /10^{-9}mol min^{-1} m^{-2}
114	4.00	2.40	-4.17	-	19.5
120	3.00	1.80	-3.52	-	11.7
121	2.00	1.20	-2.61	-	6.0
125	1.00	1.00	-1.47	-	2.0
134	1.00	0.60	-1.04	-	0.6
140	4.00	2.40	-4.17	1	3.0
141	4.00	2.40	-4.17	5	2.6
142	4.00	2.40	-4.17	10	1.7
143	4.00	2.40	-4.12	50	0.9
144	4.00	2.40	-4.12	70	0.7

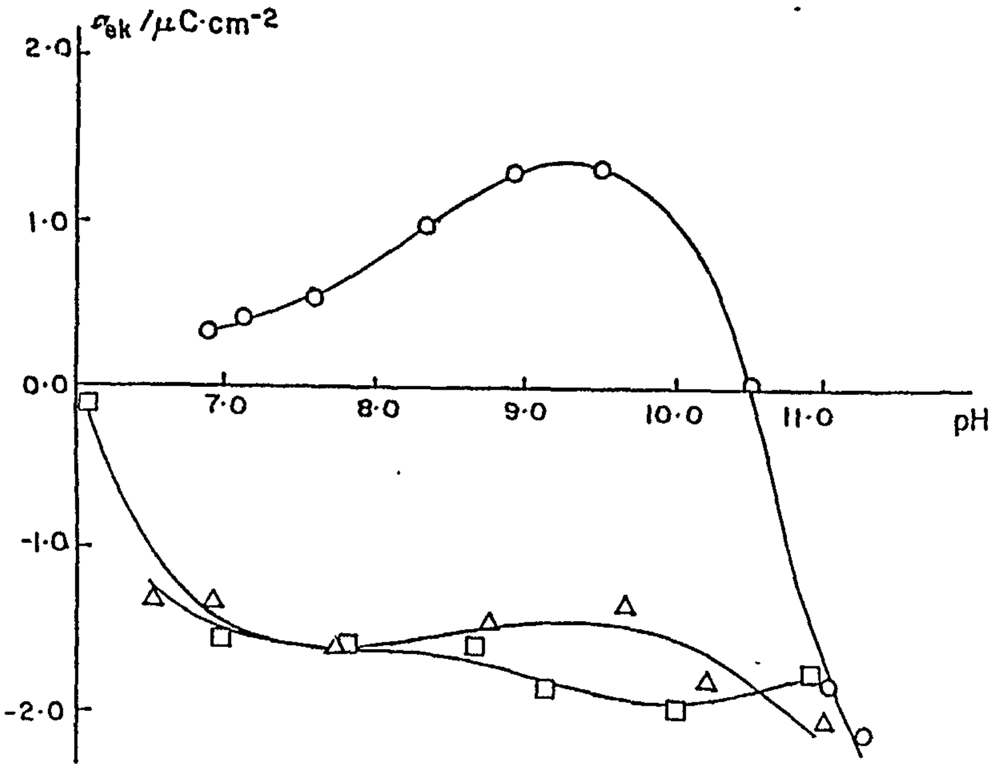

FIG.4. Electrokinetic charge of calcite particles. Effect of the adsorption of phosphate. (○) calcite particles; (△) calcite+0.75 μmole phosphate/m^2; (□) calcite+0.97 μmole phosphate/m^2.

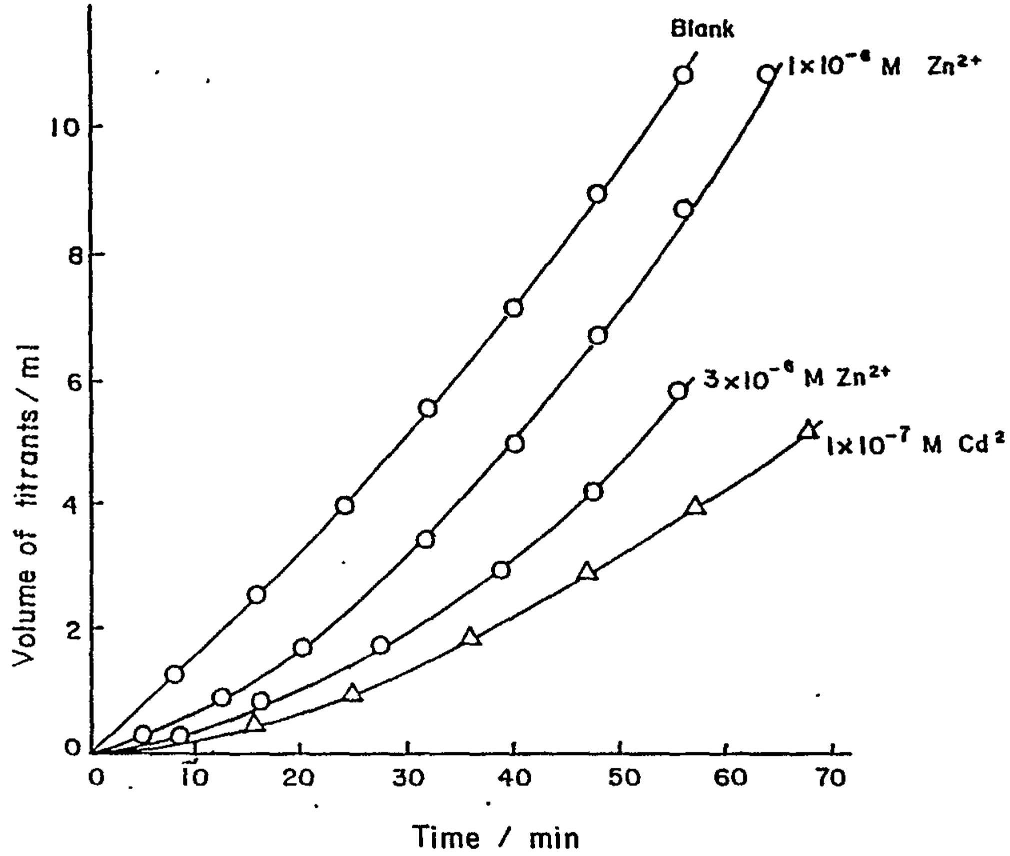

FIG.5. Crystal growth of calcite on calcite seed crystals at constant supersaturation; $Ca_t = C_t = 2.0E\text{-}03$ M. plot of titrants added as a function of time in the presence of (○) Zn^{2+}; (△) Cd^{2+}.

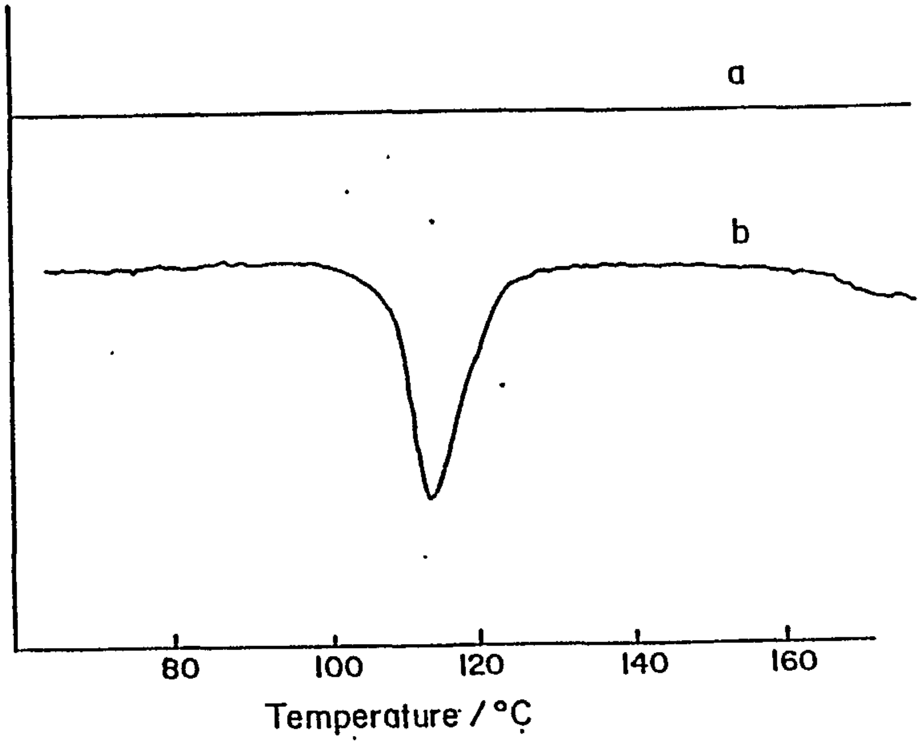

FIG.6. Calcium carbonate monohydrate formed during the crystallization of calcite in the presence of oxalate at sustained supersaturation.

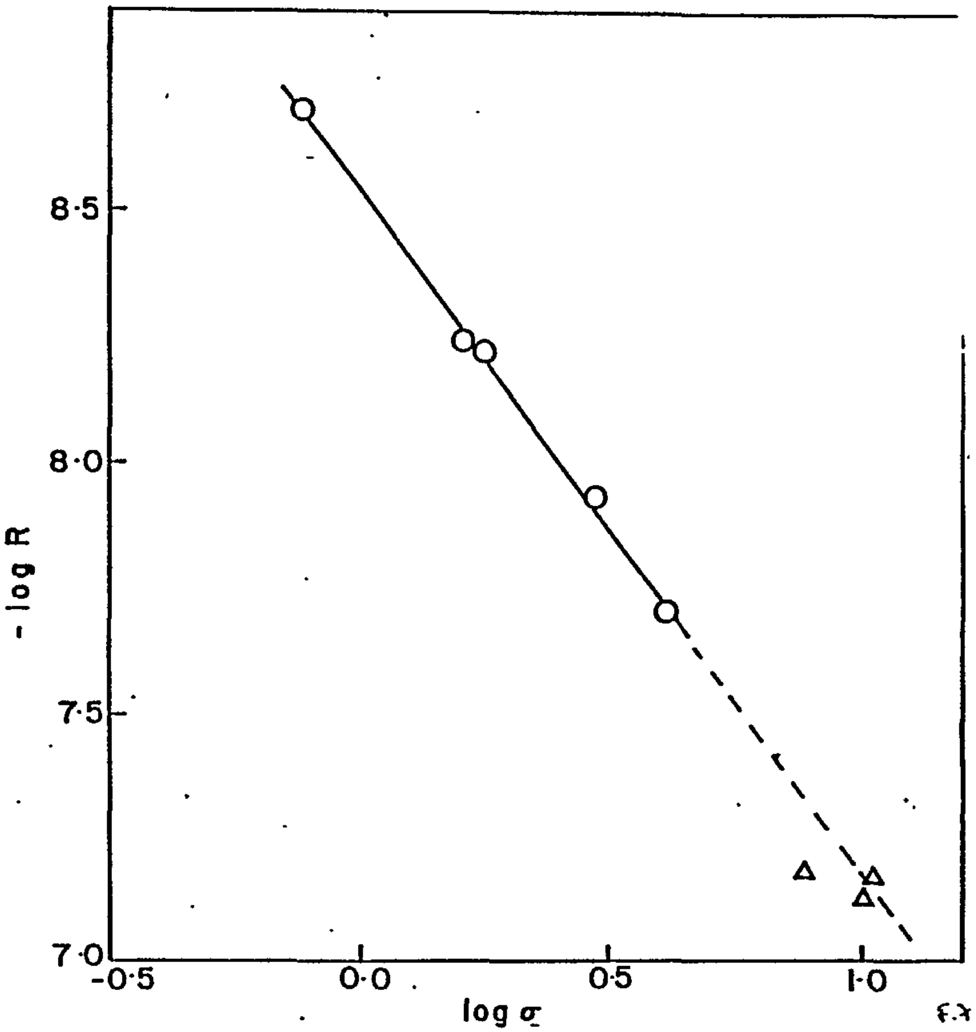

FIG.7. Kinetics of HAP seeded growth; pH 7.40, 37 C (Δ from ref.15)
$\sigma = \Omega - 1$.

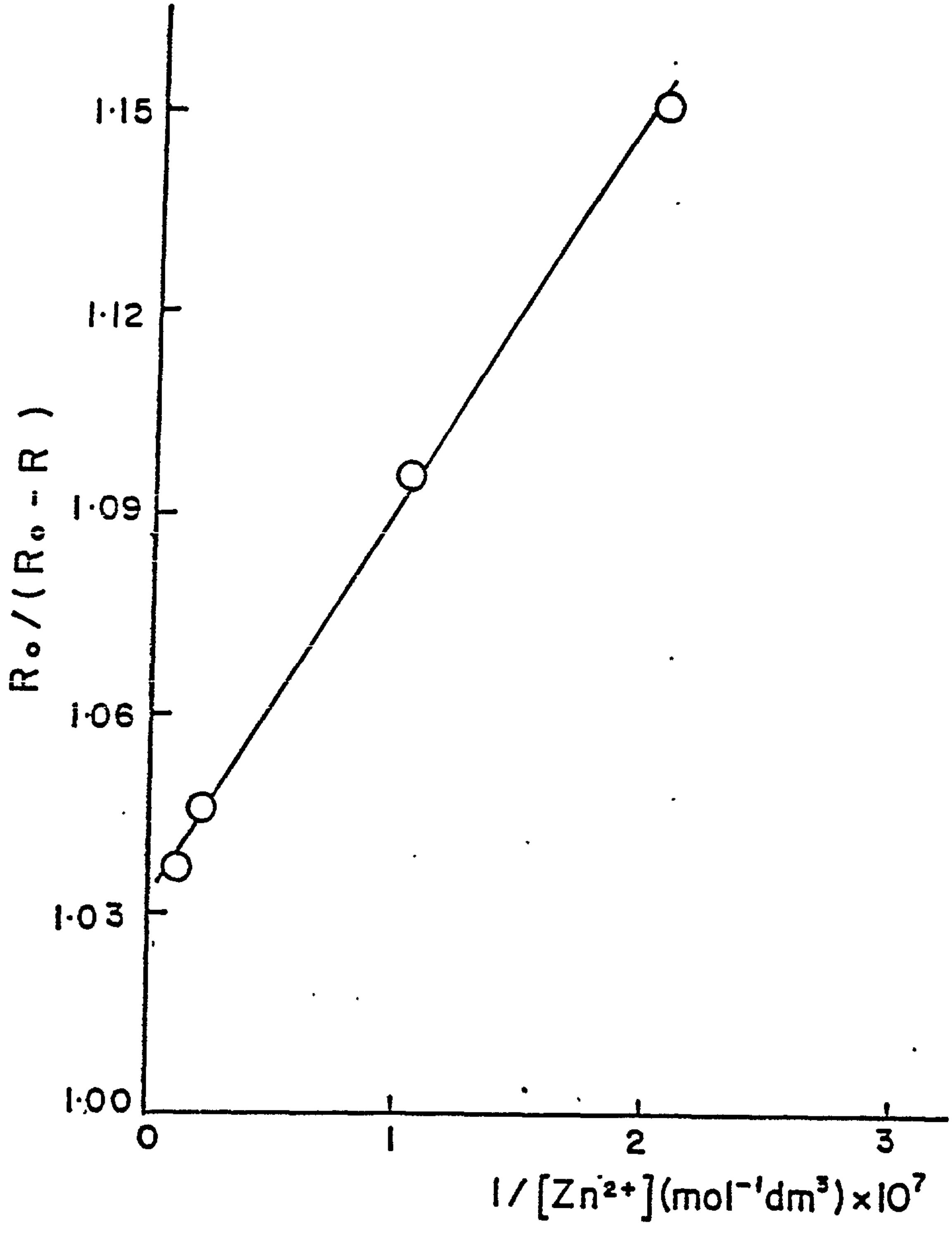

FIG.8. Crystal growth of HAP on HAP seed crystals at constant supersaturation in the presence of Zn^{2+}. Kinetic Langmuir type model.

Kinetics plots according to equation (3) yielded a straight line shown in figure 7. The apparent order of reaction was found to be n = 1.25, i.e. the same as the one reported from experiments at low ionic strength (Koutsoukos et al, 1980). The presence of Zn^{2+} ions in the supersaturated solutions caused a reduction in the rates of HAP crystal growth, probably by blocking the active growth sites on the HAP surface following adsorption. Application of the Langmuir-type kinetic model, gave a satisfactory fit shown in figure 8.

The influence of Mg^{2+} ions on the rate of HAP crystal growth, is strong, not only from the point of view of reduction of the rates, as it may be seen in figure 9, but from the effect on the electrokinetic charge of the HAP particles, which become positively charged, with a charge not varying over the pH range 4.0 - 8.0 (Zawacki et al, 1986).

Conclusion

The interaction of anionic and cationic additives with precipitating particles is a very important process for the transport of these substances. The study and precise assessment of their influence on the kinetics and the nature of the crystalline phases formed is best studied by the constant solution composition approach, which allows for studies at very low levels of foreign substance concentrations to be accurately performed.

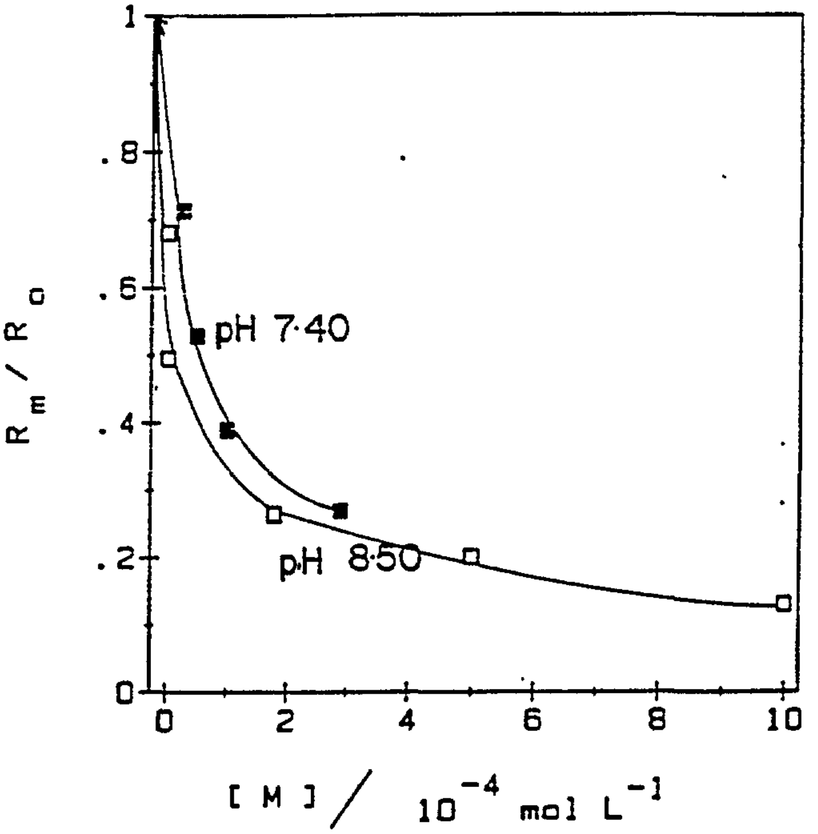

FIG. 9. Crystal growth of HAP on HAP seed crystals in the presence of Mg^{2+} ions.

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USE OF TRACE METAL DISTRIBUTION IN SEDIMENTS TO INVESTIGATE POLLUTANT TRANSPORT; HAIFA BAY, A CASE STUDY.

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ABSTRACT

In order to infer the average transport patterns of trace metal pollutants attached to particles, a study of the spatial distribution of trace metals in surface sediments was carried out. The area chosen for this case study was Haifa Bay. The trace metal content in the 250 um fraction of surface sediments was measured over a period of seven years as part of the MEDPOL/UNEP monitoring program. The measured trace metal content in the sediments is low. Once correction was made for grain size effects using iron as a conservative non-pollutant element, it was possible to show that most of the bay is almost uncontaminated by Cu, Zn, Pb, and Cd except in the southernmost portion of the bay opposite the polluted Kishon river. The whole bay is contaminated with mercury, which is derived from a chlor-alkali plant at the north end of the bay. By using the recognised point sources and the observed spatial distribution of anthropogenic trace metals, it has been possible to infer that the pollutant laden particles supplied to the south of the bay are deposited there, while those supplied to the northern part are transported to some extent to both, along the shoreline in both a north and south direction. The area, though historically one of high sedimentation, has no evidence of significant sedimentation of either fine grained or sandy sediments in the last 10 years.

INTRODUCTION

When one studies the transport of pollutants, including trace metals, which are attached to particles, there are basically two approaches which can be taken. The first is to look at the pollutant laden particles as they are being transported. Obviously this is the most direct procedure and can give valuable information directly on the processes involved. Examples of this approach are provided by Zutic and Legovic, Izdar, and Nyffeler (this volume). One of the problems with this approach is that it is not the normal conditions which move the bulk of the sediments; it is the major storm or flood. Those are exactly the conditions in which we generally avoid sampling. A second approach is to use the sediments as an integrated record of the pollution history of a given area. It is known from a number of studies that trace metals, once released to the environment, tend to attach themselves to fine grained particles and once there, are released only slowly to the biota and to the overlying waters (Salomons and Forstner, 1984; Nolan and Fowler, this volume).

Thus sediments provide an important record of the pollution history of an area (Goldberg et al., 1978, 1979; Turekian et al., 1980.) In order to use this record to investigate the transport of pollutants, one must first identify the major sources of the pollution-laden sediment to a given area. One then looks at its present distribution in the sediment biota. The observed distribution patterns can then be used to infer the transport patterns of the sediment. By using what is known about the possible current regimes in the area, it is possible to use such data to infer information on the most important transport mechanisms. This will be the approach taken in this case study and is similar to that also used by Guerzoni et al. and by Pavoni et al. (this volume).

The trace metals in marine sediments are generally held in the fine grained fraction (Forstner and Wittmann, 1979; Turekian et al., 1980). In any sedimentary regime where there is variable grain size, it is necessary to correct for this effect before it is possible to define the spatial distribution of anthropogenic metals. Salomons and Forstner (1984) describe a number of possible approaches that have been used to correct for this effect. These include extrapolation from grain size distribution, grain size fractionation before analysis, and comparison with a "conservative" element. In this case study, we use the last approach using iron as the element which is assumed to be associated with the fine grained fraction and to be relatively unaffected by anthropogenic inputs.

The example which will be used to illustrate this approach is Haifa Bay. We, at the National Institute of Oceanography in Haifa, have studied trace metals in the sediments of Haifa Bay for 15 years. In this paper we will discuss data which, in the main, has been collected over the last 7 years as part of the MEDPOL/UNEP monitoring programme for the Eastern Mediterranean. These data consist of a complete biannual monitoring from 12 stations in the inner bay for trace metals in the 250 um fraction of the sediment and in selected constituents in the biota. For a more detailed description of the use of this approach, the reader is referred to Hornung et al. (1989).

Materials and Methods

Sampling area: Haifa Bay can be divided into three distinct sedimentological regions (Nir, 1980): a shallow water zone consisting of fine-grained quartz sand sediments which follows the curve of the shore and extends to depths of 10 to 12m; a central region of rocky reefs and ridges extending to a depth of about 25m; and a deeper, smooth bottom region of fine-grained sand and silt. Two rivers flow into Haifa Bay. The main water flow in both the Kishon river and Na'aman rivers is from industrial effluents, flows from water purification plants and the penetration of seawater into the stream at the estuary. The Kishon has a mean monthly flow of 5 x 10^6 m^3 per month in winter and 0.1 x 10^6 m^3 per month in summer (Ministry of Agriculture, 1986). The Na'aman river is even smaller. This case study was carried out entirely in the shallow water zone, 3-12m depth, of the inner Haifa Bay (Fig. 1). In addition, samples were taken from unpolluted areas south of Haifa: at Tel Shikmona, at Atlit and at Zarqa, for control purposes.

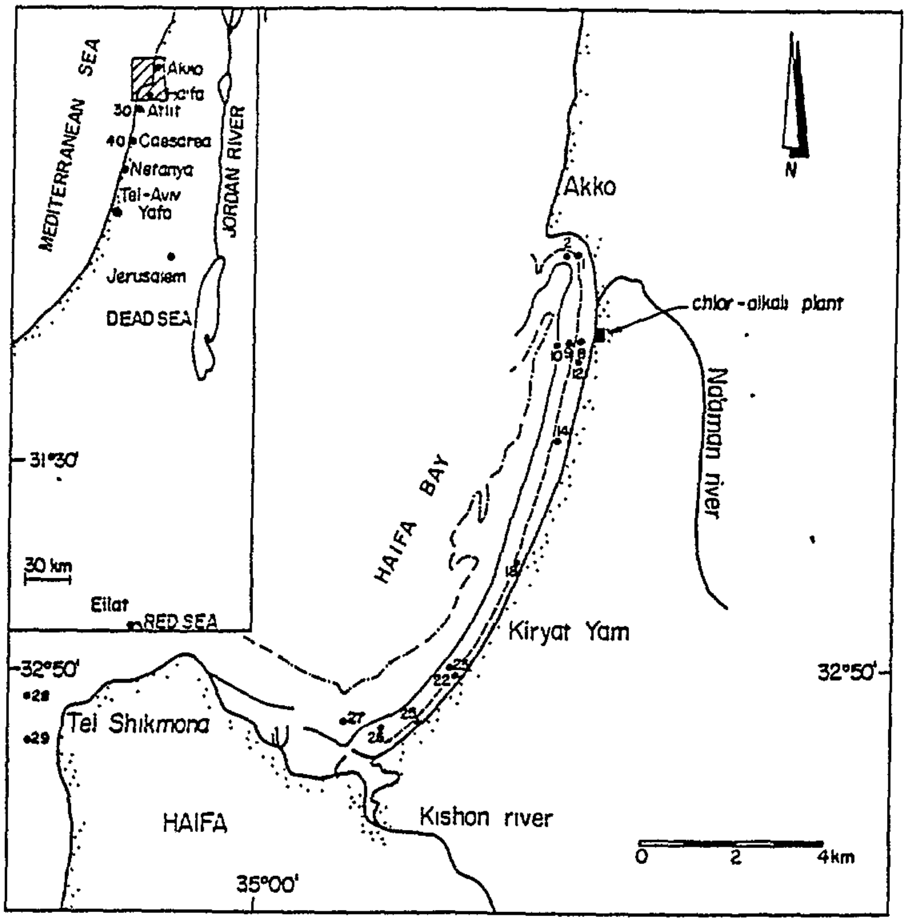


Fig. 1

Map of the study area showing locations of the sampling stations.

Depth contours. ------ 5m —·—·— 15 m
——— 10m

Sampling and sample treatment: The surface sediments were collected by divers. The sample from each site was mixed, lyophilized, and then sieved. The fraction smaller than 250 um was taken for analysis. The sediment cores were collected by diving using 50 cm long perspex tubes and frozen within hours. After slight thawing of the core tubes, the contents were slipped out and sectioned into 2cm depth intervals down the length of the core. The samples were lyophilized and treated like those of the surface sediments. Approximately 1g of dry sediment was digested for 3 hours at 140°C with concentrated nitric acid (65% wt.) in Uniseal, teflon-lined, high pressure decomposition vessels. The digested samples were colled, and transferred to aerating flasks for Hg analysis. For all other metals, digests were diluted to volume with deionized distilled water. Each sample was analyzed at least in duplicate. Accuracy was determined by the analysis of several sediment reference standards in the same analytical run with the samples. The concentration of mercury in sediments was measured by cold vapor atomic absorption spectrophotometry on a Coleman Mercury Analyzer MAS-50A. The concentrations of Cd, Pb, Cu, Zn and Fe were measured using an IL-951 atomic absorption spectrophotometer. The estimated precision based on replicate analysis of total mercury in sediments was 3.5%. For cadmium, the precision was 5.9%, lead 4.5%, copper 2.5% and zinc 2.4% (one standard deviation). For a more detailed description of the sampling method and treatment including the processing of benthic fauna from the same locations, see Hornung et al. (1989).

Results

The trace metals Pb, Cu, Zn and Cd show a highly significant correlation with each other (r > 0.78) for all locations in Haifa Bay excluding Station 27 which is opposite the contaminated Kishon estuary in the southern portion of the bay (Table 1a, Fig. 2). The correlation of Cd vs. Zn is somewhat lower (0.72), principally because the Cd values are so close to the limit of detection of the method used. The trace metals also have a highly significant correlation with iron in the sediments collected in February 1987, the only data set for which iron was measured (Table 1b). The average levels of total trace metals in these sediments (Pb 7-18 ppm, Cu 2-4.5 ppm, Cd 0.09-0.18 ppm and Zn 9-22 ppm) were low (Table 2). by contrast, the trace metal content from Station 27 was considerably higher for Pb, Cu, Zn and Cd (Table 2, Fig. 2).

Table 1a.

Interelement correlations for surface sediments from Haifa Bay sampled at 6 month intervals between July 1984 and February 1987. All stations included except Station 27.

	Hg	Pb	Cu
Pb	0.509		
Cu	0.378	0.857	
Zn	0.321	0.778	0.829

Table 1b.

Interelement correlations for surface sediments from Haifa Bay collected in February 1987. All stations included except Station 27.

	Hg	Pb	Cu	Zn	Cd
Pb	0.553				
Cu	0.413	0.930			
Zn	0.328	0.915	0.912		
Cd	0.033	0.801	0.993	0.991	
Fe	0.364	0.930	0.889	0.946	0.780

TABLE 2. Average (1984-87) total metal content and grain size distribution in surficial sediments from Haifa Bay

Stn.	Metal content						Grain size, µm (%)		
	Hg (ppm)	Pb (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Fe* (%)	125-250	63-125	<63
1	0.61	14.8	4.0	16.8	0.18	0.21	68	17.3	0.6
2	0.78	18.1	4.4	17.3	0.16	0.51	--	--	--
8	0.74	9.2	2.5	11.1	0.14	0.17	76	11.7	0.3
9	0.61	11.1	3.0	14.4	0.15	0.46	72	22.7	0.9
10	0.51	16.1	4.5	21.6	0.18	0.66	62	28.8	4.2
12	0.55	8.6	2.3	10.7	0.11	0.20	76	12.3	0.2
14	0.34	8.8	2.8	12.3	0.17	0.23	80	11.3	0.2
18	0.1	7.0	2.1	11.2	0.14	0.15	76	14.1	0.2
22	0.03	5.8	1.7	8.6	0.13	0.12	78	5.4	0.2
23	0.04	6.8	2.2	10.7	0.16	0.24	78	13.9	0.2
26*	0.06	8.7	3.2	10.8	0.15	0.24	--	--	--
27	0.30	29.9	40.6	108.7	1.25	0.93	42	30.8	11.7
Control station	0.01	4.3	1.3	3.8	0.09	0.11	71	9.9	0.3

*Station 26 and all the iron data are from the sampling in February 1987 only.

The pattern for the mercury content in sediment was different from that of the other trace metals. There is a poor correlation between mercury and the other trace metals for all locations within the bay (Table 1a). The area distribution of mercury content (Fig. 3) was similar to that found in 1980-82 by Hornung et al. (1984), with a higher content of mercury adjacent to the outlet from the chlor-alkali plant in the north of the bay and lower levels being found decreasing to the south. As with the other metals there was a higher level of mercury at station 27 than at locations immediately to the north of it (stations 22 and 23).

Fig. 4 shows the variation of mercury content in the sediment with time at stations 7,8,9, and 11 which represent a transect from the outlet of the chlor-alkali plant to deeper water. There was no significant change in amounts or pattern of the mercury content at these locations during the period sampled (1980-1987). Fig. 5 shows the total mercury content in 3 cores situated at stations closest to the outfall from the chlor alkali plant. At Station 8, closest to the outfall, there was no decrease in mercury content in the length of core measured. At Station 9 there was a zone of constant mercury content from the surface to a depth of 25 cm and a decrease below, while at Station 10, which is the most seaward of the three core stations, there was a decrease in mercury content from the surface.

Discussion

Spatial distribution of uncorrected trace metals in sediment: The concentration of Cu, Pb, Zn, and Cd in the 250 um fraction from all locations in Haifa Bay except station 27 was low (Cu < 4.5 ppm, Pb < 18 ppm, Zn < 22 ppm, and Cd < 0.18 ppm). Since the < 250 um fraction was 80-90% of the total sediment, these values represent closely the overall level of contamination in the area. These concentrations are in the range which is generally considered to be relatively unpolluted (Turekian and Wedepohl, 1961; Forstner and Wittmann, 1979; Katz and Kaplan, 1981; UNEP, 1987) and much lower than values found in many coastal shelf areas such as the New York Bight (Krom et al., 1985), Southern California Bight (Klein and Goldberg, 1970), the Firth of Clyde (Halcrow et al., 1973) or Venice lagoon (Pavoni et al., this volume).

It has generally been found that trace metals from anthropogenic sources are concentrated in the smaller size fractions of the sediment, often the silt-clay fractions (Forstner and Wittmann, 1979; Turekian et al., 1980; Salomons and Forstner, 1984). Without further consideration, it would not be possible to know whether these modest levels of metals in Haifa bay were due to low inputs of contaminant trace metals to the area or relatively high levels of contaminants in the finest fraction which is then diluted by a major input of "clean" fine sand, as is the case, for example, in certain areas of the New York Bight apex (Krom et al., 1985) and the Gulf of Venice (Donazzolo et al., 1981; Pavoni et al., this volume).

Correction of results for grain size effects: One of the ways which have been used to discriminate between these two possibilities is to examine the trace metal concentrations relative to a non-polluting element which is also principally associated with the silt-clay fraction (Forstner and Wittmann, 1979). Of the trace metals measured in this study, iron is the most suitable to be used as a conservative element. Forstner and Wittmann (1979) characterize iron as a mobile element which is subject to diagnetic remobilization. While this is truc in both freshwater and marine deposits, the amount which is remobilized is only a small fraction of the total amount which is present. This is the reason why previous studies on sediment cores from comparable marine environments have shown trace metal enrichment towards the surface while the levels of iron remain essentially constant (Goldberg et al., 1977, 1978; Kitano et al., 1980).

The plot of zinc vs iron (Fig. 2a) is a single straight line with a highly significant correlation which includes data from the control stations as well as from locations throughout the bay except station 27. There is a large range of measured iron (1000 to 7000 ppm). It is not reasonable to suggest that iron and zinc could be delivered to the entire bay in this constant ratio from an anthropogenic source. Thus it can be concluded that zinc (and iron) were derived from a single source that was not contaminated with significant amounts of anthropogenic zinc. Similarly the other trace metals, Pb, Cu and Cd, have highly significant correlations with iron and with zinc (Table 1a and b, Fig. 2b, c and d) and similar conclusions can be drawn. The values of trace metals at stations 1 and 10, close to the mouth of the Na'aman river, had somewhat higher levels of all these metals than the rest of the bay, presumably due to a higher content of the carrier phase; 18 and 32% of the sediment at these stations were less than 125 um compared to 10-20% at most locations in the bay. The control stations, which are situated outside the bay, had less trace metals probably because they contained less fine grained sediment (less than 10% is < 125 um) than elsewhere (Table 2). For six of the seven data sets reported in this study, iron was not measured. For the reasons set out above, it was possible to use zinc as a homologue for iron, and to use the calculated slopes of the metal vs zinc plots to calculate the excess trace metal in each individual sample in the entire data set. The equation used was

$$\mathrm{Mexcess} = M_{\mathrm{meas.}} - (\mathrm{Zn}_{\mathrm{meas.}} \times (M/\mathrm{Zn}))$$

where M/Zn is the best fit slope of the metal vs. zinc plot.

A similar argument for similar reasons was used to justify this same calculation for the data set collected in the New York Bight (Katz and Kaplan, 1981; Krom et al., 1985). Performing such a calculation on the data set collected between 1984-87 showed an average trace metal excess of 0.6 ppm Pb, 0.4 ppm Cu and 0.08 ppm Cd. Even if these values were real and not a result of the natural variabilities and errors inherent in such calculations, the excess of trace metals is very small compared to the levels found in polluted areas, such as Southern California Bight, New York Bight (Krom et al., 1985), and Clyde estuary (Halcrow et al., 1973).

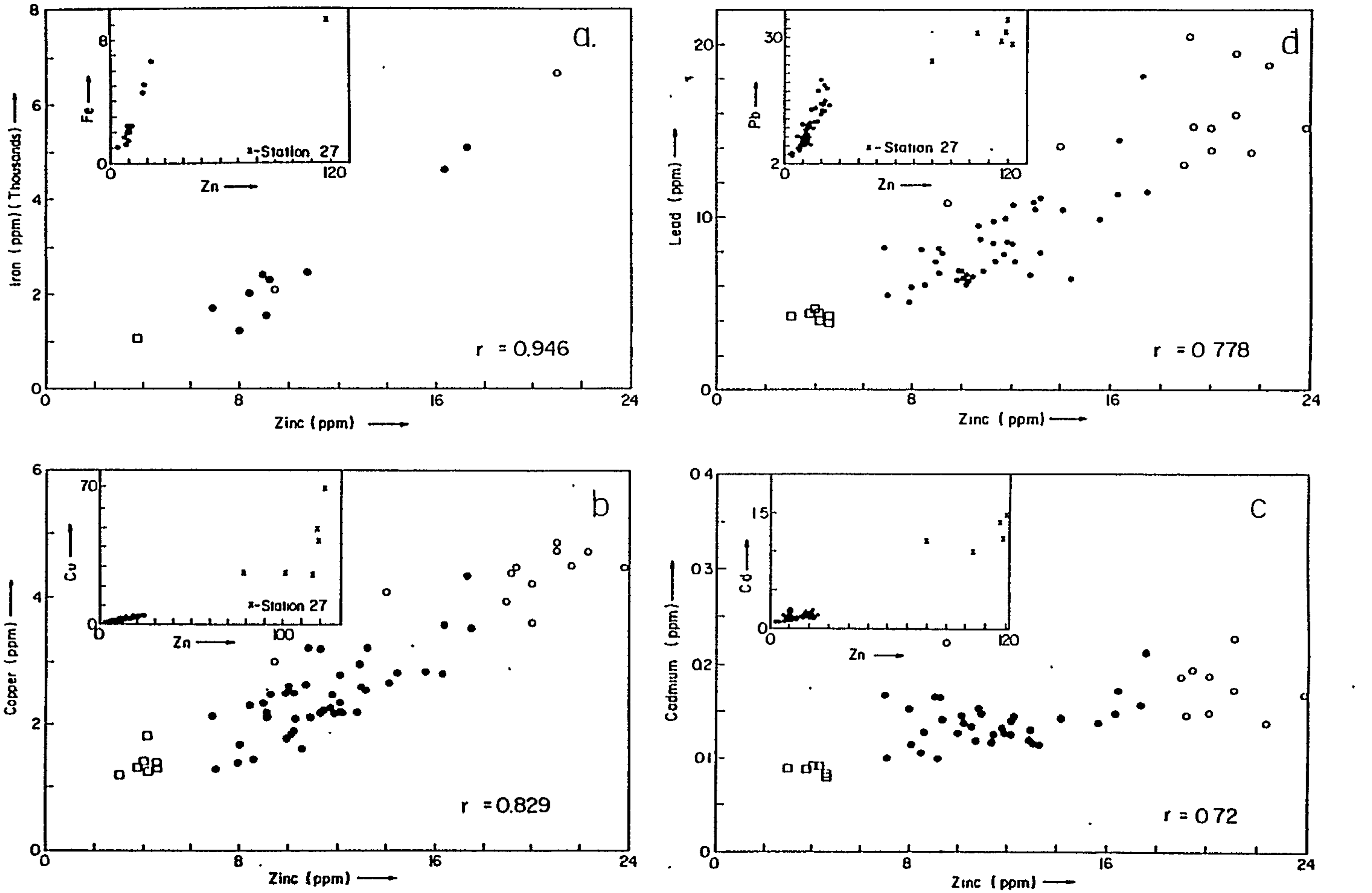


Fig. 2 : Plot of trace metals against zinc in the surficial sediments of all stations in Haifa Bay except station 27.

The samples collected in 1974 (Roth and Hornung, 1977) were not collected from the same locations as those in this study, and this it is not possible to compare the data directly. The data from 1974 show somewhat more variability than that in 1984-1987. However, if one calculates the trace metal excess using the same metal/zinc ratios as 1984-1987, the ratio for uncontaminated sediment in the region, there were also low levels of excess metal in 1974 (Table 3). There is no evidence for a significant change in the contaminant.levels of these trace metals in most of the bay.

Spatial distribution of contaminant trace metals: This pattern in which most of the inner bay shows no evidence of contamination by Cu, Zn, Cd, and Pb is confirmed by the distribution of these metals in Arcularia gibbosula, a deposit feeding gastropod, and in other components of the benthic biota (Hornung et al., 1989).

The exceptions to this pattern are the contamination by mercury which is supplied to the bay principally from a point source near Station 8 (this will be discussed further below), and Station 27. The average level of trace metals was higher at station 27 than elsewhere in the bay. There was also a complete absence of macrobenthos at that location. The values for excess trace metals (Table 3), which were calculated assuming that the Fe content at Station 27 in February 1987 was representative of the iron content in all previous samples at that station, showed that the excess Zn, Cu, Pb and Cd concentrations were higher than any other location in the bay. There was also excess Hg present but not to the same extend as was found adjacent ot the outfall of the chlor-alkali plant (see below). The excess trace metals at station 27 have a similar ratio to that measured in the Kishon river (Kronfeld and Navrot, 1974; Krumgalz and Gorfunkel unpubl. data) and were probably derived from that source. The differences probably are because the sediments in the river are not a complete representation of the metals supplied and because there is some fractionation and redistribution between the river and the bay.

The distribution of mercury in the bay was different from that of the other trace metals. The levels were high close to the outfall from the chlor-alkali plant and decreased with distance from it (Fig. 3). This pattern is similar to that found by Hornung et al. (1984), who concluded that the chlor-alkali plant was the major source of mercury pollution to the bay. It is possible to conclude that the sediments throughout the bay were contaminated with anthropogenic mercury, either by calculating a contamination factor (Hornung et al., 1984) or by expressing the data relative to a conservative element (Hornung et al., 1989). Both procedures work in this case because the amount of background mercury in natural fine grained sediment in this area was very low. The level reached, even at the most contaminated station (1 ug g^{-1}) was moderate compared to those found by previous investigators in areas which have been subject to heavy industrial pollution (Kitamura, 1968; Klein and Goldberg, 1970; Applequist et al., 1972, Halcrow et al., 1973, Pavoni et al., this volume; Guerzoni et al., this volume).

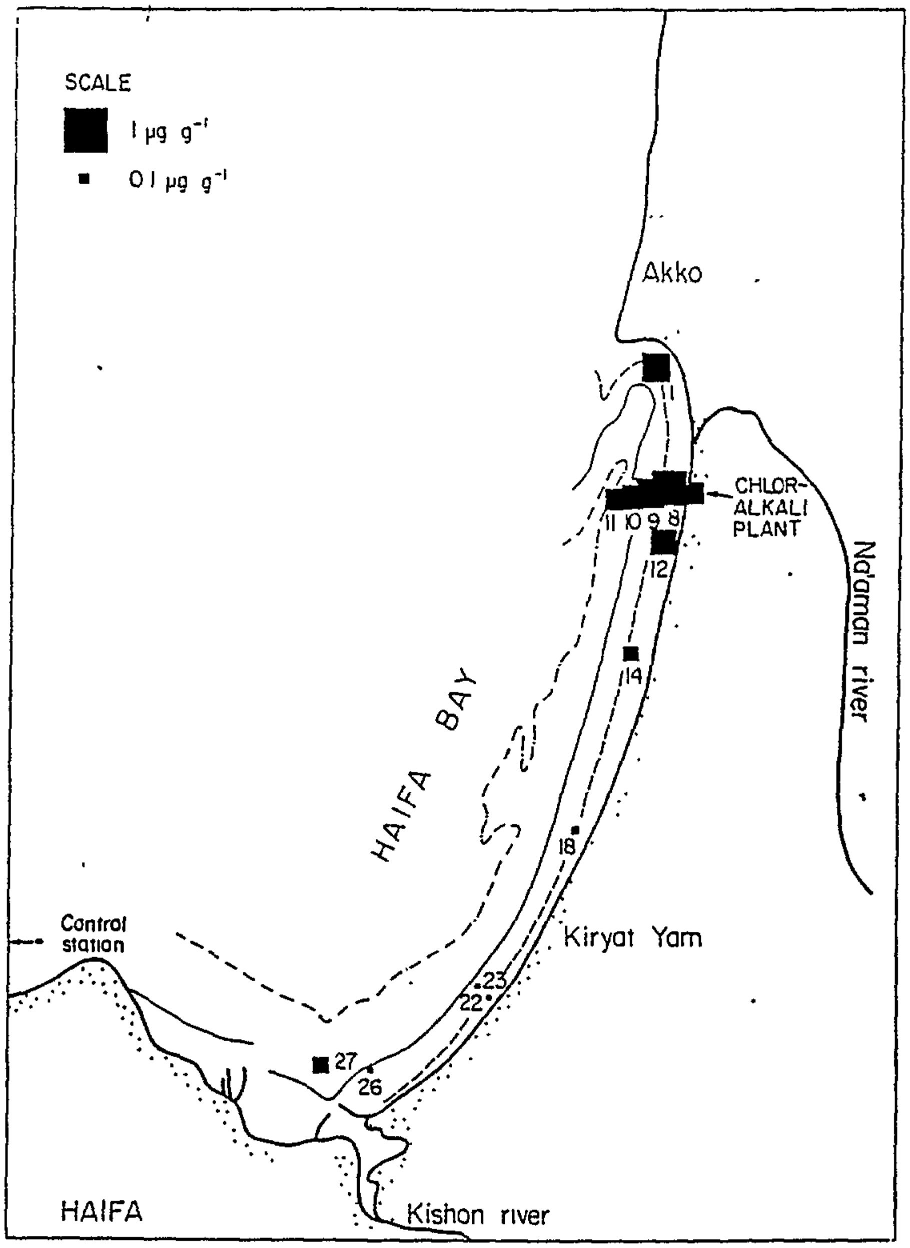


Fig 3 Spatial distribution of total mercury in surface sediments. Data from February 1987

In summary, there is no evidence for elevated levels of Zn, Cd, Cu and Pb for any of the inner bay except for station 27 and to a much lesser extent station 26. At station 27 there are high levels of all metals, which were probably derived from the Kishon river and estuary. Throughout the bay there are elevated levels of mercury in the sediment, and the Source for this is the chlor-alkali plant near the north end of the bay.

The area of Haifa bay is contaminated by trace metals from two point sources, the chlor-alkali plant and the Kishon river. There is no evidence of significant contamination from either non-point sources or from air-borne contaminants, although it would not be possible to differentiate between air-borne or Kishon-borne sources at station 27. This would be the area where one would expect to have the highest proportion of air-borne pollutants (Ganor et al., this volume). This contrasts to an area such as Long Island Sound, where Turekian et al. (1980) estimated that all of the lead and half of the copper and zinc could be explained as being of atmospheric origin. In part this is presumably because the prevailing winds, especially during rainstorms, are from the west, i.e. from the seaward direction.

Inferences concerning the transport of pollutants attached to sediment particles: The fine grained sediments which have been supplied by, or come into contact with, the trace metals from the two land based point sources can be used as tracers to follow the sediment transport pattern in the area, at least over the past 20-30 years. The sediments from these two sources have a clearly different trace metal signature. The sediments which are supplied by, or which have come into contact with, pollutants from the Kishon River are only detected at Station 27 and in the river estuary itself. There is no evidence of sediments from this source being found further north in the bay. No sediment was sampled from stations to the west or south of Station 27. Thus it appears that the southern portion of Haifa Bay is an area of net sedimentation with no transport outward (at least to the north) even of the finest grained sediment. This result is compatible with the predictions made by Goldsmith and Golik (1980), who suggested from wave modelling that Haifa Bay in general and the southern portion in particular should be an area of net sedimentation. This area has at present very little natural input of sediment from the adjacent rivers, almost all of the flow of the Kishon and Na'aman Rivers being intercepted and used for agricultural and other purposes. Almost the entire flow of the Kishon River is from the waste flow from the chemical industry next to the bay. This estuary thus accumulates a foul smelling sludge rich in organic pollution as well as trace metals. This area needs to be dredged every few years to maintain the channels open for shipping. This is the major mechanism for transport of sediment with its associated trace metal pollutants in the southern part of the bay.

For the northern part of the bay, there appears to be some natural sediment transport both to the north and to the south in Haifa Bay. The plume of mercury contamination in the bay also extends to deeper water, 6 and 12m, as well as along the 3m line. For the present, there has not been sufficient sampling to know whether the sediments which have come in contact with the point source of the chlor alkali plant are entirely restricted to the bay, or whether some fraction is present to the north of Acre along the coast or even out on the continental shelf, which is the major area of fine grained sediment in the region (Nir, 1980).

Variation in sediment transport pattern with time: Haifa bay is an area of net sedimentation, with Bronze Age ports and harbours now being found several kilometres inland (Goldsmith, 1983). Indeed, the presence of trace metal contamination in the surface sediments and mercury at depth within sediment cores confirms that within the last 30 years, there has been a net accumulation of particles contaminated with trace metals in the area. If the process of sediment movement and deposition is continuing today as it has in the past, then it would be expected that most of the pollution from the chlor-alkali plant, which was fitted with a sulphide purification plant in 1977, would remain in the bay and be buried by reworked "clean" sediment from the shelf. It is, however, clear that the surface trace metals and mercury profiles obtained in the cores are inconsistent with any continuous sedimentation, since there is not evidence of any input of uncontaminated sediment over the last 7 years (1980-1987).

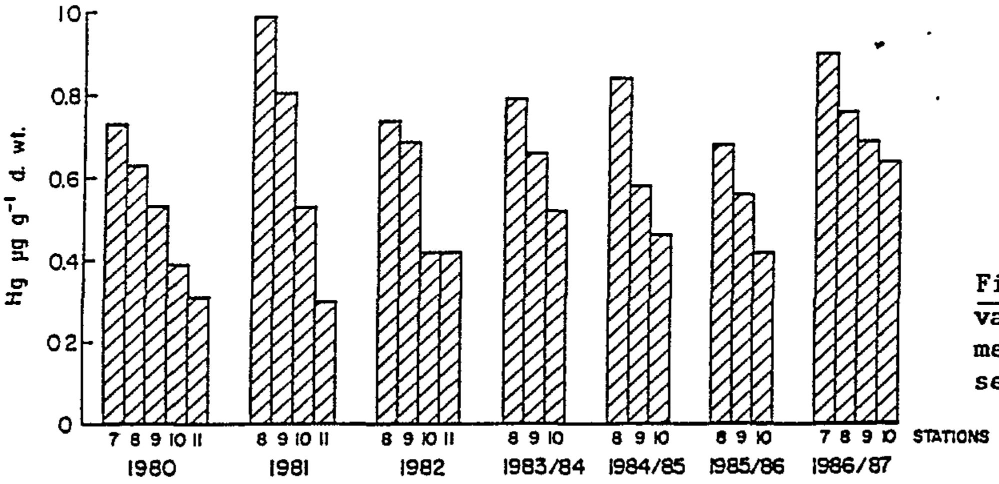
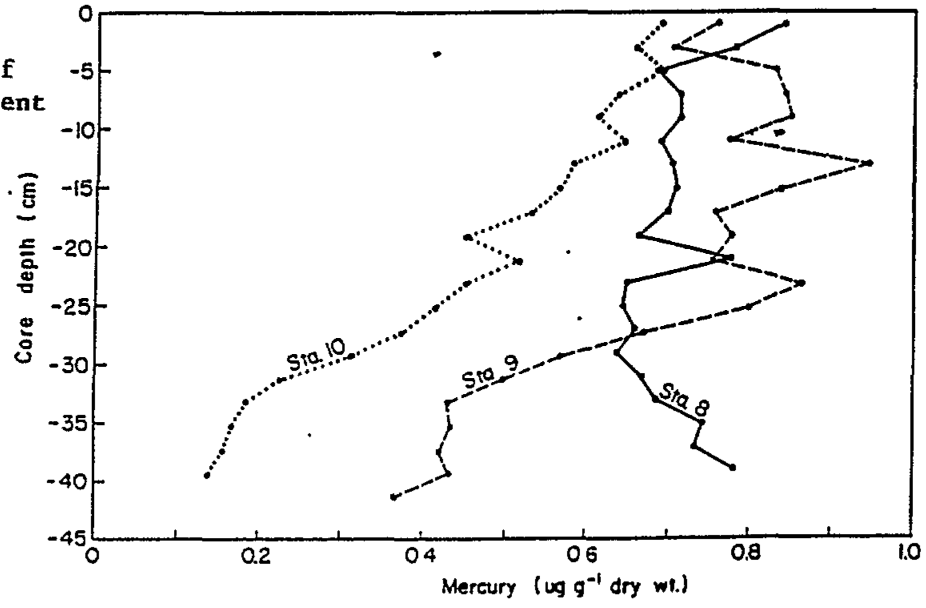


Fig. 4: Mean annual values of total mercury in surface sediments at stations 7–11 during 1980–198

Fig. 5: Distribution of total mercury in sediment cores of Haifa Bay.

(Station 9–300m distance from shore – 3m depth.
Station 9–600m distance from shore –6m depth.
Station 10–900m distance from shore –9m depth).



From an examination of the cores, if the sediment input rate was high relative to the mixing rate, a subsurface mercury maximum would be observed such as has been found in Bacci et al. (1989, as quoted in UNEP, 1987). If the sediment were subject to rapid mixing in addition to high sedimentation, there would be no maximum but the surface content of mercury would decrease systematically with time. The form of the profiles obtained is consistent with sediments where particle mixing is a major process (Benninger et al., 1979).

It is possible that the sedimentation in Haifa Bay is and maybe always has been intermittent in nature. The particular combination of factors, which presumably includes a major storm, has not taken place over the past 10 years. This is compatible with the observations made by Goldsmith (1983) that there has been widespread alteration in the sediment transport pattern along the Israeli coast north of Tel-Aviv over the last 10 years with a small net transport pattern to the south. He suggests this may be due to a slight change in the climatic regime in the area. If this is true, then at some date in the future it is expected that natural processes will result in the contaminated sediment being covered and thus removed from the biosphere. Unfortunately it is not possible to predict when this will occur.

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VERTICAL TRANSPORT OF POLLUTANTS IN THE STRATIFIED ESTUARY: BIOGEOCHEMICAL REACTIONS AT THE HALOCLINE

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ABSTRACT

Measurement of surface-active organic material along the vertical profile of a stratified estuary pointed to the existence of a well defined film at the interface. Visual observations by scuba divers confirmed the discovery. The film is formed at the fresh-water/seawater interface by accumulation and condensation of plankton-derived organic matter under the influence of salinity and shear gradients. It is composed of both dissolved and insoluble, liquid, surface-active material. The film contributes to stability of the fresh water/seawater interface and contains a potential food source for heterotrophic organisms. It affects transformation and fluxes of material on the way to the ocean by acting as an accumulation layer with increased residence time for inorganic and organic particles and solutes. It accumulates trace metals and hydrophobic pollutants. Mineral particles that sink across the film acquire organic coatings and transport the film material to the deeper layer, whereas light organic particles are accumulated on the film. This film is probably present in many estuaries where a salt-wedge exists as well as at other density and shear interfaces.

INTRODUCTION

It is well known that surface active organic matter is accumulated at the air/water (MacIntyre, 1974) and water/particle (Hunter, Liss, 1979) interfaces, thus determining their structure and reactivity. At the estuarine freshwater/seawater interface, through which the flux of organic carbon is estimated to be 10^{14} - 10^{15} g/year (Meybeck, 1982), physical, chemical and biological processes and in particular organic structures are poorly understood.

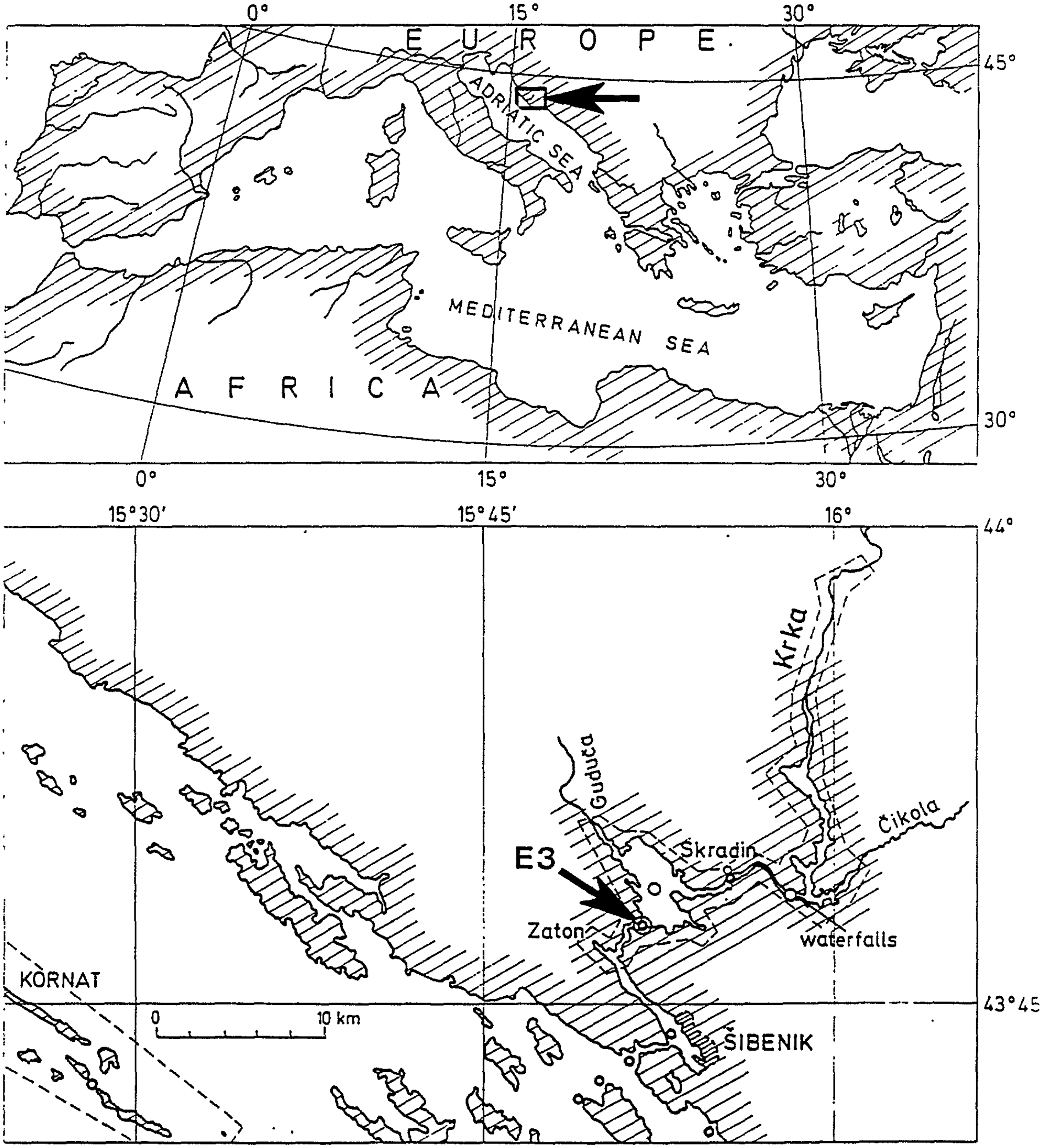
Mediterranean estuaries are predominantly of the salt wedge type. Most intensive investigations of sedimentation dynamics performed in the Golf of Lion indicated formation of mud blankets in the zone of continental influence (Monaco, 1988; Aloisi et al., 1982). Mineralogical and geochemical studies lead to the conclusion that flocculation of fine particles was the main mechanism of pro-delta formation and that organic colloids and organo-mineral aggregates formed at interfaces (haloclines, thermoclines, surface frontal zones) played an important role in the vertical transport of particles and pollutants.

Investigation of the levels and character of organic matter at the salt wedge interface has been undertaken to assess its effect on particle sedimentation. Apart from standard measurement techniques, electrochemical methodology (Zutic et al., 1984); Cosovic et al., 1985; Marty et al., 1988) was used to characterize surface active disolved and dispersed organic matter. Fine vertical profiles along the salt wedge have been studied in two small, model estuaries: of the river Aude, Gulf of Lion (Zutic, et al., 1986;) and of the river Krka, eastern Adriatic coast (Zutic and Legovic, 1987; Zutic et al., 1988). Relevant data obtained for the Krka estuary within the IOC/UNEP MEDPOL - phase II project: Vertical transport of pollutants in a stratified estuary: The importance of organic aggregates, will be reviewed here.

AREA INVESTIGATED AND METHODS

The estuary of the river Krka in the east Adriatic coast of the Mediterranean Sea (Fig. 1) is characterized by a low terrigenous input (e.g., the net average sedimentation rate at a station in the middle reach of the estuary is as low as 0.06 mm/year (Juracic, 1987) due to its Karstic drainage area and a series of magnificant cascades with travertin barriers that proceed the estuary. A high degree of stratification (common salinity gradients of 30°/oo per 20 cm) reduces the river/seawater interface to a well defined, visible region. Water samples around the interface (at 10 to 25 cm intervals) were collected by scuba divers using 1 litre glass or teflon bottles. The diameter of the orifice (2 cm) determined the vertical resolution of sampling. The reported parameters were determined in the same sample. A typical set of measurements at the station in the middle reach of the estuary during the spring cruise of 1985 (5 April) will be presented here. General hydrographic, chemical biological and pollution parameters for the whole estuary in the period 1983-1987 are presented in: Long-term research and monitoring of the pollution of the Adriatic Sea, MEDPOL - Phase II: The Krka estuary and Kornati archipelago, Center for Marine Research, "Ruder Boskovic" Institute, Zagreb, Yugosalvia.

Fig. 1. Krka estuary and measurement stations.



Only temperature was measured in situ, salinity was measured conductimetrically in the samples. Filtration (Whatman GF/F glassfiber filter) and electrochemical surfactant characterization were completed within 12 hours after sampling. Filters were analyzed for suspended matter (SM) (dried at 40°C), particulate organic carbon (POC) and chlorophyll-a and phaeophytin filtration.

Surface active organic matter in the samples was characterized as dissolved or particulate by measuring adsorption at the mercury electrode/seawater interface. The dropping mercury electrode served as a probe and a model hydrophobic surface with controlable surface charge. The parameter measured surfactant activity of a sample, is expressed as surfactant equivalent of synthetic surfactant Triton-X-100 in mg/L. This was measured both directly and in filtered samples. Besides, the electro-chemical response in unfiltered samples, the current-time signal, (Fig. 2) allowed direct counting and characterization of surface-active aggregates (aggregation number 10^9) (Zutic et al., 1984;. Each perturbation on the current-time curve at the dropping mercury electrode corresponds to a single event of coalescence and desintegration of an aggregate into the adsorbed layer. Concentration of the aggregate in a sample is estimated from the coalescence frequency (N/s). The number of coalescences per second is determined from the number of perturbations. Then, using calibration curves obtained by Coulter counting model dispersion (methyl oleate in artificial seawater), the concentration of surface-active aggregates is assessed. Surface coverage of the mercury/seawater interface (corresponding to each coalesced aggregate) can be evaluated from the amplitude of the perturbation, while relaxation time of the coalescence and reorganization event can be measured directly as the time interval of perturbation.

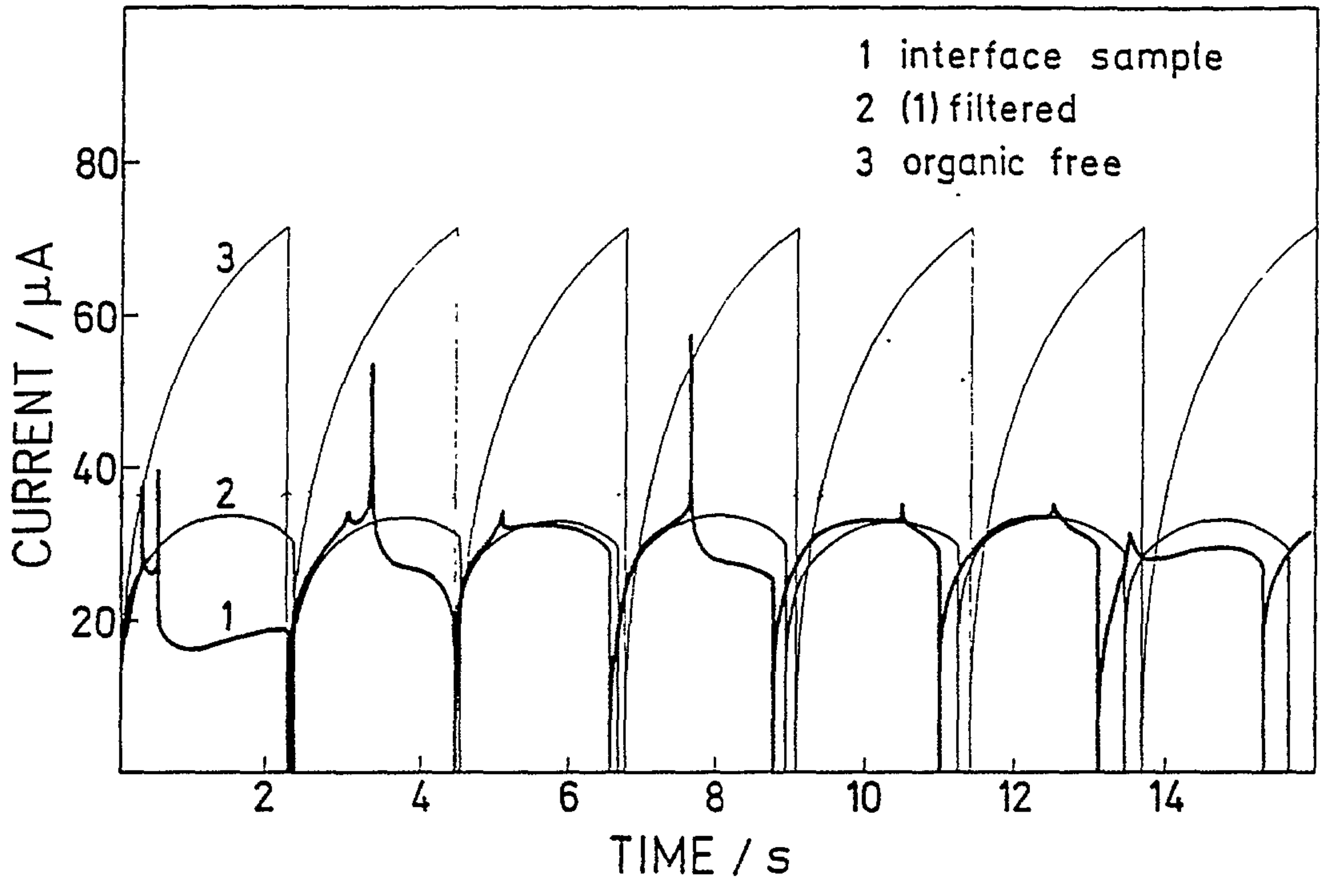
Results

As revealed from the salinity profile (Fig. 3a), the nearly homogeneous surface fresh-water and underlying saline layers are separated by a strong halocline. In the narrow zone around the halocline there is a sharp and sometimes multiple discontinuity in most, particularly surface-active, properties.

In comparison to other estuaries, the content of SM and POC in the Krka Estuary is low. Both SM and POC have maximum values at the interface. The content of SM is 80% higher than in the rest of the water column while POC content is 4 times higher (Fig. 3b).

It is important to note that the chlorophyll-a concentration in the interface sample (Fig. 3c) is lower than in the adjacent fresh-water layer, while concentration of phaeophytin, a chlorophyll degradation product, is 30 times higher.

Fig. 2. Current-time curves at the dropping mercury electrode (2.2 s drop time, potential -0.300 V vs standard calomel electrode) in the fresh interface sample (1). The curve (2) is obtained from filtered samples while curve (3) is obtained ion organic-free seawater. To each sample 10^{-3}M Hg (II) was added prior to measurement.



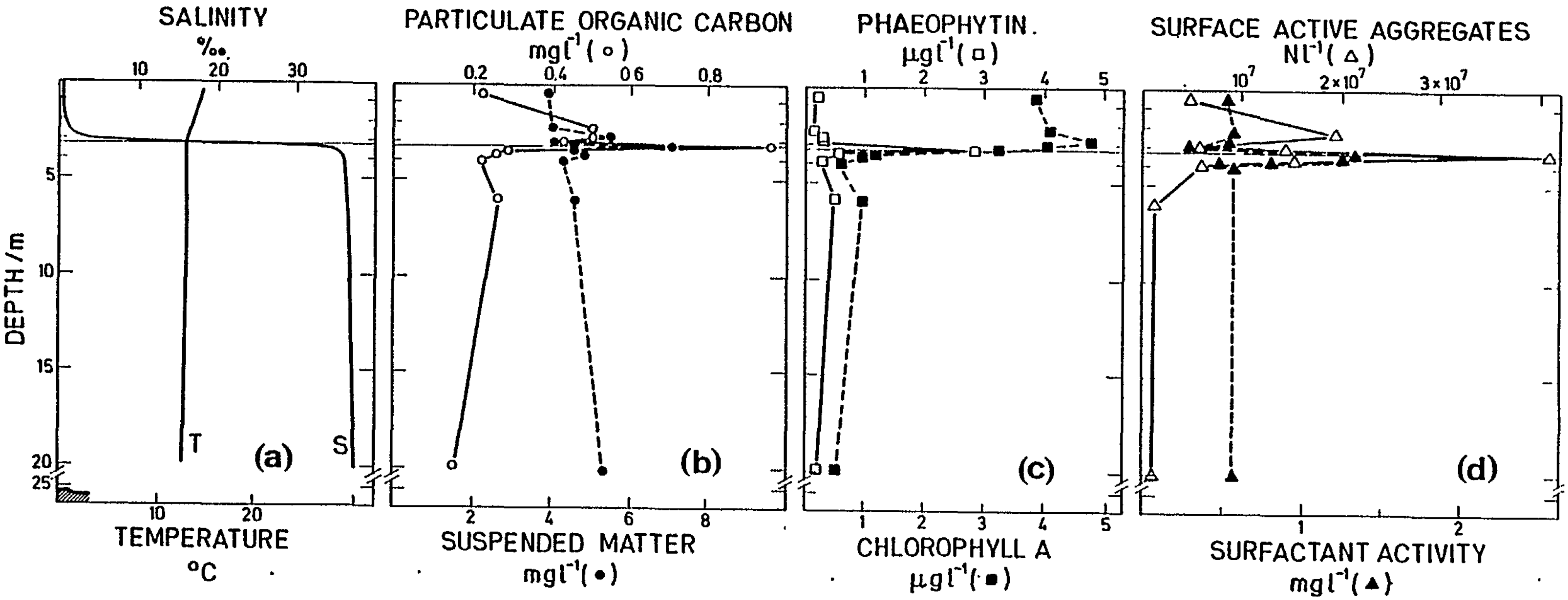


Fig. 3. Typical vertical profiles for salinity and temperature (a); particulate organic carbon and suspended matter (b); phaeophytin and chlorophyll-a (c); surface active aggregates and surfactant activity (d) at the station E3, cca 9 km down-stream of the front (beginning) of salt wedge, April 4, 1985. Surfactant activity of the samples is expressed as surfactant equivalents of Triton-X-100.

When compared to eleven other estuaries studied so far, surfactant activity in the surface layer of the Krka estuary is low. Surface-active organic material is predominantly present in soluble form with little presence of surface active aggregates (Fig. 3d). In the seawater layer below the halocline, surfactant activity is slightly higher than in the upper fresh-water layer. The electrochemical signal reveals predominantly soluble surfactants and even fewer aggregates than in the fresh-water layer.

In the sample taken at the visible interface, total surfactant activity is increased 3 times and concentration of surface active aggregates 10 times (Fig. 3d) with respect to the river-water or seawater bulk layers. Perturbations in the electrochemical response (Fig. 2) indicate a stochastic process, which corresponds to random collisions of surface active aggregates of variable size with the mercury electrode. The process takes place in the broad range of surface charges (+15 to -8 μC/cm^2). The relaxation time in the range 50-200 ms is comparable to heterodispersions of oleic acid or methyl oleate in seawater. However, a phase transition to a more ordered solid structure, as in the case of oleic films (Zutic, Plese, 1984) was not detected in natural samples. The layer formed shows characteristics of an insoluble, expanding liquid film and the aggregates could be visualised as small (0.5-10 m diameter) oily droplets. The electrochemical characterization of this material reveals close resemblence to the insoluble surface active complex (glycopeptide-acyl lipid) identified recently at other natural interfaces such as microbubbles (D'Arrigo, 1984) and sea-surface microlayer (Barger, and Means, 1985). It has been suggested that the material has been derived from the chlorophyll-protein complex present in terrestrial and aquatic plants.

In the layers adjacent to the interfaces one typically finds minima in the concentration of aggregates, total surfactant activity and POC, indicating a depletion due to accumulation and transformation in the interfacial layer.

Discussion

Vertical distributions, as represented in Fig. 3a-d, are typically obtained by analysing fresh samples taken along the salt wedge under variable meteorological conditions, biological activity, river flow rates and time within the tidal cycle. The same phenomenon was also observed in other salt wedge estuaries in the Mediterranean (Zutic *et al.*, 1986.

Measurement of vertical profiles of total mercury concentration in water samples showed a similar maximum as organic aggregates (Fig. 4).

Table 1.: Comparison of surface excess values for the parameters of organic matter at the fresh-water/seawater interface (data from Fig. 3). Data on mercury concentration are from Martincic, Kwokal and Branica, 1986; and Kniewald, Kwokal and Branica, 1987.

Parameter	Surface excess	Equivalent monolayers
Surfactant activity	20 mg/m^2	25
POC	10 mg/m^2	12
Phaeophytin	0.56 mg/m^2	0.5
Surface active aggregates	6 x 10^8/m^2	2
Total mercury	100 ng/m^2	

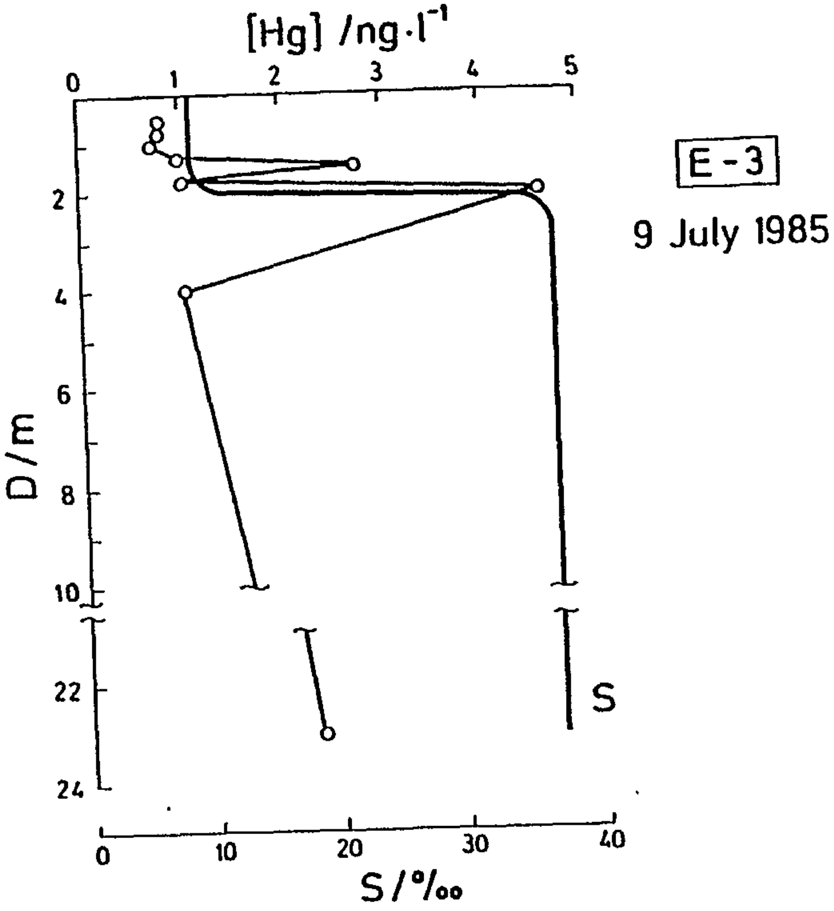


Fig. 4. Concentration of total mercury in water samples taken along the vertical profile at the Station E3, 9 July 1985 (analytical data of Martincic, Kwokal and Branica, 1986; Kniewald, Kwokal and Branica, 1987).

For comparison with the adjacent layers we evaluate the concentrations measured in the interface sample in terms of "surface excess" (analogous to the surface excess in the case of air/seawater interface (Hunter and Liss, 1981) as a measure of surface concentration per unit area of the interface.

The material, both dissolved and particulate is sufficient in amount to form several condensed monomolecular layers at the interface. Comparison of an estuarine surface microlayer sample and interface samples is given in Table 2.

The insoluble surface-active material is formed by condensation of excretion and decomposition products of phytoplankton from the fresh-water layer accumulated by differential settling at the density and shear interface where residence time of solutes and particles is longer than in the rest of the water column. The process consists of salting-out and supramolecular organization by hydrogen bonding and hydrophobic attraction which is known to take place among surfactant molecules, micelles, non-living aggregates as well as plant cell membranes and organelles when the ionic strength in an aqueous medium is approaching 0.1 M (Tanford, 1981; Staeshelin and Arntzen, 1978).

The material that appears as an unstable heterodispersion in the water sample forms a condensed film at the estuarine interface. The vertical position of the film is precisely at the depth where density of aqueous medium equals that of the organic material More soluble surface-active molecules are attached to the insoluble film and extend deeper into aqueous phases from both sides.

The film was visible during regular observations by scuba divers. When observed from the underlying saline and more transparent layer, under a high angle, it appears as a "silvery-grayish sheen", or as a "silky ceiling to the saline layer". Exactly the same appearance was reported in literature (Mueller, et al., 1962) for a bimolecular lipid membrane reconstituted in 0.1 M saline aqueous solution from solubilized membrane lipids. The membrane was stable in the absence of all other cell components and it showed some cellular functions, such as electrical excitation that was significantly affected by adsorption of surfactants from the aqueous phase. (This membrane, however, was only 10 mm^2 in surface area, suspended on a metal ring.).

The estuarine "membrane" appears as a smooth surface, very slowly moving downstream, while on other occasions slow waves might appear with amplitude of 1-2 cm and length about 10 cm.

When a lipophyllic dye, Sudan III, was injected into the saline layer it did not cross the visible interface, but spread laterally along it forming a visible yellowish film. The film gradually lost its colour in a period of 10 to 20 seconds.

TABLE 2. Comparison of parameters of surface active organic matter in the sea surface microlayer and interface layer samples at Station E-3 (Žutić et al., 1988).

KRKA ESTUARY, STATION E-3

DATE	SAMPLE	S	SURFACE ACTIVE ORGANIC MATTER					
			Dissolved			Dispersed		
		‰	Surfactant activity mg l^{-1}	Surface excess mg m^{-2}	Equivalent monolayers	Surface active aggregates N l^{-1}	Surface excess N m^{-2}	Equivalent monolayers
18 May 1986	Surface* microlayer	2.8	3.1	0.28	0.35	1.1×10^7	0.09×10^7	0.003
	0.5 m	3.8	1.7			0.68×10^7		
	Interface** d = 2.25 m	21.9	1.7	16.4	20.5	3.3×10^7	54×10^7	1.8
	d = 2.0 m	5.0	0.88			0.6×10^7		
20 May 1987	Interface d = 3.3 m	23.6	2.0	10	12.5	8.2×10^7	60×10^7	2
	d = 3.0 m	4.8	1.5			5.2×10^7		
4 May 1985	Interface d = 3.25	27.9	1.3	20	25	3.4×10^7	60×10^7	2
	d = 3.0	5.7	0.3			0.4×10^7		

* sampling depths 0.02 cm
** sampling depths 2 cm

There are several implications of the organic films on the estuarine processes:

a) we expect that the film stabilizes the density gradient by diminishing vertical turbulent mixing of freshwater and saline water; it damps the internal waves.

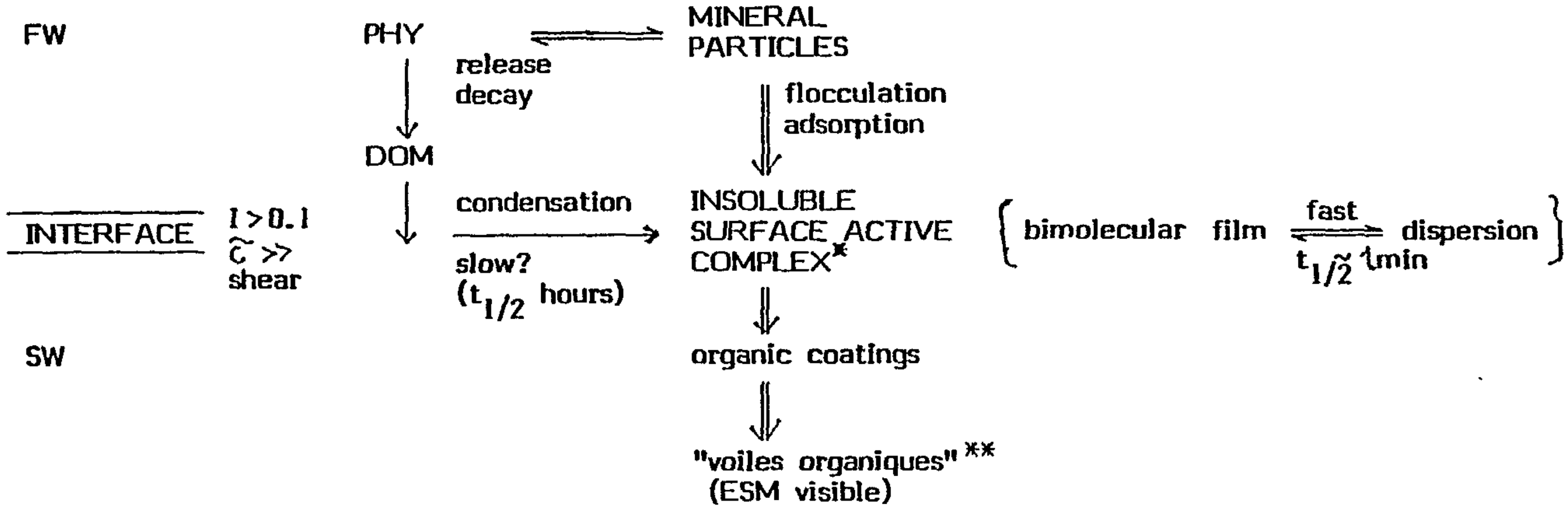
b) the film should affect all other energy and mass transport processes between overlaying fresh-water and underlaying seawater.

c) organic matter retained at the interface and the film itself represent the food source for heterotrophic organisms; thus the interface is the site of intensive biological activity, but at the same time a scavenger for pollutants ranging from mercury to chlorinated hydrocarbons.

d) all of the suspended material, riverborne and atmospheric, entering the estuary passes through the interface. Since the residence time of the material is longer than elsewhere in the water column (Sakamoto, 1972) particles and solutes have sufficient time to interact with the organic layer. The interactions such as flocculation, complexation and sorption have half-times in the order of minutes. Mineral particles that sink across the interface acquire organic coatings (Zutic, et al., 1986; Zutic and Tomaic, 1988) and transport the film material to the deeper layer (schematically presented in Fig. 5) whereas light organic particles are accumulated on the film.

Stable biogenic surface active films and a series of biogeochemically important reactions (Mantoura, 1987) identified at the haloclines of Mediterranean stratified estuaries indicate that haloclines are an important site for particle and contaminant accumulation, transformation and transport in the estuarine and coastal zones of the Mediterranean.

Fig. 5. Scheme of surface active organic matter and particle interaction at the halocline.



* glucopeptide-acyl lipid (D'Arrigo, 1984)

**Aloisi et al., 1979

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THE USE OF ARTIFICIAL RADIOACTIVE TRACERS FOR MEASURING DILUTION OF SOLID POLLUTANT PARTICULATES RELEASED IN THE SEA

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ABSTRACT

Natural solid matters in suspension in sewage are labelled by an artificial radioactive tracer. They are introduced into the sewage treatment plant and afterwards into the sea through a release pipeline.

The quantitative measurements of the radioactive particles concentration distribution are used to determine dilution and sedimentation of solid pollutants released in the sea.

INTRODUCTION

A large number of big towns built on Mediterranean coasts release directly their sewage in the sea water or after processing in a sewage treatment plant. But, however the process employed, at the present time it is in fact known that many pollutants such as heavy metals, organic and biological compounds are associated to the solid matter grains and involve three physical processes: advection, dispersion and sedimentation. So, before discussing the environment's capacity to receive a contaminant's discharge one must answer to the question: what is the behaviour of very fine grains in the area close to the release where fresh water containing suspended organic matters meets denser and colder salt water ? This problem is still more sophisticated if the ambient temperature of the sea water column presents a thermal boundary at a given depth.

These studies require field measurements and for this, it is necessary to use artificial radioactive tracers.

PRINCIPLE OF THE METHOD

A small quantity of labelled particles, representative of the natural matter, is introduced into the sewage treatment plant and afterwards into the sea through a release pipeline. The quantitative description of the movement of the radioactive tracer in the sea is used to determine solid transport versus space, depth, time and situation on the sea bottom.

Labelling of the natural particles

The solid particles (natural matter mainly organic) on suspension in the effluents are labelled by a radioactive gamma emitting isotope such a gold-198 which has a half life of 2.7 days. The chemical process involved is a redox reaction: the gold initially in solution in anionic form upon contact with the solid matter, spontaneously transforms itself into metallic gold (BOUGAULT 1970). So the labelling is irreversible in natural conditions. The efficiency of this process is in the range between 95 and 99%, if the grain sizes are smaller than 40 um and if the gold concentration is smaller than 200 mg of metal per kg of dry solid. A total activity of 3 x 10^{11} Bq (9 Ci) is needed, mixed with 100 g of mud in suspension into a large volume of effluent. The solid concentration is set equal to natural effluent's one, i.e., between 50 to 500 mg/l.

In these chemical and physical conditions the radioisotope is linked to the solid particles. For example, (Fig. 1), in quiet and fresh water, the percentage of radioactivity decreases when the solid mass in suspension decreases by siltation: it is proven that the radioactive gold is on the solid particles and flock formes by floculation process. In quiet fresh water settling velocities are in range between 0,1 and 2 mm/s.

During one field experiment the tracer is introduced, (Fig. 2), in the effluent flow during about one and a half hours.

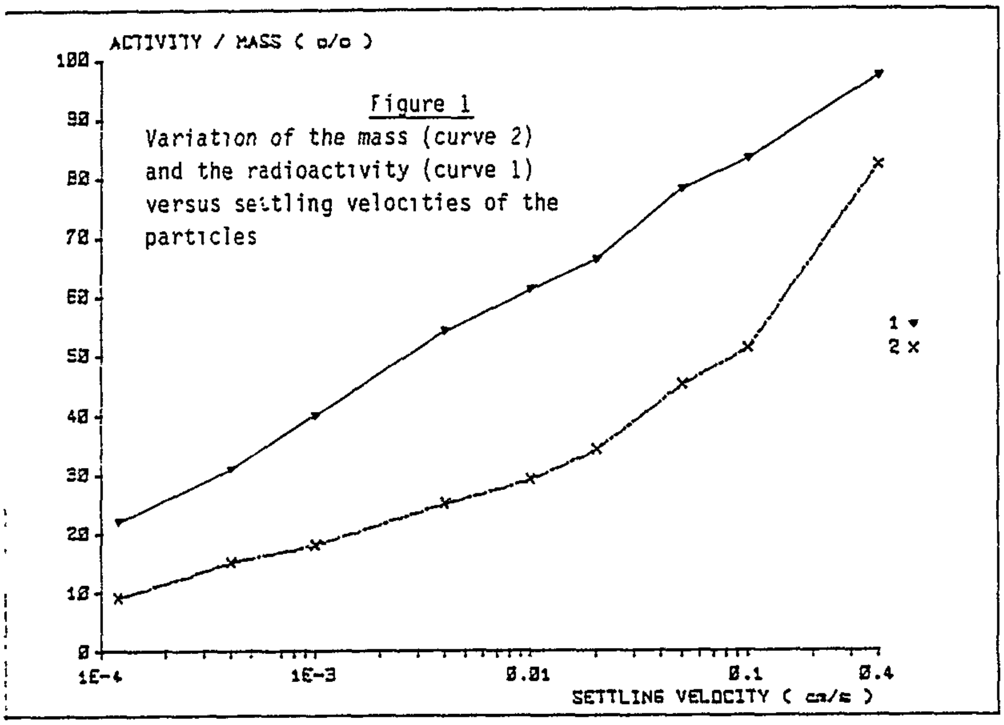
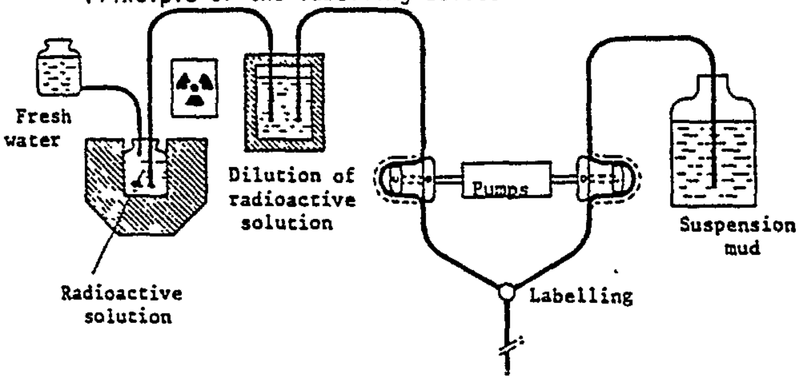


Figure 1
Variation of the mass (curve 2) and the radioactivity (curve 1) versus settling velocities of the particles

Figure 2
Principle of the labelling device



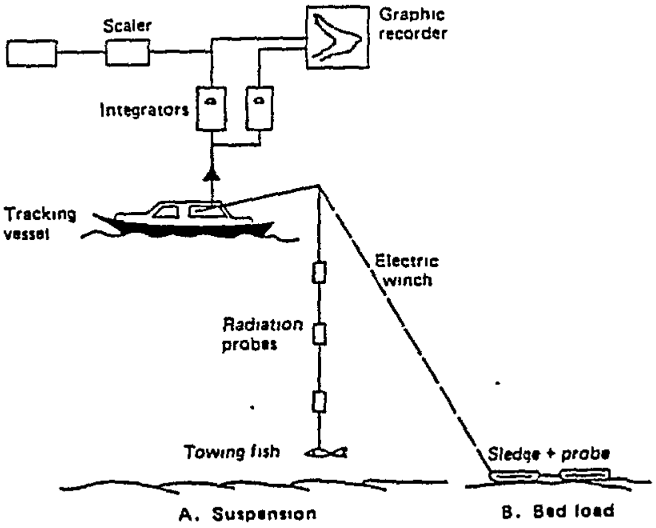
Field tracer measurements

A fixed station is set in the vertical plume formed by the effluents above the pipeline exhaust. Five radioactivity detectors are fixed at different depths: -40, -30, -20, -10 and -1 meters.

Two mobile vessels perform longitudinal and transversal detections in the horizontal plume. Each boat is equiped with five detection probes located at different depths, (Fig. 3). All detectors are equiped with depth sensors. The radioactive tracer in suspension is followed at different depths during three or four hours, along trajectories of some kilometers length.

One day after the radioactive release one proceeds to a bottom detection in order to determine the siltation rate. A location device allows regular plots, each minute. The geographical positions are immediately plotted on a large scale chart.

The radioactive tracer experiment is completed by intensive hydraulic measurements such as currents, waves and wind directions and temperature of water column. Many samples are taken too, at different depths in the radioactive cloud, in order to determine chemical and biological evolution at different levels of effluent dilution versus space and time. In these conditions radioactive information is a guide to picking up representative samples.



Detection equipment of tracking vessels.

Figure 3

EXAMPLE OF FIELD RESULTS

Three field experiments were realized, along the Mediterranean French coast. The sketch, (Fig. 4), sums up experimental conditions.

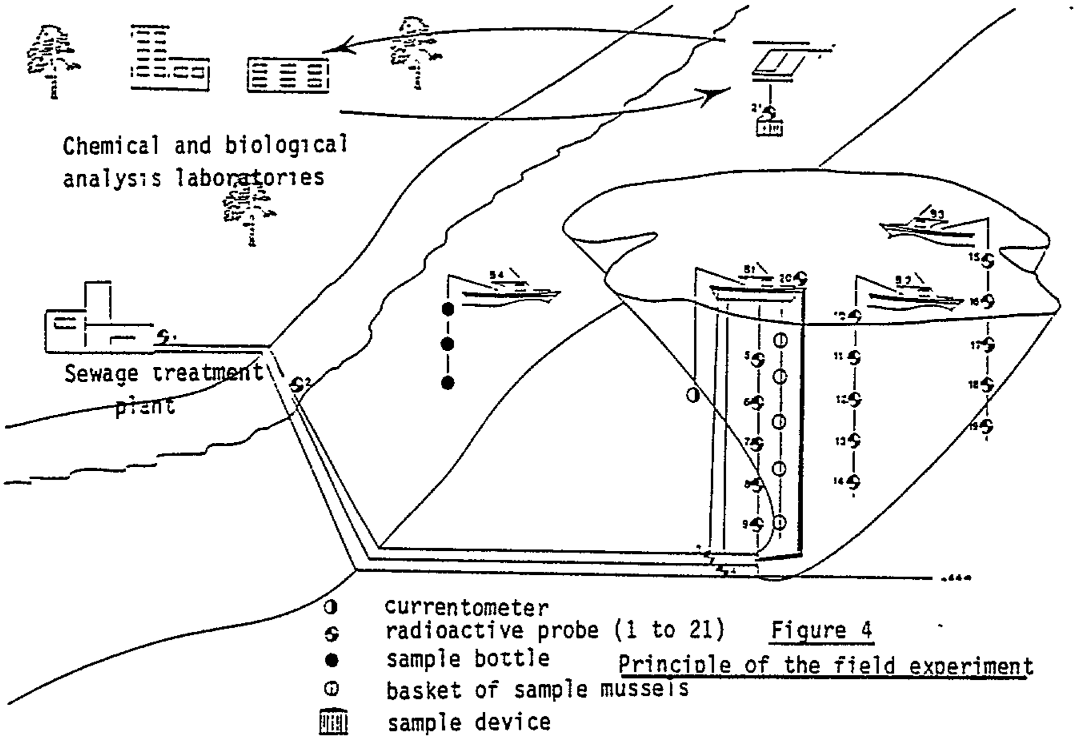


Figure 4

Principle of the field experiment

Conditions

The release area is 1800m from the beach. At such a distance the water depth is 44m. The effluent discharge rate is included between 600 and 800 m^3/h. The turbidity is less than 500 g/m^3. The sewage temperature is about 22°C whereas the sea water temperature changes: from about 19°C on the surface level to a 13°C close to the bottom. Generally the thermal boundary takes place at about -15 m, but this position depends of the season and of the wind power.

Some physical results

Ascensional velocities: Sludge particles, in fresh water, are able to reach water surface with an ascensional velocity of 0,8 m/s. But, in front of the thermal boundary, this velocity is smaller: 0,3 or 0,2 m/s.

Plume forms: Between -44 m and about -20 m the horizontal dimensions of the plume are small. But close to the water surface the cloud becomes broader and broader, in these conditions, the dilution increases with the dimensions. Spot directions are given by the wind directions. The width of the cloud is small whereas its length gradually increases as a function of the wind intensity. However the main directions of the advection are not the same at any water depth so in these conditions it is very difficult to take representative samples, having a known dilution rate. For this reason the radioactive dilution rate is important information for identifying samples. The dilution rate depends of the distance from the release and on the depth, (Fig. 5). These values change with the weather too: for example, a dilution rate of 10^{-4} has been observed at 700m or at 1500m, depending upon the wind intensity.

Vertical concentration profiles: The shape of these profiles changes with the vertical temperature profile, (Fig. 6). When there is a thermal boundary, the concentration is more important at a given depth.

Siltation rate: One day after the end of the radioactive release a detection unit was dragged on the sea bottom at a velocity of 1 or 2 m/s. The traverses were, as far as possible, perpendicular to the direction of radioactive matter deposition. About 2% of the total amount of particles were on the bottom on a large area included between 150 to 250 x 10^4 m^2 (Fig. 7). But, at this moment, an important fraction of the radioactive particles was always in suspension. So, in the future it will be necessary to use a radioactive tracer with a longer life in order to estimate the siltation rate after a longer time.

CONCLUSION

The radioactive tracers method gives access to:

1. Pollutants distribution in the close volume of the release area versus space and time.

2. Field Lagrangien measurements.

These data are used to compute dilution versus space and to calibrate mathematical models.

In the future this process will be compared with the pollution rate in the close release with or without processing by a sewage treatment plant.

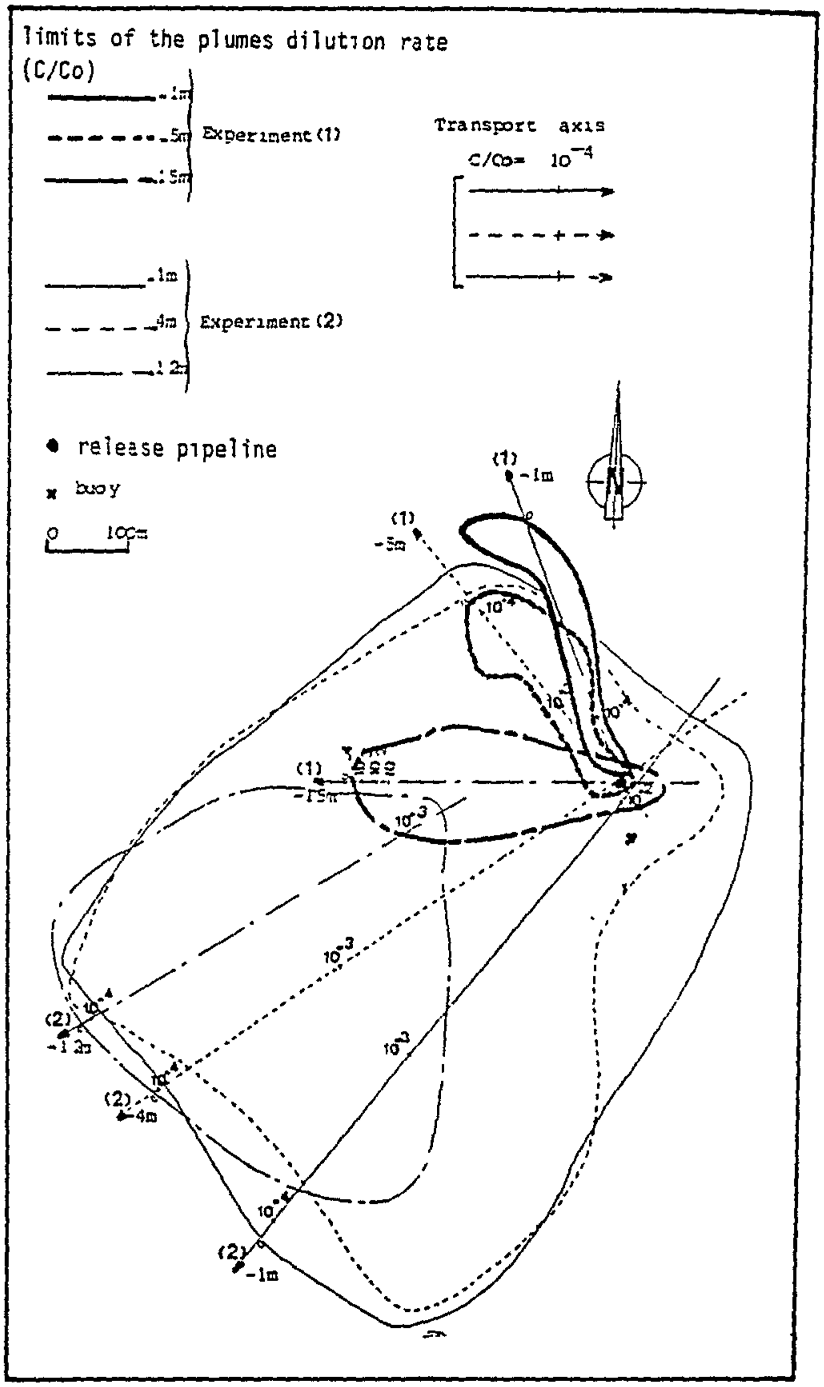


Figure 5

Comparison between spots (limits, transport axis, dilution) for continuous releases of effluents

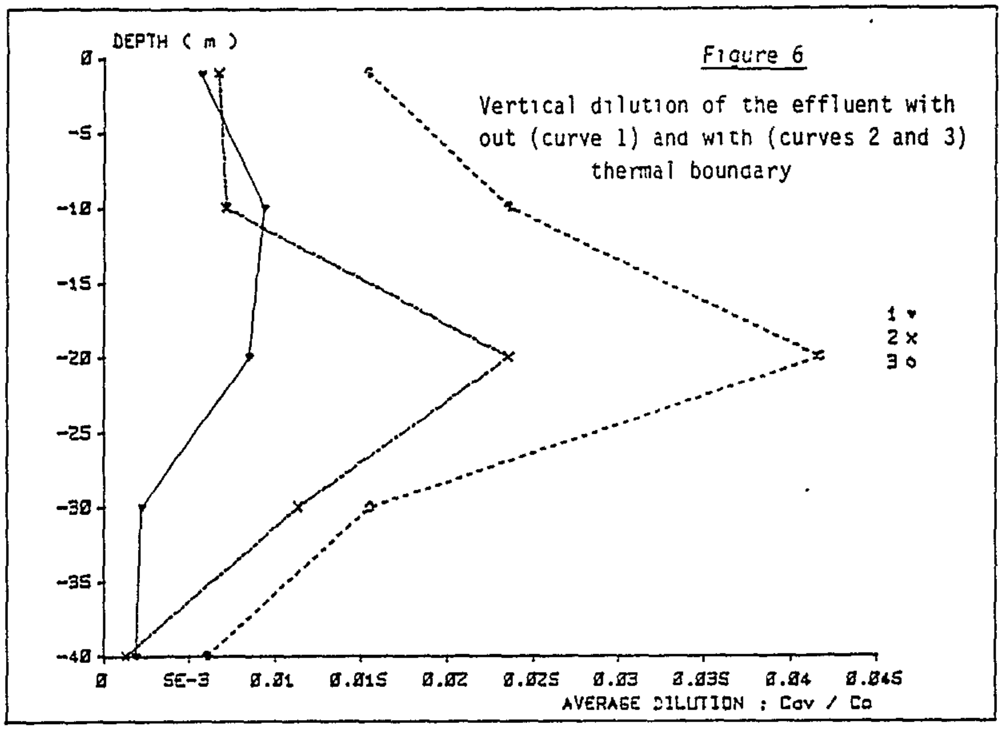
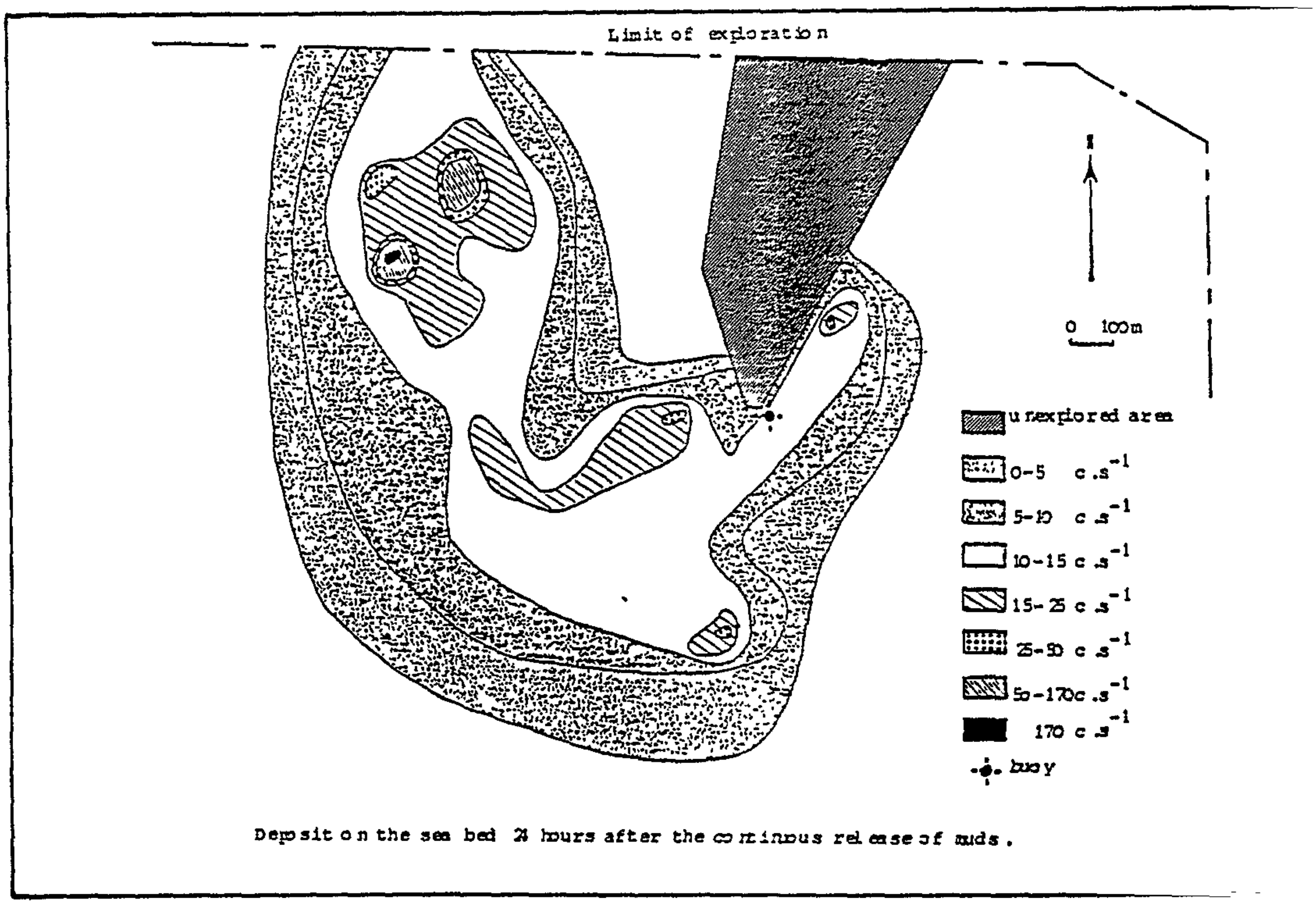


Figure 6

Vertical dilution of the effluent with out (curve 1) and with (curves 2 and 3) thermal boundary



Deposit on the sea bed 24 hours after the continuous release of muds.

Figure 7

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90 p., 70 Fig.

ACKNOWLEDGEMENTS

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ON THE DENSE ADRIACTIC WATER AND ITS ROLE IN THE CIRCULATION OF THE EASTERN MEDITERRANEAN

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ABSTRACT

A review is made of recent work on the role of the northern Adriatic as a source of bottom water in the eastern Mediterranean Sea and it's importance within the context of the general water-mass distribution in the Mediterranean. The highly dense water is sporadically formed during winter "bora" wind events and slowly sinks as it follows the eastern coast of Italy. The processes occurring during it's southwards passage are described and illustrated.

Mediterranean Water Masses

It is well known (Lacombe and Tchernia, 1971) that in the Mediterranean Sea there are three water layers (or even four, according to the classical text by Sverdrup et al., 1942), which differ from one another not only in their chimico-physical characteristics, but also in their dynamical behaviour and circulation (Fig. 1). These are:

i) A surface layer, formed by Atlantic water entered the Mediterranean through the Strait of Gibraltar, the circulation of which is ruled by a general cyclonic flux.

ii) An intermediate layer, formed by the so-called LIW (Levantine Intermediate Water), which represents one of the most important water bodies of the Mediterranean. Wust (1961) describes its formation in the Levantine Sea during winter as a result of a strong cooling and evaporation process involving the surface water, the salinity of which strongly increases. These effects are due to the blowing of the Meltemi, a North-Eastern wind typical of that area. Once formed, the LIW begins its path towards the Western basin of the Mediterranean Sea. Its initially very high salinity gradually decreases, until it runs off through Gibraltar into the Atlantic Ocean, where it is still to be easily found as the so-called Mediterranean water. The existence of a run-off of salty water re-establishes the salt balance of the basin; otherwise the Mediterranean would only have a large source of salty water (Gibraltar), a rather high evaporation rate and several but insufficient sources of fresh water (river inflows and rains).

iii) Finally a deep, or bottom, layer: the deep water is formed through a mechanism analogous to that of the formation of the LIW, i.e. through a convection process spun up by particularly strong meteorological occurences. In the western Mediterranean deep water formation places are the Ligurian Sea, the Gulf of Lion and the Catalan Sea. In the Eastern Mediterranean it forms in the Adriatic Sea, both in its Northern and in its Southern basin, and off Crete. However, the Adriatic Deep water represents the most important part of the whole Deep layer of the Eastern Mediterranean, as first evidenced in the classical study by Pollak (1951), confirmed by Wust (1961) and in very recent times by El-Gindy and El-Din (1986 - see table 1). For bathymetric reasons, the Deep water circulation of the Western and that of the Eastern Mediterranean are independent; in both cases they develop as a slow, large scale, cyclonic circulation, which can easily be explained in terms of the geostrophic balance pressure and Coriolis forces.

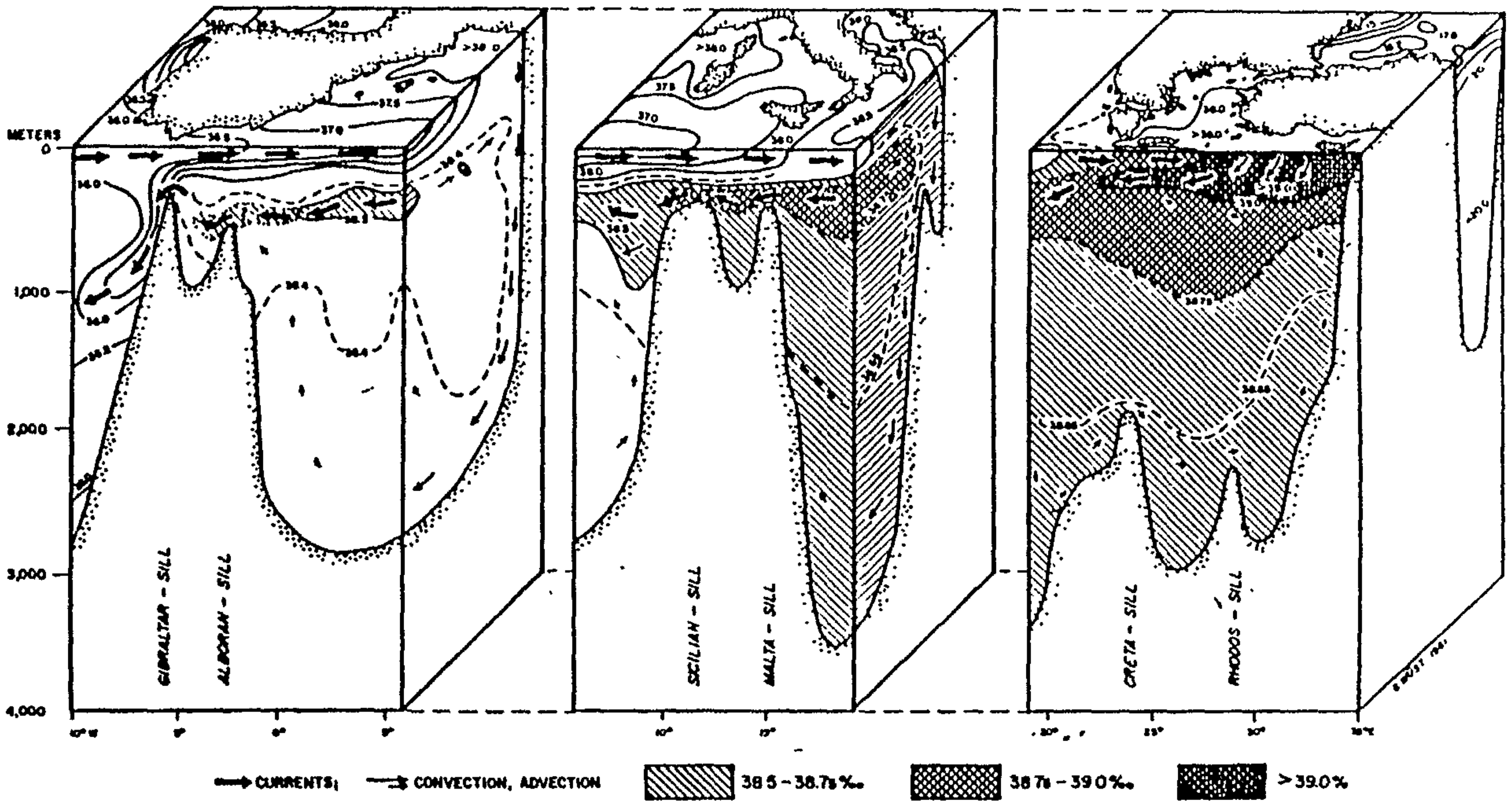
Table

Characteristics of deep water masses in the Eastern Mediterranean.

Depth (m) Season	1000					1500					2000				
	T°C	S	Ad.*	D.C.**	Lev.***	T°C	S	Ad.	D C	% Lev.	T C	S	Ad.	% D C	Lev.
A - Core of Adriatic water flow (Min.S‰ and Temp.)															
1. Warm Season	13.45 | 13.50	38.68 | 38.70			<10	13.35 | 13.45	38.66 38.68				13.30 | 13.35	38.64 | 38.66	>85 ·		10 | <15
2. Cool season	13.50 | 13.55	38.62 | 38.68	>80	<10	10 | <20	13.30 | 13.35	38.65 38.67	>80	<10	10-20	13.25 13.35	38.64 | 38.66	>90 ·	<10	5 | 10
B - Near Cretan Sea straits 1. Warm season															
Eastern Straits	13.55 |	38.75 |	40 |	40- 50	<10	13.40 13.45	38.70 |	60 |	20 |	<10	13.35 |	38.68 38.70	60 |	10 to	5 |
Western Straits	13.60	38.80	60	20- 30	<15	13.50 13.55	38.75	70	40		13.45	38.70 38.72	80	<40	10
2 - Cool season															
Eastern Straits	13.55 |	38.72 |	50 |	40 |	5-10	13.40 |	38.70	60-85	20 |	<10	13.35 |	38.66 | 38.68	60 |	10	5-10
Western Straits	13.60	38.75	60	50	<5	13.45	38.75	50- 70	40		13.40	38.70 38.75	80	<40	

N.B.
* Ad. = Adriatic water type
** D.C. = Deep Cretan Sea water
*** Lev = Levantine water type

Fig 1: Schematic block diagram of vertical circulation and distribution of salinity in the Mediterranean Sea during winter (from Wust, 1961).



The Adriatic Sea as a source of deep water

In the following, we will focus our attention in the formation and evolution of the dense water formed in the Northern Adriatic Sea (see Fig. 2). This water is formed by the blowing of the "bora", a cold and dry wind coming from Middle-Eastern Europe. The "bora" induces an intense surface cooling, with a consequent increase of the density of the well-mixed layer water. After its formation this water deepens because of its high density, reaches the sea bottom and then keeps circulating at approximately that same depth. It consequently follows the Italian shelf and shelf-break.

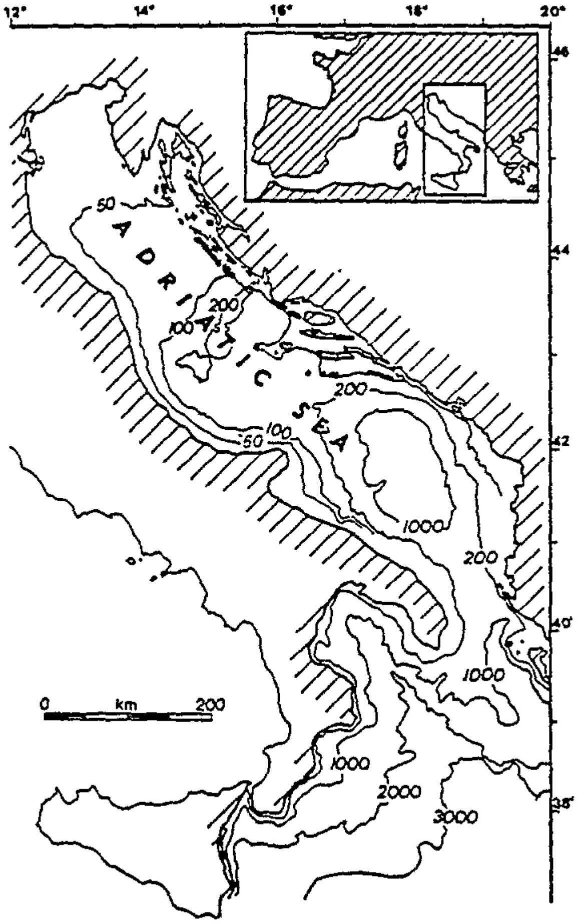


Fig. 2: Bathymetric map of the Adriatic Sea.

The typical depths this water can be found at are therefore those corresponding to the bottom of the Northern basin of the Adriatic Sea (50-70 m) and in fact the clearest observations (Fig. 3) of a very dense bottom water ($\sigma_t \hat{=} 29.8$!), due to Artegiani (1983), identify it in the Central Adriatic at a depth of between 50 and 80 m; it has also been found by Zoccolotti and Salusti (1987).

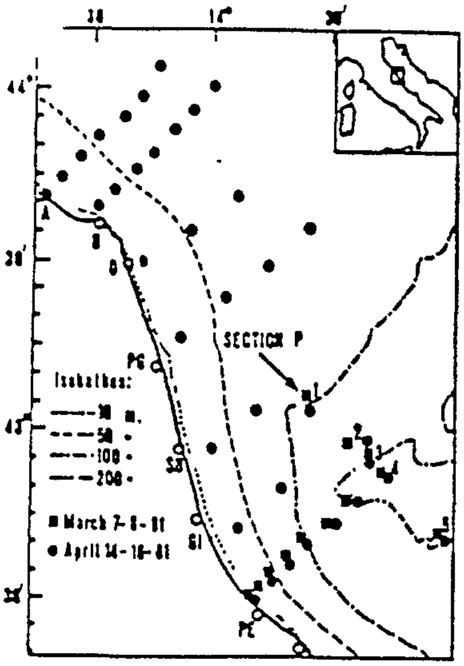
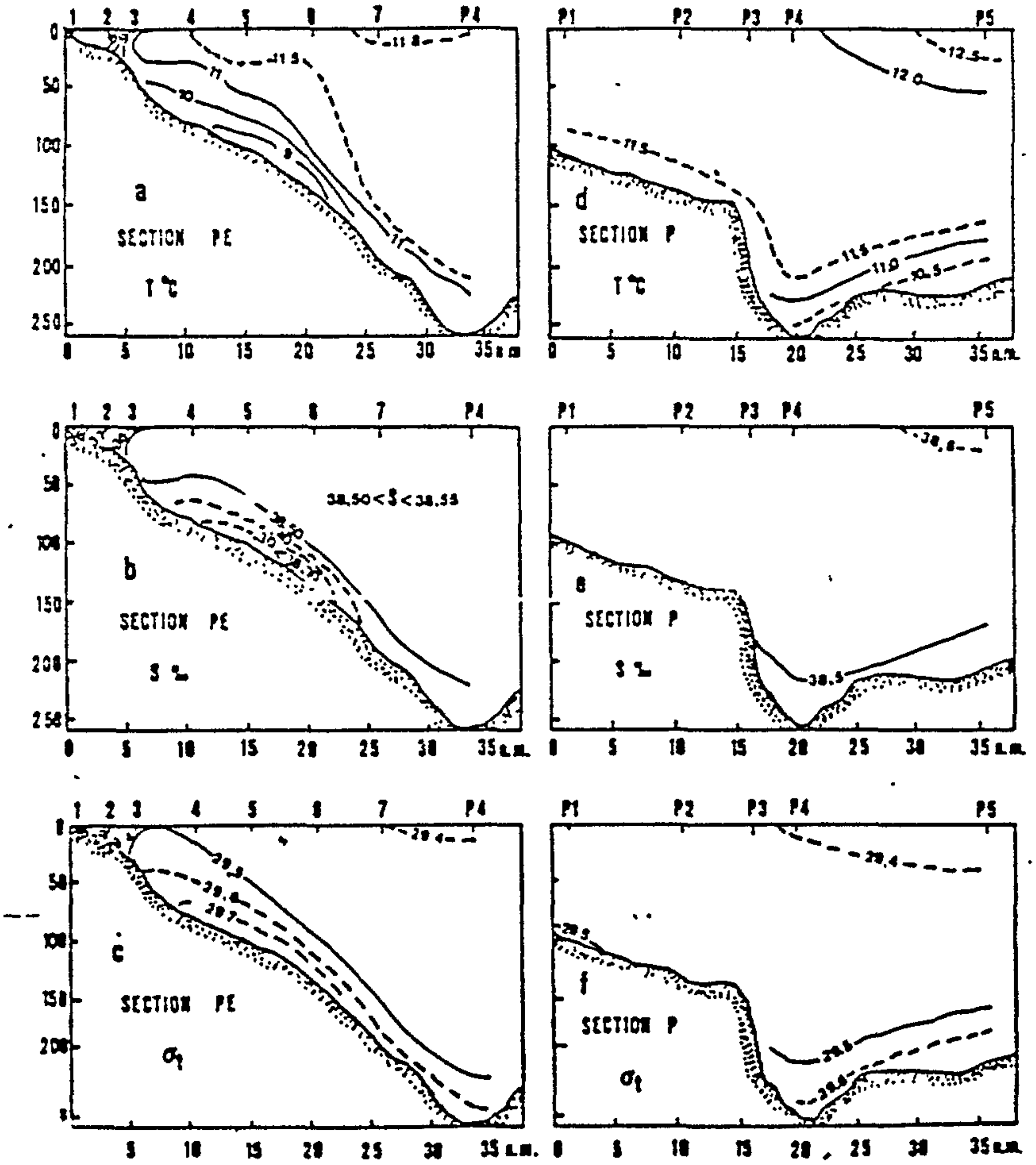


Fig. 3: Working zone and isophycnals from Artegiani (1983).



Now, on its route Southward, complex processes take place in this water, such as its mixing and dispersion with the surrounding water masses, as well as modifications of the shape of the vein due to the encountering and crossing of some bathymetric irregularities. The first of these bathymetric features is the Fossa di Pomo, or Jabuka Pit, in the Central Adriatic Sea.

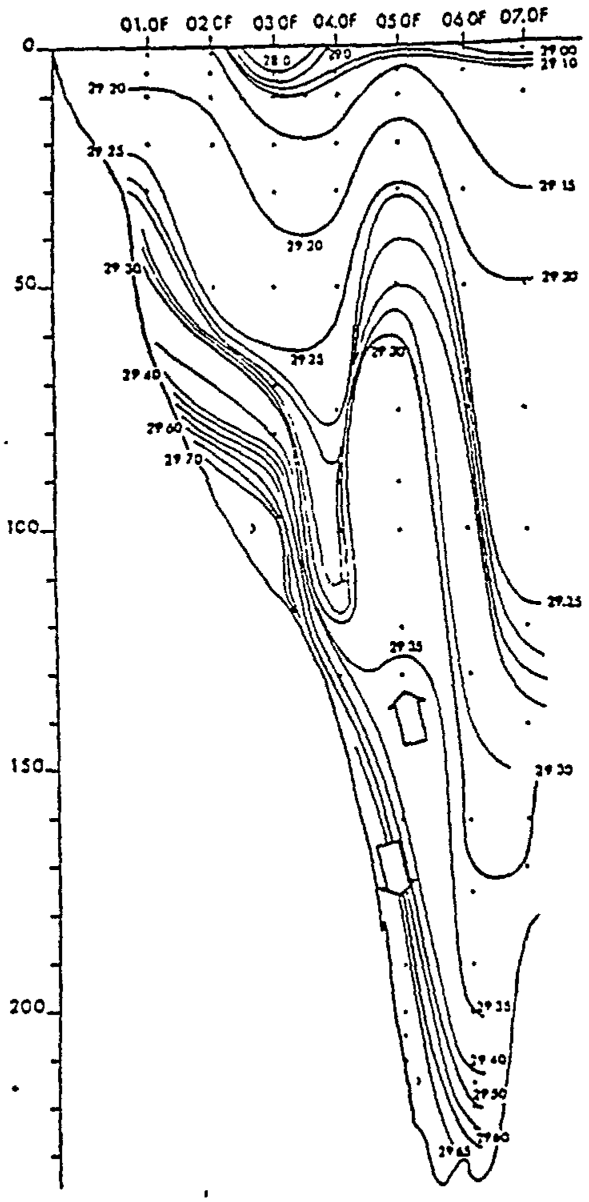
This Pit is replenished by dense water through different mechanisms which vary from year to year, as observed by Franco and Bregant (1982): either displacement and raising of the dense water lying in it (as in March 1970) or intrusion and stratification above the latter (March 1972) or - more often - through intermediate turbulent mechanisms which yield a vertical turbulent mixing of the different waters. From Franco and Bregant's (1982) study we show an impressive figure in which the dense water vein seems to destructively interact with a 10 km radius vortex (Fig. 4).

Further South, Salusti and Travaglioni (1987) detected the presence of a deep, dense water vein North of Gargano promontory (T $11.8^{\circ}C$, $S \simeq 38.7$%., $\sigma_t \simeq 29.6$) at a depth of 100 m, while Zoccolotti and Salusti (1987) report the presence of a similar vein South of the Gargano at a depth of between 90 and 120 m (Fig. 5) and find it again in the Otranto Channel, at a depth of $\simeq 400$ m (respectively, $T \simeq 12.4^{\circ}C$, $S \simeq 38.6$%., $\sigma_t \simeq 29.3$ and $T \simeq 13.5^{\circ}c$, $S \simeq 38.7$%., $\sigma_t \simeq 29.2$). In particular, they compute the velocity of the current following the model out by Shaw and Csanady (1983), which results to be a few centimenters per second (3-6 cm s^{-1}), while the typical water fluxes associated with this vein are of the order of 10^5 m^3 s^{-1} (at the moment of maximum flux).

In short, the data of Zoccolotti and Salusti allow us to reconstruct a little part of the story of this vein and it is interesting to supplement them with some more recent observations: Bignami et al . (1987a), for example, have reported a peculiar physical effect, which is also to be found in Salusti and Zoccolotti's work. During their attempt to follow the vein, they observed its presence off Bari (Fig. 6), at an approximate depth of 120 m; they kept trying to observe it further South but it practically disappeared until the Otranto Channel where it reappeared at a depth of around 800 m. That is, in the interposed area between Bari and Otranto Channel neither their CTD casts nor their observations through the Fish Finder show the presence of the vein.

This can be explained by the fact that off Bari, in a region where the shelf-break is rather regular, the outflow of the Crati river has excavated a sort of cross-shelf canyon. Here, complex phenomena of mixing, deepening and flattening of the dense water vein take place, like those which take place in the tank experiment carried out by Sugimoto and Whitehead (1983, see Fig. 7). One of the results of this experiment consists in a similar apparent disappearence of the current. In reality

Fig. 4: Isopycnals from Franco and Bregant (1982, the working zone is the same as Fig. 3).



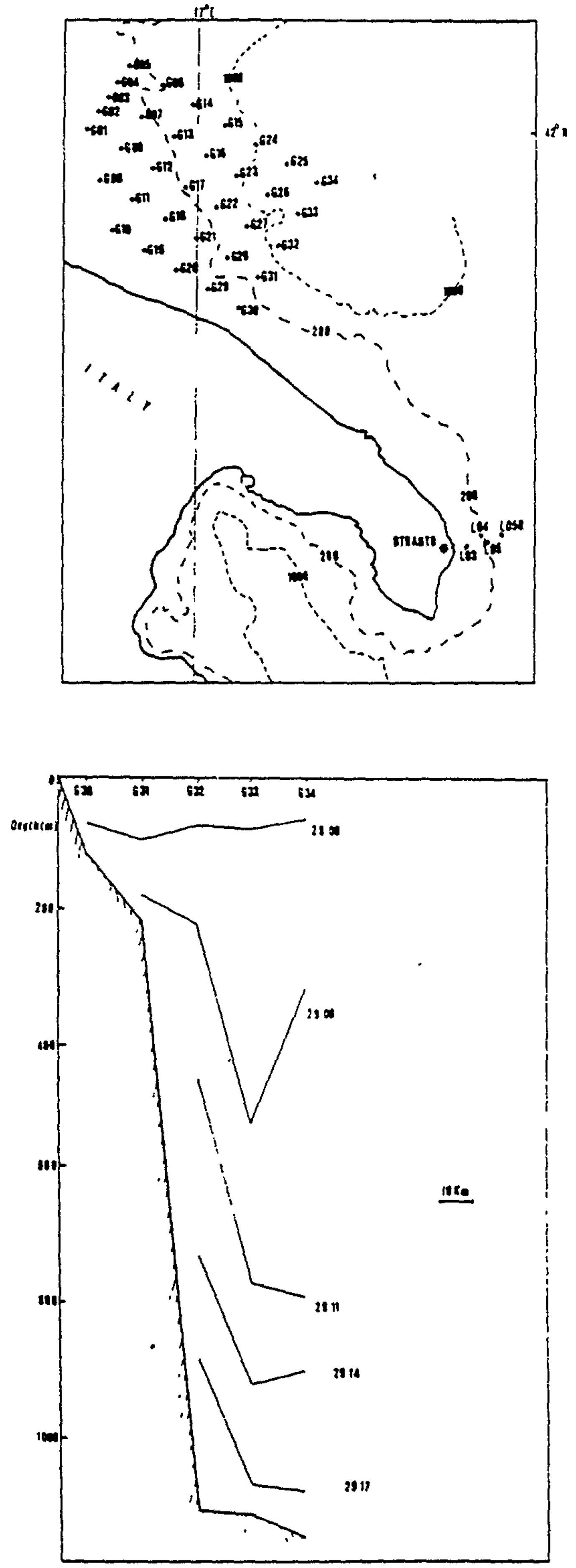


Fig. 5: Working zone and isopycnals from Zoccolotti and Salusti (1987).

it is just a strong flattening effect and the resulting flat shape of the vein makes it difficult to detect with the usual intruments, which are not easy to use inside a canyon or in particularly steep shelf-break regions.

Bigami et al. (1987c) study the further evolution of the vein along the Italian shelf-break of the Southern Adriatic and Ionian Seas. On more fundamental grounds, they show how the processes of mixing and spreading of this vein within these seas concur nicely with a model of steady motion of density driven currents is a stratified rotating fluid due to Smith (1975) and Killworth (1977). Their results are shown in Fig. 8.

As shown above - and as underlined by Bigami et al. (1987b) - the study of this phenomenon raises difficulties of an experimental, theoretical and modelling point of view. It must be borne in mind that these phenomena are strictly dependent on time, since they are typically seasonal occurences. The model by Shaw and Csanady (1983) suggests that a first-order approximation the time evolution of a vein of dense water driven by a density difference ρ' along a shelf follows Burger's equation (Fig. 9, see also Whitam, 1974):

$$\frac{\partial}{\partial t}\rho' - S\rho'\frac{\partial}{\partial y}\rho' = \frac{\partial^2}{\partial y^2}\rho',$$

where y is the alongshore coordinate, S=dh/dx is the bottom slope (x is the offshore coordinate and h is the depth of the shelf, which solely and linearly depends on x), and γ is the adimensional eddy diffusivity.

Attempts to apply these theories to such data are currently in progress.

Conclusion

It is evident that this pattern of bottom water is a typical phenomenon a basic knowledge of which is a fundamental prerequisite for understanding the dispersion and diffusion of pollutants, which are easily carried along by such dynamical features, and which... in some sense can also be used as tracers.

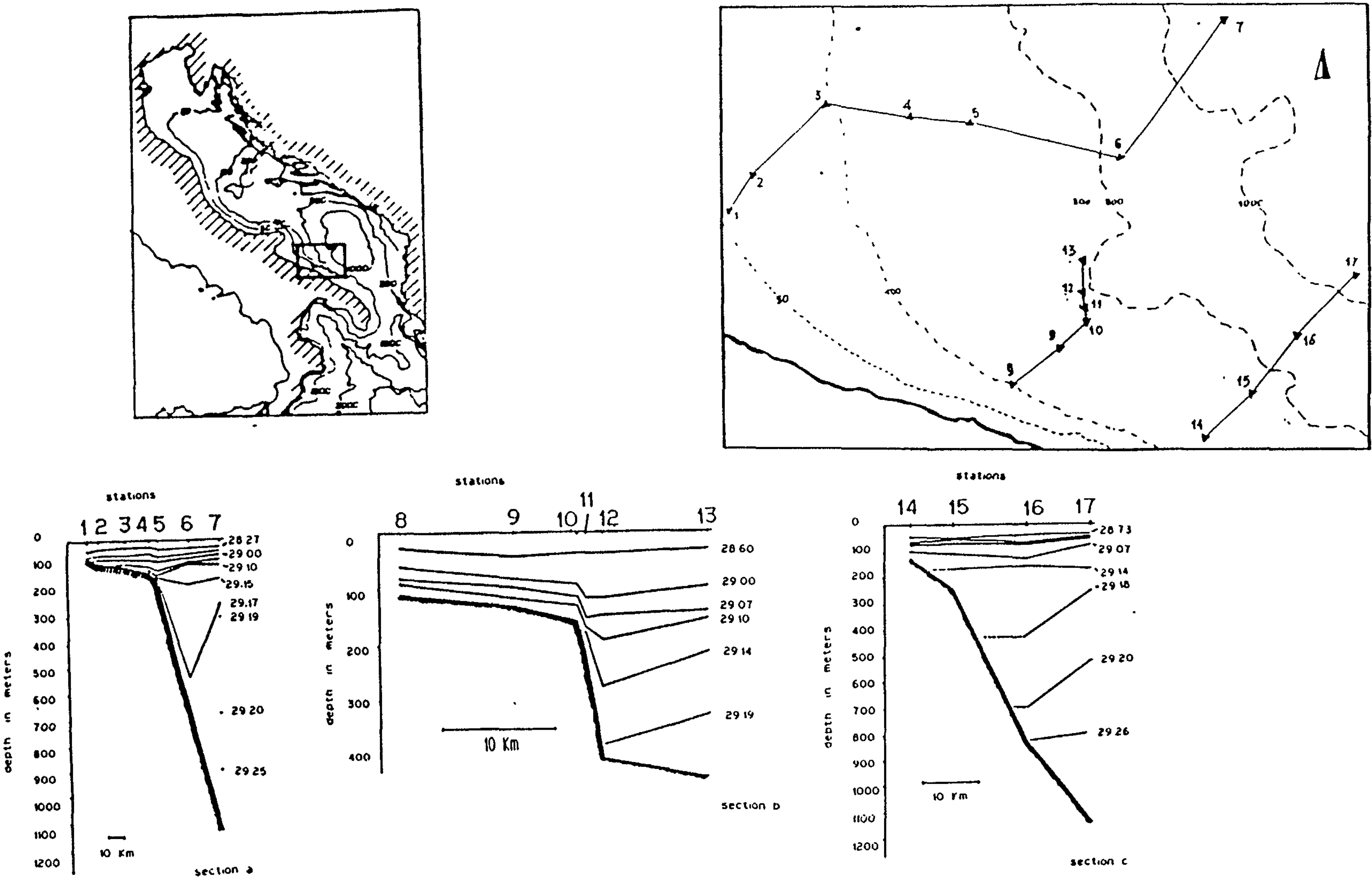


Fig. 6: Working zone and isopycnals from Bignami *et al.* (1978a).

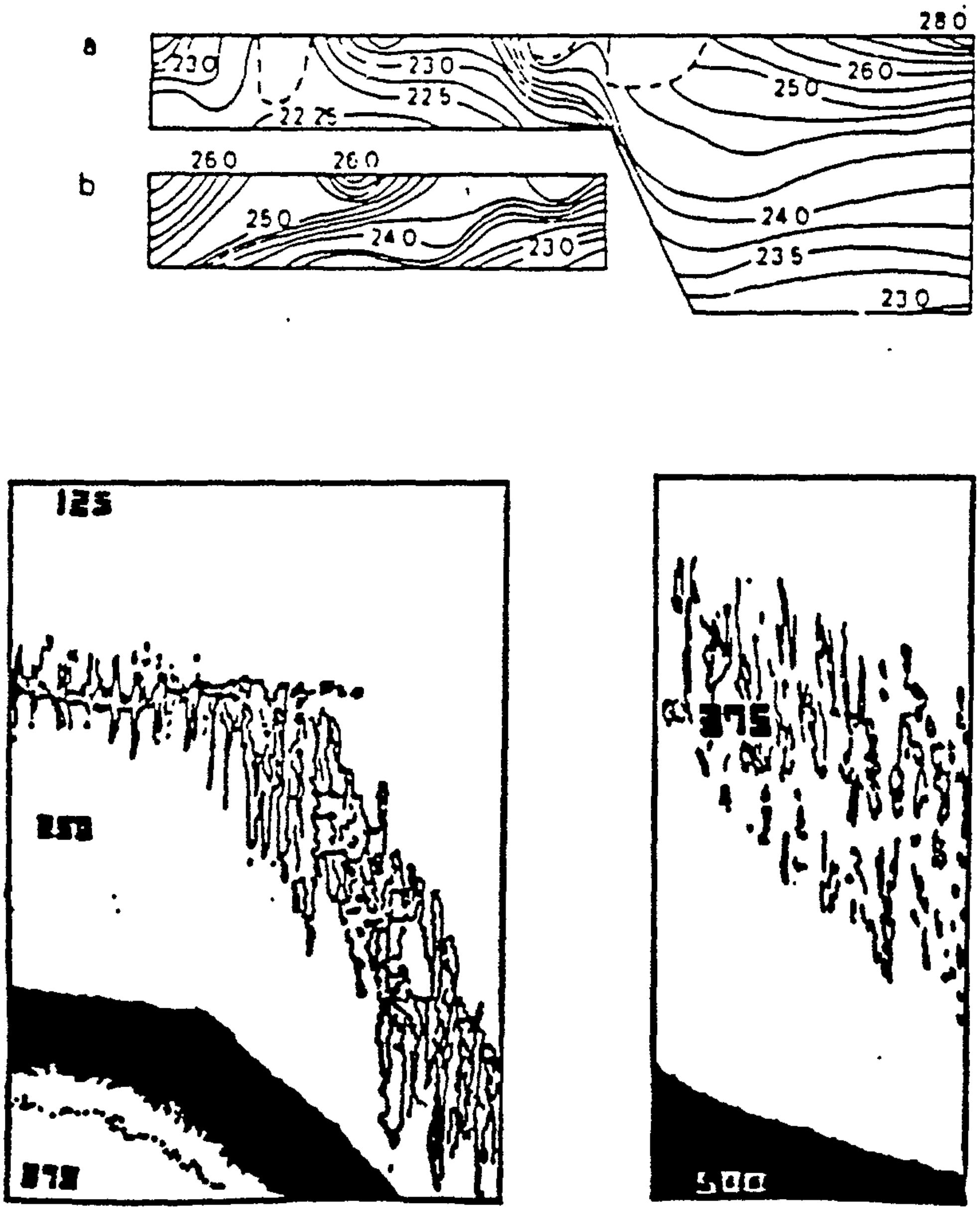


Fig. 7.: (UP) Thermal representation of the results of the tank experiment performed by Sugimoto and Whitehead (1983), and (DOWN) two drawings after fish finder images Bignami <u>et al</u>. (1978a).

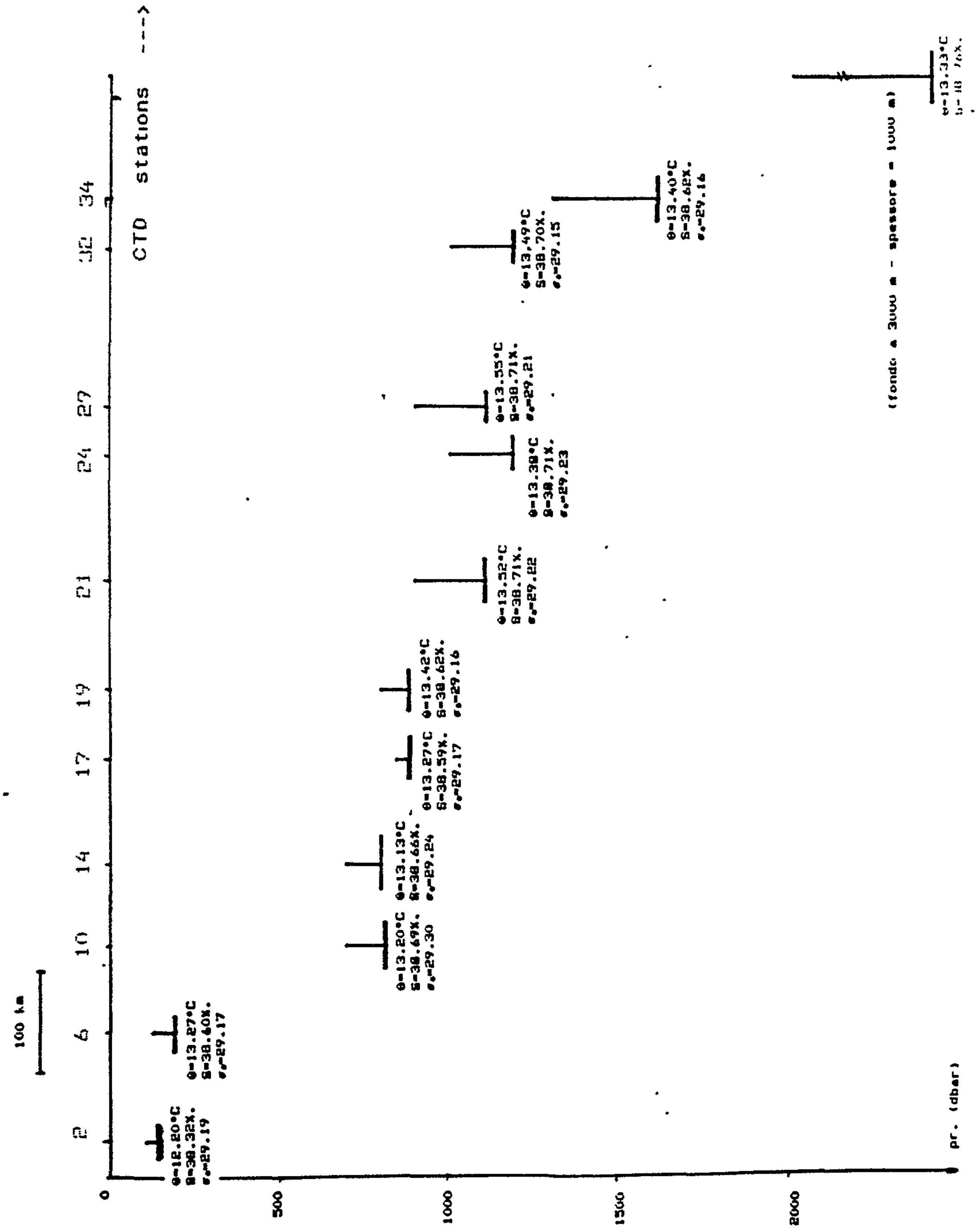


Fig. 8.: **Thickness of the Deep water current in the hydrological sections ofc the LOUISE '85 cruise (from Bignami <u>et al</u>., 1983).**

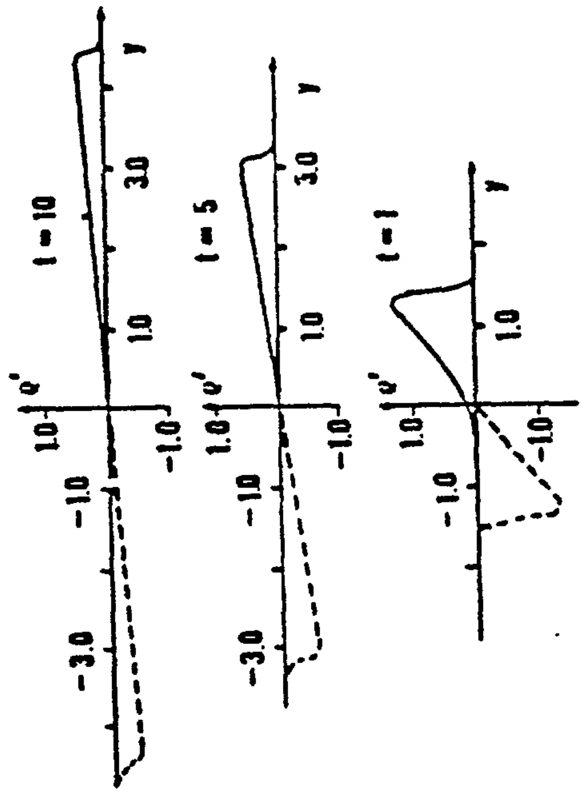


Fig. 9.: Solution of Burger's equation at t 0 showing the time evolution of a positive (solid line) and a negative (dashed line) density perturbation. The initial condition is a delta function at t=0 and y=0 (from Shaw and Csanady, 1983).

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CASE STUDIES

SEDIMENTS AS A SOURCE OF POLLUTANTS IN THE VENICE LAGOON

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ABSTRACT

Our results indicate that the Lagoon of Venice is characterized by a considerable time and space variability of nutrient concentrations (nitrogen and phosphorus compounds), chemical physical and biological parameters both in the sediments and in the overlying waters. Also the fluxes of eutrophying species released from the sediments depend to a great extent on the seasonal conditions and on the characteristics of the area in which they are measured. Laboratory experiments gave the following average values for release: Total Inorganic Nitrogen, 2 mmoles/(m^2/day); Reactive Phosphorus, 0.3 mmoles/(m^2/day).

From these data, average annual fluxes of nitrogen (2,000 ton/year) and phosphorus (600 ton/year) released from the sediments to the lagoon waters, have been calculated for the central area of the lagoon, the Lido Basin (ca. 200 km^2). These values are close to the sum of those estimated as originating from industrial, urban, agricultural and atmospheric sources (5,000 and 1,000 tons/year for nitrogen and phosphorus, respectively).

INTRODUCTION

Nutrients (nitrogen, phosphorus, carbon and silicon compounds) released in soluble forms into water bodies, are subjected to physical-chemical processes and become absorbed onto (or included into) organic and inorganic suspended materials. Finally they accumulate in the sediments that are a sink and a reservoir for such substances. A number of chemical, physical and biological reactions take place in the sediment which render nutrients available for overlying waters. Thus the nutrient supply from sediments can maintain a marine or lacustrine system eutrophic for long time periods after inputs have been stopped.

The pollution and eutrophication events that affected a water body are recorded in the underlying sediments. These records can be decoded on a short (months or years) or long (decades) historical basis by radiodating techniques.

Since few data were available in the literature on the nutrient concentrations in waters and sediments of the Venice lagoon and no data on fluxes at the sediment-water interface (despite the number of articles and books published, see e.g., Pellizzato and Scattolin, 1982, Cossu and De Fraja Frangipane, 1985), the authors undertook the research here reported. The aim was to investigate the transport mechanisms of nutrients inside the lagoon and the sea-lagoon exchanges. The distribution of concentrations in the surface sediments of the lagoon have been measured.

The eutrophication processes taking place in the Venice lagoon can be better understood if the release rates of nutrients from sediments are evaluated. Lagoon sediments are very rich in macrofauna (Avanzi et al. 1980) and benthic organisms certainly play an important role in the nutrient exchange mechanisms between water and sediment. Laboratory experiments were carried out in a large reactor containing water and sediment with and without the presence of macrofauna to evaluate the contribution of bioturbation (caused by macrofauna) to nutrient release rate and compare with other chemical-physical processes (e.g. concentration gradients).

Study Area

The lagoon of Venice (Fig. 1) has a total area of 549 km^2 (about 360 km^2 are navigable) and a mean tidal difference of 0.6m (Pirazzoli, 1974). If we do not consider the pounds bordered for fish farming, 75% of the lagoon has a depth between 0 and 2 m and only 5% is more than 5m deep (the principal navigable cannals) (Avanzi *et al.*, 1980). The lagoon receives from 1.6 to 5.2×10^5 m^3 of water from the Adriatic sea during a half tidal cycle through the Ports of Chioggia, Malamocco and Lido with an average amount of 3.3×10^5 m^3 (Cavazzoni, 1973). In the last century 32% of the lagoon surface has been barred from tidal flooding for new fishing farms or for industrial, commercial and touristic facilities.

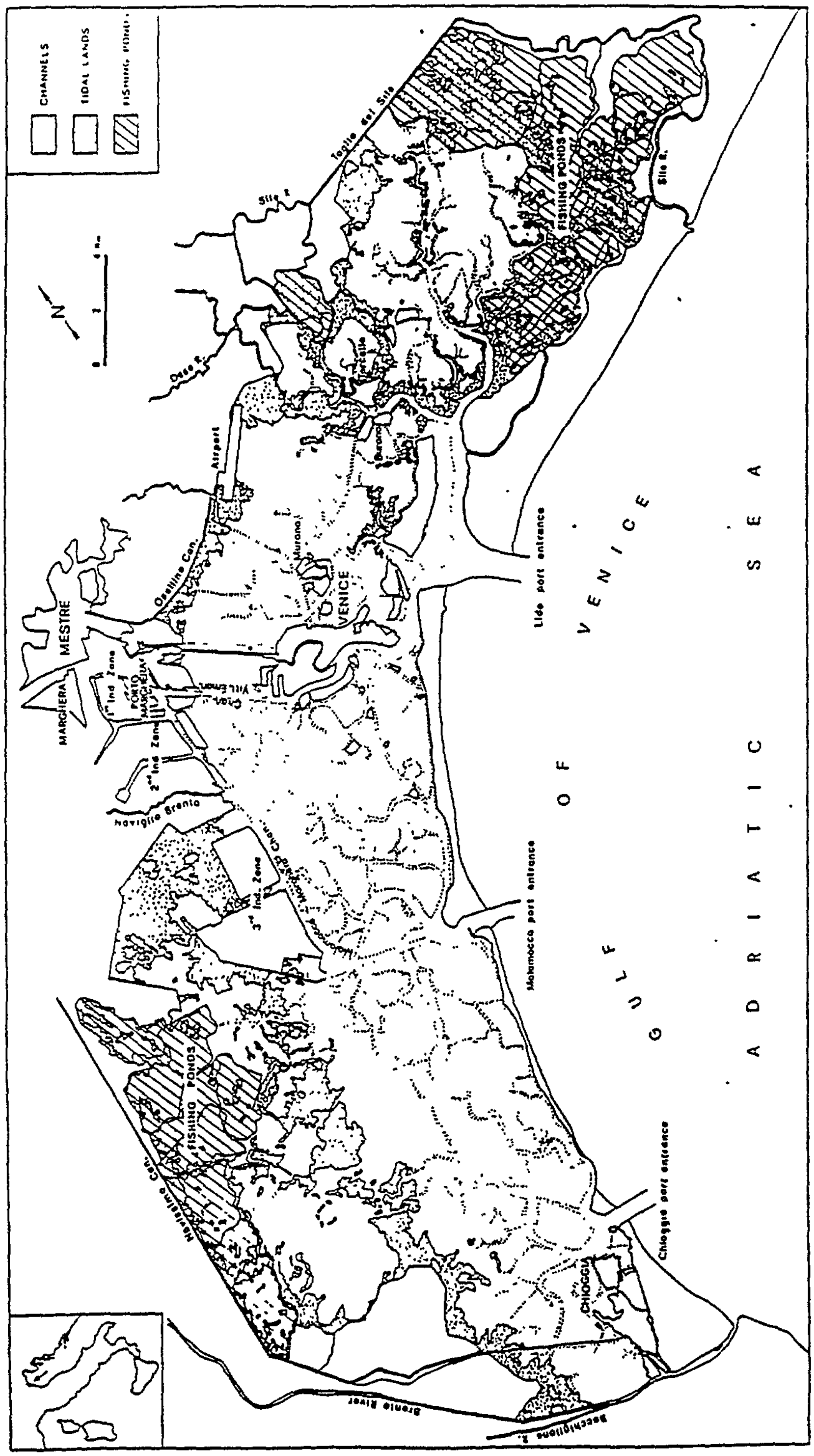


Fig. 1: The Lagoon of Venice.

Fresh water inflows, very large in the past, have been progressively reduced during recent centuries to prevent silting. At present, some 20 inputs are still active and a mean fresh water supply of 31 - 35 m^3/sec. has been estimated (Cossu and De Fraja Frangipane, 1985).

The lagoon is a marine embayment with a salinity of 25 - 36%. (Facco et al., 1986), which receives urban waste waters from Venice, Mestre and Chioggia (about 400,000 inhabitants), agricultural runoff from 2,000 km^2 of cultivated land, and industrial wastes from the area of Porto Marghera.

Analytical Methods

Sampling procedures: Surface sediment samples (upper 5 - 10 cm) were collected by a stainless modified Van Veen grab sampler or by a plexiglass cylindrical corer (i.d. 10 cm) at stations distributed all over the lagoon. These were stored in glass containers and transferred to the laboratory. Nitrogen analyses were carried out on wet samples, phosphorus determinations were performed on freeze-dried sediments. Non disturbed sediments for nutrient release experiments were collected with a box corer (30 x 40 x 80) or cylindrical corers (16 cm i.d.).

Van Dorn bottles were used to sample water. Interstitial waters were extracted by centrifuging or by squeezing in a stainless steel press.

Analytical Determinations

Water and air temperatures, water transparency, pH, Redox Potential of water, were measured in the field. The salinity was determined by a modified Knudsen method (Oxner, 1962), the dissolved oxygen was either measured potentiometrically in the field or by the Winkler method in the laboratory after sample stabilization.

Grain size determinations were carried out by wet sieving for the fractions above 63 um and by sedimentation for the silt and clay (Donazzolo et al., 1981). Carbonates were determined by measuring the CO_2 after treatment with phosphoric acid (Jobstraibizer, 1970).

Total nitrogen and total organic carbon were determined on sediment samples with a Perkin-Elmer 240 CHN Analyzer and a TOC Analyzer (Beckman 15B) after removal of carbonates (Froelish, 1980). Inorganic phosphorus in the sediments was determined after treatment of the samples with 1 M HCl for 16 hours (Aspila et al., 1976). Total phosphorus was analyzed similarily after mineralization at 550°C. Organic phosphorus was calculated by difference.

Chlorophyll$_a$ and nutrients (ammonia, nitrite, nitrate, reactive phosphorus) were determined according to standard oceanographic methods (Strickland and Parsons, 1972), with a fluorescence spectrophotometer Perkin-Elmer 44B or a uv-vis Spectrophotometer Perkin-Elmer 156 (Degobbis et al., 1986).

Nutrient Release From Sediments

The sediment samples used for the release experiments were collected in the most contaminated part of the lagoon close to the industrial area of Porto Marghera in October 1983 (first experiment) and April 84 (second experiment). The sediments from this location were used to carry out other laboratory experiments to measure nutrient release rates (Cossu *et al.*, 1983). A 10 cm sediment layer was sampled with a modified Van Veen Grab. The sediment was fine-grained (sand. 1-5%) and contained up to 5% organic carbon, up to 0.3% organic nitrogen, up to 0.03% organic phosphorus, up to 0.07% inorganic phosphorus, all expressed as dry weight).

A larger number of samples were collected at the same location by cylindrical plexiglass corers (i.d. 10 cm): vertical profiles of pH and Eh were immediately traced by inserting electrodes into suitable holes (0.3 cm) equally spaced in the corer walls. Two to 3 cm sections were then cut and the interstitial waters squeezed to determine concentrations of nitrite, nitrate, ammonium and reactive phosphorus. Phosphorus and other extractable nutrients were also determined in the whole sediment.

Experimental Procedure

The sediment for laboratory experiments was sieved through a 1mm sieve to separate larger organisms and left to compact for several days in the reactor shown in Fig. 2. Overlying water was replaced with low nutrient filtered sea water. The reactor was kept in the dark. Temperature, dissolved oxygen, pH and redox potential were monitored daily by electrodes fitted in the reactor cover. Eh profiles were measured, also daily, by a number of electrodes housed in the vertical wall. To measure nutrient exchange rates 3 x 50 ml of overlying waters were sampled daily and analyzed. The volumes were restored with filtered sea water.

Each nutrient release experiment was carried out in two phases with the same sediment. No macrofauna was present in the first; the second was performed in the presence of organisms. The macrofauna composition was the same as determined in the natural sediment at the moment of sampling. Each phase of the experiment was repeated three times with the same sediment by completely renewing the filtered overlying sea water each time. The release rates were estimated by fitting linear equations to concentration trends of nutrients in the overlying waters.

Results and Discussion

The grain size distribution of lagoon sediments has been described extensively (Barillari and Rosso, 1976, Barillari, 1978, Barillari, 1981, Hieke Merlin *et al*,, 1979). In the entire lagoon the fraction > 63 pm (pelite) is about 67%. Sediments are coarser going from the inner parts of the lagoon toward the ports. Tidal currents, which are as fast as

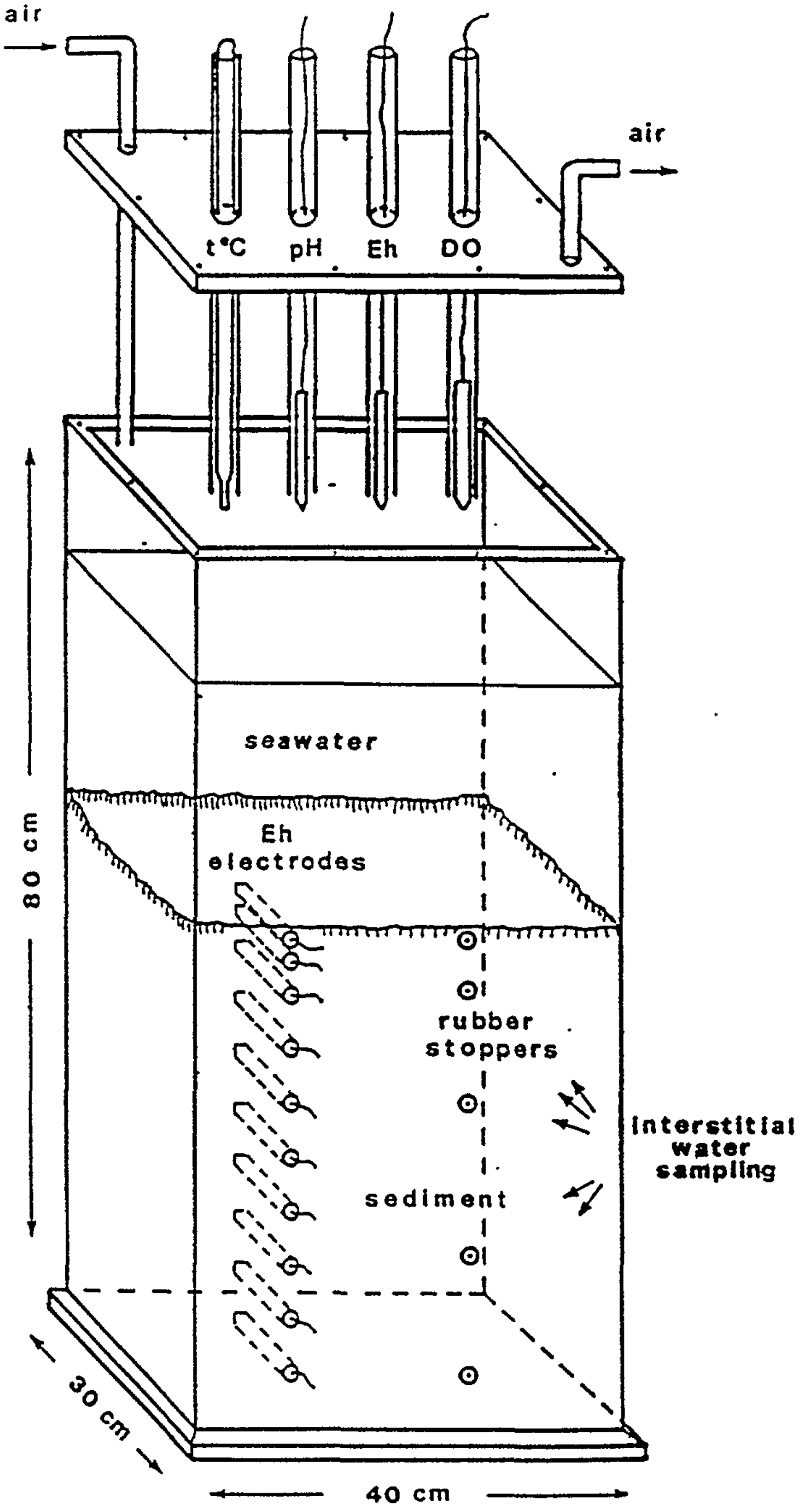


Fig. 2: The experimental reactor for nutrient release experiments.

2.68 m/sec., on exceptional occasions, (Tosi, 1970), may prevent deposition of fine materials. Carbonates are the prevailing minerals in the lagoon sediments and generally dolomite is more abundant than calcite. Other identified minerals are quartz, feldspars and clays (illite, kaolinite, chlorite).

Distribution of Nutrients in the Sediments

Isolines for total phosphorus in the surficial sediments of the lagoon are shown in Fig. 3. Concentrations below 410 ug/g have been considered "natural". This limit was obtained from the deepest sections of cores dated to more than one century ago (Pavoni et al., 1987). The concentrations above 650 ug/g have been considered indices of heavy pollution in agreement with Prater and Anderson, 1977.

From an inspection of Fig. 3 it is apparent that phosphorus concentrations above the "background" value are present in the inner parts of the lagoon where influx of fresh waters containing agricultural runoff or industrial wastes is present. The highest concentrations in the southern part are of agricultural origin, whereas the high value close to the bridge across the lagoon are due to industrial wastes from fertilizer plants and to sewage from the town of Mestre. In the northeastern part, waters from the Dese carry a heavy pollution load at the mouth of the river.

Most of the P_{tot} in the surficial sediment is inorganic. In the entire lagoon P_{inorg} is about 81.5% of the total, and the 18.5% left is associated to organic matter. Only 1.1% of the phosphorus is leachable with sea water and therefore readily available to photosynthetic processes.

Nitrogen compounds were determined in sediments sampled in the 11 stations shown in Fig. 4 in the period 1981-1982. In Fig. 4, sediment total inorganic nitrogen concentrations in sediment are presented. Almost all the inorganic nitrogen (99.12%) is ammonia. Nitrite and nitrates are 0.91% and 0.24% of the total inorganic nitrogen, respectively. Isolines have been drawn using two arbitrary limits: 14 and 28 ug/g. The lowest concentrations of total nitrogen are present in the central area bordering the Vittorio Emanuele canal, a very important waterway. On both sides of this area shallow zones are present, in which poor water exchange occurs and hypertrophic conditions are favoured (which cause periods of anoxia in spring and summer).

In this central part of the lagoon high nitrogen concentrations are due to the influence of industrial waste waters and sewage from the city of Venice and Mestre Marghera. Nutrient concentrations have also been determined in the core sections taken in the central part of the lagoon between the city of Venice and the industrial area of Marghera. Immediately after sampling, the profiles of pH and Eh of the cores have

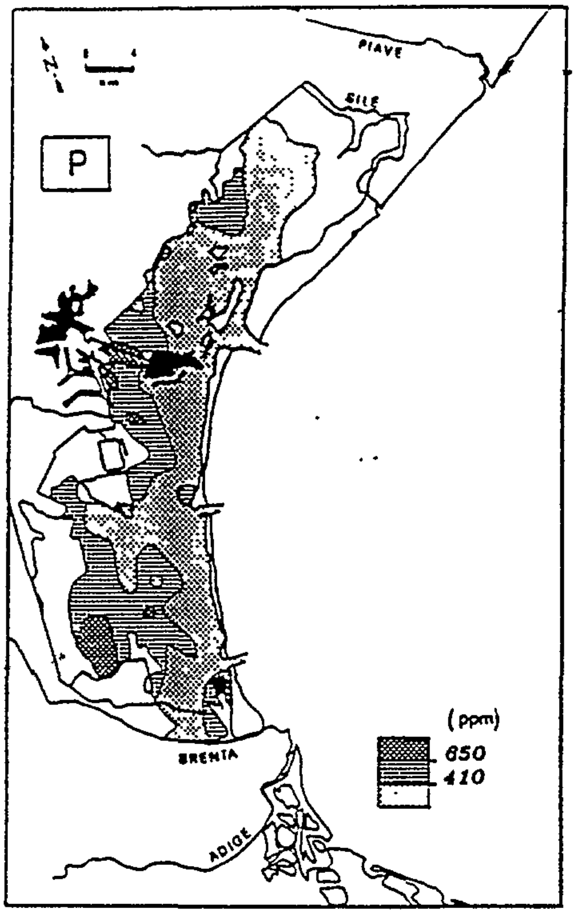


Fig. 3: Isolines of total phosphorus concentrations in the surficial sediments of the Lagoon of Venice.

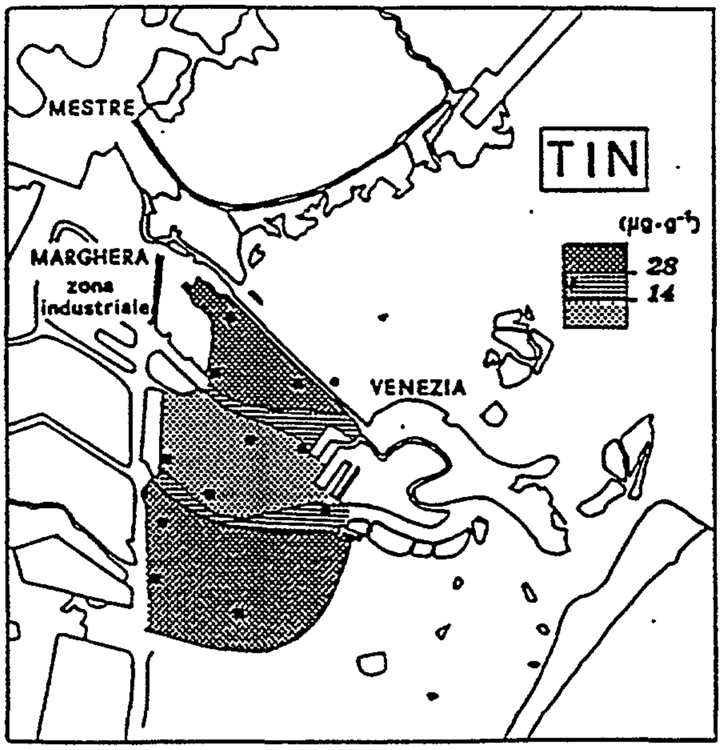
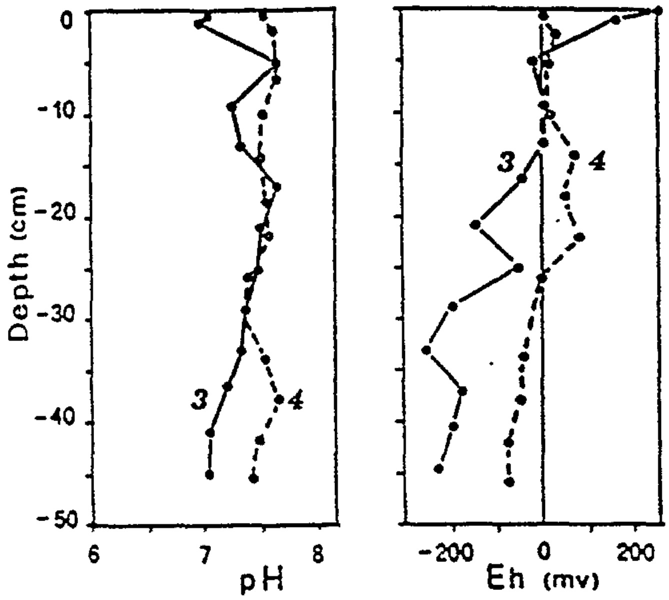


Fig. 4: Isolines of total nitrogen concentrations in the surficial sediments of the Lagoon of Venice.

been measured by inserting electrodes into suitable holes in the corer walls. These values are reported in Table 1 and shown in Fig. 5. The pH profiles are fairly flat, whereas Eh profiles significantly change as a function of the depth. Deepest strata are characterized by negative Eh values, indicating the presence of a reducing environment. A very sharp drop of Eh values (some 100 mV) is usually observed at the sediment water interface and also in the first centimeters of the sediment surface (see the trends in core 3).



In summertime a very noticeable difference is observed between the Eh value monitored in water and at the sediment surface: positive values in the water (> + 100 mV) correspond to negative values (5-100 mV) in the sediment surface. If we exclude the periods of anoxia that may occur in some areas of the lagoon, the photosynthetic processes that usually take place in the water column produce a large amount of dissolved oxygen that maintains the Eh at positive values. On the contrary, at the sediment surface a layer of dead algae is generally present that decrease the Eh values (because of depletion of the dissolved oxygen by organic matter decomposition) and renders the environment reducing. In winter upper sediments are oxidized and the Eh drop is observed few centimeters below the sediments surface.

In Table 2 and 3 the concentration of various forms of nitrogen and phosphorus in the two above mentioned cores are reported. At a depth of 30 cm, total concentrations become close to the value of 12.8 ug-at/g or 410 ug/g considered as a "background" for the lagoon of Venice. The extractable phosphorus is 1% of the total, whereas inorganic phosphorus is 60-80% and organic phosphorus 20-40%. As observed with the surficial sediment data, ammonia is almost the only form of nitrogen present in the deepest strata. This is not surprising taking into consideration that the low redox potential clearly favours the reduced forms of this element.

Fig. 5: Ph and Redox potential profiles in core 3 and 4 collected in the most contaminated area of the Venice Lagoon.

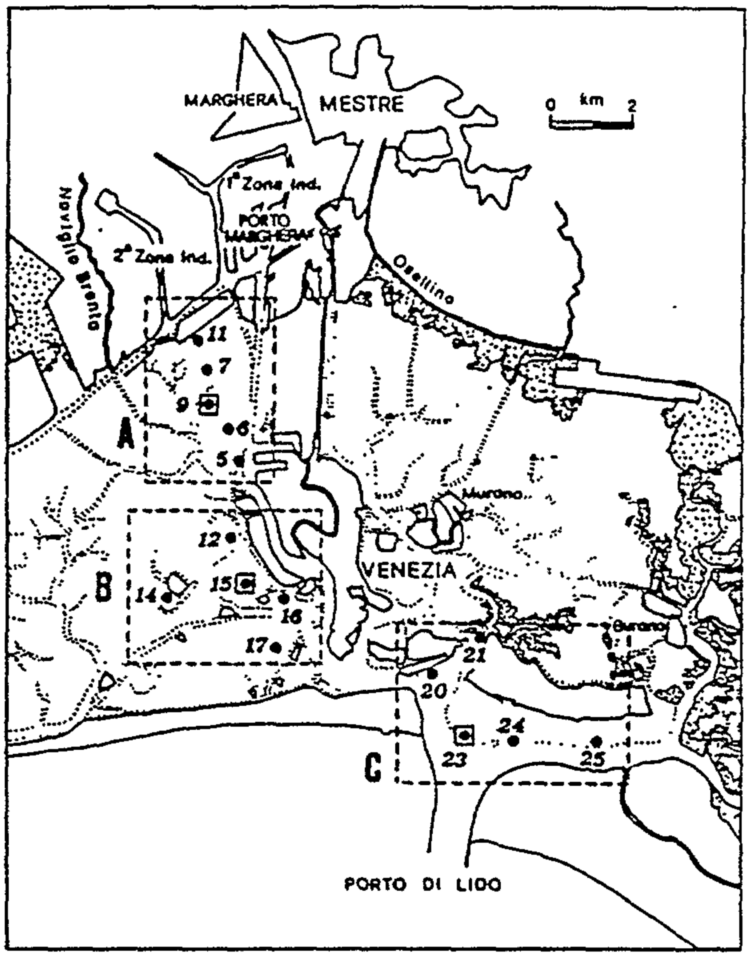


Fig. 6: Seasonal sampling stations grouped into areas.

Ammonia concentrations in the interstitial waters of core no. 4 (Table 4) are about one order of magnitude lower than those observed in the solid phase. Also in the interstitial waters the percentages of nitrites and nitrates are almost negligible (ca. 0.5%). Interestingly, nutrient concentrations in the interstitial waters constantly decrease in the upper sections of the core. This observation combined with the one that concentrations in the interstitial waters are significantly higher than those in the overlying waters (Facco et al., 1986) shows that a release of nutrients is taking place from the sediment and therefore that sediments play a primary role in maintaining eutrophic conditions in the lagoon.

Nutrient concentrations in lagoon waters (Table 5) have quite a large range (typical of coastal environments) and are usually decreasing going from the border of the industrial zone toward the center of the lagoon. Average values of nutrients determined in lagoon waters are about one order of magnitude higher than those found in the surficial waters of the Adriatic Sea and of the same order of magnitude than those determined in the waters of the River Po, which is the main nutrient source for the Adriatic. However, whereas in the river Po the ratio between total inorganic nitrogen and reactive phosphorus is ca. 50, the same ratio in the lagoon waters ranges between 12.3 and 27.3 and much closer to the value of 16 which is considered characteristic of non contaminated waters (Horne, 1969) and optimal for algal growth (Redfield et al., 1973).

Seasonal sampling has been carried out in the period from February 1984 - June 1985 in the stations indicated in Fig. 6. These expeditions were carried out to monitor areas receiving different pollution loads. Data are schematically represented in Figs. 7 and 8. Very different concentrations are determined from zone to zone, typical of shallow water systems with high anthropic influence. The "A" zone shows the highest values of inorganic nitrogen and phosphorus. In this part of the lagoon, run-off waters from agricultural lands flow in and waste waters from fertilizer plants are discharged. Furthermore, in this area the highest differences from station to station are observed. In fact, in station 11 located close to the industrial area, concentrations are 2 to 10 times higher than those found in station 5 located close to Venice. As an example, in the samples of April 1985 at stations 5, 6, 9 and 11, concentrations of total inorganic nitrogen and reactive phosphorus were: 3.6, 7.1, 11.8, 17.3, 68.4 and 0.85, 1.43, 1.96, 1.77, 5.95 ug-at/l, respectively, with a constant increase along the above mentioned transect. Despite such relevant differences, no corresponding variations have been found in the concentrations of Chlorophyll$_a$ (19, 27, 33, 6.4 and 7.9 ug/l). This indicates that the phytoplancton growth may not be in strict relationship with the concentrations of nutrient in the dissolved phase in a hypertrophic environment such as a lagoon. Much less important differences (2 to 3 times) are monitored in the stations of areas B and C.

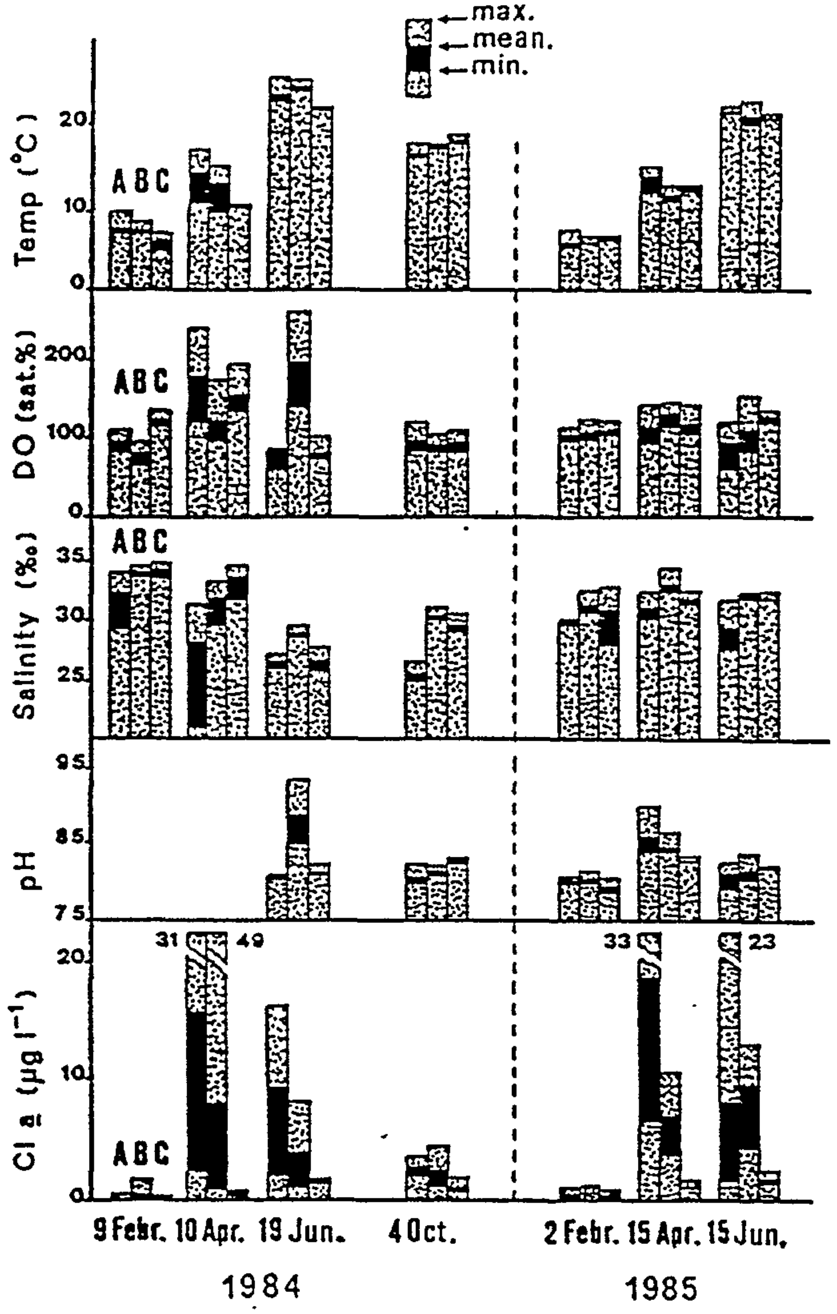


Fig. 7: Seasonal variations of water temperature, oxygen saturation (%), salinity, pH and chlorophyll$_a$ in the areas of Fig. 6. Minimum/maximum and average values are reported.

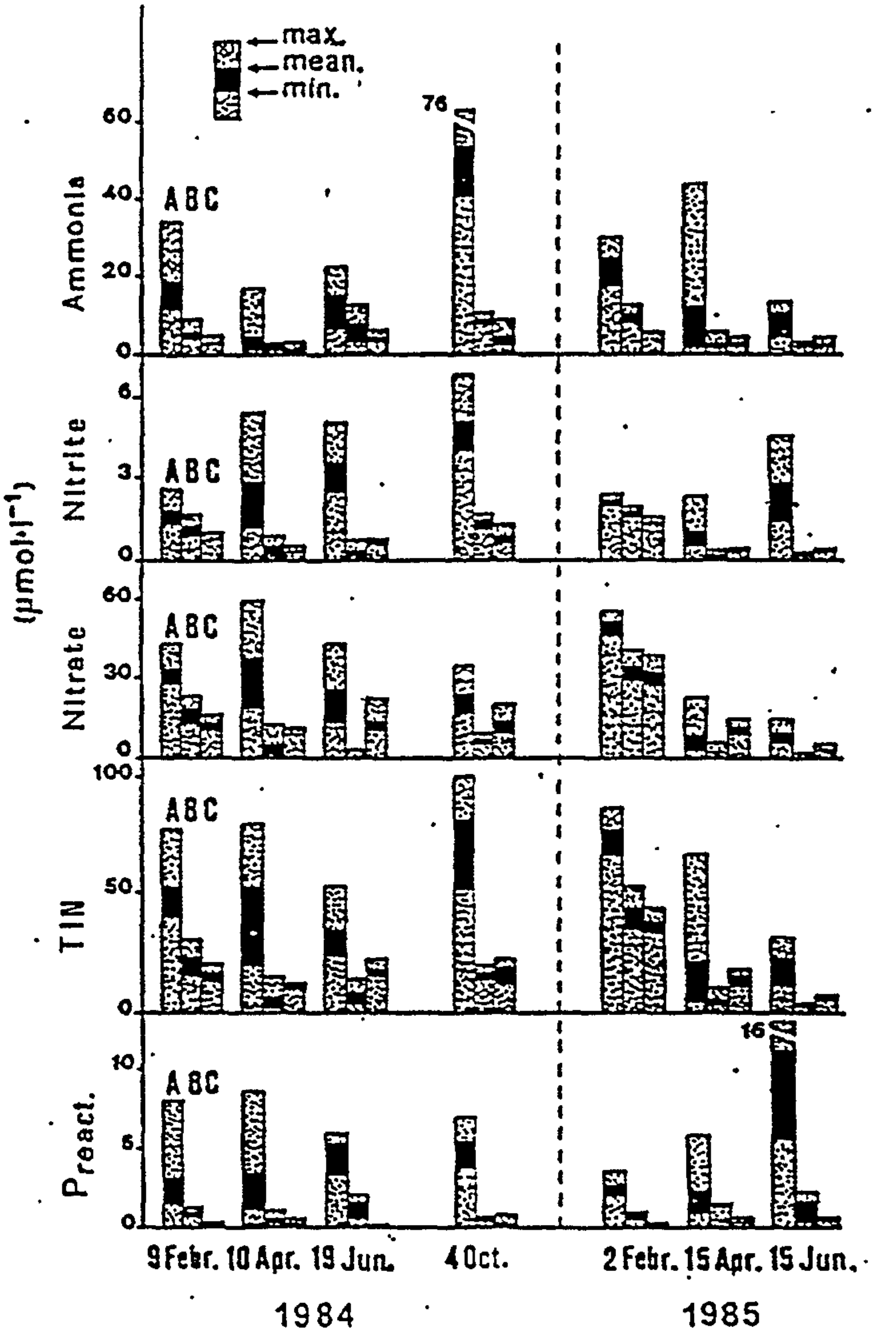


Fig. 8: Seasonal variations of nutrient concentrations in the waters of the areas of Fig. 6. Minimum/maximum and average values are reported.

All the parameters measured undergo high seasonal variations related to biological processes. Concentrations of inorganic nitrogen are higher in autumn and winter and lower in spring-summer. This trend is the reverse of that of Chlorophyll$_a$. Highest nitrate concentrations were measured in February. In this period well oxygenated water favours the oxidized forms of nitrogen. On the contrary, highest concentrations of amonia were found in October when decomposition processes were already much more important than the photosynthetic ones. Highest concentrations of reactive phosphorus were monitored in June and October during periods of high organic matter regeneration and release from sediments.

Nutrient Release Experiments

In both experiments, sediment Eh vertical profiles were reproducible and below 1 cm were almost flat, ranging from -180 to -230 mV in the first experiment and from -200 to -280 mV in the second. In both cases a noticeable drop was observed in the first layer (from 0 to -200 mV). Sediment redox potential profiles were not significantly changed by the presence of macrofauna, when added in the second phase. Physical-chemical parameters in overlying water remained almost constant during experiments: temperature was around 19°C, dissolved oxygen was ca. 6 mg/dm^3, Eh 400 mV and pH ranged from 8.15 to 8.60. Inorganic phosphorus and exchangeable ammonium and orthophosphate concentrations in the surface sediment did not change from before to after the experiments. Exchangeable reactive phosphorus was ca. 10 mmole/kg, inorganic phosphorus and ammonium ranged from 12 to 16 and from 0.2 to 2.0 mmole/kg respectively.

In Fig. 9 the nutrient trends observed in the first experiment are shown in the phase with no macrofauna. Results of the second experiment were similar. The first experiment was prolongated for 6 months to test the stability and reproducibility of the system. In the first period of the experiment, nitrogen was mainly released as ammonium, afterwards as the surface sediment became more oxidized (in a few days a brown layer was formed, which increased with time) and oxidation processes also took place in the overlying water, the dominant form became nitrite and then nitrate. When the experiment was restarted by changing the overlying water, nitrogen was released as nitrate. Reactive phosphorus was released during the first days at a lower rate; this also decreased in time.

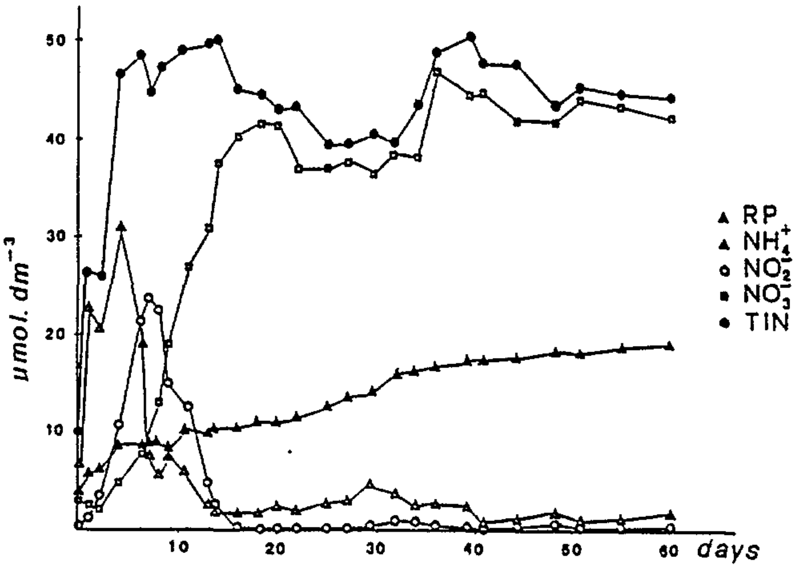


Fig. 9: *Concentration changes of inorganic nitrogen species and reactive phosphorus in the overlying water of the experimental system during the first experiment without macrofauna.*

When macrofauna was added in both experiments, nitrogen was again released as ammonia and after the second and third water changes, the release of ammonia concentration was still important, even though a noticeable release of nitrite was observed. Macrofauna considerably perturbed the sediment both mechanically, by drilling burrows, and chemically through their physiological functions. Another important effect of the presence of macrofauna in the experimental system was a considerable increase of nutrient release from sediment. From Table 6 it is apparent that macrofauna increased the release of reactive phosphorus from the sediment by 2 to 3 times and the release rate of total inorganic nitrogen by up to an order of magnitude. From these results it is clear that macrofauna can play a very important role in the processes involving nutrients at the sediment-water interface, a role much more important than other processes such as diffusion.

CONCLUSIONS

Due to the industrial and urban development that took place in the territory surrounding the Lagoon of Venice in the last century, a heavy load of polluting and eutrophic substances has been conveyed into the lagoon and in large part they have accumulated in the sediments.

Even though the lagoon bottom is often perturbed by dredging, fishing and boating activities, some undisturbed areas can be found in which positive sedimentation occurs and radioisotopic techniques can be applied to date sediment core strata. Mean ages of sections, sedimentation rates, and fluxes of pollutants through the sediment surface, can therefore be calculated and historical records of the sediment contamination can be reconstructed. Different areas of the lagoon experiment different contamination levels and the most polluted and eutrophicated part was undoubtedly the one located between the industrial area and the city of Venice, i.e., the Lido basin.

The lagoon sediments contain nutrients that undergo regeneration processes and they act as an inexhaustible supply for the growth of algae and phytoplankton. Laboratory experiments carried out to measure fluxes of nutrients from the sediments gave 2 mmol/m^2/day) of TIN and 0.3 mmol/m^2/day) of reactive phosphorus (Table 6). By extrapolating these results, one can estimate that some 10 ton/km^2/year) of TIN and 3 ton/km^2/year of phosphorus can be released from sediments with concentrated in nutrients as those of the central area of the lagoon. Taking into consideration the water surface (ca. 200 km^2) it gives some 2,000 ton/year of TIN and 600 ton/year of phosphorus released from sediments.

From sediments perturbed by the presence of macrofauna, releases of nitrogen more than ten times as high and fluxes of phosphorus up to three times as high, were observed in the laboratory experiments.

From the figures reported above one can assess that the present contamination in the sediments constitute a source of nutrients almost as important as the sum of industrial, urban, agricultural and atmospheric inputs (5,000 and 1,000 ton/year for nitrogen and phosphorus respectively, Cossu et al. 1984).

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TRANSPORT OF TRACE METALS BY SEDIMENTATION IN THE ADRIATIC SEA:

A CASE STUDY

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ABSTRACT

A detailed analysis is presented of available data concerning the input and distribution of trace metals in the northern Adriatic Sea. The importance of sediment transport of anthropogenically introduced metals is demonstrated. By determining "background" metal levels and fluxes for land-based sources, it was possible to identify distribution patterns and areas of maximum impact. The prodeltas of rivers are shown to be important sites for pollutant trapping and serve as a good indicator of pollutant loading to the system. Future research strategies and perspectives are discussed.

INTRODUCTION

Adriatic basin

The Adriatic Sea (Fig. 1) has always been regarded as a completely closed basin, with very little water exchange with the rest of the Mediterranean. A considerable amount of freshwater (2500-3000m^3/sec) is discharged into the entire basin. A big fraction of this discharge (1500 m3/sec) comes from the Po River (Grancini and Cescon, 1973), which is the largest italian river and drains a very industrialized as well as intensively cultivated area. Moreover, both sides of the basin are very popular sea resorts and attract millions of people every summer.

Problems of the open and coastal water pollution of the Adriatic Sea have therefore been the concern of scientists and administrators for some time. There was particular concern when some scientists predicted that the pollution phenomena was likely to damage the whole Mediterranean ecosystem in a short span of time as people were afraid that the Northern Adriatic Sea could have been the worst area affected.

Many national and international research programmes were formulated to study on the Adriatic Sea. Presently, in Italy, the most important are the ones sponsored by the National Research Council and another in the frame of the "Italian/Yugoslavian Treaty on Cooperation", a joint multidisciplinary programme on the investigation of pollution phenomena in the Adriatic Sea, operating since 1978 (Degobbis et al., 1986).

Hydrodynamics

The freshwater discharge, as shown in Tab. 1, is prevailingly due to the Po River (approximately 65% of the total); the smaller rivers discharging to the north and to the south contribute 35% of the total.

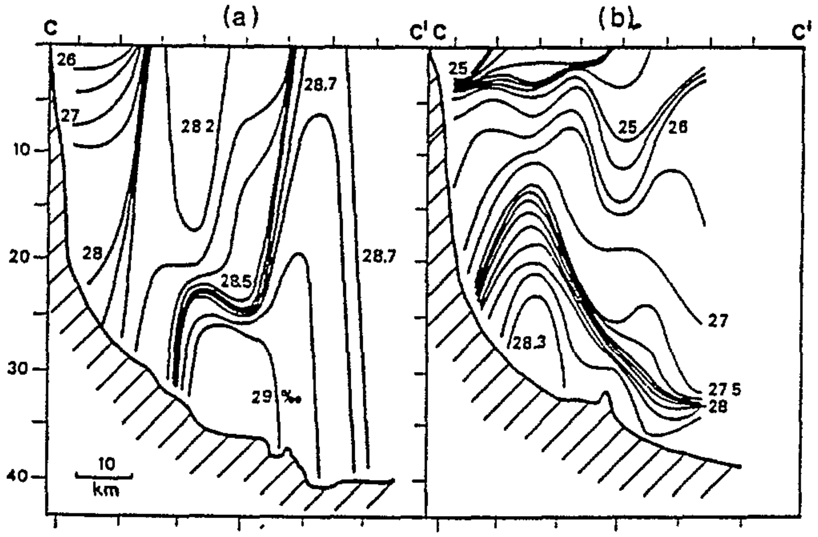
Table 1: Freshwater discharge (m^3/sec) into the northern part of the Adriatic Sea basin.

Area	Discharge	% of the total
North of Adige R.	350	14
Adige River	260	10
Po River	1570	63
South of Po R.	320	13
Total	2500	

Oceanographic studies carried out in the recent years (Malanotte Rizzoli et al., 1983) describe the water circulation in detail and report values of water residence time (one year approximately) shorter than those presented previously (Franco 1982).

Two different contrasting situations can explain the dynamics of the Northern Adriatic waters:

1. In winter, intensive vertical and horizontal mixing of water masses occurs which leads to a uniform distribution of physical oceanographic parameters. The circulation is essentially of thermohaline origin, and is governed by high salinity water dilution and heat exchange processes. The water column is therefore vertically homogeneous and the riverine waters flow southwards along the western coast, separated from the high salinity water of the central part of the basin by a sharp vertical discontinuity (fig. 2a).



2. In the summer the water column is vertically stratified; the distribution of the density field is mainly controlled by thermal variation of the water column produced by solar radiation. Two water masses are formed in the whole Northern Adriatic, separated by a marked pycnocline. An intermediate water mass is also observed (as a result of mixing phenomena and a lateral injection). The deeper densest layer consists of low temperature-high salinity winter water. The thickness of this layer tends to decrease at the end of the summer, and a dome structure can be isolated north of the basin in October/November (Fig. 2b).

The winter circulation can therefore be described as a cyclonic system, from which a secondary gyre separates on the isobath of 50 mn (fig. 3a). The overall cyclonic circulation, on the other hand, is very weak in summer (fig. 3b).

The wave motion and the tidal currents prevent stratification of the coastal waters (down to a depth of 10-12 m) and the waters of minor rivers (q = 10-250 m^3/s) often remain confined to this area.

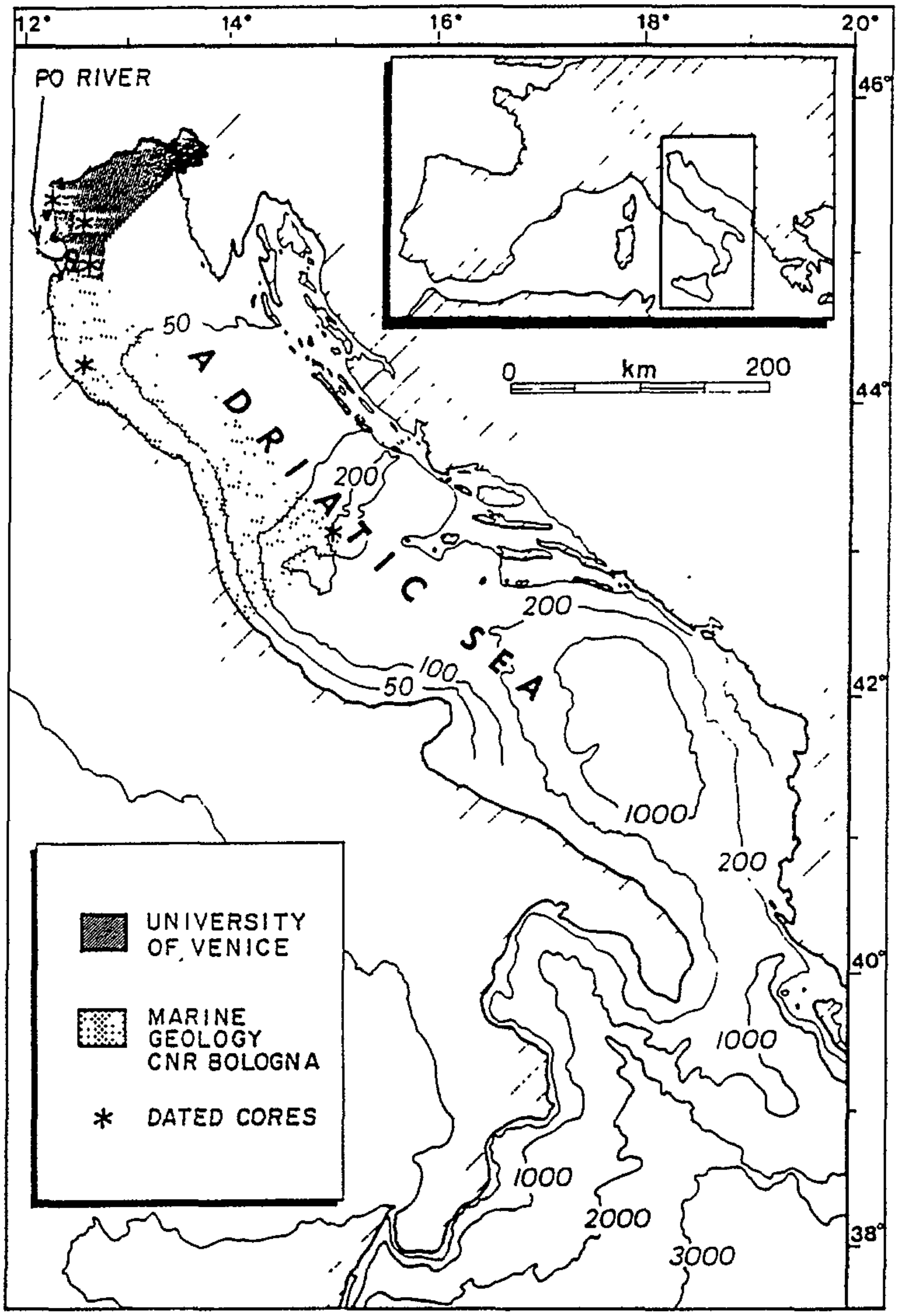


Fig. 1: Adriatic basin; the Po River outflow is in the NW part of the basin; contour lines are bathymetry in meters; the asterisks indicate the locations of the cores used for background calculations; the shaded areas are the most studied ones, from the two Institutions in legend.

Sediment Distribution

Morphology, sedimentology and mineralogy of the area have been discussed by several authors, among them Nelson (1970), Colantoni et al. (1979), Tomadin (1979) and Boldrin et al. (1988).

During the Wurmian regression (10,000 years ago), the whole Northern Adriatic basin emerged down to the Meso-Adriatic deep. During the Post-Glacial transgression the sea level underwent rise and stagnation periods. The actual shore line is slightly regressed in comparison with the transgression peak (nearly 2000 - 3000 years ago). The Po river transports relatively large amounts of solid material (about 14,106 ton/yr). Considering its restricted flow (1500 m^3/sec) and the fine materials settle either in the prodelta areas in front of the mouths, or further on, after having been transported in suspension by currents.

Silts and clays are found to prevail along the northern and western edges of the basin beyond the depth of 6-7 m. High contents of dolomite in sediments deposited in a belt at 20 to 25m depth (Frascari, 1986) SE off the Po River, indicate a transport pathway of fine materials from northern rivers. This material might be responsible for the transport to the south of some trace metals (cd, Hg, Zn). In the eastern part of the basin almost no recent fine material is deposited, (only a small amount of fine material is deposited) and only a small amount of fine material is transported into the Meso-Adriatic deep, down to 150-200m depth (Fig. 4).

The thickness of the holocenic fine deposits vary from 0 to 25m and therefore the average sedimentation rates, over a period of several centuries, range from few mm/yr to 2-4 cm/yr. The velocities were lower in the older sediments, becoming higher towards the more recent deposits. In particular the Holocene mud belts and the present prodeltaic deposits (related to the river discharges onto the large continental shelves of the Mediterranean Sea) show sedimentological affinities (Got et al., 1985). The Po River prodeltaic area shows sediment patterns that are similar to the ones described by Aloisi and Monaco (1975) for the Gulf of Lion (Boldrin et al,, 1988).

Methodology

Bottom sediments were collected using a box corer and core samples were recovered with a modified gravity corer (Busatti et al., 1980) and a sediment-water core sampler (Busatti et al., 1988).

Different analytical procedures have been used in our laboratory and other Italian ones during the period of studies. The aim was to find out an extraction method capable of dissolving the anthropic fraction leaving the lithogenic one undissolved. Two of the most used widely employed leaching procedures were those with cold 1N-HCl and hot HNO_3 (Guerzoni et al., 1984; Donazzolo et al., 1981). Complete dissolution of the sample, with teflon bomb digestion at 170°C, with a mixture of aqua-regia and HF, was also used. The analyses were performed with an AA Spectrophotometer, equipped with a graphite furnace for some elements (Pb, Cd). Analytical precision, together with comparison among different procedures, are presented in detail elsewhere (Guerzoni et. al, 1987).

Results

Trace metal input to the area: Most of the available data on the metal input to the studied area are from analyses of riverine suspended matter and of a few atmospheric and dust samples.

Provini and Pachetti (1982) studied the Po River and calculated (over a period of 18 months) total metal fluxes for Cr, Cu and Pb of 760, 970 and 1080 ton/yr respectively. For the Adige river, the same paper gives a metal flux of 40, 60 and 56 ton/yr for Cr, Cu and Pb respectively. Other estimates for the amounts of heavy metals entering

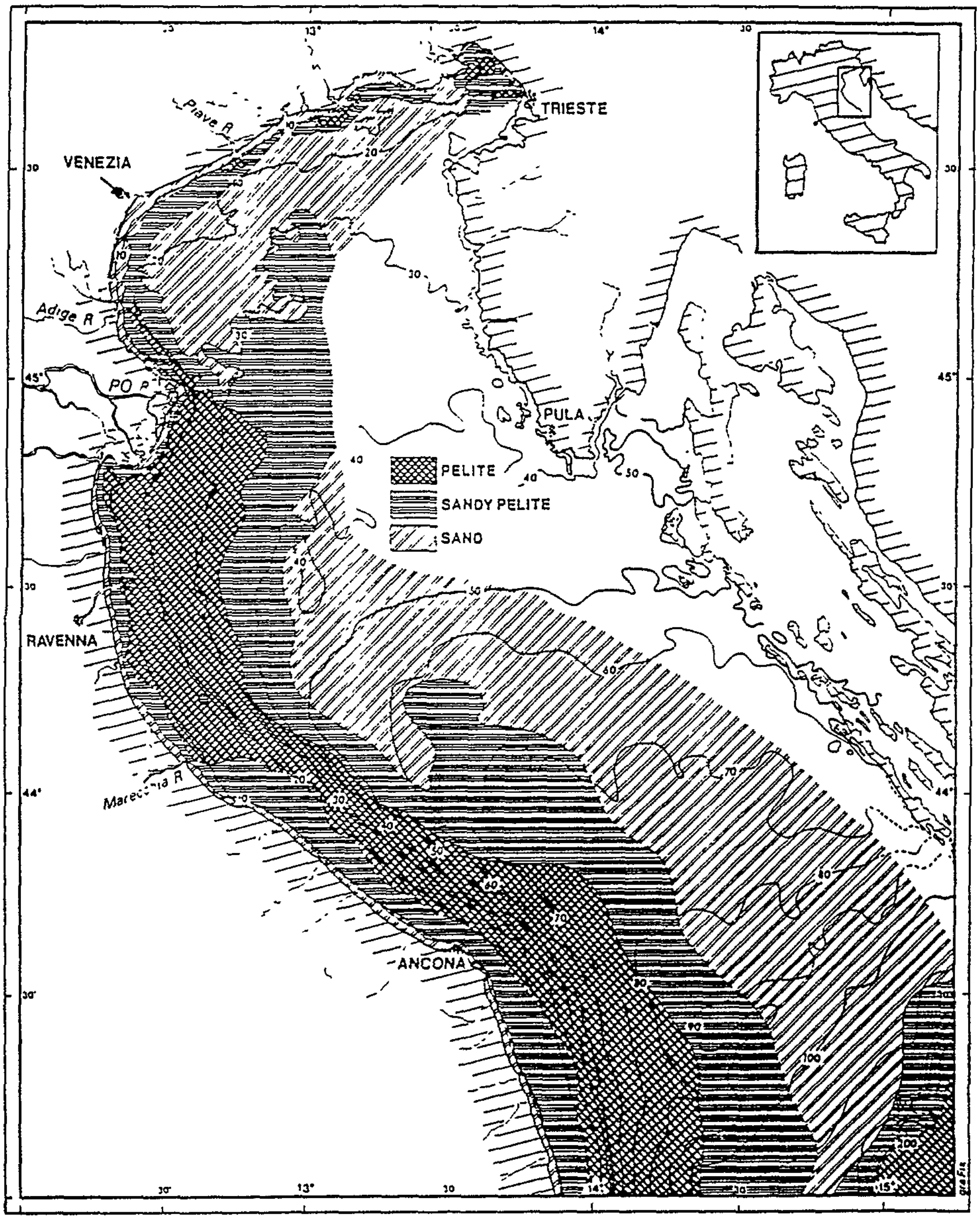


Fig. 4: Lithological composition of surface sediments (from Brambati et al., 1986).

the sea from the Po River give over 2500 tons of Zn, 89 of Ni and 65 of Hg (IRSA, 1977). Those figures are approximately twice as great as those observed in the Rhone River (430 t/yr of Pb and 1330 for Zn. Oregioni *et al.*, 1978). Guerzoni *et al.* (1985) estimated that the total annual natural metal fluxes from the Po are about one third of the present day fluxes.

Recently, some new data was made available on dust samples collected at the sea-air interface in the southern part of the study area. The calculated eolian fluxes averaged 121 ng cm^{-2} y^{-1} for Pb, 185 for Zn, 20 for Ni and 0.6 for Cd (Guerzoni et al., 1987). The data, transformed for an area of approximately 130,000 Km2, gives an average flux from the atmosphere of about Pb = 150, Zn = 200, Ni = 25 and Cd = 1.0 ton/yr.

Table 2 summarizes the available data.

Table 2: Trace metal load (ton/yr) delivered to the Northern Adriatic Sea; (a), (b) Provini & Pachetti, 1980. (c) Guerzoni *et al.*, 1987b.

Input	Cr	Cu	Pb	Zn	Hg	Ni	Cd
Adige River (a)	40	60	56				
Po River (b)	760	970	1080	2500	65	89	
Other Rivers		?	?	?			
Atmosphere-particulate(c)		?	150	200	?	25	1

General Studies

Most of the recent studies in the Northern Adriatic Sea sediments can be summarized from the papers of Marine Biology Institute and University of Venezia, and Marine Geology Institute in Bologna (Donazzolo *et al.*, 1981, 1982, 1984a; Mantovani *et al.*, 1985; Frignani *et al.*, 1978; Frascari *et al.*, 1979; Guerzoni *et al.*, 1984; Frascari *et al.*, 1988).

The whole Northern Adriatic Sea can be subdivided in two sub-areas, one from Trieste (TS) to Chioggia and the other from Chioggia to Ancona (AN). It was clearly apparent from the data on these geochemical regions that the composition of the marine sediments is directly influenced by the nature of the materials transported by various rivers, with some important differences due to the role of the Po River in the Southern sub-area. In table 3 the average data and ranges for the two sub-areas are reported.

The principal accumulation sites are: (a) The marine area in front of a chlor-alkali plant and the mining district of Idria, with high content of Hg; (b) offshore from the Venice Lagoon, where anomalous quantities of Zn and Cd were detected; (c) at the mouth of the rivers Brenta and Adige, with extremely high (200 ppm) values of Cr were associated with leather industries along the rivers; (d) in front of some tributaries of the Po River.

South of the Po River, the fine-grained sediments show lower levels of almost all metals, decreasing with distance from the Po, and some local accumulations, especially Cr, in front of the mouths of small rivers.

Table 3: Average and range of metal data (mg/kg, dry weight) in two sub-areas north and south of the Po River delta (from Frascari *et al.*, 1988.

Area	Cd	Cr	Cu	Hg	Pb	Zn
N. of Po River	1.1	24	15	0.8	35	94
	0.1-5.6	4-273	2-52	0.1-16.9	5-96	2-870
S. of Po River	0.5	44	17	0.2	30	71
	0.1-1.2	16-74	1-48	0.1-1.0	4-75	15-171

Lagoons

The most studied lagoonal areas of the Northern Adriatic area are the Venice Lagoon, shallow lakes ("Valli") near Ravenna and the lagoons of the delta of the Po River. Those environments are perfect natural collectors of the fine-grained sediments and usually retain all the inorganic and organic wastes (industrial and agricultural) discharged into them.

Venice and Ravenna lagoons are reported to be polluted from industrial discharges, but Guerzoni et al. (1984) found that deltaic lagoons did not show the maximum concentration among the metals studied (Cd, Cu, Cr, Hg, Zn) except for Pb, in comparison to riverine or prodeltaic sediments. Donazzolo et al. (1984b) reported that the sources of trace metals (especially Hg, Pb, Co, Cu, Zn and Cd) in the sediments of the Venice Lagoon is the Marghera industrial zone. High organic carbon levels were found in the SE part of the lagoon. Anconelli et al. (1980) studied Ravenna salt-marshes and found extremely high levels of Hg and high values of Pb, Zn and Cu, indicating industrial pollution due to direct dumping of petrochemical wastes. In Table 4 the data of metals in the semi-enclosed environments are presented.

Table 4: Range of metal values (mg/kg, dry weight) in three closed environments of the studied area (from Frascari et al., 1988).

Lagoon	Cd	Cr	Cu	Hg	Pb	Zn
Venice (a)	0.6-20.8	6-34	5-180	0.1-3.5	15-164	18-3000
Po delta (b)	1.2- 1.6	47-85	46- 65	0.3-0.6	59- 81	156- 210
Ravenna (c)	0.5- 9.5	—	12-280	0.1-245	12-122	19- 303

Off-shore Studies

Following the classical studies of Stirn (1974) and Paul and Meischner 1976), in the recent years Frignani & Giordani (1983) analyzed some offshore samples (surface and core) and the previously cited ASCOP programme gave more data on a basin-wide scale (Giordani et al., in press). Table 5 summarizes the offshore data, together with averages of coastal (less than 12 miles offshore) data (from the general study), and a nearshore Mediterranean environment, for comparison.

Table 5: Comparison of metal concentrations (mg/kg, dry weight) in offshore and coastal sediments of Adriatic and Mediterranean Seas; (a) Frignani et al., 1983; (b) Giordani et al., in press; (c) Paul & Meischner, 1976; (d) Frascari et al., 1986; (e) Donazzolo et al., 1984a; (f) Renfro & Oregioni, 1974.

Area of Study	Cu	Pb	Zn
Frignani & Giordani (off-shore) a	21	30	61
ASCOP (offshore Adriatic) b	25	31	75
Paul & Meischner (offshore)c	20	15	90
Northern Adriatic (coastal) d (Po + Emilia Romagna)	23	37	88
Gulf of Venice (coastal) e	20	35	80
Renfro (nearshore Mediterranean) f	18	56	73

Po River delta area

The deltaic area of the Po River is approximately 400 km^2 and, apart the contribution of the river itself, it receives a small (10-20%) amoung of fine-grained sediments from the north.

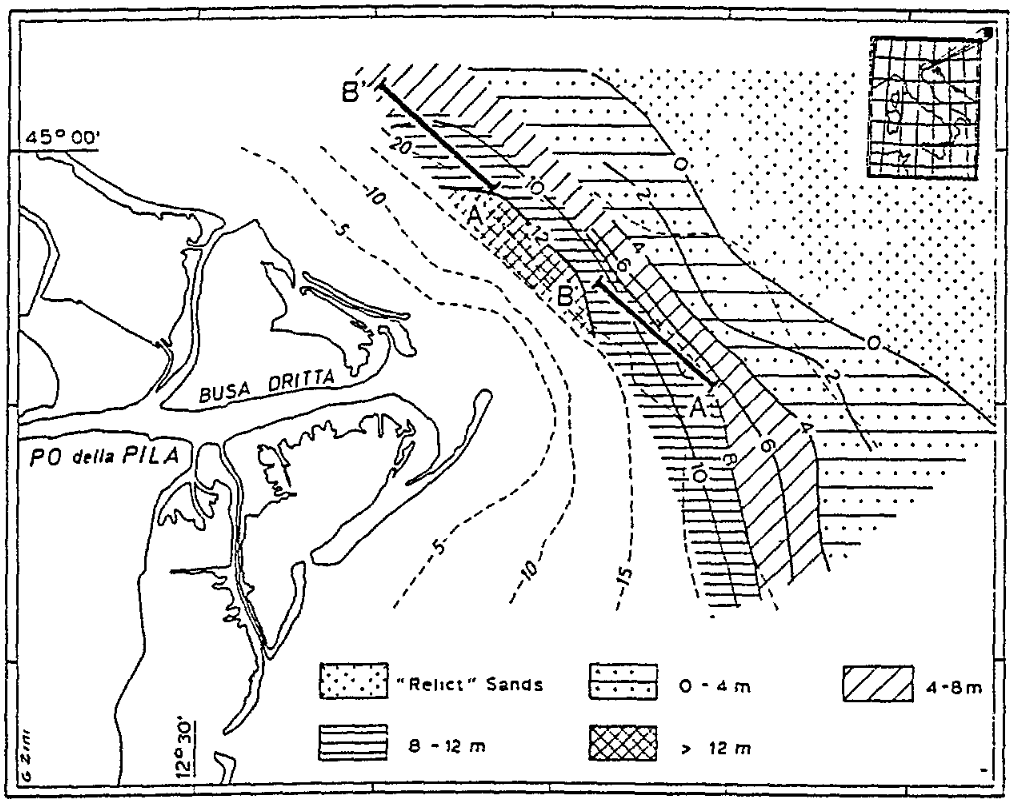


Fig. 5: Thickness (m) of the Holocene muds off the Po River delta (solid lines); dashed lines indicate the bathymetry (m); (from Boldrin <u>et al</u>., 1988).

As described previously, the nearshore prodeltaic area is characterized by rapidly accumulating deposits (2-4 cm/yr) enriched in smectite, gas, organic material and trace metals. The thickness of the muddy sediments reaches 10-12m in front of the main mouth and thins seaward, and is only a few centimetres thick, 8 km offshore (Fig. 5). During the summer, the marine waters of the area present a typical multi-layer system with three distinct water bodies (Fig. 6a): (1) riverine and diluted waters, (2) middle depth waters (10-20m), and (3) bottom waters (Boldrin et al., 1988). The bottom water layer, between 15 and 20 m, has a dome structure that interacts with bottom sediments with the highest content of organic matter (Fig. 6b).

Fig. 6· (a) Density Sigma-t and total suspended matter (TSM) (mg/l) off the main mouth of the Po River. The 21 and 24 Sigma-t contours separate three different water (typical of the summer). Particle size spectra at the surface (0.5 m deep), at 19 m deep and at the sea bottom are shown for a station just inside the nearshore prodeltaic area (from Boldrin et al., 1988).

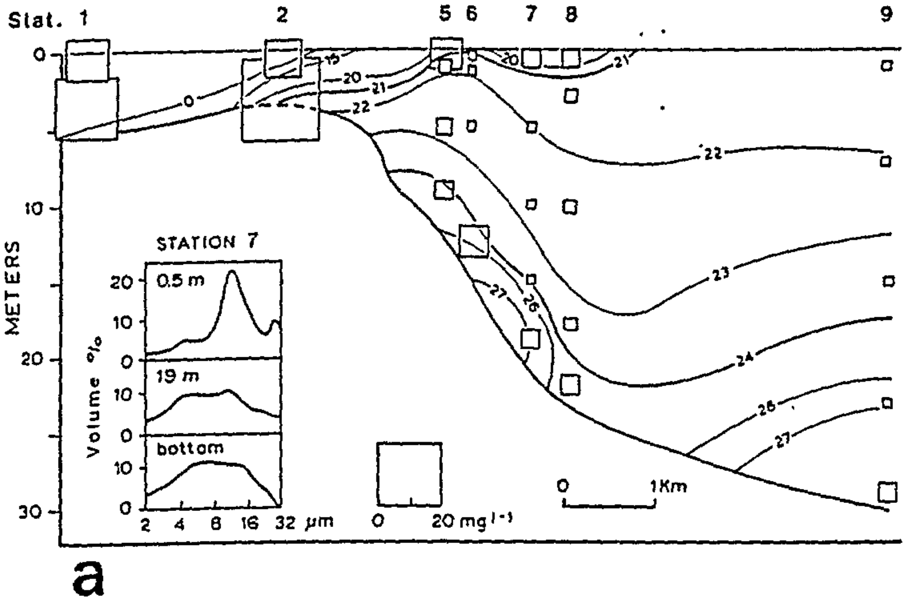
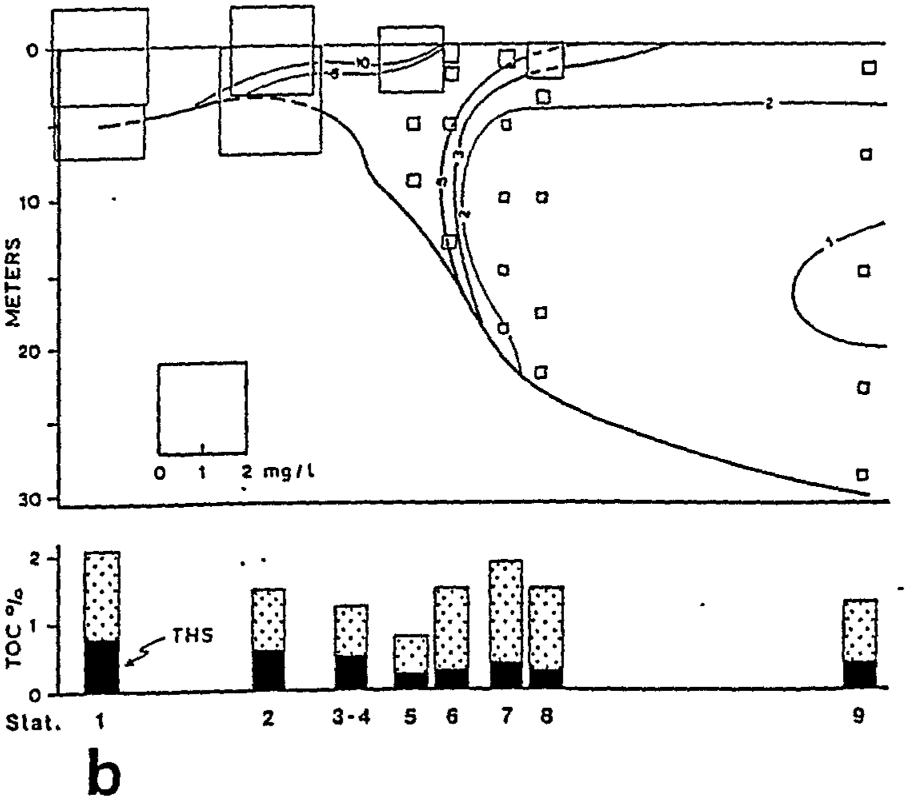


Fig. 6: (b) Particulate organic carbon (POC) (mg/l) of suspended sediments (squares) and yellow substance distribution (arbitrary fluorescence unit AF contours) off the Po River delta. The histograms show total organic carbon (TOC) (%) and total humic substances (THS) (%) content of bottom sediments at the same stations (from Boldrin et al., 1988).



Trace metal concentrations of Cd, Cu, Hg, Pb and Zn in the upper sediment layers of studied cores appeared to be higher than the average values found for surficial fine-grained sediments from the surrounding area (Guerzoni et al., 1985; Frascari et al., 1986). Fig. 7 shows the area of the maxima around the main mouth of the river and Table 6 shows the average values, in comparison with the surrounding Po delta area.

Discussion

Background values:

Different methods were tentatively applied to define the background values of the area for some trace elements. Among them, the most valuable is the use of trace metal values of radiodated core segments that extend far enough back in time beyond anthropogenic influence. Some sets of surficial data were compared with independent 137-Cs measurements, assuming as baseline values those of samples with a correspondent zero value of the nuclide. In other cores, trace metal data of pre-holocenic sediments were presented. Fig. 8 shows two examples of trace metal profiles with depth, in cores with different sedimentation rates. One core was collected just off the Po River (2-4 cm/yr) and the other in front of Ravenna (0.5-1 mm/yr).

Natural background concentrations of fine-grained sediments have been proposed for the Lagoon of Venice, for the Po delta and south and for the Middle Adriatic Sea by Selli et al. (1980), Donazzolo et al. (1982) and Guerzoni et al. (1984) and are in good agreement (within 15-20%) with each other. Some uncertainties for Cd data still remain, especially after low values were found in some cores of the N. Adriatic.

On the basis of our data, and after taking into account the values proposed from other authors, we propose for this area the following natural background concentrations: Cd = 0.20 ppm, Cr = 25, Cu = 20, Hg = 0.12, Ni = 35, Pb = 23 and Zn = 70. As a comparison, Whitehead et al. (1984) proposed the following values as background for the entire Mediterranean Sea: Cd=0.15, Cu=15, Pb=25 and Zn=50.

The values of the Adriatic Sea are quite close to the general ones and represent, as expected, the local variability due to geochemical background. From this data, a good estimate of the sediments indicating a high level of contamination is possible, and concentration factors (actual vs. background) can be calculated.

Accumulation areas

In Fig. 9 we present a synthesis of the relative importance of different depositional environments in accumulating Zn, Pb, Cd and Hg. The data are averages of those presented through the paper in the different environments, and are plotted in comparison with the background levels. Pb and Zn correlate very well, whilst Cd and Hg display some differences. The highest pollutant accumulations are found in the prodelta of the rivers and in areas of low hydrodynamic energy (lagoon of Venice, Ravenna and Po).

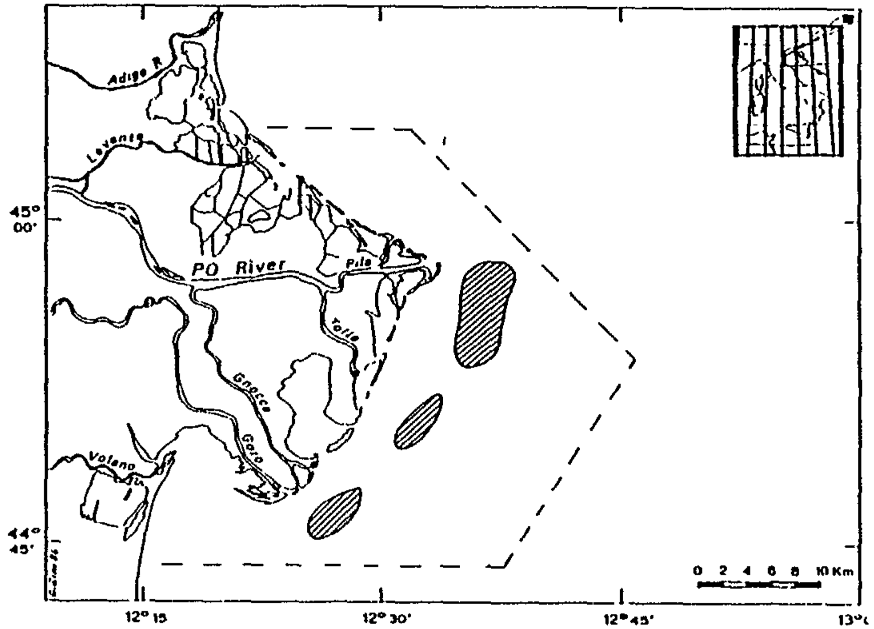


Fig. 7: Prodeltaic areas off Po River main mouths (40 km^2); the dashed line indicates the Po River deltaic area with *fine-grained sediments* (400 km2, *see also table 6 for metal* concentrations).

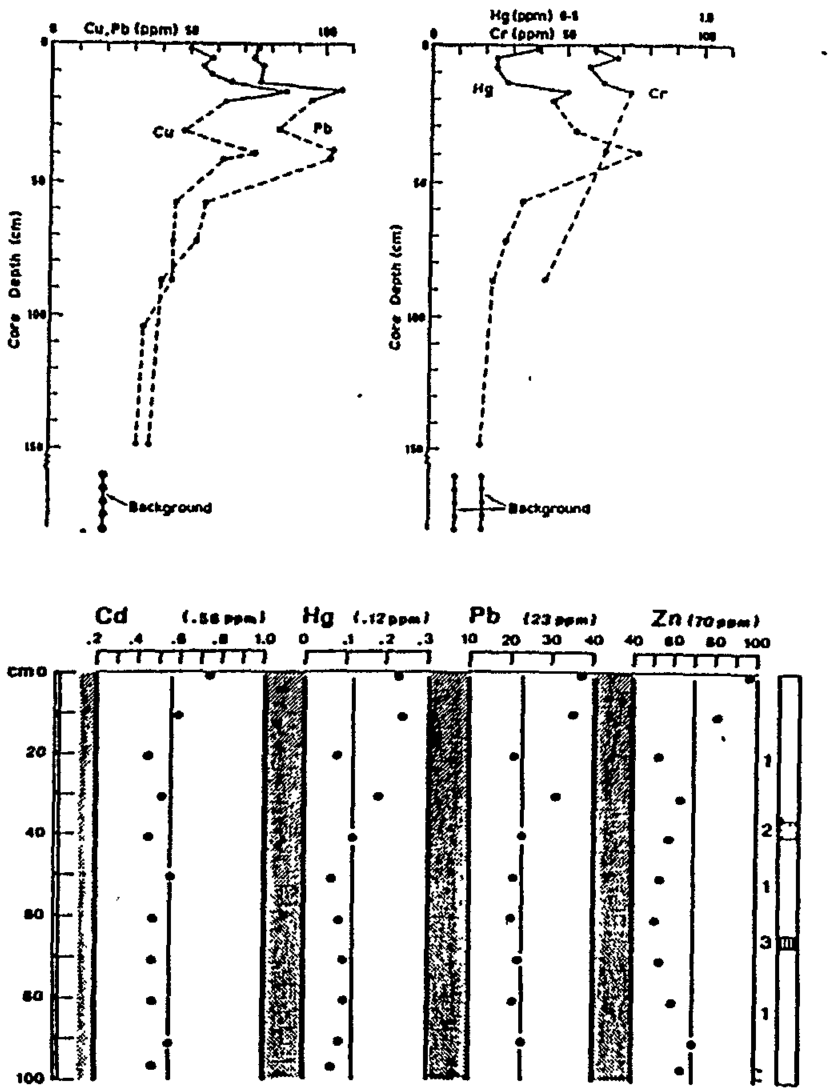


Fig. 8: Trace metal concentrations (mg/kg, dry weight) versus depth profiles (cm) for a core just off the Po River main mouth (above) and another in front of Ravenna (see Fig. 1 for locations).

The Po River and industrial areas are responsible for the largest input of Zn and Pb (high values in lagoons, prodelta and Po area), whilst industrial discharges and northern rivers are responsible for the delivery of Hg and Cd.

Storage capacity

Miserocchi (1987) studied Cu, Pb, Hg and Zn in surface and core samples in the Ravenna lagoon and estimated respectively in 100, 100, 40 and 230 tons the amount of the metals stored in the sediments deposited in approximately the last 20 years.

Donazzolo *et al*., (1984) reported figures of 1600, 1300, 16500 and 35 ton for the same metals stored in the first 10 cm (about 20 yr) of the sediments of the lagoon of Venice.

The estimate for the nearshore prodeltaic area (shown in Fig. 7) was made multiplying the area (approximately 40 Km^2) for the sediments deposited in the last 20 years (about 40 cm) for the average concentrations listed in Table 6.

In Table 7 we present a comparison of the metals stored in the last 20 years, in two lagoonal environments (Venezia and Ravenna) and in the nearshore prodeltaic area of the Po River.

Table 6. Average metal data (mg/kg, dry weight) in front of the Po River delta (400 Km2) and in the prodeltaic area off Po River main mouth (40 Km2).

Area	Cd	Cu	Hg	Pb	Zn
Po delta	0.3	23	0.3	37	88
Prodeltaic	0.9	60	0.6	85	190

Table 7. Trace metals stored (ton) in different reservoirs. (a) Donazzolo *et al* , 1984b; (b) Miserocchi, 1987; (c) estimate for the nearshore prodeltaic area shown in Fig. 7 (see text for explanations).

Area	Cu	Pb	Zn	Hg
Venice lagoon (a)	1600	1300	16500	35
Ravenna "Valli" (b)	100	100	230	40
Prodelta Po (c)	100	1300	3000	10

This table shows that the extremely large amount of Hg in the lagoon of Ravenna and the large amount of Zn in the lagoon of Venezia affects the concentration of the same element in the marine area offshore. Both are related to industrial discharges.

As far as the prodeltaic area is concerned, if we compare the fluxes of the Po River (annual load from Table 1) multiplied for 20 years, with the amount of metals stored in this small area (0.03% of the total), it comes out that approximately 5% of the load of Cu, Pb and Zn and 1% of the Hg is retained in 1/300th of the total area.

CONCLUSIONS

Rivers carry large quantities of heavy metals into the marine environment, some of which are natural and some of which are derived from pollution. It is often difficult to assign a quantitative estimate of the riverine flux of pollutant metals to the sea because of the lack of data on the heavy metal chemistry prior to the era of significant pollution. Careful measurement of the composition of the marine sediment cores combined with independent indicators of the "age" of particular sediment layers, can help to provide estimates of the riverine metal fluxes in the past.

The results of most of the studies confirm that the concentration of trace elements in the marine sediments is essentially depending on its mineralogical composition and on the size of the deposited particulate matter. In particular the fate of the pollutants in the marine environment is mainly associated with the transport, distribution and sedimentation phenomena of fine materials (silt and clay).

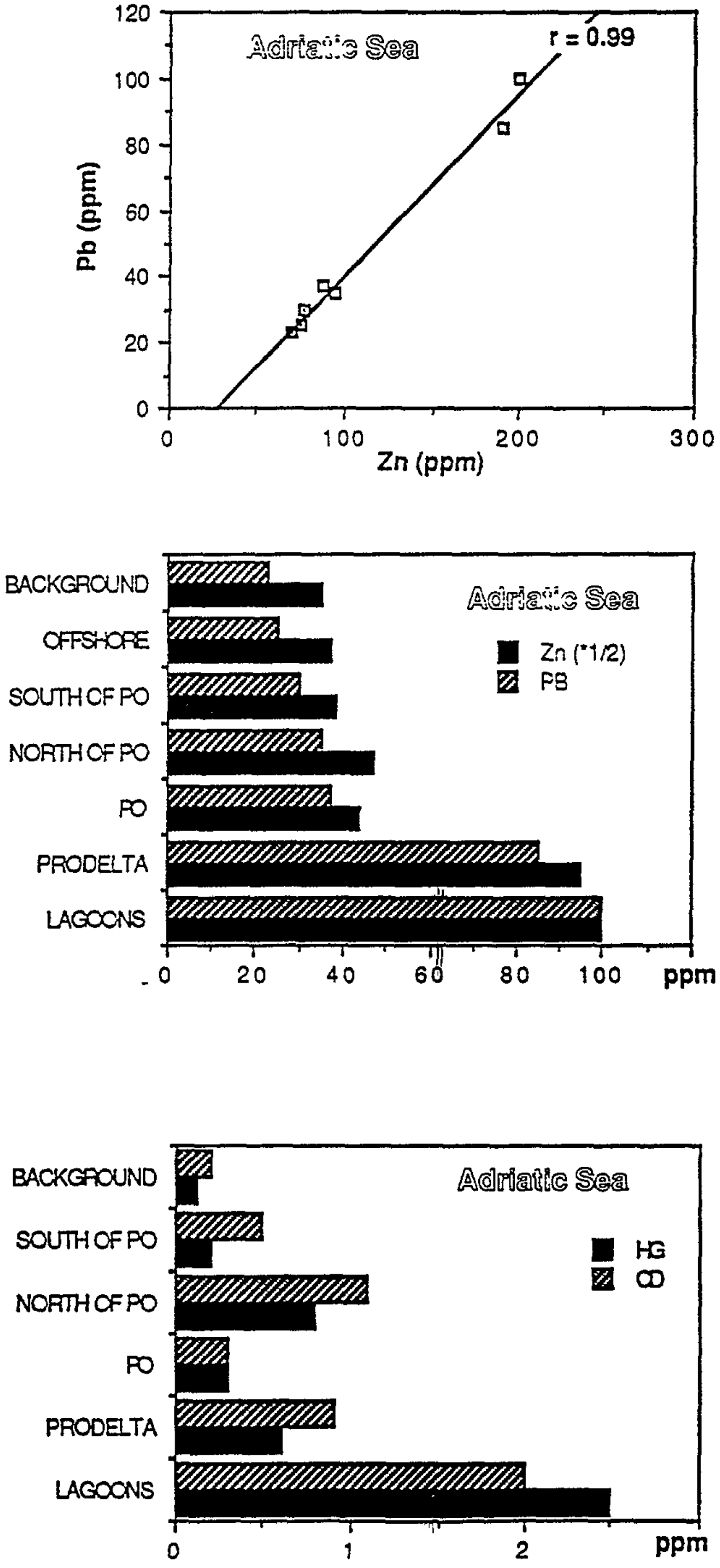
Target sites to study

We have previously reported (Guerzoni *et al*., 1984) analytical data for a sediment core, just off-shore from the Po River discharge, which should be representative of the fine sediments derived from this river over the past few decades. These data, examined in conjunction with pre-industrial metal concentrations from other similar types of detrital sediment deposits, indicate the proportion of metals accumulating in marine sediment near the Po which were derived from pollution.

The results of the investigation of the nearshore prodelta, directly in front of the main outlets of the river, demonstrate the meaningful use of this area as a "sensitive barometer" for pollution problems. The efficiency in "concentrating" the toxic metals was calculated to be 30 (1%/0.03%) to 150 (5%/0.03%) times higher than other nearby areas. The prodeltas therefore could be targeted areas to provide advance warning of environmental problems.

Both of these approaches should be applied to all the principal rivers entering the Adriatic Sea, and related offshore areas. The proportion of pollutant metals in these nearshore marine sediments, combined with measured present-day fluxes of metals, will provide a good indication of the natural and pollutant metal fluxes to the Northern Adriatic Sea.

Fig. 9: Average concentrations of Zn, Pb, Hg and Cd (mg/kg, dry weight) of different depositional environment (see text for explanations).



Open problems and future effort

- More detailed studies are needed, especially to describe the depositional processes, the distribution of the suspended load and biogeochemical processes in the water column.

- The mud deposits at shallow depths and the structure of a multilayer system offshore from the freshwater-seawater mixing zone probably present considerably seasonal differences, that have to be investigated. Some preliminary results confirm the hypothesis of different seasonal sedimentation velocities, with high levels of deposition rate during summer period (may to September), followed by a partial erosion of the previously deposited sediments.

- The use of different methodologies to evaluate the specific background levels of the area is required to avoid misunderstanding of the proportion between natural and pollutant inputs.

- The large range of the atmospheric flux data and the lack of long-period sampling, stress the need of more work to study the atmospheric input. More data on small rivers will be also useful to understand their importance.

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SOURCES AND FLOW OF SUSPENDED ORGANIC MATTER IN THE GULF OF TRIESTE (NORTHERN ADRIATIC): C AND N ELEMENTAL AND C AND H ISOTOPIC EVIDENCE

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ABSTRACT

Measurements of the C:N ratios and the isotopic composition of C and H various classes of autochthonous (pelagic and benthic autotrophs, net-zooplankton and jellyfish) and allochthonous organic matter (riverine and sewage) in the Gulf of Trieste were used to elucidate the origins of marine POM and sedimentary organic matter. The causes for C and N elemental and C and H isotopic fractionations in the primary producers and pelagic consumers were found to be primarily the differences of source of dissolved inorganic carbon and reactions occurring prior to CO_2 fixation in the cell, and selective respiration of $^{12}CO_2$, respectively. The mixing models, constructed with $\delta^{13}C$ values and C:N ratios, indicate the POM in the Gulf of Trieste is prevalently of autochthonous marine origin (60%), while sedimentary organic matter is a mixture of marine POM and benthic producers in the ratio 2:1. Pelagic food web analysis demonstrated that the labile fraction of marine POC (phytoplanktonic carbon) is primarily a food for net-zooplankton.

^{13}C depleted detritus of riverine and sewage origin is probably deposited on the surficial marine sediment or exported out of the waters of the Gulf of Trieste.

INTRODUCTION

The composition of suspended particulate and sedimentary organic matter in coastal waters is presumably controlled by mixing of autochthonous organic matter produced by marine producers and allochthonous organic matter of riverine and sewage origin. Terrigenous organic matter can be identified in marine sediments by its high C:N ratios (Kukal, 1971) and recently, the presence of lignin was assumed to be a sensitive indicator of terrigenous input (Pocklington, 1976). On the other hand, a sensitive biomarker of anthropogenic inputs was found to be coprostanol (Hatcher and McGillivary, 1979) as an indicator of the introduction of sewage organic matter in coastal waters.

Nearshore gradients in the stable carbon isotope ratio ($\delta^{13}C$ of sedimentary organic matter have been assigned to a mixing of autochthonous marine and allochthonous land-derived organic matter. This rationale was based on observations that riverine inputs produce ^{13}C depleted values in contrast to ^{13}C enriched autochthonous marine organic matter (Tan and Strain, 1979; 1983; Sackett and Thompson, 1963; Hunt, 1970). Shifts in stable C isotope ratios can also provide evidence of the introduction of petroleum contamination (Sackett <u>et al</u>., 1986) and sewage derived organic matter in the marine environment (Sweeney and Kaplan, 1980; Sweeney <u>et al</u>., 1980).

The rather straightforward presumption is, however, complicated by several factors which govern the distribution of heavy C isotope in the marine environment. Among them, the most important appears to be the differences in the fractionation of C isotopes during CO_2 fixation between C_4 (Hatch-Slack) and C_3 (Calvin-Benson) photosynthetic pathways. It was pointed out that primary producers fixing inorganic C by the C_4 pathway are considerably less enriched in 12_C than C_3 primary producers (Smith and Epstein, 1971; Bender, 1971). Also, for marine phytoplankton a relationship between sea water temperature and photosynthetic fixation of inorganic C was proposed based on the observation that phytoplankton in cold waters is more ^{13}C depleted than in warmer seas (Sackett <u>et al</u>., 1965). This statement was criticized by others (Fontugne and Duplessy, 1978; Fry <u>et al</u>., 1984). Fractionation of stable C isotopes in higher pelagic and benthic tropic levels as well as microbes, has been asigned to their dietary $\delta^{13}C$ values (Monson and Hayes, 1982; Rau and Anderson, 1981, Fry and Arnold, 1982; Fry and Sherr, 1984). Based on this statement, the shifts in stable C isotope ratio can also provide evidence of the transfer of sewage-derived organic matter (Sweeney <u>et al</u>., 1980;. Rau <u>et al</u>., 1981) and petroleum (Spies and Desmarais, 1983) to marine organisms. On the other hand, the biochemical components of organisms exhibit significant differences in their C isotopic composition, the lipids being the most deplated in $\delta^{13}C$ values (De Niro and Epstein, 1977) and carbohydrates approaching the isotopic composition of the bulk organism.

The wide range of $\delta^{13}C$ values found in marine organic matter is in general retained in marine sediments, since isotopic changes during burial and diagenesis or organic matter are low, although in some cases changes, though not substantial, do occur. Therefore, the primary carbon sources are not seriously changed in marine sediments (Schidlowski et al, 1983; Schidlowski, 1986). Isotopic modifications of sedimentary organic carbon proceed through separation of the isotopically light lipid fraction and their hydrocarbon derivatives from the bulk kerogen, preferential cleavage and subsequent loss of isotopically distinctive functional groups, such as heavy - COOH, during biological and thermal degradation, and selective disruption of ^{12}C - ^{13}C bonds in response to increasing thermocatalytic processes (Peters et al., 1980; Schidlowski, 1986). Re-equilibration of stable C isotopes between sedimentary organic matter and coexisting carbonates at elevated temperatures has been reported due to the preferential volatilization of ^{13}C during metamorphic decarbonation processes in carbonates. These carbonates remain isotopically ligher (Schidlowski et al., 1983).

The mechanism and role of stable H isotope fractionation in marine organic matter is not yet completely clear, although it was reported that animals in the majority of cases have δ D values similar to their diet (De Niro and Epstein, 1981). Furthermore, δ D values seem to be a good indicator of fresh-water influence on the diet in the marine food web due to the great difference of δ D values between the sea water and fresh-water environments (Taylor, 1974). The great δ D enrichment of marine organic matter with respect to sea water is also reflected in sedimentary organic matter (Schidlowski et al., 1983), although it has been suggested that during early diagenesis the compounds enriched in D are preferentially lost leaving a residual D depleted organic matter (Schliegl and Vogel, 1970).

In this paper we summarize our recent results on the study of the sources and fate of suspended and sedimentary organic matter in the Gulf of Trieste (Northern Adriatic). In order to define better and unequivocally the origins of POM and sedimentary organic matter in the Gulf, which are presumably a complex mixture of allochthonous and autochthonous derivation, we used a multiple tracer study consisting of chemical and isotopic analyses. C/N elemental ratios were supplemented by $\delta^{13}C$ and δ D values of different classes of organic matter, i.e., riverine and sewage POM, phytoplankton, marine POM, net-zooplankton, the jellyfish Pelagia noctiluca as the top pelagic consumer, benthic macrophytes and sedimentary organic matter, in constructing multiple source mixing models for POM and sedimentary organic matter. We also tried to decode the mechanisms of C and H isotopic fractionation involved in this study, since their isotopic data are dependent on their basic biochemical processes. Also, $\delta^{13}C$ and D values provided some interesting data on the pelagic food web structure in the Gulf, thus helping to resolve the fate of POM in the sea water column. Moreover, the C and H composition of total dissolved inorganic C and environmental water, respectively were checked to relate them to the C and H isotopic composition of organic matter. These data were also tested in relation to trace the possible implications of petroleum contamination of sediments in the Gulf.

Study Area

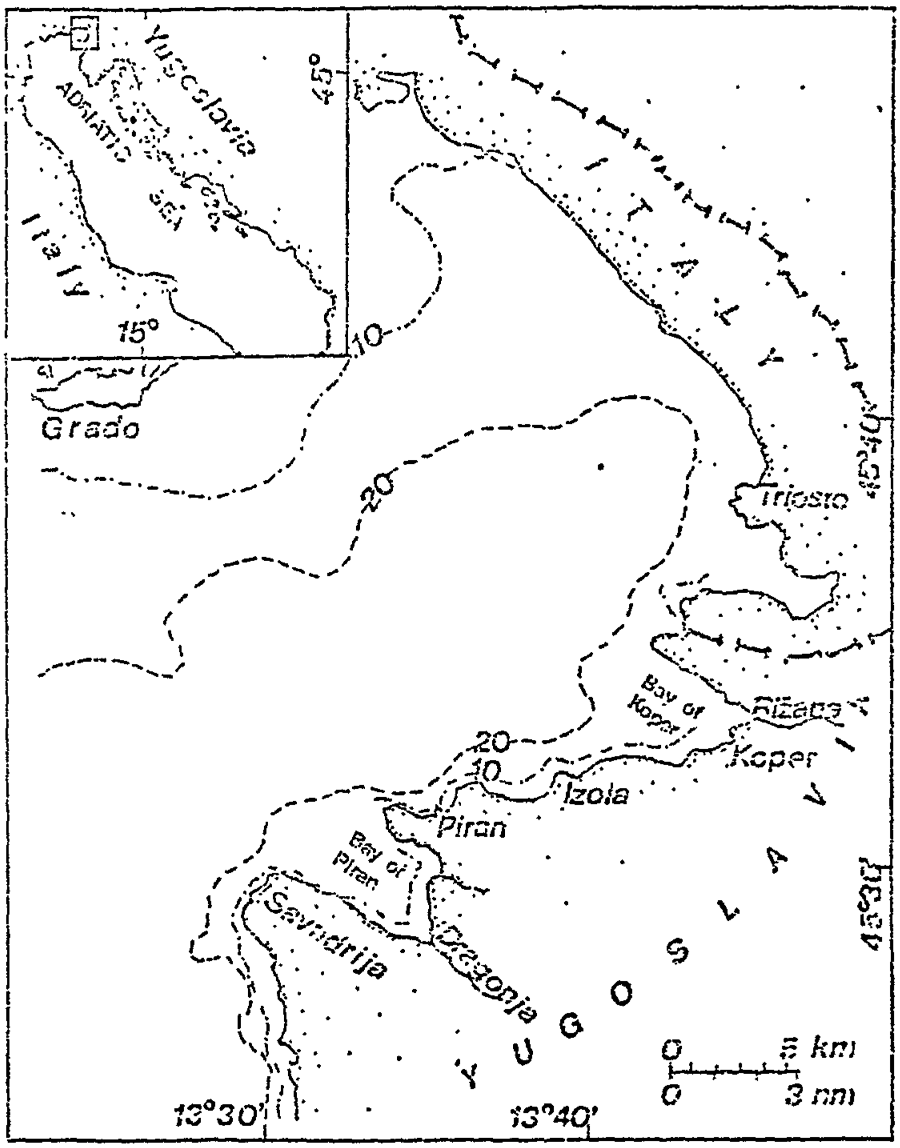
The present study was conducted in the central and southern part of the Gulf of Trieste, the Northernmost and shallowest part of the Adriatic Sea (Fig. 1). The maximal depth of the Gulf of Trieste does not exceed 30 m and about one fifth of the area has a depth of less than 10 m. It is strongly influenced by winds (Bora) and local fresh water discharges. The salinity of the waters is typically marine, ranging between 33 and 38 ^{o}/oo. The waters of the Gulf in general remain permanently oxygenated throughout the water column, except when the strong pycnocline is located just above the bottom (approx. 1 m) and horizontal sea water dynamics are reduced (for example in September 1983). The water circulation of the Gulf is mostly controlled by tides (approx. 0.5m) and winds (mostly NNE), although it is also affected by the main counterclockwise circulation pattern of the Northern Adriatic. These factors, superimposed on each other, lead to a complex circulation pattern not consistent with any of the proposed models.

The near-shore sediments of the Gulf consists principally of sandy silt and silty clay, while the sediment of the central part of the Gulf is composed of silt. The coarse fraction is mostly composed of foraminifera and skeletons of moluscs. The silty fraction of the sediment in the central part of the Gulf is continuously flushed by a near-bottom current, going mostly in the direction SW-NE. The carbonate content and the grain-size composition decrease from the central part of the Gulf towards the shore. The mineral composition of the surficial sediments is fairly uniform. Quartz prevails over clay minerals, carbonates and feldspar. The authigenic minerals are aragonite and pyrite, the latter being an indication of a reducing environment in the sediment, which usually appears few centimeters below the surface.

Experimental Samples

Samples for $\delta^{13}C$ analyses in total dissolved inorganic carbon (DIC) and δD in water were collected periodically in 1982. Samples for POM, net-zooplankton, jellyfish *Pelagia noctiluca*, benthic macrophytes *Fucus virsoides* and *Ulva rigida* and surficial sedimentary

Figure 1. Sketch map of the study area in the Gulf of Trieste (Northern Adriatic)



organic matter were collected periodically during 1980-85. A dinoflagellate bloom of Gyrodinium sp. was sampled in September 1984 in the Bay of Koper and a diatom bloom of Hemiaulus hauckii in the central part of the Gulf of Trieste in December 1987. Samples for riverine POM were taken in the Rizana river in 1985 and those for $\delta^{13}C$ in DIC and δ D in brackish and riverine water in the rivers Dragonja and Rizana and their mouths in 1982. Sewage samples were collected in the Koper and Piran sewage systems.

Sea water samples for all analyses were taken at the sea surface (0.5m) and in the bottom layer (1m above the bottom) using Niskin samplers. Marine POM was sampled by the filtration technique and using cylindrical sediment traps (i.d. 4 cm, height/width ratio of about 5) located approx. 1m above the bottom to reduce resuspension. Samples of POM and phyto plankton blooms were filtered through preignited (4 hours at 480°C) Whatman GF/C glass fibre filters. Zooplankton samples were collected by standard IO 250 µm mesh size net. Macrophytes were collected by hand in the mediolitoral and jellyfish were collected using plastic beakers. Surficial sediment samples (0-4 cm) were taken with a Meischner-Rumohr (1974) gravity core sampler (i.d. 4 cm) at water depths of 15 - 20m.

Analyses

Samples for C and N elemental and δ D analyses of POM, plankton and macrophytes were freeze-dried without pretreatment. Samples for organic analyses of marine sediments were first acid-treated with 1 N HCl and subsequently freeze-dried. Lipids in homogenized benthic macrophytes were extracted with CCl_4 under reflux for 4 hours. Amino acids and globular proteins were extracted with water from residue.

C and N contents of the Samples were determined with a commercial CHN elemental analyzer (Coleman), calibrated with acetanilide. DIC in waters was determined by precipitation of carbonates with NaOH and $CaCl_2$ and subsequently dissolution of carbonates in H_3PO_4, producing CO_2. Hydrogen from water samples was produced by reaction of water with hot Zn wool at a temperature of 350 - 400°C. For isotopic C and H analyses of organic matter the samples were ignited to CO_2 and H_2O at 1200 °C in oxygen. The isotopic composition of all samples were determined with a Varian MAT 250 mass spectrometer. The results of C and H isotopic analyses are reported relative to Pee Dee Belemnite (PDB) and Standard Mean Ocean Water (SMOW) standards, respectively, as:

$$\delta X = ((R_{sample}/R_{stand.})-1)\times 10^3 \ ^o/oo,$$

Where X = ^{13}C or D and R = $^{13}C/^{12}C$ or D/H content. The analytical precisions of ^{13}C and D measurements were ± 0.2 °/oo and ± 0.6 °/oo, respectively.

C:N Ratios

Table 1 lists the mean C and N contents and C:N ratios (atomic) of various organic material from the Gulf of Trieste. The C:N ratio of organic matter in surficial marine sediments has been frequently used as an indicator of terrigenous addition to marine sediments (Trask, 1955; Pocklington and Leonard, 1979). The rationale was based on observed enrichment of organic C over N in land-derived organic matter (C:N atomic ratio $\geqslant$ 12; Kukal, 1971), as compared to autochthonous marine C:N ($\leqslant$ 10; Parsons, 1975). Blooming phytoplankterss Gyrodinium sp. and Hemiaulus hauckii had, for example, C:N ratios (atomic) of 5.0 and 7.9, respectively. Factors contributing to such high C:N ratios of land-derived organic matter are especially forest humus and terrestrial plants and wood debris containing lignin (Pocklington and Leonard, 1979). Our mean C:N ratio of sedimentary organic matter (13.1) and that of Rizana riverine POM (15.2) would indicate that surficial marine sediments were affected by terrigenous organic matter. On the other hand, high C:N ratios could also be derived from benthic macrophytes.

Another allochthonous source of organic materials considered was sewage. The low C:N ratios of organic particulates from untreated sewage indicate the presence of a rather high content of proteinaceous matter. Enhanced breakdown of organic N relative to organic C during decomposition in the marine environment leads to organic matter with higher C:N ratios, probably similar to partially digested organic matter in treatment plants. We found, for example, the C:N ratio of the primary treated sewage in the Piran treatment plant to be 6.3 thus, the C:N or organic effluent does not behave as a conservative component in the marine environment, as was also reported by Sweeney and Kaplan (1980).

In spite of the considerable variability in the C:N ratios of suspended POM, sediment POM and sedimentary OM (Table 1), a distinct trend in these ratios can be ascertained, with higher values in the sedimentary OM. These results indicate the preferential degradation of N relative to organic C during sedimentation. Thus, the C:N ratios along could not provide an answer to the question of the origin of sedimentary organic matter in the Gulf of Trieste, especially with the respect to allochthonous sources (sewage organic particulates and terrigenous organic matter).

^{13}C Values

The few δ ^{13}C values of the total DIC analysed in sea water of the Gulf of Trieste varied between -5.8 and -6.1 ^{o}/oo, with a mean value of -5.9 ± 0.2 ^{o}/oo (n = 3; Fig. 2) which is much lower than the average value for ocean waters (0 ^{o}/oo; Tan and Strain, 1983). The ^{13}C depleted total DIC in the Gulf of Trieste is a consequence of fresh water inflow having lower δ ^{13}C values. Total DIC δ ^{13}C values from the river Dragonja exhibited variations in the range -12.4 to -12.8 ^{o}/oo with a mean value of -12.6 ± 0.1 ^{o}/oo (n = 3; Fig. 2). Intermediate values ranging between -9.8 and -10.6 ^{o}/oo (mean value of -10.3± 0.3 ^{o}/oo, n = 3; Fig. 2), were typical for brackish waters found in the mouths of the rivers Rizana and Dragonja.

Table 1: Mean values ± SD (n) of organic carbon and nitrogen and C:N rat (atomic) of various organic material from the Gulf of Trieste.

	%C	% N	C:N
Fucus virsoides	31.4 ± 5.1(18)	2.6 ± 0.7(18)	15.4 ± 5.7(18)
Ulva rigida	26.5 ± 7.1(19)	3.0 ± 0.7(19)	11.1 ± 4.8(19)
POM (marine)	13.5 ± 10.8(31)	2.3 ± 1.7(31)	8.5 ± 7.1(31)
Gyrodinium	21.7	5.0	5.0
Net zooplankton	20.3 ± 7.5(58)	4.4 ± 1.5(58)	4.2 ± 1.3(58)
Pelagia noctiluca	8.6 ± 0.8 (5)	2.8 ± 0.2 (5)	4.0 ± 0.2 (5)
Sedimented POM	2.5 ± 1.0(16)	0.4 ± 0.3(16)	8.1 ± 4.2(16)
Sedimentary OM	1.38 ± 0.5(34)	0.13 ± 0.13(34)	13.1 ± 10.7(34)
Sewage POM	26.9 ±23.7(10)	11.0 ± 7.3 (10)	4.7 ± 0.9(10)

Primary producers in the Gulf of Trieste, both benthic algae and phytoplankton, were ^{13}C depleted with respect to DIC to about 11 - 15 $^{o}/oo$. Benthic algae exhibited $\delta^{13}C$ values in the range between -14.2 and -17.7 $^{o}/oo$ (mean value -15.6 ± 0.9, n = 16; Fig. 2) in <u>Fucus virsoides</u>, and between -15.7 and -19.5 $^{o}/oo$ in <u>Ulva rigida</u> (mean value -17.6 ± 1.0 $^{o}/oo$, n = 17; Fig. 2). Different causes may influence the degree and variations of ^{13}C fractionation in marine benthic algae; i.e., colonization by epibionts (Fry and Parker, 1979), changes of the isotopic composition of source DIC (McMillan and Smith, 1982), differences and changes in bio-chemical composition (McMillan et al., 1980), different utilization of HCO_3 ion and free CO_2 (Smith and Walker, 1980; Osmond <u>et al</u>., 1981), differences between C_3 and C_4 photosynthetic pathways (Benedict <u>et al</u>., 1980; McMillan and Smith, 1982) and diffusion of CO_2 into and out of the photosynthetically active plant tissue (O'Leary, 1982). Although thought to belong in general to C_3 plants and partially to PEP carboxylase reaction (Wong and Sackett, 1978), we attributed ^{13}C differences in both algal species primarily to different sources of DIC (HCO_3 or free CO_2) used in the photosynthetic process or to various reactions occuring prior to CO_2 fixation in the cell, such as the diffusion of HCO_3 ion and CO_2 across the stagnant boundary layer at the leaf surface and the dehydration of HCO_3 in the cytoplasm (Smith and Walker, 1980). We considered that differences and variations of biochemical composition of both species were an unlikely explanation for the ^{13}C fractionation observed, since $\delta^{13}C$ values were independent of the C:N ratios. However, the $\delta^{13}C$ differences between lipid and protein components (Table 2) in both algal species and also between two different metabolisms in Ulva species, deduced from significantly different $\delta^{13}C$ vs. δD values (Fig. 4; denoted as Ulva (A) and Ulva (B)) were strongly verified. The reason lies in the different metabolic pathways. The two metabolic pathways starting from Acetyl CoA forming amino acids and fatty acids (as a predominant component of the lipid fraction), respectively, showed that the biosynthesis of amino acids requires the loss of CO_2, which provides an additional step for C isotope fractionation. Therefore, amino acids and proteins are isotopically heavier than lipids which are produced from acetyl CoA without the loss of CO_2 (Bassham, 1971).

Table 2: Mean ^{13}C values ($^{o}/oo$) of lipid and protein fractions as compared to residue in benthic algae.

Algae	Lipids	Proteins and amino acids	Residue	Total plant
Fucus virsoides	-21.5	-16.2	-13.4	-15.6
Ulva (A)	-22.9	-17.7	-15.8	-17.0
Ulva (B)	-25.5	-20.1	-17.7	-18.5

Figure 2. Mean values ± SD of carbon isotope composition of dissolved inorganic carbon (DIC) in waters and organic matter in the Gulf of Trieste.

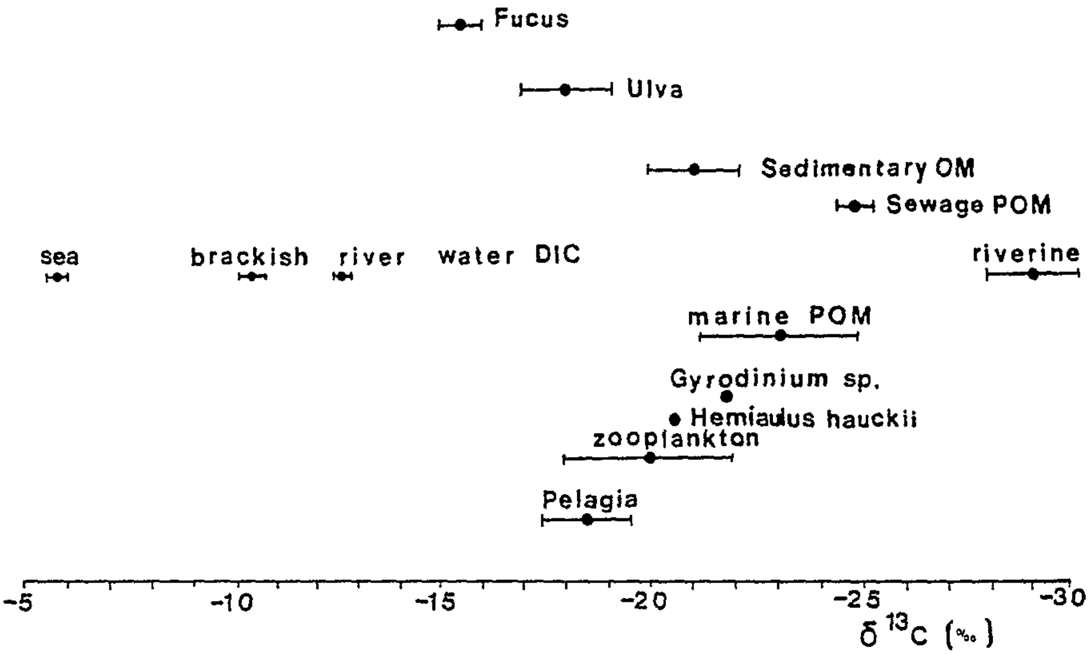
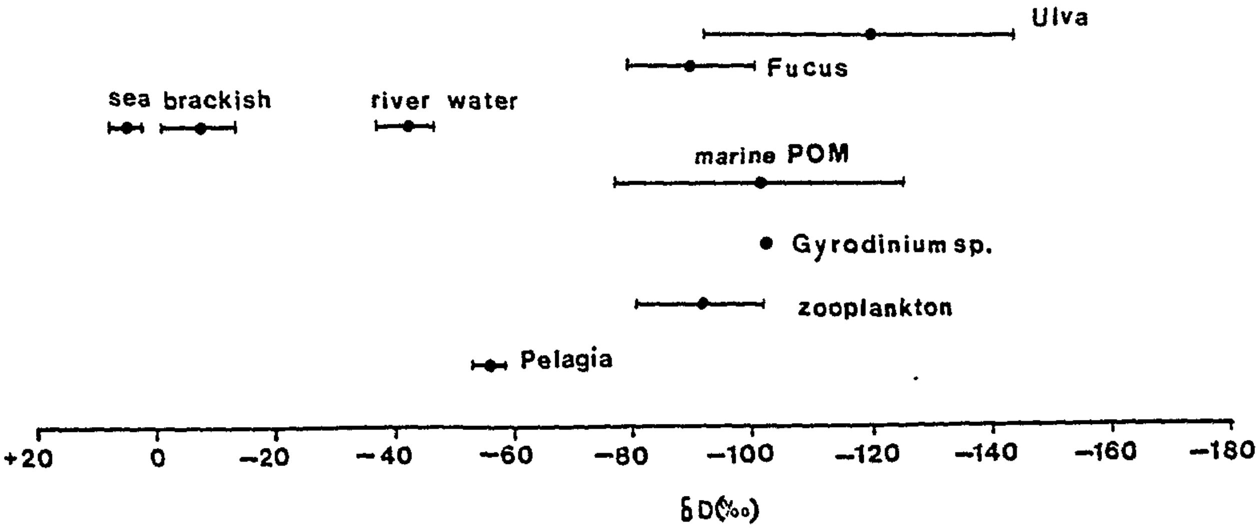


Figure 3. Mean values ± SD of hydrogen isotope composition of waters and organic matter inthe Gulf of Trieste.



$\delta^{13}C$ values of blooming phytoplankters, the dinoflagellate *Gyrodinium* sp. and the diatom *Hemiaulus hauckii*, were -21.5 °/oo and -20.6 °/oo, respectively. Five cultured phytoplankters (Faganeli *et al.*, in press), two of them isolated from the Gulf of Trieste (*Chaetoceros affinis* and *Navicula* sp.), showed higher $\delta^{13}C$ values, ranging between -13.9 and -19.7 °/oo. The most ^{13}C enriched was *Nitzschia closterium* (-9.3 °/oo) probably a typical C_4 plant, although all eukaryotic algae seem to belong to the C_3 class, and only partially to C_4 plants containing the PEP carboxylase reaction in CO_2 fixation (Wong and Sackett, 1978). The reasons for the wide ^{13}C fractionation observed among cultured phytoplankters lies in the different utilization of source DIC (HCO_3 ion and free CO_2), a diffusion-limited CO_2 supply in aquatic environment and also in different biochemical composition. *Nitzschia c.*, containing the highest $\delta^{13}C$ values, revealed the lowest lipid content.

$\delta^{13}C$ values of net-zooplankton as a pelagic consumer ranged between -18.0 and -23.5 °/oo, with a mean value of -20.9± 1.9 °/oo (n = 9; Fig. 2). The secondary pelagic consumer, the jellyfish *Pelagia noctiluca* exhibited a narrow range of $\delta^{13}C$ values between -16.9 and -19.5 °/oo (mean value 18.4 ± 0.8 °/oo, n = 8; Fig. 2), indicating a significant ^{13}C fractionation between consumers and their diet. A positive relationship between respiration rates of both consumers and ^{13}C isotopic composition suggests that the selective respiration of $^{12}CO_2$ is the mechanism primarily responsible for ^{13}C enrichment in pelagic secondary and tertiary trophic levels in the Gulf of Trieste (Malej *et al.*, in prep.).

POC samples collected in the Gulf of Trieste showed $\delta^{13}C$ values in the range between -21.1 and -25.3 °/oo, with a mean value of -23.1 ± 1.2 °/oo (n = 11; Fig. 2). The isotopic composition of phytoplankton species and their growth conditions control the composition of natural phytoplankton and consequently POC. Sewage and riverine POM $\delta^{13}C$ values were most negative, averaging to -25.0 ± 0.05 °/oo (n = 3; Fig. 2) and -27.9 ± 1.0 °/oo (n = 3; Fig. 2), respectively, and influence the rather low $\delta^{13}C$ values of marine POM in the Gulf. On the other hand, it has been reported that lower $\delta^{13}C$ values observed in open waters sometimes indicate the more refractory nature of POC (Eadid *et al.*, 1978). ^{13}C values obtained for sedimentary organic matter in the surficial sediments of the Gulf lay within a narrow range between -19.9 and -23.0 °/oo, with a mean value of -21.1 ± 1.1 °/oo (n = 8; Fig. 2), and were enriched in ^{13}C with respect to POM but depleted in comparison with benthic algae.

δ D Values

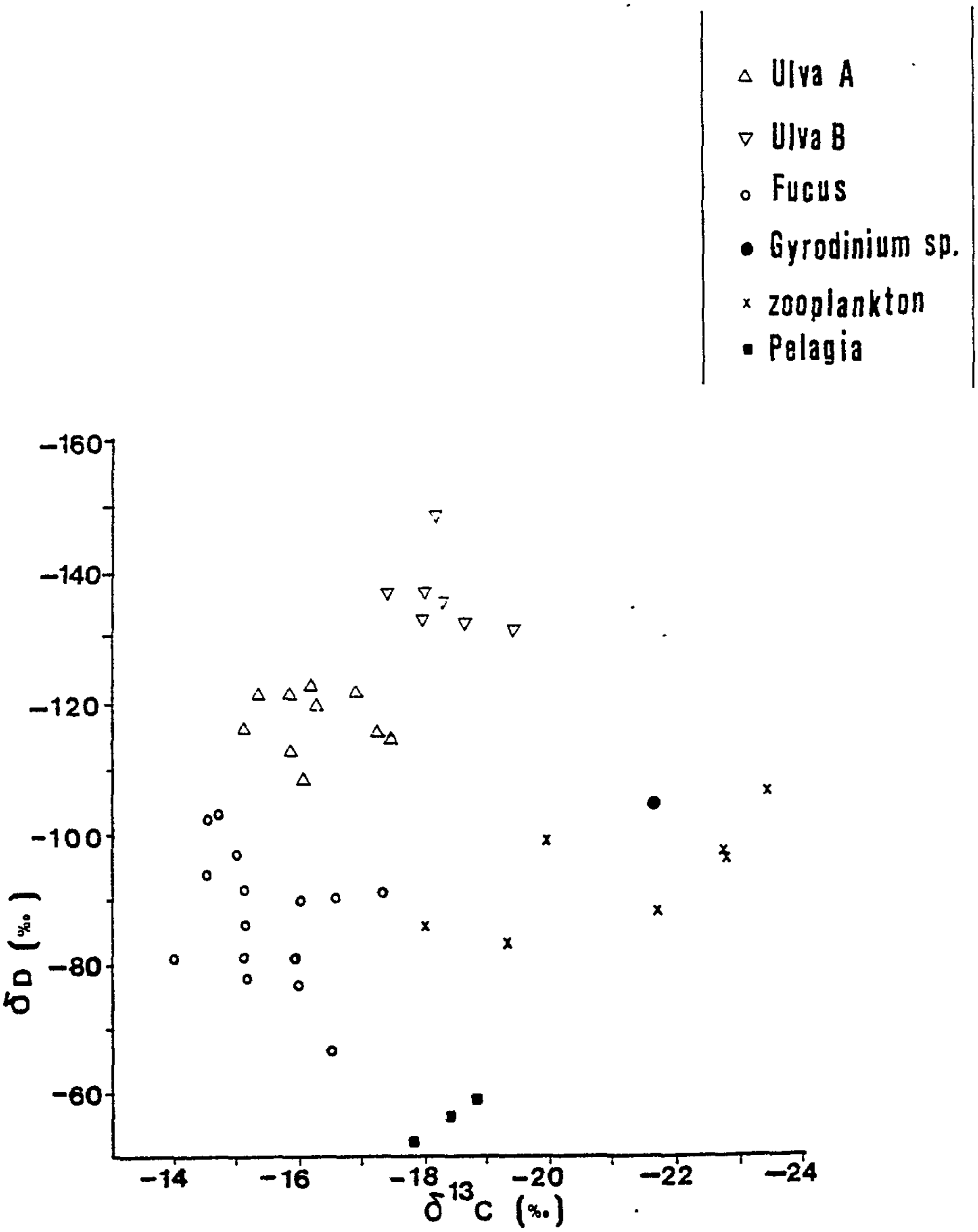
D values in sea water of the Gulf of Trieste ranged between +1.5 and +7.0 °/oo, with a mean value of +4.6 ± 2.3 °/oo (n = 13; Fig. 3), and were lower than those analysed so far in the Southern Adriatic (+8.25 °/oo; Cotecchia *et al.*, 1974). The difference observed is a consequence of the influence of D isotopically lighter river waters on the waters of the Gulf of Trieste. δ D values in the rivers Rizana and

Dragonja ranged between -29.5 and -47.2 °/oo (mean value -42.1 ± 5.2 °/oo, n = 10; Fig. 3), as a function of precipitation. D values of brackish waters varied between -2.3 and -11.9 °/oo with a mean value of -8.9 ± 6.4 °/oo (n = 5; Fig. 3). δ D values found in Adriatic sea water in comparison to ocean water (δ D = 0 °/oo) are typical of seas subjected to intense evaporation (Faure, 1977).

δ D values of benthic algae were rather scattered (Faganeli et al., 1986). δ D values of Ulva ranged between -109.2 and -150.3 °/oo, with a mean value of -126.2 ± 28.3 °/oo (n=18; Fig. 3) and that of Fucus between -68.5 and -104.7 °/oo, with a mean value of -89.7 ± 10.8 °/oo (n = 15. Fig. 3). δ D values of a primary pelagic producer, a blooming phytoplankter Gyrodinium sp. (-104.1 °/oo) were in the same range as POM with a mean value of -102.1 ± 24.0 °/oo (n = 5; Fig. 3) and were similar to values reported by Estep and Hoering (1980) for natural phytoplankton populations taken from various geographical locations. Our results for some cultured phytoplankton species, i.e., Tetraselmis suecica and Dunaliella tertiolecta (Faganeli et al., in press), revealed D values of -108.7 and -101.8 °/oo, respectively, and hence that different phytoplankton species have different δ D values as reported by Estep and Dabrowski (1980). Identifying the causes for different D fractionations in marine primary producers (benthic macroalgae and phytoplankton), we observed a linear relationship between δ ^{13}C and δ D values (Fig. 4), suggesting that the fractionation of both isotopes proceeds in parallel. Hydrogen isotope fractionation probably takes place during the catalytic decomposition of the HCO$_3$ ion, forming CO$_2$ and OH ion in the cytoplasm which is enriched in the heavy hydrogen isotope. A source of D fractionation could also be the differences in lipid content, since Hoering (1974) and Estep and Hoering (1980) found that δ D values of the lipid fraction was about 100 °/oo lighter than the δ D value of the whole organism.

δ D values of net-zooplankton were in the range between -82.1 and -105.6 °/oo with a mean value of -92.1 ± 11.1 °/oo (n = 7; Fig. 3). δ D of Pelagia noctiluca as a top consumer in the pelagic food web ranged between -53.0 and -60.0 °/oo, averaging to -56.5 ± 3.5 °/oo (n = 3; Fig. 3). A positive relationship between respiration rates of pelagic consumers and δ-^{13}C values and D (Malej et al., in prep.) values, as well as a linear relationship between ^{13}C and D fractionation in the pelagic food web (Fig. 4), suggests that the fractionation of both isotopes proceeds in parallel and that the selective elimination of H by respiration is a possible mechanism of D enrichment along the food web. This observation is not in accordance with that of Estep and Dabrowski (1980) and Macho et al. (1983) that stable H. isotopes in animals have δ D values similar to their diet with little isotope fractionation. Strong fractionation in the jellyfish Pelagia, however, could also be influenced by exchange of hydrogen isotopes between bonded water in the organism and organic matter (De Niro and Epstein, 1981).

Figure 4. δ D and δ ^{13}C values of benthic macroalgae, <u>Gyrodinium</u> sp., net-zooplankton and jellyfish <u>Pelagia noctiluca</u>.



Origins of Suspended POM and Sedimentary Organic Matter In the Gulf of Trieste

Suspended POM and sedimentary organic matter in the Gulf of Trieste are probably mixtures of autochthonous and allochthonous organic matter with different origins. In order to determine the sources we constructed mixing models using C:N ratios (Table 1), and δ^{13}C values of different sources of organic matter and POM and sedimentary organic matter (Faganeli *et al.*, in press). C:N ratios and δ^{13}C values alone cannot provide definitive answers about the origins of organic matter since the ranges of both values in different classes of organic matter studies overlap (Table 1; Fig. 2) although the mean values were statistically unique (t-test between means). Ranges of δ D values are, however, wider and thus not usable as a marker for constructing mixing models.

We tried first to quantify the contributions of allochthonous (riverine and sewage) and autochthonous (phytoplanktonic) organic matter in POM in the Gulf of Trieste using C:N ratios and δ^{13}C values of source organic matter (end-members) as tracers. For the solution of a three component mixing system, consisting of riverine, sewage and phytoplanktonic organic matter, we used the method of linear programming (Dantzig, 1963). Generally, for the solution of an n-component mixing system we can combine the equations:

$$\sum_{i=0}^{n} \alpha_i = 1 \quad (1) \qquad \text{and} \quad \sum_{i=0}^{n} \alpha_i = X_T \quad (2) \quad ,$$

where n is the number of constituents and ${}_i$ denotes the fraction of the individual i-th component and X_i is the ^{13}C value or C:N ratio of the individual i-th component in the mixture X_T. For a three component mixing system the elimination of ${}_3$ fraction in the system of two equations with three variables gives the equation of a line in the plane α_1 α_2 :

$$\left(\frac{X_1 - X_3}{X_T - X_3}\right)\alpha_1 + \left(\frac{X_2 - X_3}{X_T - X_3}\right)\alpha_2 = 1 \qquad (3)$$

where α_i lies between 0 - 1 and i = 1, 2, 3 (Fig. 5). Considering the mixing of three δ^{13}C end-members, i.e. sewage (X_1 = -25.0 ^{o}/oo), riverine POM (X_2 = -27.9 ^{o}/oo) and a mean value of the *Gyrodinium* sp. and *Hemiaulus hauckii* blooms as a representative of phytoplanktonic organic carbon in the Gulf of Trieste (X_3 = -21.0 ^{o}/oo), we obtained the intervals of solution for fractions of three end-members in the mixture in POM (X_T = -23.1 ^{o}/oo). The contributions of riverine POC ranged between 0 - 33%, sewage POC between 0 - 60% and phytoplanktonic carbon between 40 - 67%. A similar mixing model constructed with C:N ratios (atomic) as end-member, i.e., sewage POM (X_1 = 4.7), riverine POM (X_2 = 15.2), and phytoplanktonic organic matter X_3 = 5.0), mixed in POM (X_T = 8.5) would yield the contribution of each end-member in the ranges between 0 - 64%, 34 - 36% and 0 - 66%, respectively. Constructing this model it was assumed that the compositional alteration of this organic matter in the sea water column is of minor importance, especially in the period of intense vertical mixing or above the pycnocline. Comparison of the two mixing models showed that the contribution of sewage POM to marine POM is the most variable, depending primarily on the distance of the pollution sources. In the absence of sewage-born POM, the contribution of riverine POM amounts to about one third of the total POM in the Gulf of Trieste. Simplifying a three-source mixing model towards a two source model, consisting of phytoplanktonic carbon and allochthonous POC, as a combination of riverine and sewage POC ($\delta^{13}C$ = -26.5 $^{o}/oo$), we calculated on the average a total allochthonous contribution to POC in the Gulf of Trieste of about 37%.

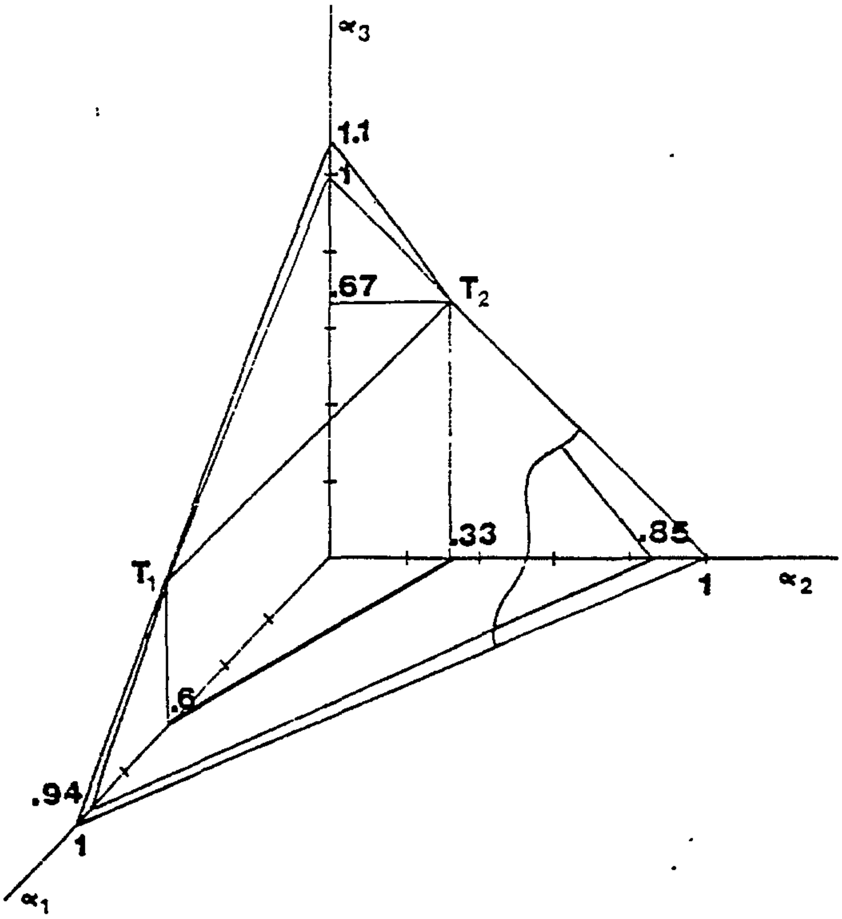
The application of the two source mixing model of $\delta^{13}C$ to the sedimentary organic matter (X_T = -21.2 $^{o}/oo$) consisting of a marine POM fraction (X_1 = -23.6 $^{o}/oo$) and a macrophytic fraction (X_2 = -17.0 $^{o}/oo$), and supposing that the latter could be a reasonable value for the whole benthos (Fry and Sherr, 1984), gave the contribution of POM in the mixture forming sedimentary organic matter of about 64%.

The $\delta^{13}C$ signatures of POM and sedimentary organic matter could not be used as indicators of petroleum contamination in the Gulf of Trieste since the $\delta^{13}C$ values of Middle East petroleum, principally imported through Adriatic harbours (varying between -25 and -30 $^{o}/oo$; Hoebs, 1980), overlap with those of allochthonous organic matter in the area.

Food Web Analysis

The elucidation of marine food webs are generally based on the observation that consumers usually have similar stable C and H isotopic compositions as their food (Fry and Sherr, 1984). The maximal ^{13}C enrichment in the pelagic food web of the Gulf of Trieste between phytoplankton and net-zooplankton is about 1.5 $^{o}/oo$ and between net-zooplankton and jellyfish is about 2 $^{o}/oo$. ^{13}C enrichment in the pelagic food web of the Gulf of Trieste is similar to that found in some other marine areas, for example in the offshore waters of the Gulf of Mexico (Thayer *et al.*, 1983). On the other hand, in other areas controversial results were reported, indicating essentially no ^{13}C. enrichment in the pelagic and also in some benthic food webs (Tan and Strain, 1983; Mc Connaughey and Mc Roy, 1979; Rau *et al.*, 1983). The solution of this controversy probably lies in the observation that POC probably consists of two fractions; a labile one, composed mainly of living phytoplankton, and a refractory detrital fraction (Incze *et al.*, 1982) with lower $\delta^{13}C$ values (Eadie *et al.*, 1978). This supposition is also valid for the waters of the Gulf of Trieste with POC more $\delta^{13}C$ negative than phytoplanktonic carbon by about 2 $^{o}/oo$, at least in part due to the contribution of allochthonous sources to marine POC.

Figure 5. The intersection of equations (1) and (2) of two planes in the space with azes $\alpha_1, \alpha_2, \alpha_3$. The solution of the three end - members system lies on the line segment between points T_1 (0.60, 0, 0.40) and T_2 (0, 0.33, 0.67). The equation (3) is represented as a projection of this line on the $\alpha_1 \alpha_2$ plane.



Therefore, from our food web analysis based on $\delta^{13}C$ values it emerged that the "labile" phytoplanktonic fraction of POC is primarily the food for net-zooplankton due to the closer ^{13}C isotopic similarities of phyto and zooplankton. The ^{13}C depleted detritus, partially of riverine and sewage origin, is probably deposited on the surficial sediment or exported from the Gulf.

D enrichment in the pelagic food web between phytoplankton and net-zooplankton is about 10 °/oo and that between net-zooplankton and jellyfish is much higher, amounting to about 35 °/oo. The latter enrichment is probably somewhat influenced by exchange of hydrogen isotopes between water and organic matter (De Niro and Epstein, 1981). Studies of stable hydrogen isotopes in the pelagic food web in the Gulf of Trieste have shown the usefulness of this isotope as a marker for the flow of pelagic organic matter.

Summary and Conclusions

1. Different classes of organic matter, i.e., phytoplanktonic, POM, net-zooplankton, jellyfish, sedimentary organic matter and benthic macrophytes, and allochthonous inputs, riverine and sewage POM in the Gulf of Trieste, were distinctly characterised by C:N ratios and stable C and H isotopic composition. In order to use these markers in elucidation of sources of POM and sedimentary organic matter and the flow of POM in the pelagic system, it is important to decode the naturally occurring causes for C and N elemental and C and H isotopic fractionation.

2. A distinct trend in C:N ratios has been ascertained in the Gulf of Trieste, with higher values found in the sedimentary organic matter due to the preferential degradation of N relative to organic C during sedimentation.

3. The causes for $\delta^{13}C$ fractionation in primary producers (benthic macroalgae and phytoplankton) lie primarily in different utilization of source DIC and reactions occuring prior to CO_2 fixation in the cell, rather than in changeable photosynthetic pathways (C_3 and C_4) and differences in bio-chemical composition and their growth rates. The causes for ^{13}C differences and variations in pelagic consumers, i.e. net-zooplankton and jellyfish, is probably the selective respiration of $^{12}CO_2$. The most ^{13}C depleted organic matter was found to be of allochthonous origin, i.e riverine and sewage.

4. The causes for D fractionation in primary producers appear to be the same as in ^{13}C fractionation, since the fractionation occurs during the catalytic decomposition of HCO_3 in the cytoplasm, forming CO_2 and OH^- ion. D fractionation in pelagic consumers is probably caused by selective respiration. The relationship between $\delta^{13}C$ and δD demonstrates the parallel fractionation of both isotopes.

5. Mixing models using C:N ratios and $\delta^{13}C$ values were used to assess the origins of POM and sedimentary organic matter in the Gulf. A three component mixing model, consisting of phytoplanktonic, riverine and sewage organic matter C:N ratios and ^{13}C values, indicated that marine POM in the Gulf of Trieste is a mixture of about 1/3 of riverine POM and 2/3 of phytoplanktonic organic matter in the absence of the input of sewage POM which is the most variable. The two source $\delta^{13}C$ mixing model indicated the contribution of marine POM to sedimentary organic matter to be about 2/3. The possible effect of petroleum contamination on marine POM and sedimentary organic matter could not be ascertained by ^{13}C values due to the overlap between $\delta^{13}C$ values of Middle East petroleum and allochtonous riverine and sewage POM.

6. Pelagic food web analysis in the Gulf of Trieste showed ^{13}C fractionation in the pelagic food web amounting to about 1.5 - 2.0 °/oo per trophic level. The D enrichment in the pelagic food web is higher, amounting to about 20 °/oo between POM and net-zooplankton and as high as 35 °/oo between net-zooplankton and jellyfish. Pelagic food web analysis in the Gulf of Trieste demonstrated that the labile fraction of POC is primarily a food for net-zooplankton and the latter for jellyfish. ^{13}C depleted detritus of riverine and sewage origin is probably deposited on the surficial sediment or exported out of the Gulf of Trieste.

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PARTICULATE MATTER AND HEAVY METALS IN THE LIGURIAN SEA

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ABSTRACT

Results are reviewed, of studies of heavy metals in particulate matter conducted over a seven year period in Ligurian coastal waters. The data includes studies along transects and studies of seasonal variations. Enrichment of some metals (notably Cu, Cd and Ni) was observed in the coastal waters and a relationship was established between metal enrichment and phytoplankton blooms in the study area.

Introduction

This paper is a short review of a part of the results we have obtained till now in the study about concentrations of heavy metals in particulate matter, about their distribution in time and space in reference to hydrological and environmental parameters as well as about the relationship between metals in particulate matter and biological events (Baffi et al. 1984, 1986; Fabiano et al. 1985, in press; Frache et al., 1986, 1987).

These researches are included in the study programme of G.R.O. - G. and were supported by the financial contributions from the Ministero della Pubblica Istruzione (Fondi 40%) and from the International Atomic Energy Agency of Vienna within the MEDPOL Programme.

The study of the chemistry and the behaviour of settling particulate matter is very important in various fields such as sedimentology, marine chemistry, biology and particularly in pollution problems. Infact we know that some pollutants, such as heavy metals, can interact with the particulate matter and are involved in sedimentation processes and in trophic chains. The chemical, physical and biological mechanisms that regulate these interaction processes depend on a large number of parameters, such as ionic force, relative concentrations of the major elements, the pH and redox conditions, the concentration and the nature of the organic matter, chemical form of the elements in solution, morphology and mineralogy of the particles. They also depend on the biological parameters related to the biochemical processes concerning the living and detrital particles and the dynamic and structure features of vegetal and animal populations involved. Besides all this has to be considered within the physical framework of typical processes of advection and vertical movement (upwelling, divergence, convergence).

Figure 1 shows the sampling zones considered till now in Ligurian Sea. Sampling was carried out in the coastal area and the open sea. The coastal zones were chosen in order to have information about an area that is strongly influenced by anthrophic inputs and constitutes the interface between land and open sea. In this area, the particulate matter plays an important role in regulating the dissolved fraction of metals both by equilibrium kinetics between the two components (dissolved and particulate substances) and by biological events of the seston organisms. The Canyons facing Genoa's harbour were selected on the basis of previous research (Pierce et al. 1981; Picazzo e Tucci 1983). This work showed very high values of particulate matter that were related with the peculiar dynamic of the water masses in this area. Finally the transect Imperia - Capo Corso was selected as an example of an open sea area and also for the more or less stressed presence of the Ligurain Sea divergence.

Sampling was carried out during the G.R.O. - G. oceanographic surveys by the n/o "Bannock", "Marsili" and "Minerva" of C.N.R. or by a properly equipped fishing-boat.

METHODS

The sampling details and the analytical methods are described in the publications previously cited.

RESULTS

Coastal waters

The research on the concentration and the distribution of heavy metals in particulate matter in relation to the environmental features began by a study of Ligurian Sea coastal waters (Baffi et al. 1984). A first sampling of surface and deep waters in 25 stations at different distances from the coast (between 0.5 and 6.1 nautical miles) in five transects facing the towns of Alassio, Savona, Genova, Chiavari and Corniglia was carried out in February 1981. The data are reported in Table 1.

The vertical distribution of hydrological parameters, oxygen and nutrients concentrations shows an environmental situation characterized by winter mixing of the water column. The values of chlorophyll-a are typical of the algal bloom period in this area: in fact the phytoplankton populations sampled on the stations nearer the coast show chlorophyll-a values between 1-2 µg/l. As for heavy metals concentrations in particulate matter, Cd and Fe are the same magnitude of those reported by Buat-Menard et al. (1980) for the Ligurian waters, while Cu concentrations are elevated. Generally each transect seems to be characterized by its own chemical "facies" ; Genoa presents highest values for Cd, Chiavari the lowest ones for Cu, Corniglia the highest one for Fe. Therefore it would seem that metal concentration in coastal particulate matter can record the different urban and industrial settlements and the different geochemical characteristics of the coast. This consideration is strenghtened by the results of a contamporary research (Cosma et al. 1982) on the heavy metals contents in sediments of the Legurian continental shelf, that confirm the chemical peculiarity of the different transects and reveale some correspondance with the data concerning the particulate matter (Tab. 2). With regard to the relationship between the phytoplankton biomass (chlorophyll-a) and the heavy metals we have found a significant correlation ($r = 0.93$ and $r = 0.90$) for Cu and Fe only on the Corniglia Transect.

The data led us to believe that this relationship must be investigated at specific periods of the phytoplankton cycle. A series of samples, collected monthly from January to October 1979 in a station placed offward Chiavari on a depth of 250 m, allowed us to perform a study on this subject (Fabiano et al. 1985).

In superficial waters, the highest concentration of Cu was found in February, in the same period of phytoplankton bloom. By using chlorophyll-a concentration as an expression of the vegetal biomass, we therefore verified a significant correlation ($r = 0.81$) between algal growth and particulate Cu concentration for the whole yearly cycle ; if we consider the samples coming from the photic zone, correlation is significant only for the period of active production (February-March). These different results help to explain the different interpretations we met in literature about this relation.

Moreever, data analysis allowed us to obtain a further significant result in indentifying a seasonal cycle of metal concentrations, particularly for Cu. Table 3 summarizes the data. The cycle is characterized by a highest concentrations during the winter-spring period. In this time of elevated algal activity, a relationship appears between phytoplankton biomass and heavy metals in the photic layer. Then an increase over the whole column appear in summer, during the period of zooplankton grazing and organic detritus formation. Finally in winter, when water mixing occurs, a reduction and homogenization of values along the column is evident. These results confirm the role of plankton organisms in concentrating large quantities of metals from seawaters with mechanisms probably involving biochemical processes within the organisms (Fowler 1977).

Genoa Gulf Waters

As for coastal waters in July 1983 the sea water facing the town of Genoa and overlaying the Bisagno and Polcevera Canyons was sampled. Previous studies (Picazzo and Tucci 1983) were systematically carried out in these zones which have a complex hydrodynamic regime; an upwelling phenomenon was described along the Canyons end and large suspended matter concentrations were found out. Furthermore, the distribution of the total inorganic and organic suspended matter did not reveal a land-based source.

The most recent studies (Fabiano et al., in press ; Frache et al. 1987) have been carried out by sampling the surface and different depths on some stations placed along the Canyons's axis as well as offshore and inshore waters. Table 1 reports the values of mean total concentrations.

The analysis of the data did not permit the detection of the above mentioned upwelling phenomena and therefore to confirm the data referred by Frache et al. (1986) on the Fe enrichment in the supended matter sampled on the stations placed on the head of the Canyons. Considering that the sampling period was in July, the biological activity and the consequent production of organic matter was low and it was impossible to point out a correlation between the metal concentration and the algal biomass or other biochemical components (lipids, proteins and carbohydrates) of the organic particulate matter. It was possible to obtain an interesting information by comparing the qualitative information on the particles of the Bisagno and Polcevera Canyons in terms of organic components and of heavy metals content: so we verified that the two Canyons show marked differences.

Offshore waters

As for open sea waters, marked differences were observed while examining the metal concentrations in terms of ug/l or of ug/g. Concentrations referred to volume seem to point out more clearly the differences between the coastal and the open sea water masses. Table 4 reports the mean concentration (ng/l) of the 0-50m layer of Genoa Gulf, both in coastal and open sea waters. On the contrary, considering the values referred to the unity of weight, the concentrations of the surface samples of the transect Imperia - Capo Corso stations nearer to the coast appear to be similar to those of the more coastal stations (Gulf of Genoa). These results seem to point out that the differences between the water masses, as for chemical composition of particles, keep themselves longer from a qualitative (metal contents in the particles, metals ratio) than from a quantitative point of view.

As for vertical distribution of metal concentrations in the particulate matter, the lack of a "trend" points out the dynamics of waters in these zones. We also observed a significant relation among the metals (Fe, Cr and Ni) and the trend of AOU (Apparent Oxygen Utilization) values, pointing out the close relation between metal content in particle and intensity of the organic matter oxidizing phenomena. In the upper 200-400 m, where the processes of bacterial degradation are more intense, the quantity of metal that passes from the particulate to the dissolved fraction of the chemical system is greater.

Another aspect of the problem is the evaluation of the concentration factors referred to as the earth crust mean composition. As we could not get the data of Al concentrations, we referred to the Fe concentrations that we believed to be sufficiently constant. The results, always referring to the 0-50m water layer, show an enrichment in Cu, Ni, and Cd of the coastal water samples, about 10 times greater than the samples of Genoa Gulf waters and of the open sea waters (Table 5).

CONCLUSION

Ligurian coastal waters present heavy metal concentrations higher than open sea waters. Concentration factors indicate a remarkable enrichment in Cu, Cd and Ni with regard to the mean Fe content of the earth crust. Distribution of metal in particulate matter overlying the Canyons of the Genoa Gulf shows us that it can record the different characteristics of its different origins.

There is a relation, even if not always clearly evident, between some metals and organic components, particularly the relation between the phytoplankton biomass and Cu concentrations in the particles. It could indicate that this relation is strictly related to the particular moment of the growth of algal populations. The concentration increase in particulate matter is contemporary with the exponential stage of growth at the surface and, more remarkably, with the final stage of the phytoplankton bloom along the whole water column.

Our future research will be dealing with the role played by degradation of particulate and dissolved forms of metals along the water column.

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TABLE 1

Mean total values, minimum and maximum in brackets, of the whole water column.

	Coastal	Genoa Gulf	Open Sea
Cd ng/l	11.0 (6-22)	0.66(0.05-4.3)	0.09(0.002-0.64)
Cd ng/mg		0.22(0.01-1.23)	0.36(0.005-0.93)
Cu ng/l	160.4 (5-820)	73.1(10-974)	5.6(0.03-56)
Cu ng/mg		23.9(1.2-269.9)	22.9(1.5-128.0)
Cr ng/l		41.5(1.5-217)	2.2(0.012-25.3)
Cr ng/mg		14.0(0.5-85.2)	11.7(0.24-54.7)
Fe ng/l	518.4(5-2000)	578.6(50-4490)	29.2(0.105-4178)
Fe ng/mg		185.0(18.7-1185)	99.6(5.0-312-0)
Ni ng/l	182.0(130-890)	40.9(8.6-210)	5.5(0.14-32.4)
Ni ng/mg		13.3(3.2-34.6)	25.0(6.6-61.5)

TABLE 2

SEDIMENTS (attack with 0.5 N HCl) g/g

	Fe	Cd	Cr	Cu	Ni
Allassio	4317	1.77	15.3	14.5	24.1
Savona	4725	1.75	46.6	20.0	25.2
Genova	6453	2.04	56.9	51.9	20.7
Chiavari	5477	1.69	13.4	25.4	22.0
Corniglia	6605	2.16	19.1	22.2	15.1

TABLE 3

Cu concentrations in particular matter (ng/l)

Layer	feb - mar	apr - may	jun - oct	nov - jan
0- 25 m	128.4	175-0	47.0	32.8
50-100 m	34.3	277.3	81.0	24.5
150-200 m	4.5	34.5	185.2	16.7

TABLE 4

Mean values of heavy metals concentrations (layer 0-50 m)

	Coastal	Genoa Gulf	Open Sea
Cd ng/l	14.79	0.80	0.42
Cd ng/mg		0.26	0.13
Cu ng/l	128.82	49.04	37.09
Cu ng/mg		16.60	6.54
Cr ng/l		32.30	16.36
Cr ng/mg		18.85	2.31
Fe ng/l	327.8	331.86	129.36
Fe ng/mg		106.47	34.40
Ni ng/l	160.0	36.72	34.06
Ni ng/mg		11.63	8.04

TABLE 5

Concentration factors

	Coastal	Genoa Gulf	Open Sea
Ni/Fe (0-50)	2135	166	215
Ni/Fe (column)	1380	120	273
Cu/Fe (0-50)	4182	194	241
Cu/Fe (column)	1984	158	198
Cr/Fe (0-50)		72	63
Cr/Fe (column)		62	81
Cd/Fe (0-50)	84500	1071	1156
Cd/Fe (column)	49592	721	2112

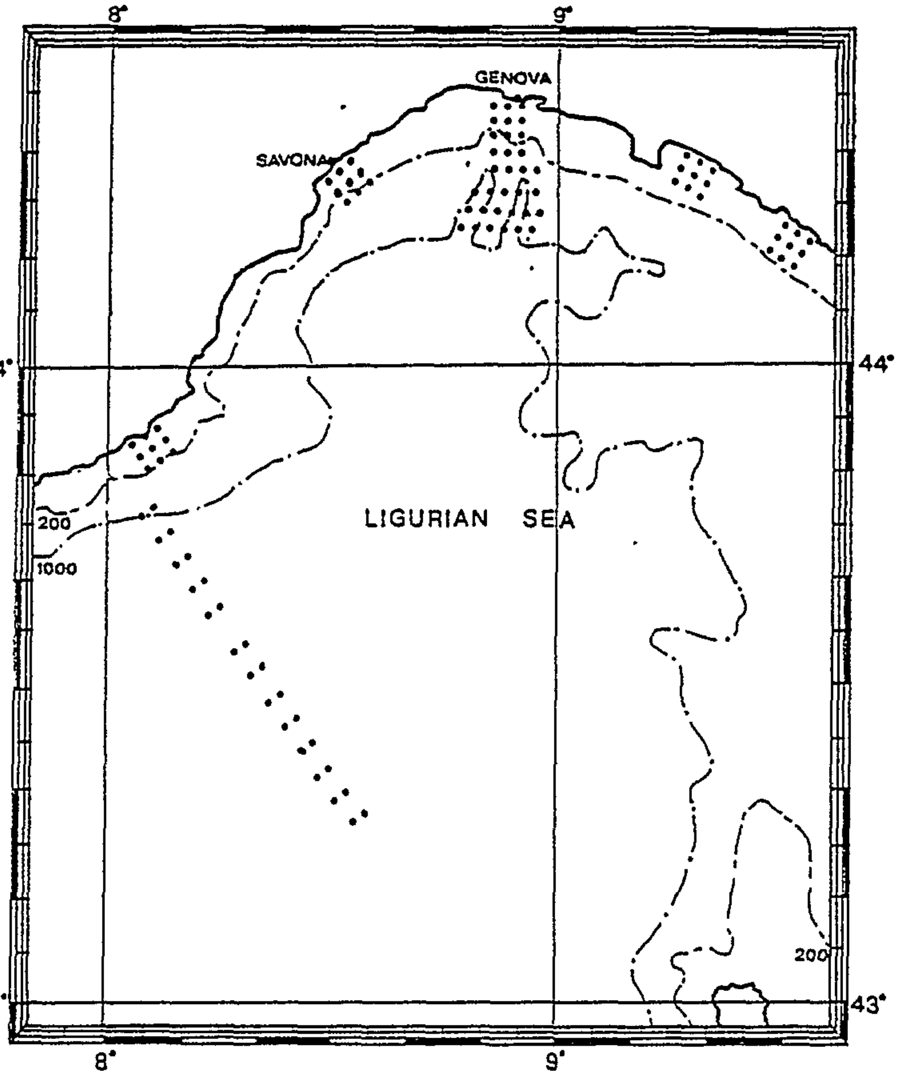

Fig. 1. Sampling areas

TRANSPORT MECHANISMS, DISTRIBUTION AND MOBILIZATION OF HEAVY METALS IN WATER AND SEDIMENTS OF AXIOS RIVER AND ITS ESTUARIES

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ABSTRACT

A five step sequential extraction technique was used to determine the chemical association of heavy metals (Pb, Cd, Cu, Fe, Mn, Zn, Cr) with major sedimentary phases (exchangeable cations, easily reducible compounds, organic sulfidic phases, carbonates and residual components in samples from the Axios River in Northern Greece.

The influence of different organic and inorganic complexing agents on the remobilization of heavy metals from sediments to water was also studied, and the verticle distribution as well.

From the obtained data it can be suggested that the surplus of metal contaminants introduced into the aquatic system from antropogenic sources usually exists in relatively unstable chemical forms. The higher proportions of the elements studied remain in the residual fraction. Most of the non-residual portions are bound to the ferromanganese oxides and to the organic matter.

INTRODUCTION

Environmental pollution is clearly reflected in the high concentrations of heavy metals in water and aquatic sediments in highly industrialized and populated areas. Most of these sediments are enriched with metals from municipal, industrial wastes and surface runoff. The chemistry of contaminated sediments is complex since the composition of heavy metals varies significantly (Lapin et al, 1983, Chester et al. 1967). Dredged material may contain appreciably high concentrations of heavy metals but the question arises as to what percentage of the total concentration of heavy metals will be available for release to the water over a long period of time (Gibbs, 1973, Gibbs, 1977).

Knowledge of the total amount of metals alone is not sufficient to indicate the risk of toxicity or even to understand the various geochemical processes (Salomons, 1985, Presley et al., 1972, Aoyama et al. 1982). Studies have previously not yielded enough information regarding the partitioning of trace elements among the various components of the sediments and their potential to affect water quality under different environmental conditions (Salomons, 1985, Guy et al. 1978).

Heavy metals are released into rivers, lakes and sea either dissolved (complexed ions) or as part of minerals or organic solids. A large fraction of the dissolved metals are immobilized by precipitation, ionic exchange or adsorption. On the other hand, heavy metals can be mobilized from suspended material and from sediments by changes in pH - Eh conditions, by complexing with synthetic complexing agents (e.g., NTA, EDTA, etc.) or with natural chelating agents such as soluble humic substances (Banat et al., 1974), Muller and Forstner, 1976, Sanchez and Lee 1973). Synthetic complexing agents have recently come into use as partial substitutes for polyphosphates in detergents. Large amounts of heavy metals are solubilized (complexed) when highly polluted river sediments are treated with solutions containing e.g., NTA.

Such chemical transformations could endanger the drinking water supplies in areas using river and lake water. Experiments with polluted river sediments indicate a high percentage mobilization of heavy metals with Cu, Cd and to a lesser extent Ni all of which show a positive correlation with both concentration of NTA and time of shaking. Other metals show negative correlation or no mobilization at any concentration or with any time of shaking.

Axios River

The Axios river, which originates in Yugoslavia and flows into the Thermaikos Gulf, is characterized by high zinc, iron and mercury levels. The main pollutants which flow into the Axios originate in Yugoslavia and are derived from domestic effluents and industrial wastes (chemical, metal plating industries, acid mine-drainage, steel industries and oil refineries).

About 650,000m^3/day of untreated or partially treated domestic sewage and industrial effluents are discharged in the Axios river in the Yugoslavian region. In Greece, the communities in the Axios area are relatively small and consequently no problems of local water pollution are foreseen. The mean water discharge of Axios is 170 m^3/sec(max. 310 m^3/sec in Winter and min. 37 m^3/sec in Summer). (Fytianos et al., 1986).

It appears that in station 1 (near the estuary) a slight improvement has occurred in comparison with station 2 (Greek/Yugoslavian border). This improvement is probably due to the sedimentation caused by coagulation or coprecipitation of the heavy metals.

The Axios river flows into the Thermaikos gulf. The Thermaikos gulf acts as a receptacle for municipal, industrial and agricultural wastes. About 120,000 m^3/day of untreated sewage from the city of Thesaloniki (with a population of more than 1,000,000 inhabitants), partially treated industrial effluents and agricultural effluents, are directly discharged into the bay of Thessaloniki (Samanidou et al., 1987).

The scope of this work was to investigate the distribution of heavy metals, their transport mechanisms in different water and sediment phases in the Axios River, the chemistry of sediments and the association of trace metals with each chemical fraction. Various forms and attachments of heavy metals such as the exchangeable form, existence in carbonate mineral phase, easily reducible form (Fe-Mn oxides), interactions with organic and sulfide fractions and presence in the lattice structure (residual) of sediments were studied. It was found to be the most adequate means to obtain detailed information about the origin, the mode of occurence, the biological and physicochemical availability, the mobilization of metals and their transport media (Welte et al., 1983). The influence of different organic and inorganic complexing agents on the remobilization of heavy metals from sediments to water was also studied.

Materials and Methods

The Axios River in Northern Greece was examined. Three sampling stations were installed as shown in the map. Station 1 is located before the estuarys of the river, station 2 near the Greek/Yugoslavian Border and Station 3 in the estuary. Samples of surface sediment were collected every three months over a one-year period (November 1986 - October 1987).

The following heavy metals were determined by A.A.S.: Pb, Cd, Cu, Fe, Mn, Zn and Cr. The distribution of these metals was examined in the different sediment phases. The speciation of heavy metals in sediments was examined by using a sequential extraction method in order to obtain the concentration of metals bound in cation exchange positions, carbonates, Fe-Mn oxides, organic matter, sulfides and crystal lattice, (Tessier et al., 1979, Etcheber, et al., 1983, Calmano, 1983, Rapin et al., 1982, Gupta et al., 1975). The vertical distribution of metals in the sediment (0-30 cm depth) was also studied.

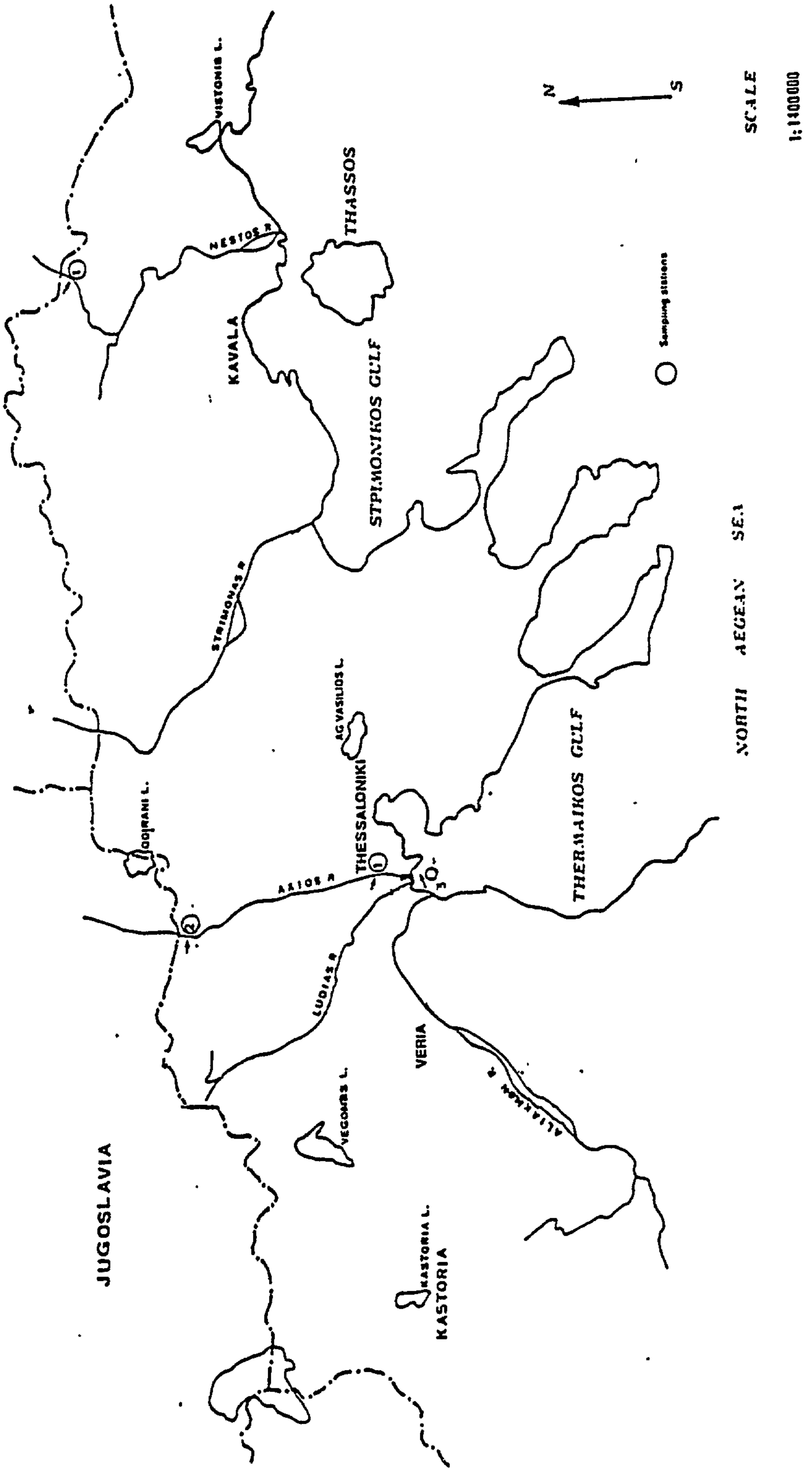
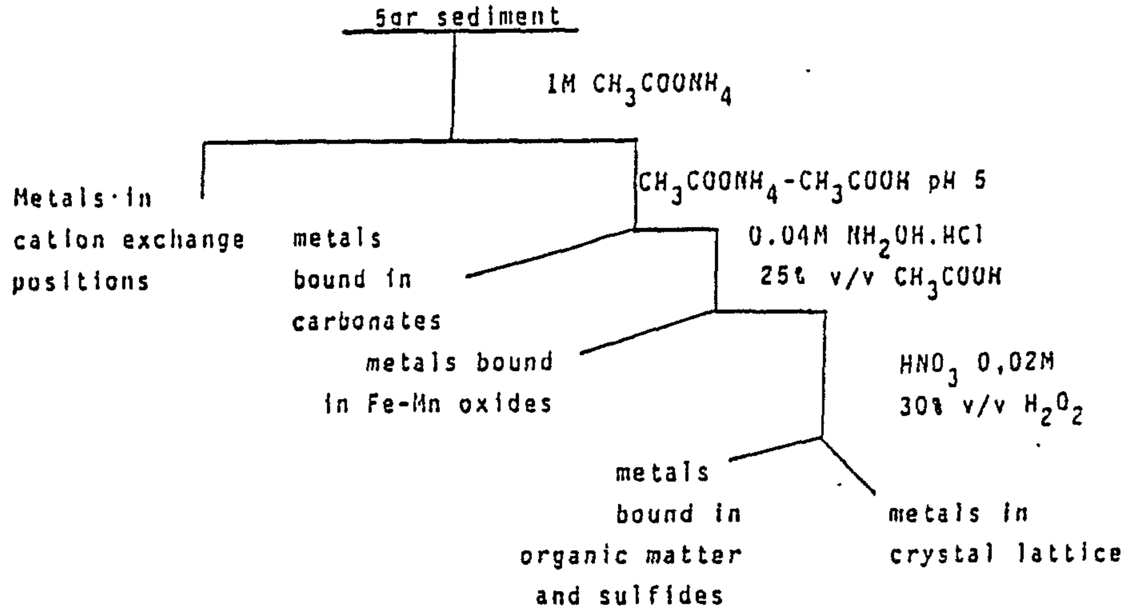


Fig.1.Map of Northern Greece.

The sequential extraction method which was followed is shown at the following scheme:



For the determination of the heavy metals associated (chelated or adsorbed) with humic and fulvic acids, the sediments were treated with 0,1N NaOH for 10 hours. An easy and fast extraction method using 0,5 N HCl has also been used for the evaluation of the pollution level of the examined areas (Agemian 1976). This extraction removes mainly the "anthropogenic" trace element fraction from the sediment.

The remobilization of heavy metals from sediments to water was examined using different organic and inorganic agents such as NTX, EDTA, STPP, Triton X100 using distilled and river water. For these experiments the influence of shaking time (1/2-96 hours) was examined in a 100 ppm concentration of the complexing agent on 1 g. of river sediment with 1L of solution. The efficiency of the total metal analysis was tested using standard reference material (river sediment SD-N-1/2). The results obtained are as follows:

Fe	3,20%	CV	3,72%
Zn	386,12 ug/g	"	2,79%
Cu	63,90 "	"	3,91%
Cr	80,42 "	"	2,36%
Cd	7,76 "	"	2,45%
Pb	140,50 "	"	6,48%
Mn	763,33 "	"	0,89%

CV = coefficient of variation

Results and Discussion

The % mobilization of heavy metals from the Axios River sediments by the different complexing agents is shown in table 1. The data obtained indicate high percentage mobilization of copper and cadmium and to a lesser extent for lead and chromium. No mobilization of iron and manganese was observed of at this concentration.

Table 1. Mobilization (%) of heavy metals from the Axios River sediments by different complexing agents.

Complexing Agents	Cu	Pb	Fe	Mn	Cr	Cd
NTA	72,5	5,2	1,27	3,4	5,0	31,2
EDTA	31,2	3,5	0,50	1,7	0,2	75,3
Triton X100	24,4	4,8	0,53	1,3	9,0	5,0
STPP	16,1	1,7	0,72	1,0	1,3	10,0

The heavy metal concentrations in the core samples were estimated in 3 depths (10-20-30 cm) for two of the three stations (1 and 2). Maximum concentrations were observed for the 10-20cm depth as shown in table 2. In general, the leached metal concentrations in this study were very low below 20 cm. The low concentration in depth 0-10 cm, in comparison to that at the depth 10-20 cm, is probably due to mobilization from the superficial sediments by changes in pH-Eh conditions or by complexing with natural or synthetic chelating agents.

Table 2. Concentrations of heavy metals in sediments from different depth in Axios River (mg/g).

Depth(cm)	Pb	Zn	Cu	Mn	Fe(mg/g)	Cr	Cd
			Station 1				
0-10	130,4	210,0	52,0	623,5	7,93	252,0	28,8
10-20	293,9	333,1	67,6	710,2	7,95	294,3	39,8
20-30	103,8	142,5	43,8	610,6	7,0	173,0	22,3
			Station 2				
0-10	252,7	255,5	64,1	710,2	8,29	226,5	28,9
10-20	260,2	281,0	59,9	720,3	7,84	391,1	30,3
20-30	441,8	430,1	47,8	735,6	8,22	225,2	12,9

Concerning the total heavy metal analysis in the Axios sediments, it appears that in station 2 (near the Greek/Yugoslavian border) a significant increase of concentration has been observed in comparison to station 1 (near the estuaries). This increase is probably due to sedimentation caused by coagulation or coprecipitation of heavy metals.

The partitioning range of heavy metals extracted by different chemical extractants for the 2 sampling stations in the Axios river, is presented in tables 3 and 4 respectively (see also Samanidou et al., 1987). The values (average from one year's measurements) shown are expressed as the ratio of the extracted amount to the total amount of metals in percentages. In most cases, the sum of the sequential extractions of trace elements was satisfactorily close (± 10%) to the "total" metal concentrations.

Based on this selective leaching procedure, it has been possible to define the percentages of the various elements which are associated with certain fractions of the sediments, and also the distribution patterns of each of these in the sediments of the Axios River. The main conclusions which can be drawn from the chemical fractionation of sediments are the following:

The heavy metals showed distinct distribution trends. The distribution patterns of the total metals were similar in some cases. However, on separating the metals in the separate fractions differed considerable differences were noted. This stresses again the importance of knowing the form of trace metals in the environment. The cation exchangeable fraction which represents the elements loosely adsorbed on the sediments, was comparatively small except for that of Cd for the Axios River. Hydrous Mn and Fe oxides in sediments are generally stronger scavenging agents for heavy metal ions (Schor, 1985, Chao, 1972). Mn oxides in Axios sediments were found to be readily dissolved by hydroxylamine hydrochloride solution, leaving the major part of Fe oxides in the residue.

More than 50% of the Cd was associated with the carbonate and reducible fraction. It therefore seems that Cd occurs incorporated within Fe and Mn oxides and/or with carbonates. A relatively small percentage of the total concentration was removed. The hydrogen peroxide treatment should remove mainly sulfides and organic matter and have only a minor effect on the silicate lattice. The distributions of metals as organic complexes in sediments were very sensitive indicators of contamination. Of the metals examined in this study, Cu had the highest relative amount in this fraction. This is probably an indication of the often-proposed close association of Cu with organic matter.

Table 3 Partitioning range % of heavy metals extracted by different chemical extractants in the Axios River (Mean values).

AXIOS 1	Pb	Zn	Cu	Mn	Fe	Cr	Cd
Cation-exchangeable	1.16	0.99	0.98	5.57	0.91	0.19	9.59
Carbonates	13.26	9.08	2.19	21.94	0.96	0.63	35.53
Fe-Mn Hydrous oxides	23.82	27.08	6.01	27.55	18.31	9.69	22.16
Organic-sulfides	33.13	29.12	42.98	23.99	37.28	30.70	10.77
Residual	28.63	33.71	47.84	20.95	43.26	58.79	22.13
Total ug/g/* mg/g	153.71	220.05	45.71	814.57	15.64*	166.97	13.52
"Anthropogenic" (non lithogenous phases)	63.80	37.05	44.24	44.52	15.47	22.50	56.45
Humic and fulvic acids	9.98	10.92	13.59	0.69	0.84	1.34	4.88

Table 4. Partitioning range % of heavy metals extracted by different chemical extractants in station 2 of Axios River (Mean values).

AXIOS 2	Pb	Zn	Cu	Mn	Fe	Cr	Cd
Cation-exchangeable	0.96	0.76	0.87	7.24	0.14	0.52	10.79
Carbonates	15.54	8.36	1.47	19.64	1.60	0.52	24.89
Fe-Mn Hydrous oxides	25.50	28.41	3.08	27.36	18.81	8.52	29.60
Organic-sulfides	29.80	32.03	44.65	22.44	37.06	32.51	19.05
Residual	28.20	30.44	49.69	23.32	42.39	57.93	15.67
Total ug/g/* mg/g	216.92	249.38	46.91	983.63	17.37*	193.48	17.59
"Anthropogenic" (non lithogenous phases)	72.47	44.80	57.52	43.33	15.05	28.25	62.14
Humic and fulvic acids	4.24	6.69	17.32	0.58	1.05	1.60	3.49

The residue remaining after the hydroxylamine hydrocloride, acetic acid, and hydrogen peroxide leaches, could be expected to consist almost entirely of detrital silicate minerals and organic matter, such as humic material, which is resistant to peroxide attack. This residual solid should contain mainly primary and secondary minerals which may hold trace metals within their crystal structure. These metals would not be expected to be released in solution over a reasonable time span under the conditions normally existing in nature.

The treatment of the residue with nitric-perchloric acid mixture, shows that for Axios river the metals Fe, Cr, Cu and Mn were concentrated mainly in this fraction of the sediment. The amount of trace metals in the residue decreases in the order Cr> Cu> Fe> Zn> Pb> Mn> Cd. Most of the Cr in the sediments in the Axios was associated with the residual fraction. Therefore, it appears that in these sediments Cr is probably terrestrially derived.

About 50% of the total copper was found in the residual fraction of the Axios River which which means that copper is probably bound in terrestrially derived materials. Approximately 35% of the Fe concentration was incorporated in the organic and sulfide phase. The percentate of Fe in this fraction was however, variable. This variability probably results from competition between Fe organic complexes and hydrous Fe oxide forms. This situation is complicated because hydrous Fe oxides themselves can complex with organic (especially humic) substances in sediments (Smith et al, 1979, Nembrini et al., 1982).

About 43% of the total Fe was found in the residual phase. Approximately 14% of the iron was associated with the reducible phase, although this showed considerable variation. An average of about 30% of tht total Mn was associated with the reducible fraction probably in the form of Mn oxides. The Mn in the residual fraction arises from precipitation of Mn minerals. As regards to the respective concentrations in the sediment, the following list of relative levels was found: Fe Mn Zn Pb Cr Cu Cd. Iron was shown to have the highest concentration factor.

Comparing the partitioning range of heavy metals between the two stations in the Axios we can conclude that, there is no significant variation in the different fractions.

Table 5. Heavy metal distribution in the different fractions in St. 1 (ug/g).

	Pb				Mn				Fe*(mg/g)			
Fraction	1	2	3	4	1	2	3	4	1	2	3	4
Cation Exchangeable	0,17	0,30	0,39	0,95	11,6	40,9	74,4	38,5	0,54	8,26	2,14	12,1
Carbonates	24,3	15,0	25,7	50,3	114,3	87,8	200	267,5	38,2	8,75	168,6	430,8
Fe-Mn hydrous oxides	32,2	28,1	14,3	29,7	127,9	145,7	145,9	147,5	672,7	285,8	426,1	801,6
Organic sulfides	53,9	54,3	47,6	36,6	117,7	140,0	204,0	142,5	*1,05	427,9	741,5	*1,21
Residual	33,9	25,5	27,6	29,5	62,7	118,7	165,2	162,5	*1,01	537,4	792,3	472,3
Total	40,8	120,8	120,4	140,5	470,8	580,1	705,9	780,9	*3,01	*1,45	*2,85	*3,4
Anthropogenic	86,67	96,1	80,9	98,6	171,9	237,1	372,9	255,7	894,6	559,1	801,9	*1,5
Humic-Fulvic acids	12,1	5,40	3,24	5,08	3,09	2,29	6,21	4,24	38,19	72,6	95,68	67,4

	Zn				Cr				Cu				Cd			
Fraction	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Cation Exchangeable	0,83	2,70	1,61	3,06	0,07	0,27	0,47	0,14	0,14	0,41	1,08	0.36	0,08	1,5	0,14	0,09
Carbonates	26,33	15,4	14,64	34,81	1,22	0,77	2,09	1,83	1,01	0,78	2,26	1,86	7,84	1,67	3,19	5,6
Fe-Mn Hydrous oxides	66,33	38,2	2,19	33,53	26,0	3,26	5,68	3,61	6,0	1,75	0,29	2,59	4,64	3,33	0,28	2,72
Organic-sulfides	95,83	35,8	47,7	56,5	87,0	40,0	45,0	20,8	24,0	16,42	23,7	11,79	3,84	2,33	0,25	0,19
Residual	28,17	41,6	45,95	45,8	104,4	106,89	82,5	90,6	11,6	14,11	12,8	10,4	3,20	2,17	2,98	3,7
Total	210,40	140,5	143,5	201,4	219,51	51,2	145,0	120,7	48,8	33,87	46,5	25,8	28,4	11,9	7,59	13,4
Anthropogenic	88,01	68,45	64,14	98,5	27,47	36,7	26,6	23,8	17,6	18,9	18,3	17,63	10,5	9,14	7,0	9,4
Humic Fulvic Acids	14.9	18,95	18,76	23,2	1,34	1,44	1,17	4,9	4,36	2,5	6,04	4,13	0,42	0,48	0,31	0,47

1 = Winter 1987, 2 = Spring 1987, 3 = Summer 1987, 4 = Autumn 1987.

Table 6. Heavy metal distribution in the different sediment fractions in St 2. (ug/g)

	Zn				Cr			
Fraction	1	2	3	4	1	2	3	4
Cation exchange-able	1,25	2,80	1,79	4,77	0,7	0,25	,12	0,14
Carbonates	26,33	12,0	16,43	58,04	1,36	0,70	2,14	2,43
Fe-Mn hydrous oxides	62,5	44,0	28,1	70,9	27,8	3,21	3,11	8,59
Organic sulfides	85,67	54,4	45,95	83,3	100,8	56,47	40,5	47,2
Residual	40,0	52,3	48,6	67,7	86,0	123,5	65,0	110,4
Total	216,25	160,8	156,5	260,3	215,4	184,2	120,4	170,8
Anthropo-genic	110,10	78,93	64,73	137,5	35,85	35,2	28,32	34,4
Humic Fulvic Acids	15,44	13,87	23,32	20,1	1,50	1,82	1,13	2,77

	Cu				Cd			
Cation exchange-able	0,09	0,44	0,66	0,21	0,07	2,17	0,13	0,11
Carbonates	0,88	1,02	2,24	0,8	6,08	2,33	3,40	6,9
Fe-Mn Hydrous oxides	6,4	1,1	0,27	2,15	4,16	5,33	0,28	2,72
Organic sulfides	21,8	27,16	22,9	20,0	2,88	4,67	0,24	4,64
Residual	15,0	17,68	12,8	11,65	13,19	2,33	2,98	4,48
Total	43,6	50,3	40,8	33,4	30,5	15,5	6,98	19,5
Anthropo-genic	23,82	32,03	20,0	26,3	12,03	14,13	6,5	17,8
Humic Fulvic Acids	3,27	10,5	6,8	10,5	0,41	0,35	0,27	0,51

Table 6. Heavy metal distribution in the different sediment fractions in St 2. (ug/g).

	Pb				Mn				Fe(mg*/g)			
Fraction	1	2	3	4	1	2	3	4	1	2	3	4
Cation exchangeable	0,49	0,98	0,52	1,71	24,1	63,24	71,3	51,2	1,98	5,47	0,60	1,4
Carbonates	40,86	26,3	30,5	56,2	124,7	115,8	187,3	256,0	112,8	13,13	124,6	475,4
Fe-Mn Hydrous Oxides	41,74	54,2	20,5	44,6	118,2	164,5	165,9	187,0	787,3	377,9	451,5	858,6
Organic Sulfides	49,56	73,6	40,95	70,6	116,0	142,6	201,9	232,5	*1,07	463,7	725,6	*1,23
Residual	37,4	33,7	28,6	33,14	79,6	127,9	174,1	143,9	*1,04	536,3	794,8	633,1
Total	178,1	190,5	130,6	210,8	480,6	610,8	830,4	875,6	*3,2	*1,83	*2,4	*3,9
Anthropo-genic	111,2	157,6	80,9	168,5	172,2	256,2	364,7	326,3	921,8	588,1	788,5	*1,6
Humic-Fulvic Acids	12,3	4,59	3,07	7,95	3,59	2,49	4,86	15,48	51,27	42,4	76,2	46,3

Table 7. Heavy metal distribution in the different sediment fractions in St 3 (ug/g) (estuaries)

	Zn			Cr			Cu			Cd		
Fraction	2	3	4	2	3	4	2	3	4	2	3	4
Cation exchange-able	1,50	1,40	2,60	0,07	0,03	0,16	0,22	0,97	0,44	0,14	0,19	0,08
Carbonates	14,4	17,20	17,4	0,70	3,31	0,98	0,27	3,73	1,95	1,5	2,47	2,72
Fe-Mn Hydrous Oxides	34,7	16,90	20,6	17,65	4,97	2,20	1,58	0,24	2,0	3,67	0,25	0,11
Organic-Sulfides	38,1	44,7	46,1	55,3	42,5	15,1	23,16	24,53	14,74	2,0	0,21	0,10
Residual	45,5	52,86	63,40	61,2	14,8	16,5	21,26	17,07	11,37	2,33	4,04	4,48
Total	147,7	146,8	163,5	150,4	64,3	37,3	50,25	53,6	35,81	8,4	7,1	6,7
Anthropogenic	60,5	49,7	62,75	32,4	7,93	10,3	25,26	17,67	15,0	7,71	4,0	5,0
Humic-fulvic Acids	10,26	7,86	16,4	1,03	1,3	6,62	1,79	6,37	7,61	0,34	0,32	0,49

	Pb			Mn			Fe*(mg/g)		
Fraction	2	3	4	2	3	4	2	3	4
Cation exchange-able	0,34	0,61	0,76	9,76	23,35	25,5	4,0	3,3	8,0
Carbonates	19	37	33	68,55	175,3	181,8	13	400	389,4
Fn-Mn Hydrous Oxides	40	19,05	25	149,4	133,4	123,0	383,7	53,22	915,4
Organic-Sulfides	39	49,0	32	95,32	154,6	143,5	758,5	756,2	1,3*
Residual	26	24,76	39	117,1	185,2	177,5	537,4	796,9	1,5*
Total	165,0	145,1	160,1	500,25	708,3	610,5	1,92*	2,8*	5,1*
Anthropogenic	95,0	71,43	71,43	206,7	295,0	356,0	575,7	851,9	1,5*
Humic-Fulvic Acids	4,69	3,35	5,82	0.22	5,21	5,04	42,8	119,9	47,5

1-Winter 1987, 2-Spring 1987, 3-Summer 1987, 4-Autumn 1987.

The various fractions vary generally from higher to lower concentrations for the metals Cr, Cu, Fe and Zn in the following orderÑ

Residual fraction> organic fraction> easily reducible fraction> carbonate fraction> cation exchangeable fraction. The anthropogenic heavy metals in sediments follow the order:

Pb> Cd> Cu> Mn> Zn> Cr> Fe.

Analytical data concerning the metal distribution in the different sediment fractions for the 4 seasonal samplings during the period of November 1986 to October 1987 are given in tables 5, 6 and 7 for stations 1, 2 and 3 respectively.

Conclusions

From the results of the present investigation the following conclusions can be drawn:

- Concerning the total concentrations in sediment, the Axios River is highly polluted especially for the metals Fe, Mn, Zn, Pb, and Cd.
- Iron has shown to have the highest concentration factor.
- The heavy metal concentrations in the different phases obtained by sequential extraction show distinct distribution trends.

As regards the respective concentrations in the sediment the following list or relative levels was found: Fe> Mn> Zn> Pb> Cr> Cu> Cd.

The heavy metal concentrations were found to be greater for the depth 10-20 cm. Below 20 cm, these concentrations decreased.

Concerning the influence of different complexing agents it can be concluded that NTA and EDTA have a strong complexing effect on certain heavy metals in sediments of the Axios River.

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THE AQUATIC CHEMISTRY OF THE LAGOON OF MESSOLONGHI

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ABSTRACT

The lagoon of Messolonghi is an area of Western Greece with productive fisheries. In recent years, problems arose as the results of irrigation works that are believed to have affected the chemistry of the lagoon waters, which in turn may adversely affect the fisheries resources of the area.

During the period from October 1985 until September 1986, we investigated the chemistry of the lagoon of Messolonghi by taking samples from both the surface and bottom. It should be noted that for the most part, the waters are shallow, their depth ranging from 0.70 - 1.50 m. Parameters such as pH, temperature, conductivity, dissolved oxygen and turbidity were measured in situ. The samples, transported to the laboratory, were analyzed for BOD_5, density, salinity, chlorophyll concentration (a, b and c), Ca, Mg, Zn, Cd, Pb, Cu, total phosphorus, nitrate and Cl. The ratio of Ca/Mg was found to be constant as is the case in the seawater and the ratio of NO_3/PO_4 was found to vary linearly with NO_3 concentration. The physiochemical parameters of the lagoon were found to depend on the characteristics of the output from the pumping stations.

INTRODUCTION

The lagoon of Messolonghi is an area in Western Greece, traditionally used for systematic fish production. Fishing is of primary importance for the local economy. A few years ago, in the early seventies, the water from the lake of Lysimachia (North of Messolonghi) shown in Fig. 1, was used to irrigate the valley between the lake, the city of Messalonghi and the river Acheloos.

The waters from irrigation along with the draining waters, were transferred by channels to four pumping stations and were discharged in the lagoons of Messolonghi (outer) and of Aetoliko (inner lagoon). As a consequence of the water discharge, seaweed grew rapidly, extensive areas covered with algae appeared and there was an unpleasant odor during some seasons (Spring - Summer). As a result, certain varieties of fish completely disappeared from the inner lagoon of Aetoliko while the remaining stock of fish were drastically reduced. After additional public works and reduction of the output of pump stations into the lagoons the situation was somewhat improved with fish quantities increasing again, though never reaching the previous levels. Certain varieties of the more sensitive fish never returned in the inner lagoon of Aetoliko.

The purpose of the present study was to investigate the status of the lagoons of Messolonghi and Aetoliko from the point of view of their aquatic chemistry. Parameters such as pH, conductivity, dissolved oxygen, turbidity, calcium, magnesium, phosphorus, nitrate concentrations, chlorine concentrations, chlorophyll levels (which are proportional to algal growth), salinity, biochemical oxygen demand (BOD_5) and heavy metal ion concentrations including Zn^{2+}, Cd^{2+}, Cu^{2+} and Pb^{2+}, were measured.

Eutrophication is the process of alteration of the physiochemical parameters of lakes or estuaries and lagoons in a way that the water rendered cannot be used for water supplies and recreation. Aquatic environments rich in nutrients are called eutrophic while those poor in nutrients are called oligotrophic. Inorganic Phosphate, nitrate and carbon dioxide are key parameters regulating the biological productivity of natural waters. Excess of nutrients in water, however, results in increased algae populations rendering waters turbid. Moreover, algae, upon decomposition sediment out, causing reduction in dissolved oxygen. The process, results in elimination of the preferred food-fish varieties and their replacement by fish which are more tolerant in the new environment. A major source of nutrients input to estuarine waters is from soil fertilization which becomes even more serious when over-fertilization is practiced. Algal growth developed in the epilemnion, where light is abundant, may settle in the hypolimnion and upon decomposition, may deplete the dissolved oxygen. Reduced dissolved oxygen, has been associated with a reduction in commercial fish (Hammer 1977). Once a eutrophication situation is established, it remains for a long time, because of the long turnover times.

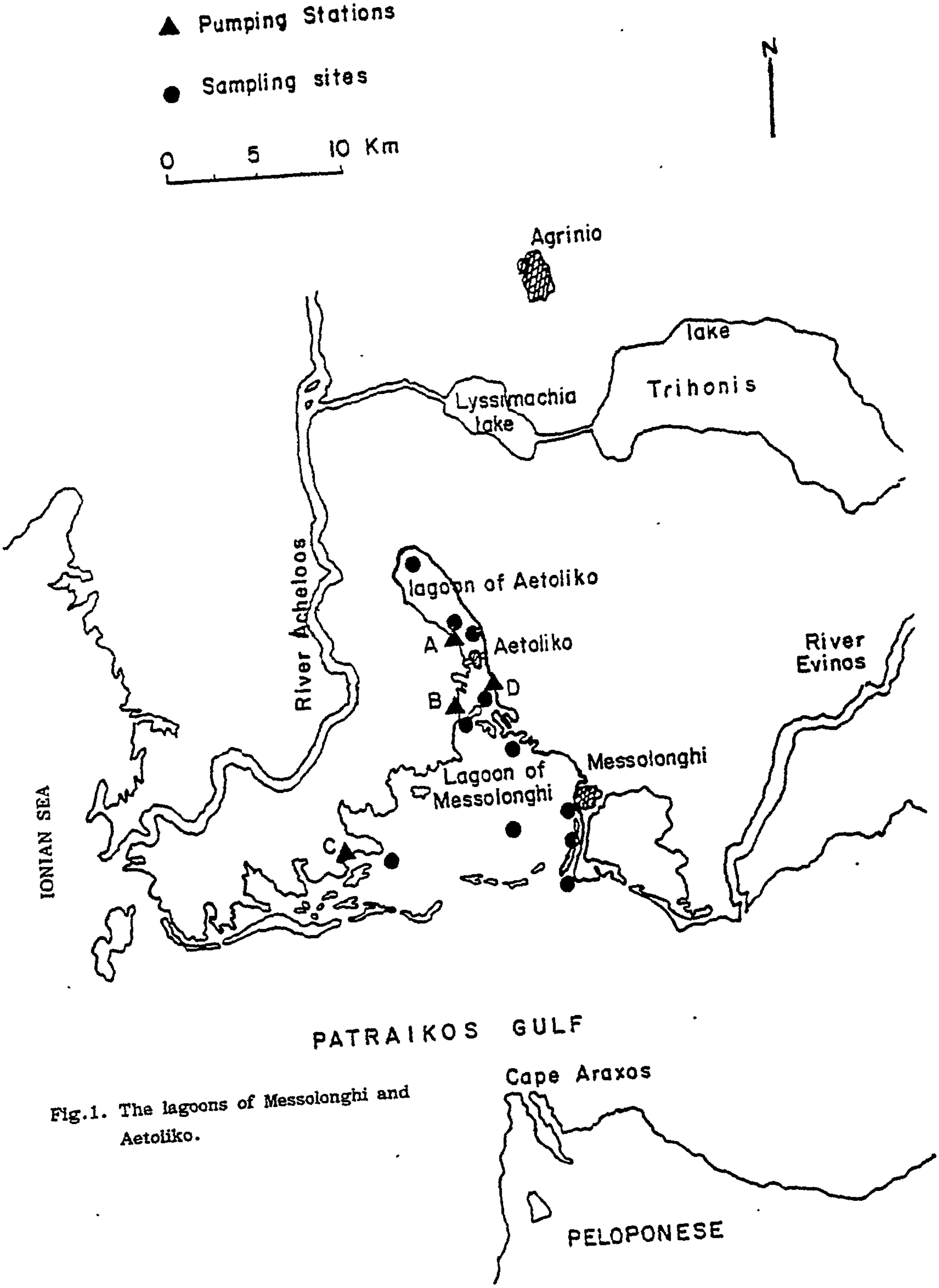

Fig.1. The lagoons of Messolonghi and Aetoliko.

The lagoon of Messolonghi is very likely to be markedly influenced from the influx of irrigation drainage from areas which may be over-fertilized. In the present work, the investigation was extended to the parameters of the waters discharged from the four main pumps located in the lagoon.

MATERIAL AND METHODS

Water pH, temperature, conductivity, turbidity and dissolved oxygen were measured in situ with a Horiba Model U-7 water checker. The instrument employed a pair of glass/saturated calomet electrodes for the pH measurements (± 0.1 pH), a thermistor for the temperature measurement (± 0.5°C), a membrane oxygen electrode/saturated calomel electrode pair for the dissolved oxygen measurement (± 1.0 ppm), a four electrode sensor for the conductivity measurement (+ 2.5 mmho/cm) and a ratio turbidimeter for the measurement of turbidity (± 20 ppm). 1.8 dm^3 samples were collected using a horizontal PVC sample collector (Cole-Palmer). The water samples were placed in 1L acid-washed polyethylene bottles and were stored at 4°C. Within 4 hours from the collection from the field, BOD_5 was measured in special 500 ml glass bottles incubated at 20°C for five days. The BOD_5 was estimated from the dissolved oxygen (DO) before and after the five day incubation by equation (1):

$$BOD_5 \text{ (mg/l)} = \text{Initial DO (mg/l)} - \text{Final DO (mg/l)} \qquad (1)$$

The depletion of dissolved oxygen is directly related to the amounts of degradable organic matter. Chlorophyll a, b and c were determined by the trichromatic method (APHA, 1980) according to equations (2) - (4):

$$\text{Chla (mg/l)} = 11.64\ (OD_{663}) - 2.16\ (OD_{645}) + 0.10\ (OD_{630})$$
$$\text{Chlb (mg/l)} = 20.97\ (OD_{645}) - 3.94\ (OD_{663}) + 3.66\ (OD_{630})$$
$$\text{Chlc (mg/l)} = 54.22\ (OD_{630}) - 1481\ (OD_{645}) + 5.33\ (OD_{663})$$

The optical density, OD at 630, 645 and 663 were corrected for the reading at 750 nm. OD_{750}. The concentrations of Zn^{2+}m Pb^{2+}, Cd^{2+} and Cu^{2+} were measured by anodic stripping polarography, using a Kemula Hanging Mercury Drop Electrode (HMDE), (Radiometer, Polarite P04). The density of the water samples were determined by precision hydrometers of various ranges (Gallenkamp, ± 0.0005). The salinity was computed from the densities (APHA, 1980). Cl^- and NO_3^- concentrations were measured potentionmetrically by ion selective electrodes (Radiometer) using as reference saturated calomel electrodes. Calcium and Magnesium were measured by atomic absorption spectroscopy (Varian 1200) and phosphate spectrophotometrically (Murphy and Riley, 1962). Samples to be analyzed for metal ions (Ca, Mg, Zn, Cd, Pb and Cu) were acidified in glass bottles ans stored at 5°C. The rest of the analyses were done within 48 hours from arrival in the laboratory.

RESULTS AND DISCUSSION

The present work describes the results of analysis conducted for a year, starting from October 1985 and ending September 1986 (inclusive). Sampling was done between the 20th-30th day of each month. Sampling stations are shown in the map of Fig. 1. A, B, C and D are the locations of the four pumping stations. It should be noted that in the inner lagoon of Aetoliko there is an additional open drainage channel. The waters in the lagoon of Messolonghi are shallow, their depth ranging between 0.70 - 1.50m. In the inner lagoon of Aetoliko the depth reaches 30m.

The data discussed in this report is of the surface water samples (20cm from the surface). Sampling at 50 cm and at the bottom (1.50m) did not show any significant differences. There sampling stations were located in the inner lagoon of Aetoliko and the rest were in the lagoon of Messolonghi. It should be noted that pump station D is located very close to the entrance of the inner lagoon to the east of the town of Aetoliko. From the temperature profiles shown in Fig. 2, it may be clearly seen that the average temperature of the waters is rather high and shows typical seasonal variation. The temperature is rather uniform in all sampling stations in both lagoons and slightly higher as compared with the temperature in the pumping stations especially during the warm months (May - August).

The pH at various locations, as may be seen in Fig. 3, both for the pumping stations and the lagoon sites, has an average value about pH 7.0. In Fig. 3a, it may be seen that the output of pump station A is significantly acidic (pH 5.0). The pH of seawater is also low (<7) for the months of November and December (Fig. 3b) probably because of the acid rain in the area (Glavas 1987). Again, a relative drop in pH was observed towards the end of September 1986, as the samples were collected following the beginning of the raining season. Examination of Figs. 4a and 4b shows that in general, the input from the pump stations has lower conductivity values, except for the high values of pumping station B shown during the months February, March and April (Fig. 4a).

The values of the conductivity of the lagoon samples show that those corresponding to the inner lagoon are quite lower and comparable to the values of the input water from the pumping stations (lower part of Fig. 4b). Moreover, a similar trend is shown in the salinities, as it may be seen in Figs. 5a, b, c. During the winter season the salinity is lowered even in the outer lagoon probably due to increased input from the pump stations and the drainage channels or small channels bringing water from rainfall. It is obvious, that the physiochemical factors of the incoming waters influence the waters of both lagoons, particularly those of the inner lagoon of Aetoliko.

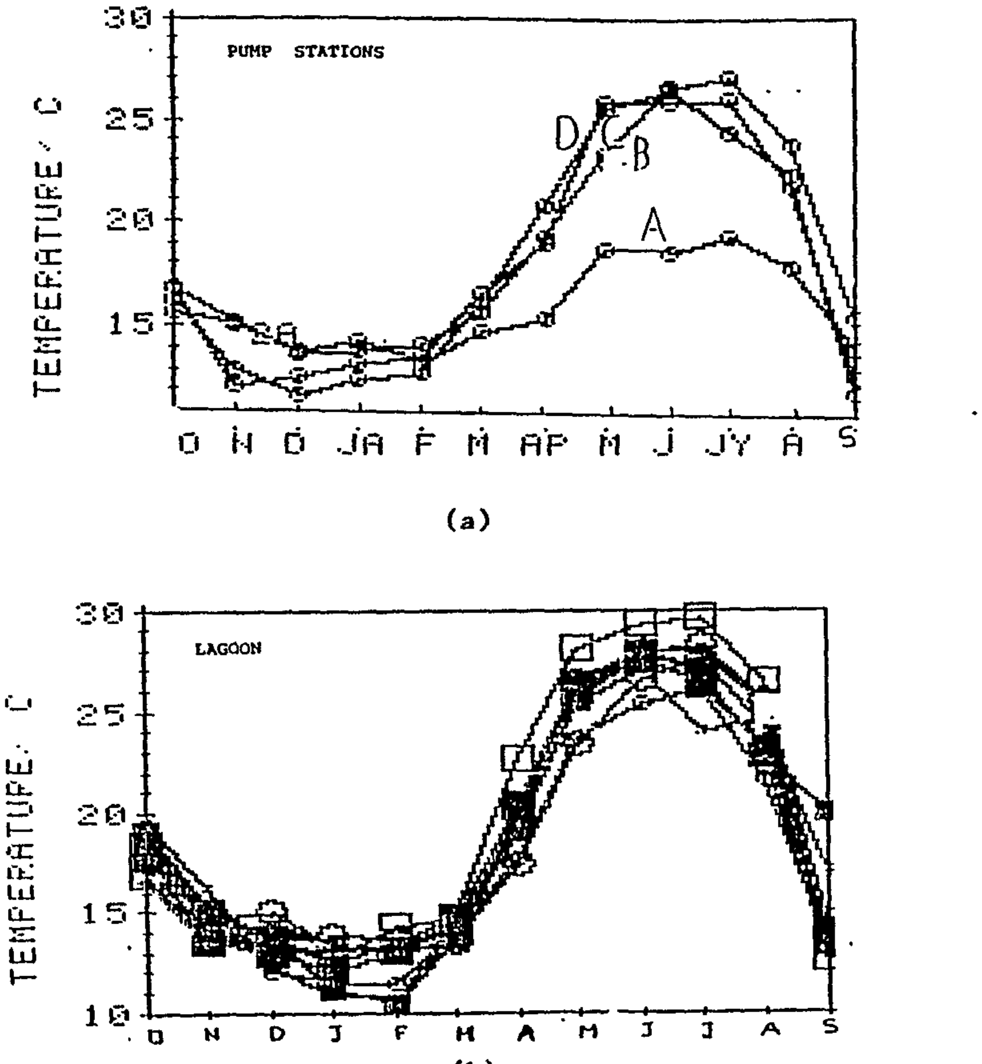

Fig. 2: Variation of temperature from Oct. 1985–Sept. 1986

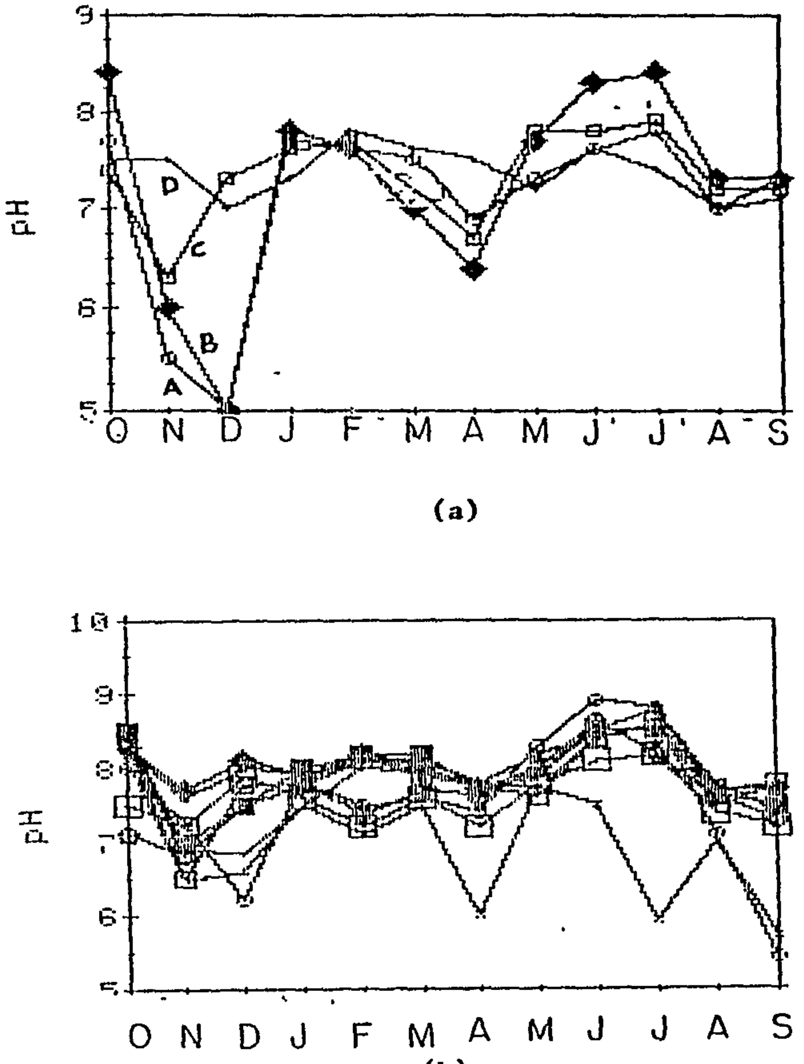

Fig. 3: pH variation for a period of 12 months (Oct. 1985–Sept. 1986)

a. Pump station b. Lagoons

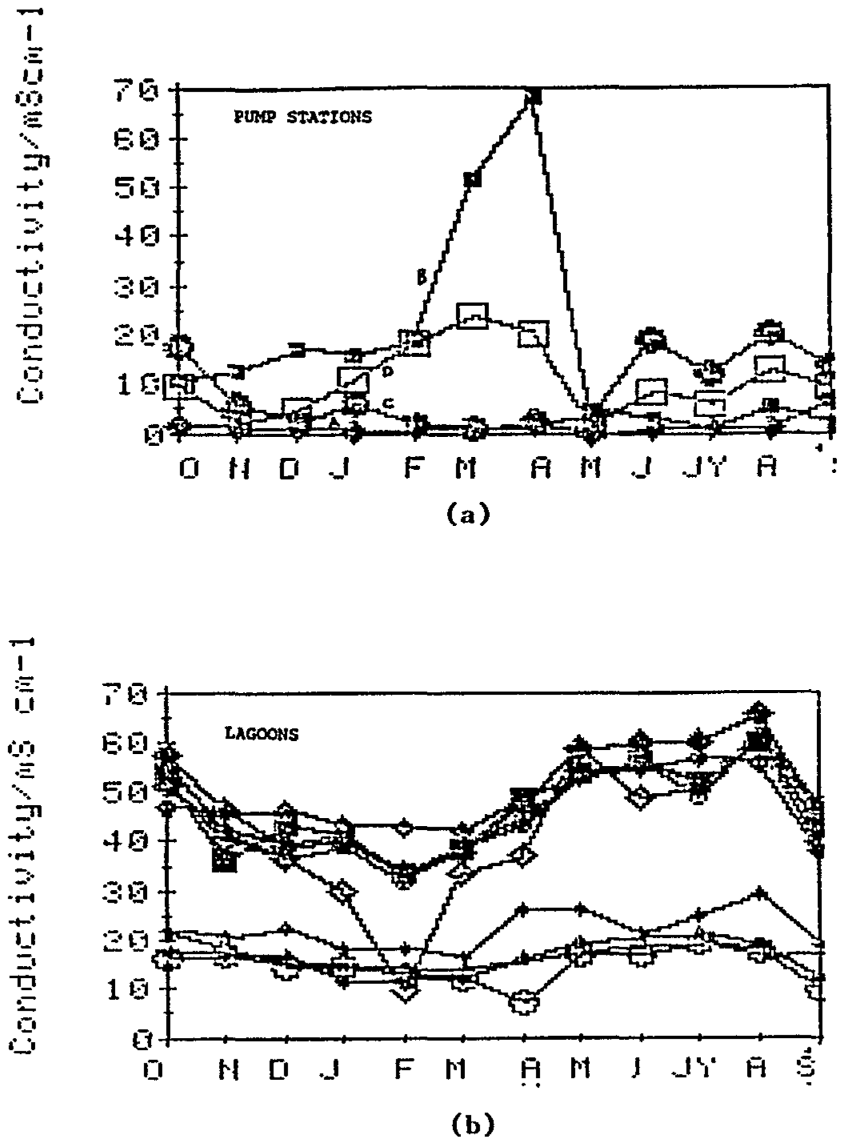

Fig. 4: Conductivity variation (Oct. 1985-Sept. 1986)

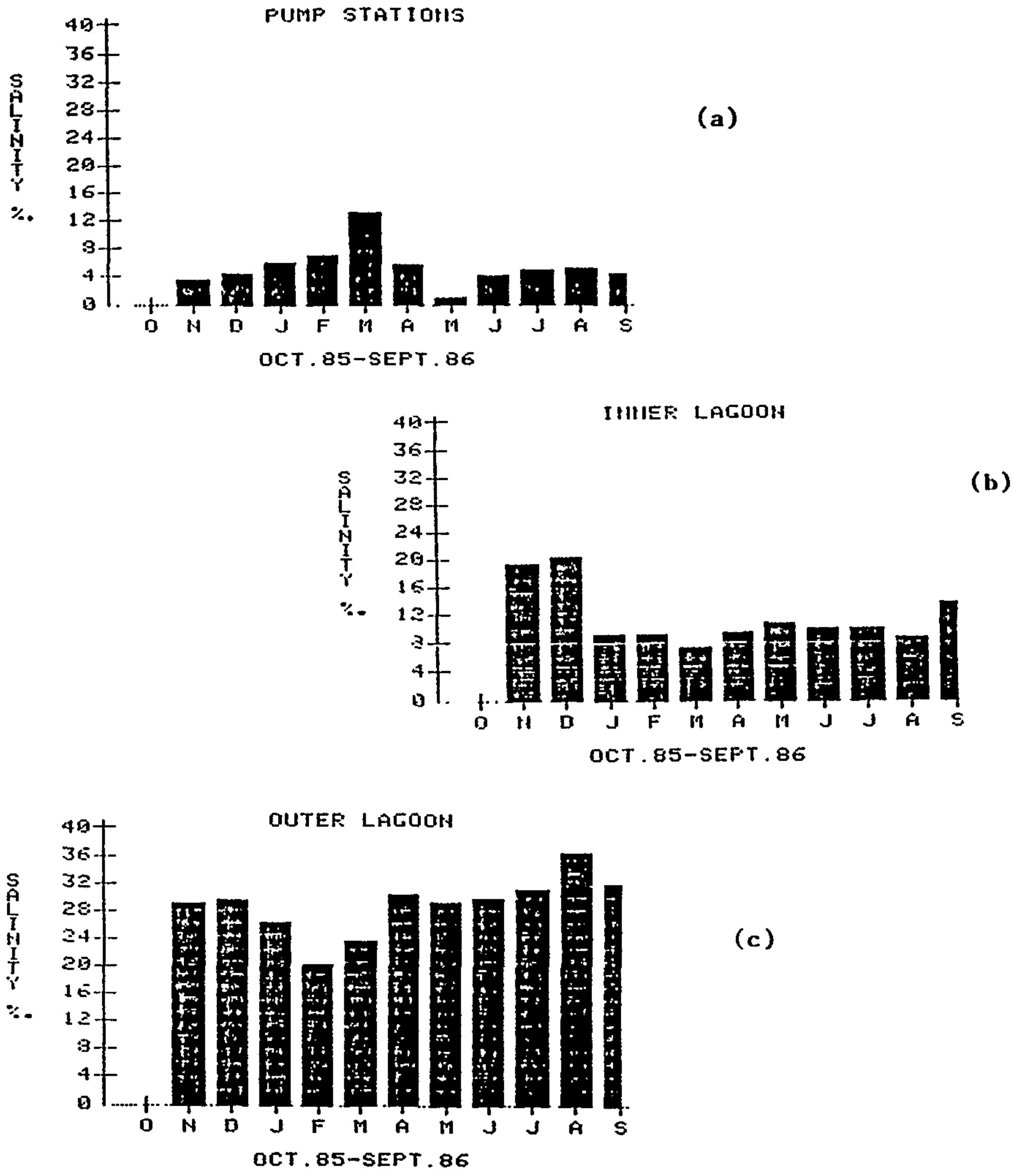

Fig. 5: Salinity variation (Oct. 1985-Sept. 1986)

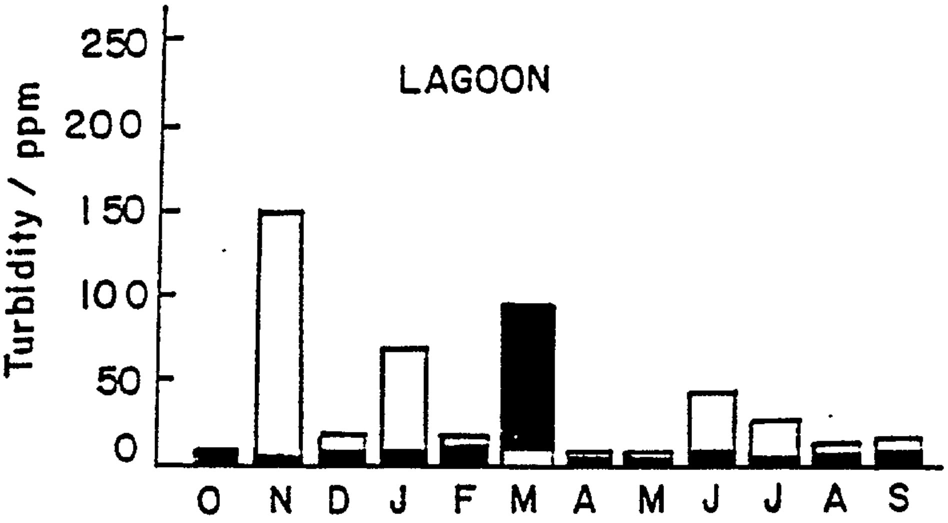

Fig.6. Mean turbidity of the sampling stations of the Lagoon of Messolonghi for 12 months (Oct.1985-Sept.1986) Blank bars correspond to pump stations

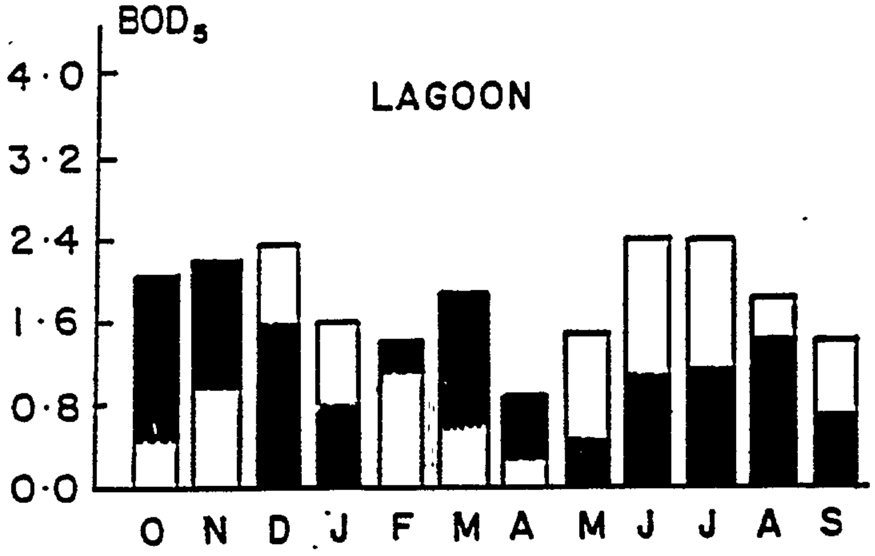

Fig.7. Variation of the biochemical oxygen demand over a period of 12 months. Solid bars:lagoon Empty bars:pump stations

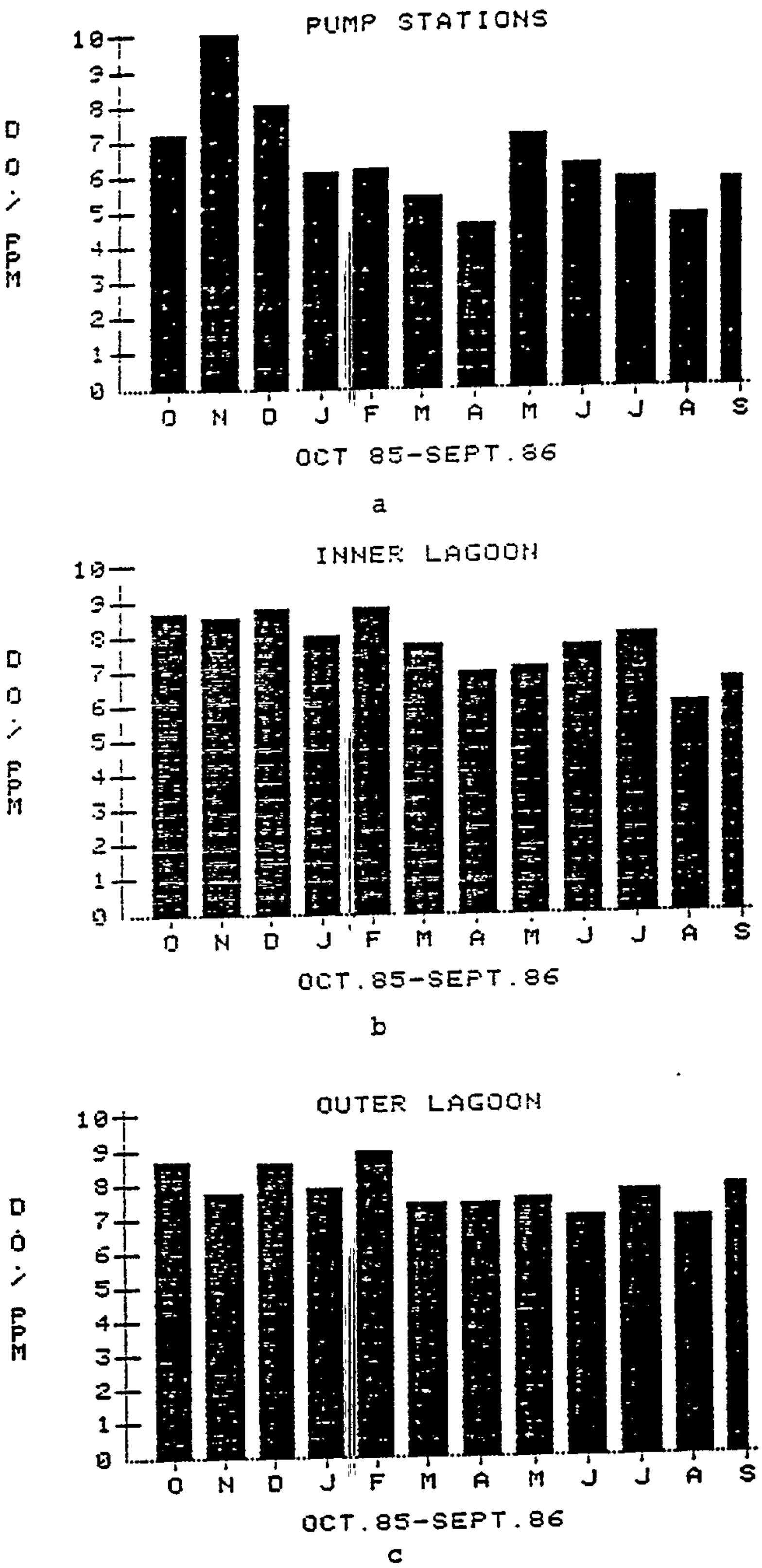

Fig.8. Dissolved oxygen variation:
a:pump stations
b:Lagoon of Aetoliko (inner)
c:Lagoon of Messolonghi

The turbidities of the lagoon samples shown in Fig. 6 are low except for March, when the average water turbidity is significantly higher. Similar findings have been related to high abundance of diatoms (Adeniji 1977, Yoshimura 1930). It should be noted that the maximum seawater turbidity (solid bars) follow, with a delay of a few months, the maximum of the turbidity in pump stations. Turbidity is caused in general by insoluble particles of soil, organics, microorganisms and other materials, impeding the passages of light through water by scattering the light beams. In a typically clear lake, turbidity is about 25ppm, which is the case in the lagoons for most of the months. In March, in conjunction with the rough waters and the input of muddy waters from the drainage channels, the water becomes turbid (turbidity > 100 ppm). Fig. 7 shows the variation of the biochemical oxygen demand during the year, while in Figs. 8a, b and c the dissolved oxygen variations are shown. These plots reflect the fact that the organic load in the lagoon of Messolonghi, depends strongly on the input from the irrigation and drainage works. The values of dissolved oxygen, in most cases exceed 100% saturation but it has been reported that dissolved oxygen may vary drastically during the day (Krom et al. 1985) probably reaching critically low levels for some organisms. Another parameter related to algal growth is chlorophyll a, and the variation of this parameter for both the pump stations and the lagoon stations is shown in Figs. 9a and b in which increased algal growth is observed during Spring and Summer, decreasing during winter. Chlorophyll a could not be correlated with nutrient concentrations such as phosphate and nitrate.

Of interest for the quality of the water is the concentration levels of heavy metal ions. We have investigated the concentration levels of Zn^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+}. The first three metal ions have been found to induce cancer in experiments in animals (Sunderman 1978). In figs. 10a-d and 11a-d, the variation of the concentrations of the four metal ions throughout the year is shown for the pump stations and the lagoon respectively. As the concentrations of these metal ions are below 1ppm, they may be classified as ultra-trace elements (Dulka and Rishy 1976). Thus, the anodic stripping polarography technique was employed since it makes it possible for ppb levels to be determinated. The analysis (performed directly in the lagoon samples without any treatment other than acidification) gives results for free metal ions in solution. It was found that the cadmium concentrations, eventually rise beyond the levels normally encountered in seawater (< 0.1ppm) (Beliles 1975).

Of particular interest in defining the eutrophication status of natural waters are the concentration levels of nitrate, which may also prove dangerous (for example for the health of young children, Weber and Wadworth 1976), and of phosphate. The generally accepted upper concentration limits for waters free of algae is 0.3 mg/l of ammonia plus nitrate nitrogen and 0.02 mg/l of orthophosphate at the time of the spring overturn. Mean annual levels of 0.8 mg/l and 0.1 mg/l for nitrogen and phosphate are shown respectively. The high levels of nitrate during

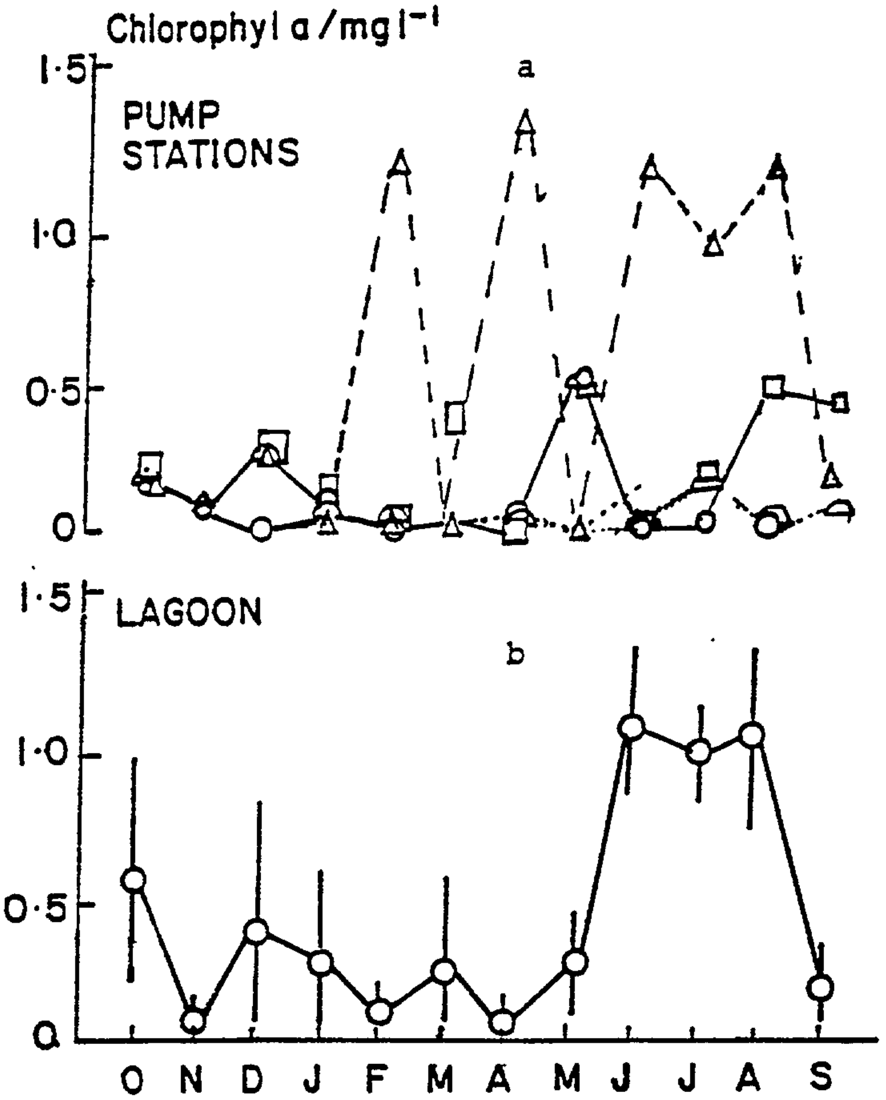

Fig. 9: Chlorophyll a variation for a period of 12 months (Oct. 1985 - Sept. 1986) for:

a: Pump stations

b: Lagoon of Messolonghi (mean values)

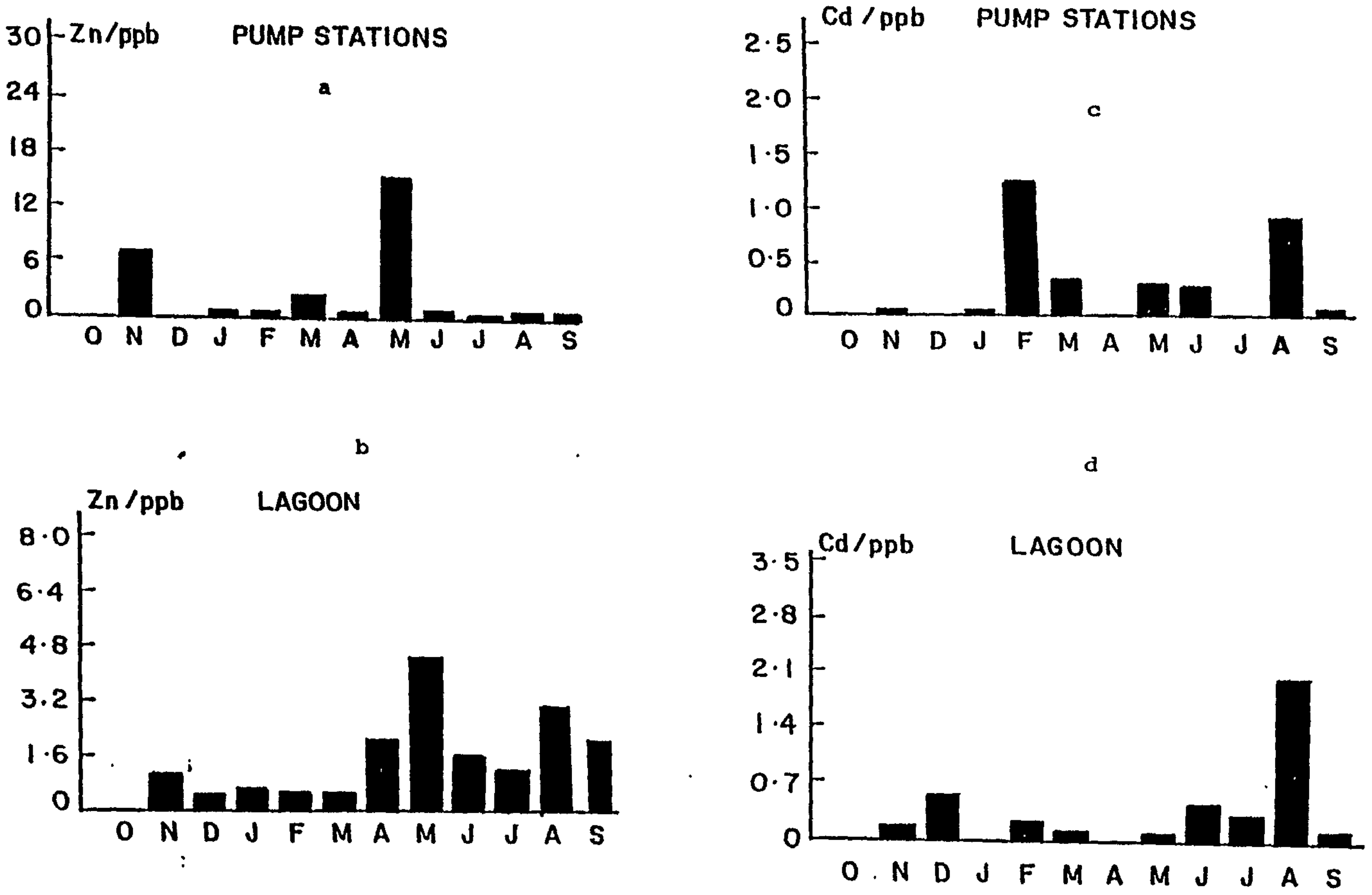

Fig.10.Variation of: a. Zn^{2+} concentration in pump station b. Zn^{2+} concentration in lagoons
c. Cd^{2+} concentrations in pump stations d. Cd^{2+} concentrations in lagoons

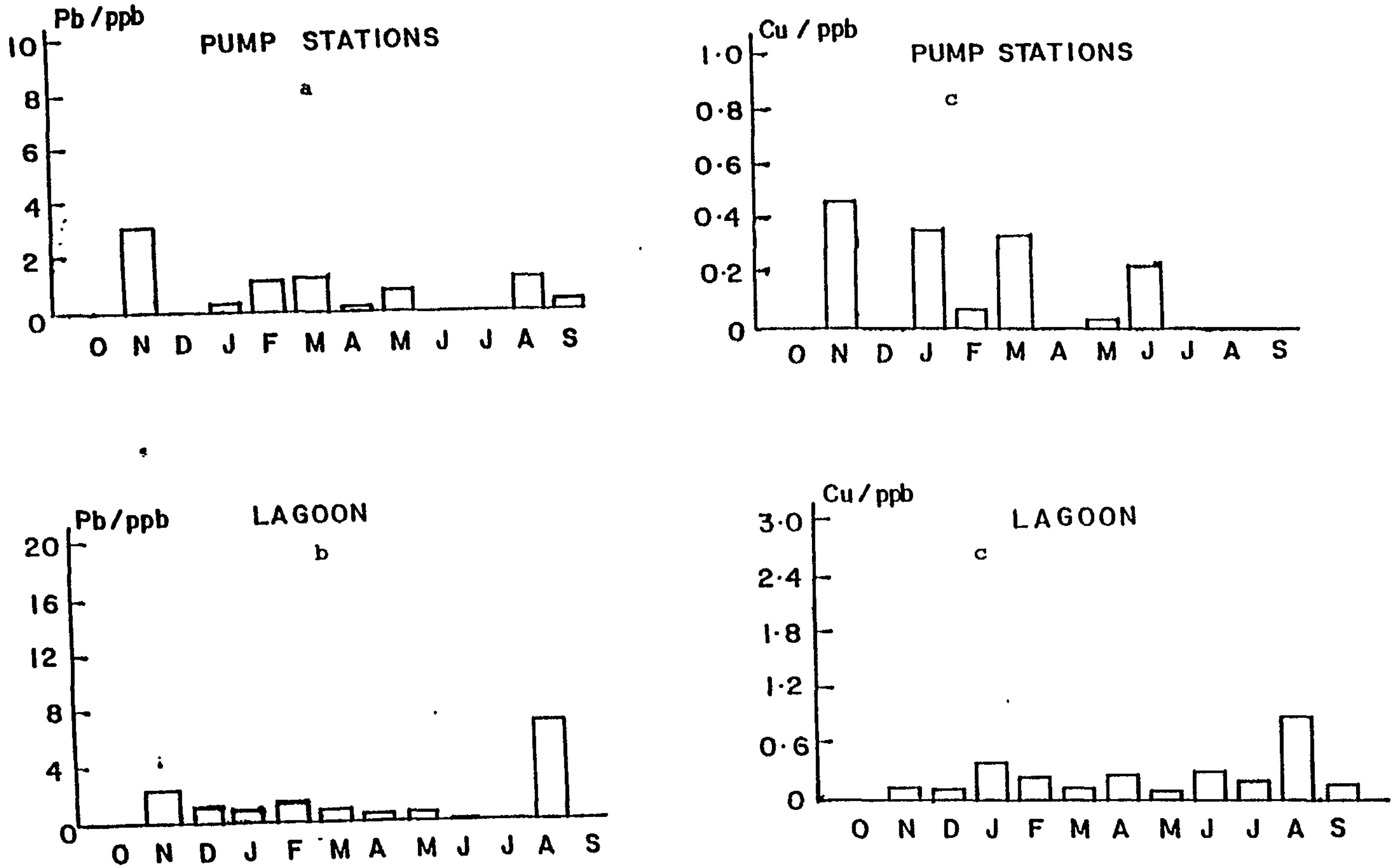

Fig.11. Variation of: a. Pb^{2+} in pump stations b. Pb^{2+} in lagoons
c. Cu^{2+} in pump stations d. Cu^{2+} in lagoons

spring time seem to follow the input from the pump stations. Phospate on the other hand, shows a maximum at the end of the spring both in the inner and the outer lagoons, while the input from the pump stations seems to be rather steady. Again in this case the input from the pump stations seems to regulate the phospate levels in the lagoons. The ratio NO_3/PO_4-P as a function of nitrate concentration yielded a straight line:

$$(NO_3) / (PO_4) = - 2.46 + 1.13 (NO_3)$$

with $r = 0.97$. The linear relationship is shown in Fig. 14.
Finally, it should be noted that the ratio of Ca/Mg was found for the lagoon sites to be constant and equal to 0.4, value which is lower than the average value of 0.78 found in the ocean. The constancy of the Ca/Mg ratio is believed to reflect equilibrium between the waters, calcite and dolomite. The correlation is shown in Fig. 15.

CONCLUSIONS

Following the analysis of the chemical and the physiochemical characteristics of the lagoon of Messolonghi it was found that the waters are polluted. It is believed that a serious source is the input from the pump and drainage systems (including a high suspended sediment loading) which end at the lagoon. Improvement of the eutrophic state may be slow and it would definitely demand further quantitative study in order to accurately assess the input rates and their actual share of the whole problem.

ACKNOWLEDGEMENTS

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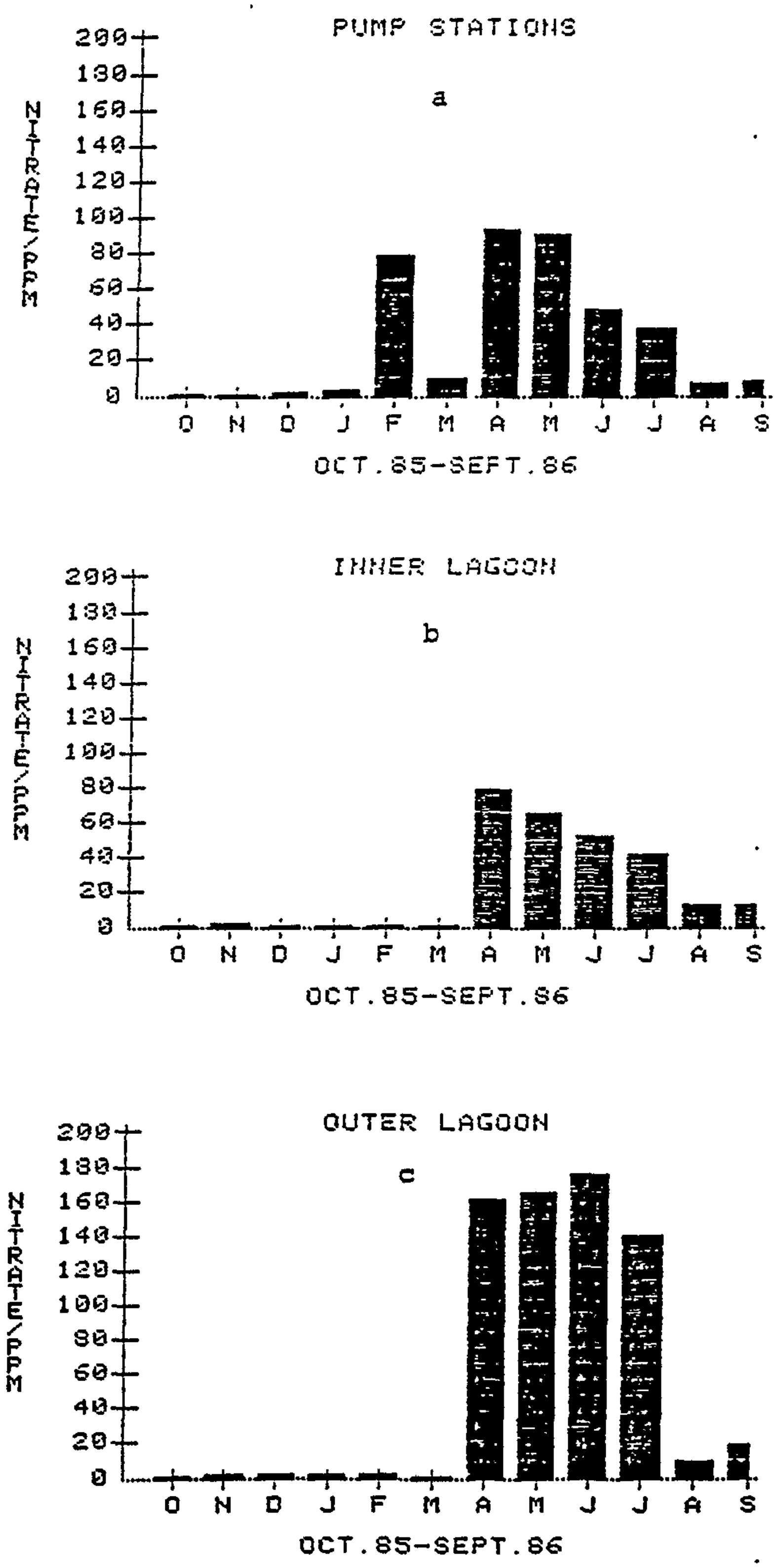
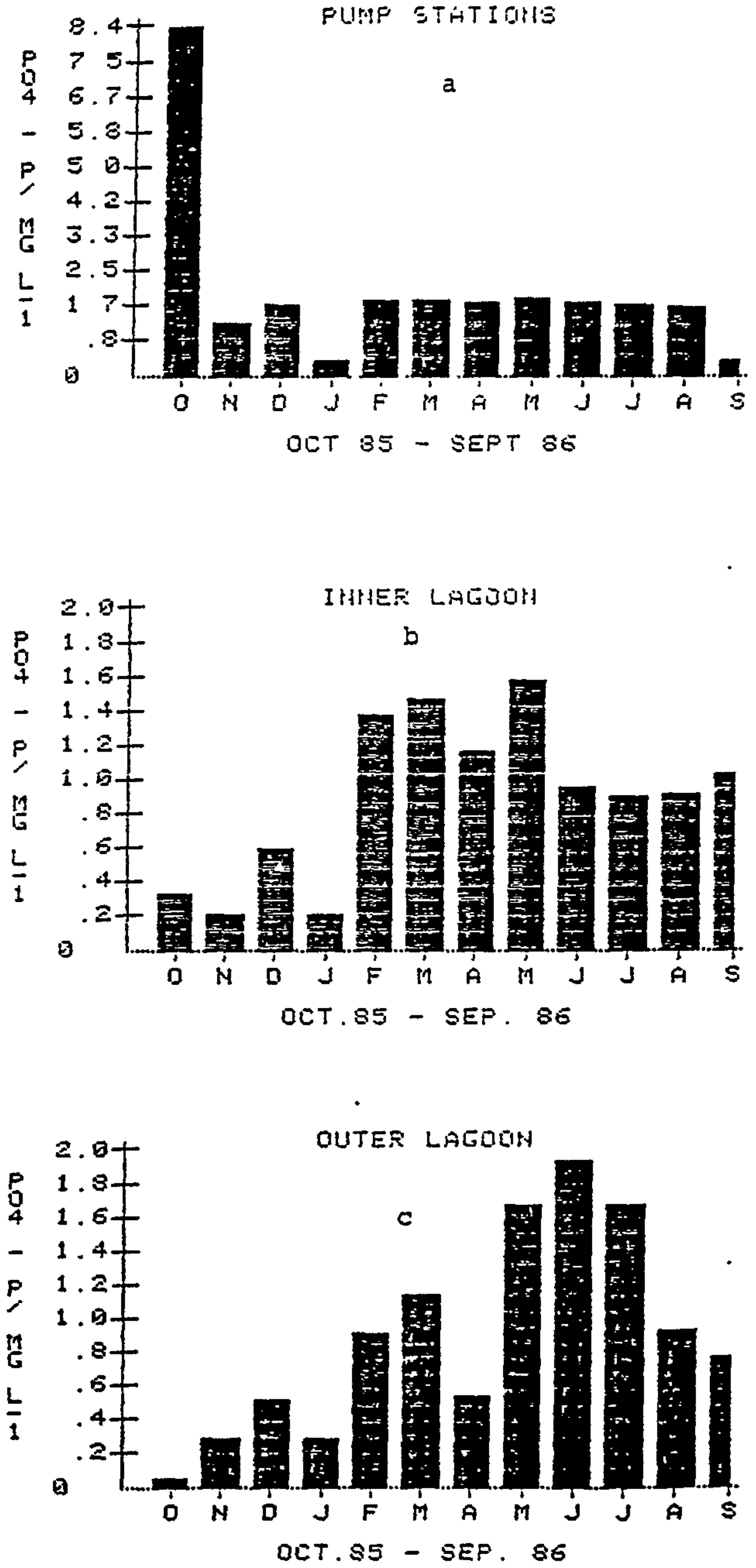


Fig.12. Nitrate variation over 12 months



Fi.13.Phosphate concentration over 12 months

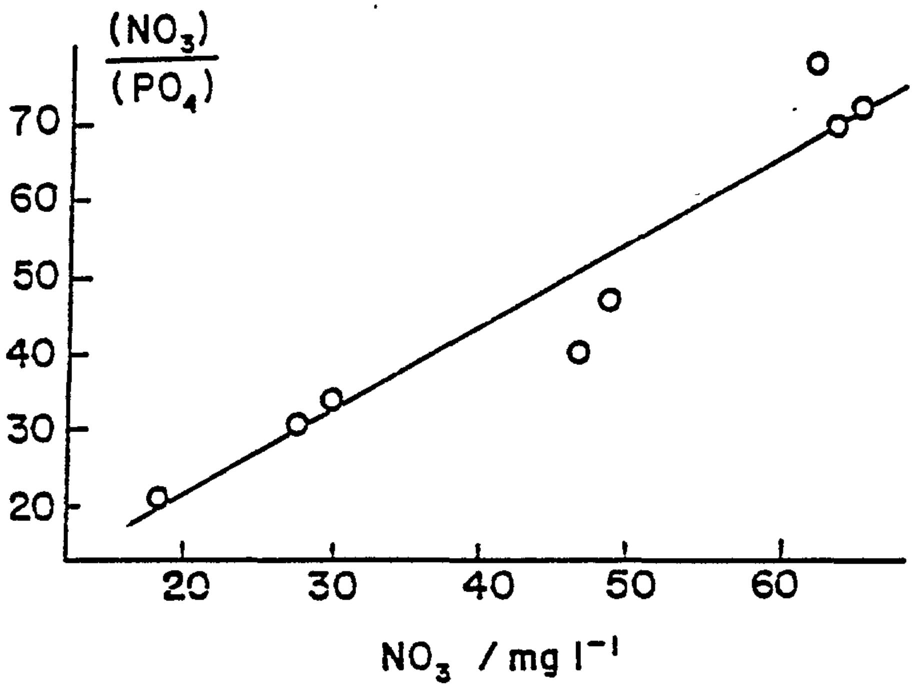


Fig. 14: Dependence of the molar ratio $(NO_3)/PO_4)$ on (NO_3) concentration for the lagoons (Mean annual values).

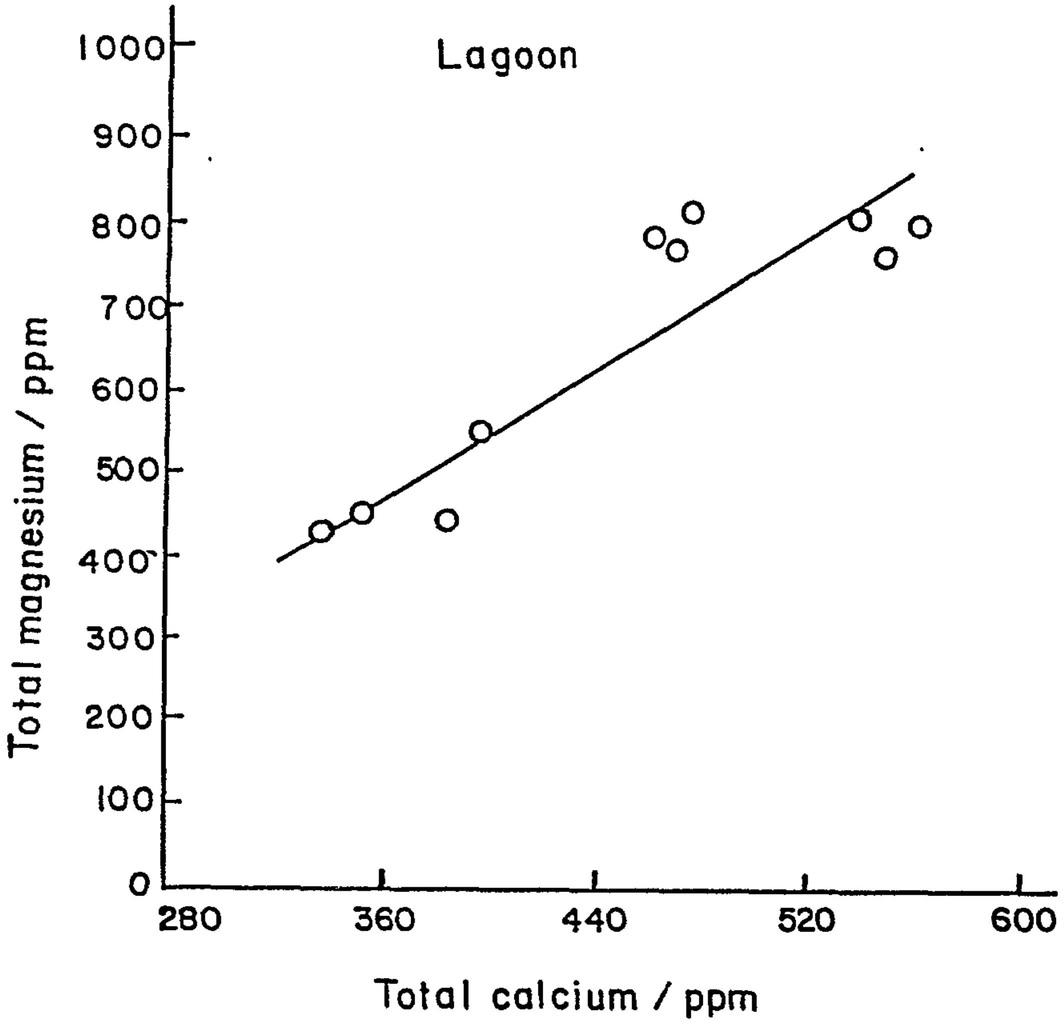


Fig.15. Dependence of Ca on Mg concentration in the lagoons (mean an
values)

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DETERMINATION OF PARTICLE SIZE DISTRIBUTION (PSD) OF COLLOIDAL POLLUTANTS IN COASTAL WATERS BY PHOTOSEDIMENTATION. CORRELATION OF PSD WITH THE CONCENTRATION OF POLLUTANTS.

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ABSTRACT

The particle size distribution of the suspended matter in various coastal waters collected in the vicinity of Patras City in Greece, together with the mean distribution of particle diameters, has been determined as a function of time by means of a simple, quick, inexpensive and relatively accurate photosedimentometer devised by the authors.. The concentration of dissolved heavy metals (Cu, Zn, Cd and Pb) in these water samples, were also measured by a polarographic method. Finally the electrophoretic mobilities of the suspended particles were measured using a microelectrophoresis apparatus. The particle size distributions were found to be self-preserving and independent of time, heavy metal load and particle mobility. As an average, the dependence of the distributions on the particle diameter was found to be -1.1 to -2.4. The flocculation processes of the suspended particles taking place upon mixture of the river water with sea water were also investigated.

INTRODUCTION

The interactions of colloidal pollutants with dissolved species in sea waters are of particular importance, because suspended solids may participate via sedimentation in the process of transporting solutes from the water body into the sediments. The suspended solids have relatively large surface areas per unit mass and can serve as carriers of often insoluble harmful substances such as heavy metals and lipophilic organic compounds. An important parameter for the characterization of the suspended solids in the particle size distribution (p.s.d.). A change of the p.s.d. would be reflected in a change of the transportation characteristics, since transport rates are strongly influenced by particle size. One of the methods used for the determination of particle size distributions of suspended particles is the photosedimentation.

The photosedimentometer combines gravitational settling with photoelectric measurement. The principle of the technique is that a narrow horizontal beam of parallel light is projected through a suspension at a known depth on to a photocell. Assuming an initially homogeneous suspension, the concentration of particles in the light beam will be the same as the concentration in the suspension. If the particles are allowed to settle, the particles leaving the light beam will be balanced by the particles entering it from above. However, after the largest particle present in the suspension has fallen from the surface to the measurement zone, the emergent light flux will begin to increase since there will be more particles of this size entering the measurment zone from above. The concentration of particles in the light beam at any time will be the concentration of particles smaller than the relevant Stokes diameter.

The photosedimentation technique has many advantages over most other particle size analysis methods: the suspension is not disturbed by the insertion of a probe or other measuring device; the attenuation of a beam of light can be measured accurately; the required concentration is low (which lowers the possibility of particle-particle interaction); and experimental results are obtained in a form which lends itself to automatic recording of the cumulative particle size distribution curve. The method has not yet become popular due to the breakdown in the law of geometric optics which occurs as the particle size approaches the wavelength of the incident radiation.

Since particle size distribution and coagulation are closely related, it is the purpose of this work to discuss the particle size distributions in terms of coagulation phenomena.

The concentrations of dissolved heavy metals together with the mobilities of the suspended particles were also measured in order to be investigate the influences of these parameters on the particle size distributions.

Experimental

The coastal water samples for our studies were gathered from the Gulf of Patras in the vicinity of Patras city, Greece. Figure 1 shows the sampling locations (1,2,...,8). The locations 1 and 4 are close to mouths of rivers. In the time period from 1 November 1986 to 31 October 1987, 96 samples were collected, i.e. 8 samples per month. Sample preservation consisted of chilling the samples on ice during their transportation to the Laboratory where they were stored at 2°C. The samples were partly characterized by monitoring the temperature, pH, conductivity, turbidity and dissolved oxygen by the Horiba water checker U7 at the time of collection.

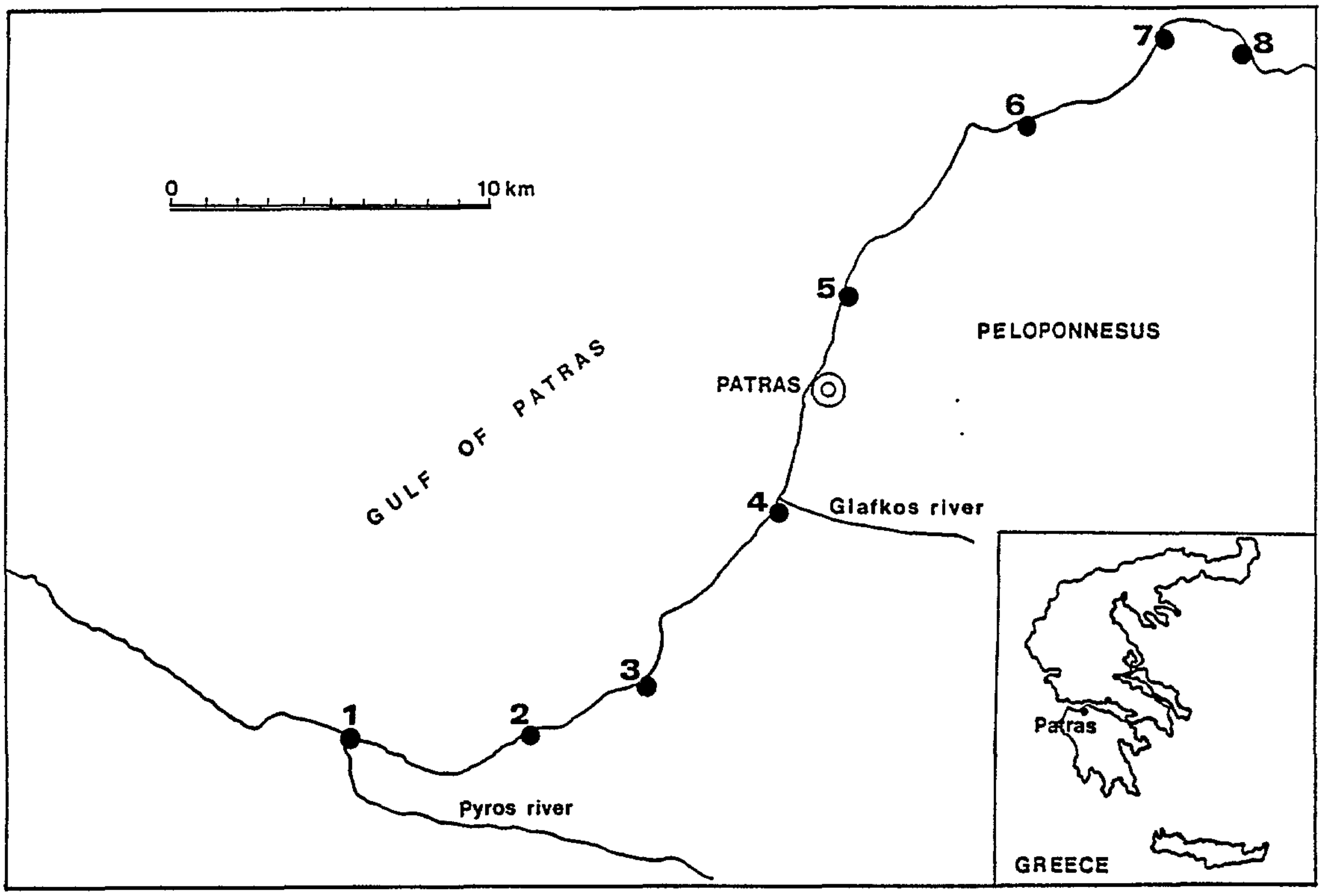

Figure 1

Map showing location of sampling sites.

The determination of particle size distribution of colloidal pollutants in coastal waters was made on those samples which had a significant concentration of suspended particles. This was performed using a simple and inexpensive photosedimentometer devised in our Laboratory. The accuracy of the sedimentometer was tested by comparing the particle size distribution of a well characterized by Coulter Counter calcite sample with that found by our method.

A multichannel Coulter Counter, Model TAII from Coulter Electronics Ltd., was also used to determine the particle size distribution of one water sample and to compare it with that found by our photosedimentometer.

In all water samples the concentrations of dissolved heavy metals (Zn, Cd, Cu and Pb) were measured by using a polarographic method (Polarograph, Model PO4 from Radiometer).

The microelectrophoretic mobilities of the suspended particles in coastal waters were measured in a microelectrophoresis apparatus (Rank, Mark II) by using a four electrode, capillary cell. The velocities of at least twenty particles in each direction of the electric field, were measured at the two stationary layers.

The treatment of the experimental data was performed on a Model RT-Unitron computer.

Results and Discussion

The Stokes diameter of a spherical particle, d_i, suspended in a medium, can be determined from its sedimentation rate in a gravitational field. The diameter d_i is given by the relation:

$$d_i = \left[\frac{18n\upsilon}{(\rho-\rho_o)g}\right]^{\frac{1}{2}} = \left[\frac{18nh}{(\rho-\rho_o)gt}\right]^{\frac{1}{2}} \qquad (1)$$

where n is the viscosity of the suspended medium, υ is the sedimentation velocity of the spherical particle under the influence of gravitational acceleration g, ρ and ρ_o are the densities of the particles and the medium, respectively, h is the sedimentation distance and t is the time.

When the particles are irregularly shaped the diameter d_i represents the equivalent diameter of a sphere of equal diffusitivity with the studied particles. Since the suspended particles in sea waters are polydispersed an average number particle diameter, $\bar{d}$, is given defined by the relation:

$$\bar{d} = \frac{\sum_i f_i d_i}{\sum_i f_i} \tag{2}$$

Where f_i is the frequency, i.e. the percentage of particles with diameter d_i.

The light beam travelling through the homogeneous suspension in the photosedimentometer, is attenuated by the particles which intersect and adsorb light, the attenuation being dependent on particle size distribution, particle concentration and length of the path of the light beam. The determination of the particle size distribution may be done by measuring the change of light attenuation with time. The resulting sedimentation curve (see Figure 2) can be converted into the cumulative curve as follows. The time axis is divided in about ten equal intervals wherein particle diameter, d_i, determinated from Eqn.(1), is considered to be constant. From all these d_i values of a sedimentation curve, a numerical average particle diameter, d, is computed via Eqn.(2). The frequency factor f_i of each class size is found from the relative intensities of the light (see Figure 2). More details for the conversation of a sedimentation to a cumulative curve (see Figure 3) are given by Terence (1980).

As Eqn.(1) shows, for the determination of the particle diameter d_i it is necessary to know the density of the suspended particles. In our case, where we do not know the exact composition of the suspended particles in sea water, this is a serious problem. In order to solve this problem we have measured the particle size distribution, and hence the average numerical diameter of the suspended particles in a given water sample, by using a Coulter Counter and we have compared it with that found by our photosedimentometer. This comparison has showed that the average density of the suspended particles must be about 5 $g.cm^{-3}$. Supposing that the composition of particle is approximately the same in all the sea water samples, we can use the value of $\bar{\rho}$ - 5 $g.cm^{-3}$ in all the collected samples. This assumption agrees with the previous study by Hohl and Vagenknecht (1979), according to which suspended particles in sea water consists mainly of iron oxides, that have densities around 5 $g.cm^{-3}$. It is noteworthy that big variations in the particle density, ρ, as Eqns.(1) and (2) show, lead to small variations in d. For instance, a variation in density from 4 and 6 $g.cm^{-3}$, i.e. a 50% variation, leads to a variation from 39.4 to 30.4 um in particle diameter, i.e. a 22% variation. Even if the assumption of ρ -5 $g.cm^{-3}$ is inaccurate, Sedimentation curve obtained by the photosedimentometer for the sample 1 collected in October 1987.

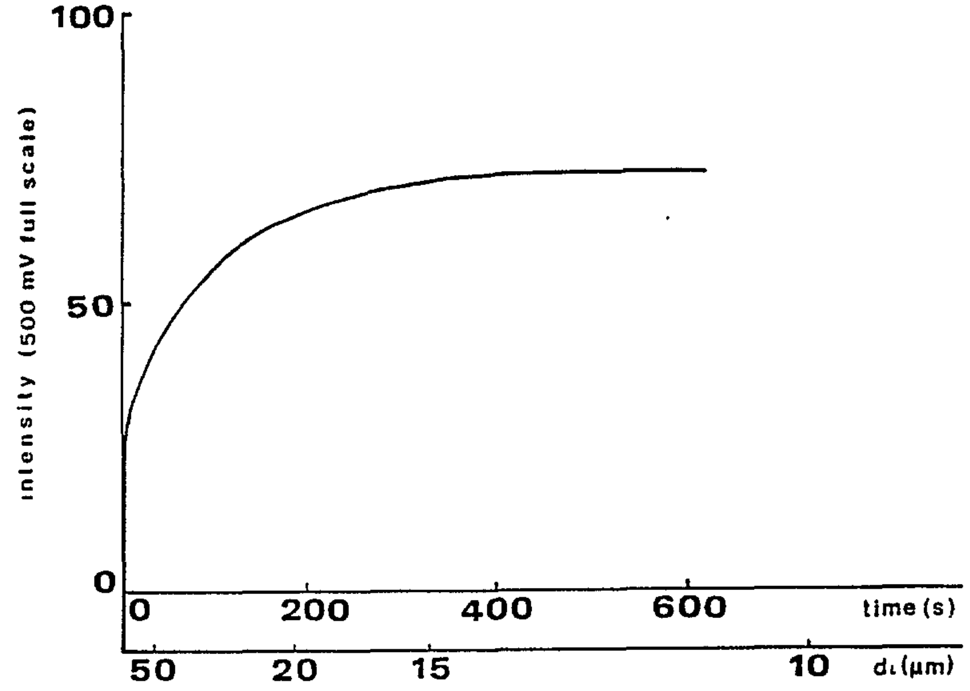

Figure 2

Cumulative curve obtained by photosedimentometer for the same sample as that of Figure 2.

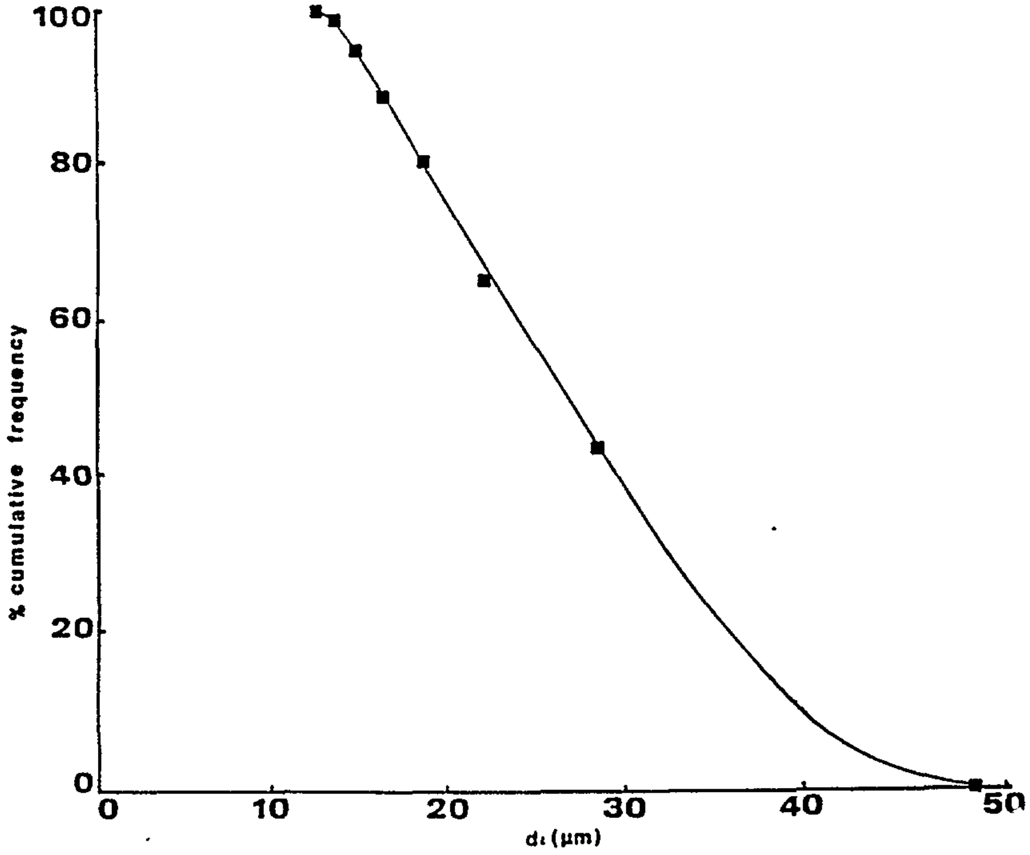

Figure 3

our final conclusions would be valid, since we are mainly interesting in the C_0 variation of particle size distributions with some other important parameters.

The slope at each point of the cumulative particle size distribution is called the particle size distribution and is represented as $\underline{b}_i$. The size distribution of atmospheric aerosols and of aquatic suspensions is often found to follow a power low of the form given by Stumm and Morgan (1981).

$$\underline{b}_i = \underline{A}\underline{d}_i^{-\beta}$$

or

$$\ln\underline{b}_i = \ln\underline{A} - \underline{\beta}\ln\underline{d}_i \qquad (3)$$

in which $\underline{A}$ is a coefficient related to the total concentration of particulate matter in the system. The exponent β has been determined experimentally and has also been shown on theoretical grounds to result from the interaction of various physical processes such as coagulation and settling.

Eqn.(3) shows that a plot of $\ln\underline{b}_i$ should be a straight line with slope equal to β .

Friedlander (1960) and Hunt (1980) have examined the effects of flocculation by Brownian diffusion and removal by sedimentation on the shape of the particle size distribution function as expessed by Eqn.(3). For small particles, where flocculation by Brownian diffusion is predominant, β is predicted to be 2.5. For larger particles, where removal by settling occurs, β , is predicted to be 4.75. When flocculation by fluid shear (velocity gradients) is predominant, β is predicted to be 4.0. Finally when flocculation by differential settling predominates β is predicted to be 4.5.

Eighteen size distributions derived from sea water samples collected at various locations and at various time yielded values of β scatter between 1.1 and 2.4. The β values, contrary to the theory mentioned previously, are even below the smallest value of 2.5 which is expected for a Brownian coagulation mechanism. A reasonable explanation for this is the fact, that many particles may consist of living organic matter, i.e. plankton. The latter is capable to act against sedimentation and thus maintains a given depth in the water body. Therefore we can exclude settling and differential sedimentation as dominating coagulation mechanisms for large particles. We can also exclude the shear coagulation mechanism, since the shear rates in coastal waters, as Hunt (1980) proposed, are too low. Thus Brownian motion becomes the dominant factor for coagulation and the β value should be 2.5, which is closer to what was measured. Similar surprising results for the β values have also been presented by Hohl and Vagenknecht (1979).

A Test for self preserving distributions is done by plotting log $\underline{f}_i$ against the logarithm of the dimensionless parameter $\underline{d}_i/\underline{d}$. The $\underline{f}_i$ is the cumulative frequency of particles with diameter equal to or larger than $\underline{d}_i$ and $\underline{d}$ is the numerical average particle diameter. If the plot shows the same functional dependence at various times, then the distributions are self preserving. Figure 4 shows the test for self preservation as a function of time (during a period of one year) in sample 1 and in sample collected from the Pyros river entered to the location 1.

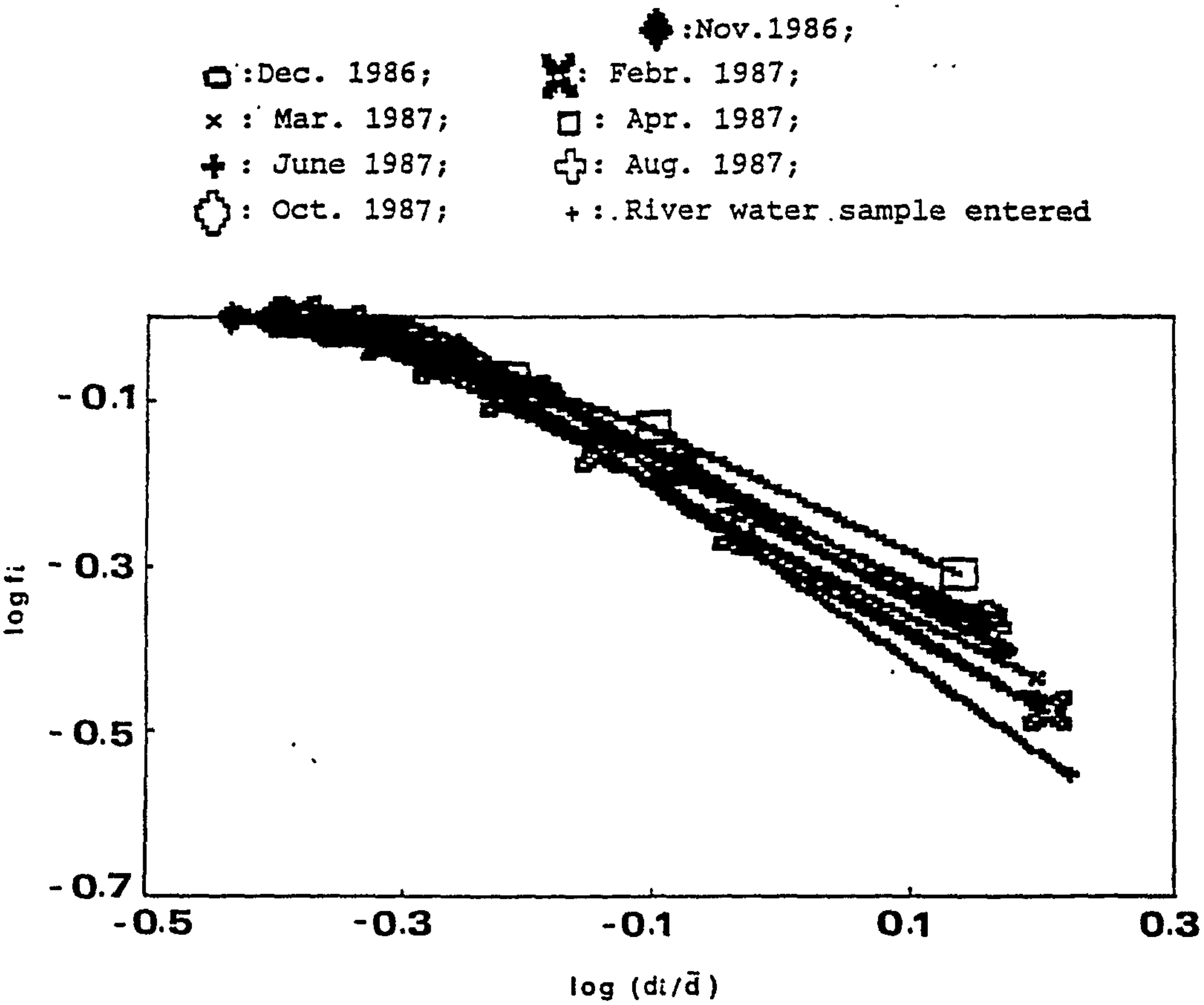

Figure 4

Test for self preserving distribution as a function of time in the sample 1.

In October 1987 together with the eight coastal water samples (1,2,...,8), a sample was collected from where the Pyros river enters the sea in sample location 1 (see Figure 1). The average numerical diameters of the suspended particles in samples 1 and that collected from the Pyros river were found to be 34.4 and 21.8 μm, respectively. This is reasonable since the increase of ionic strength during mixing of fresh and sea water induces flocculation of the suspended matter transported by river and, as a consequence, intensive sedimentation and accumulation of this material occurs generally in a somewhat restricted zone of the estuary. Theory predicts that colloid stability decreases with increasing ionic strength. Hence most colloids are less stable in sea water than in fresh water, and the total number of suspended particles in a given sample volume decreases as the number average particle diameter increases. This is in accord with our results presented in Figure 5. Figure 5a shows the variation of number average particle diameter, $\underline{d}$, with time for the sample 1, while Figure 5b the variation of the parameter $\underline{h}_{tot.}$, which is proportional to the total number of suspended particles in a given sample volume, with time for the same sample. In both plots the data of the Pyros river water are also included. Figure 5 shows that $\underline{d}$ increases as $\underline{h}_{tot.}$ decreases and vice versa.

Figure 6 shows that for sample 1, the variation of tubidity with time is independent of the variation of the total number of suspended particles with time (see Figure 5b). This might be due to the fact that, apart from the total number of suspended particles, the size, shape, and refractive index of the particulates also affect the light-scattering properties of the suspension. Figure 6 shows that the higher turbidities correspond to the sample location 1, which is close to the mouth of the Pyros river. This observation shows that a relatively large fraction of the suspended matter, such as clay, silt, finely divided organic and inorganic matter, soluble colored organic and inorganic matter, soluble colored organic compound, plankton, and other microscopic organisms, which causes turbidity in water, it is transported into the sea by the rivers.

The concentrations of dissolved heavy metals as a function of time and sample location show large variations. These variations are mostly attributed to seasonal variations and are more or less strongly affected by anthropogenic inputs. Some fluctuations also seem to occur accidentally and climatological changes are often neglected.

The highest concentrations of dissolved heavy metals in all the collected samples over a period of one year (from November 1986 to October 1987) were found to correspond to Pb. These concentrations vary between 120 and 0.3 $\mu g.l^{-1}$. These unusually high values may be due to the exhausts of cars and boats since all the samples were collected in close to coast roads. The lower concentrations were found to correspond to Cd, which was detected only in few cases. These concentrations vary between 9 and 0.3 $\mu g.l^{-1}$. The concentrations of Zn were found to vary between 34 and 0.06 $\mu g.l^{-1}$, while those of Cu between 42 and 0.08 $ug.^{-1}$.

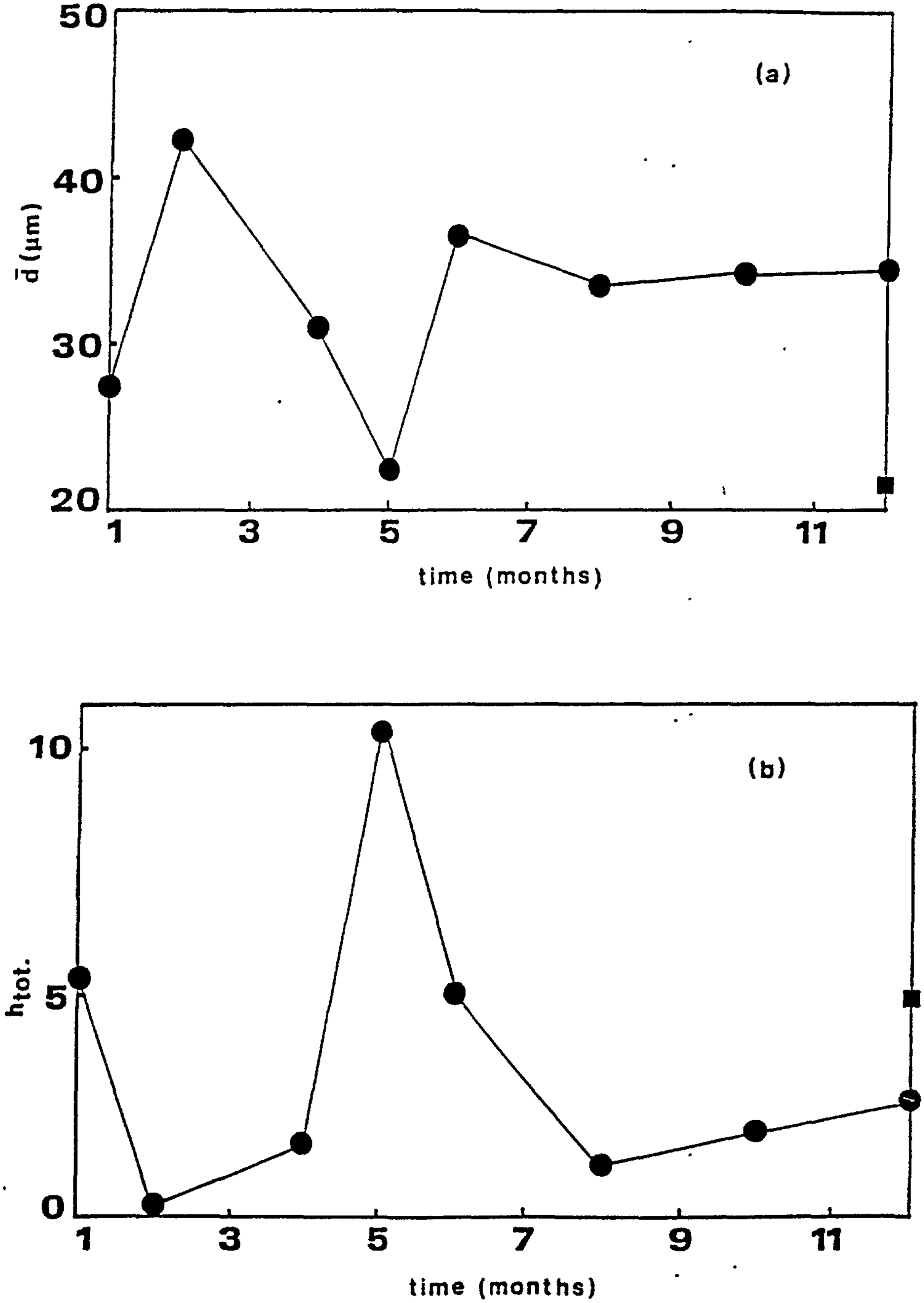

Figure 5

Number average particle diameter of the suspended particles in sample 1 as a function of time (a) and variation of the parameter $h_{tot.}$, which is proportional to the total number of suspended particles, with time (b) over a period of one year. Month 1: Nov. 1986; month 2: Dec. 1986;..., month 12: Oct. 1987. The points ■ correspond to the river water sample.

As a general conclusion the concentrations of dissolved heavy metals in all the collected sea water samples around to the Patras city in Greece, over a period of one year, are relatively low and within of the acceptable limits.

The total heavy metals concentrations in all the collected samples over a period of one year are given in Table I. This Table shows that the lower total concentrations of dissolved heavy metals were found in locations 1, 4 and 5, while the corresponding higher concentrations were found in locations 3, 6, 7 and 8.

Locations 1 and 4 are close to mouths of small rivers, where particles are flocculated (when the fresh water meets the salt water). During the flocculation, dissolved coumpounds and heavy metals are adsorbed and eliminated from solution, thus decreasing the concentration of dissolved heavy metals in locations 1 and 4. It must also be pointed out that the concentrations of dissolved heavy metals in the Pyros river water are lower to those corresponding to sea water in location 1. This is probably due to the variation of salinity in these two samples as according to the work of Duinker (1980), dissolved concentration-salinity plots are characterized by minimum concentrations at low salinities (because of the formation of insoluble metal species at low salinities). Locations 3, 6 and 7 are close to industries and the high concentrations of dissolved heavy metals in these places are probably due to the discharge of trace metals from waste waters.

From all the samples collected in location 1, those collected in January 1987, May 1987, July 1987 and September 1987, were found to have the lowest values of turbidity and the highest values of the total concentration of dissolved heavy metals. As a consequence, the total numbers of suspended particles in these samples were negligible, thus preventing the measurement of the particle size distribution of the suspended particles.

Correlation of the average numerical diameter of the suspended particles with the concentration of dissolved heavy metals is difficult, given that the concentration of the heavy metals in sediment, the organic material adsorbed on trace metals and various important physical properties also affect the particle size of the suspended matter. In previous work by Hohl and Vagenknecht (1979) the particle size distribution was also found to be independent of the concentration of dissolved heavy metals.

The measured particle mobilities in the sea water samples are negative and fall within a narrow range (about -0.27 to $-0.88\times10^{-8} m^2 s^{-1} V^{-1}$). The observed small variation of the electrophoretic mobility of particles with time and sample location may be due to the variation of adsorbed organic material in these particles. Recent work by Hunter (1980), has confirmed the importance of adsorbed organic matter in this role. Particle size distributions of the suspended particles were found to be independent of their mobilities, since the particle sizes are mainly affected by the flocculation processes that occur at the high ionic strength sea water, while electrophoretic mobilities were measured in 0.1 M KNO_3.

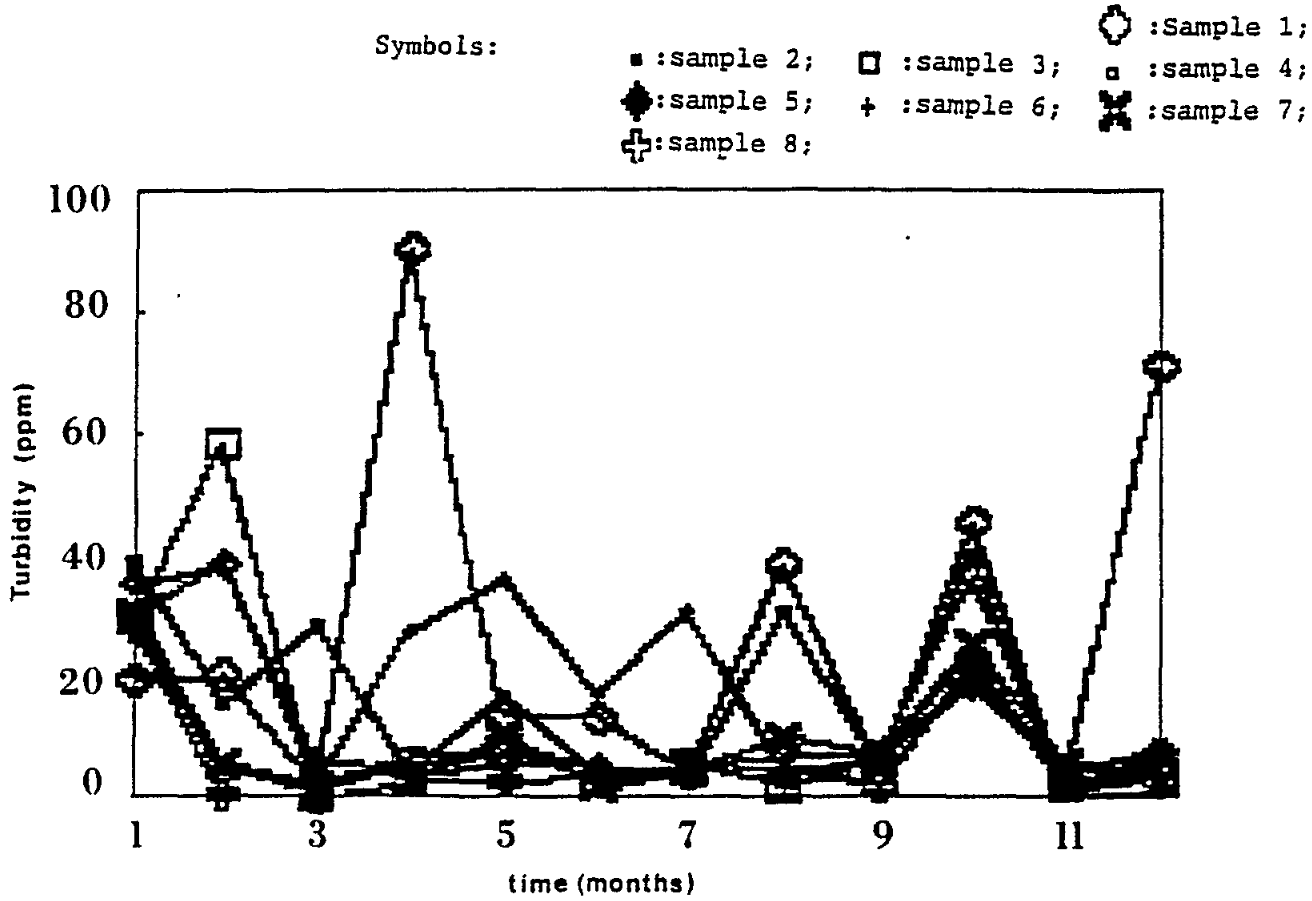

FIGURE 6: Turbidity as a function of time for the collected samples (1, 2,...., 8).

TABLE I: Total concentration of dissolved heavy metals in various water samples (1,2,...,8) collected over a period of one year with a frequency of one sample per month.

Sample / Metal	1	2	3	4	5	6	7	8
Zn ($\mu g.l^{-1}$)	14.1 *	20.3	31.6	14.2	28.5	53.2	37.7	37.0
Cd ($\mu g.l^{-1}$)	0.60	2.1	9.7	1.3	2.2	6.8	5.1	4.8
Pb ($\mu g.l^{-1}$)	84.3	86.9	93.9	67.1	34.6	60.5	152.0	156.6
Cu ($\mu g.l^{-1}$)	16.7	47.6	93.0	53.6	37.0	63.2	15.2	21.2
(Zn+Cd+Pb+Cu) ($\mu g.l^{-1}$)	115.7	156.9	228.2	136.2	102.3	183.7	210.0	219.6

* All the values of this table are cumulative concentrations of 12 samplings.

Some important ancillary parameters measured were the biochemical oxygen demand (BOD), conductivity, pH and temperature. Dissolved oxygen is a measure of a body of water's ability to support aquatic organisms. Conductivity is a numerical expression of the ability of the aqueous solution to carry an electric current. Conductivity is lower in the sample locations where fresh water meets the sea water. Measurement of Ph is one of the most important and frequently used tests in water chemistry. Every aspect of the present problem, e.g., precipitation, coagulation and corrosion control, is pH-dependent. Temperature measurements in sea water samples give information about the identification of source of water supply and have significant ecological impact.

Figure 7 shows that the variation of BOD with time its almost the same for all the collected samples. The higher values of BOD appear in locations 1 and 4 which are close to mouths of river. Figures 8, 9 and 10 show the variation of conductivity, pH and temperature, respectively, with time for all the collected water samples. All the plots show the same functional dependence at various locations, except for some conductivity, pH and temperature fluctuations which seem to show random variability.

Conclusions

A simple and inexpensive photosedimentometer devised by us was used to measure the particle size distributions of the suspended particles in coastal waters. These distributions were found to be self-preserving and independent on time, heavy metal load and particle mobility. A significant part of the suspended particles is transported into the sea by the rivers. The increase of ionic strength during mixing of fresh and sea water induces flocculation of these suspended particles. The dominant factor for flocculation processes taking place in coastal waters was confirmed to be the Brownian diffusion.

Acknowledgements

We would like to express our appreciation to Dr. Peska of The Institute of Macromolecular Chemistry, in Prague, for the Coulter Counter Measurements. A Grant from International Atomic Energy Agency, No.4621.EP, in support of this work is greatfully acknowledged.

Variation of Ph with time for all the collected samples. The symbols are the same as those of Figure 6.

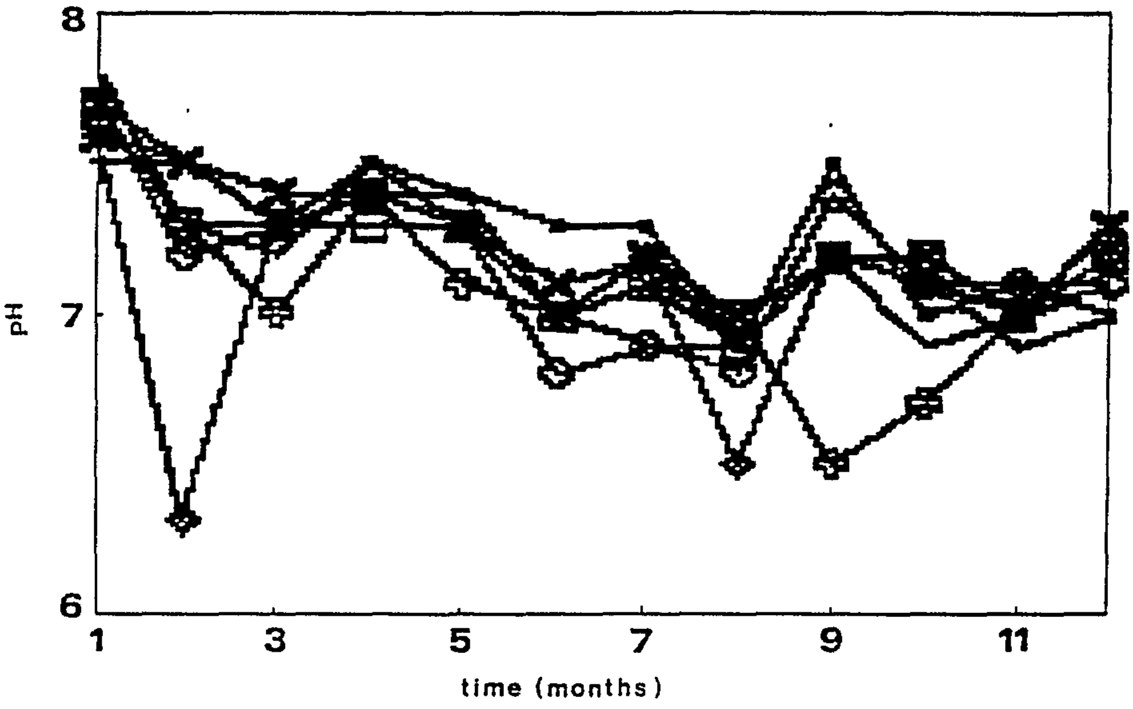

Figure 9

Temperature as a function of time for the sea water samples collected over a period of one year. The symbols are the same as those of Figure 6.

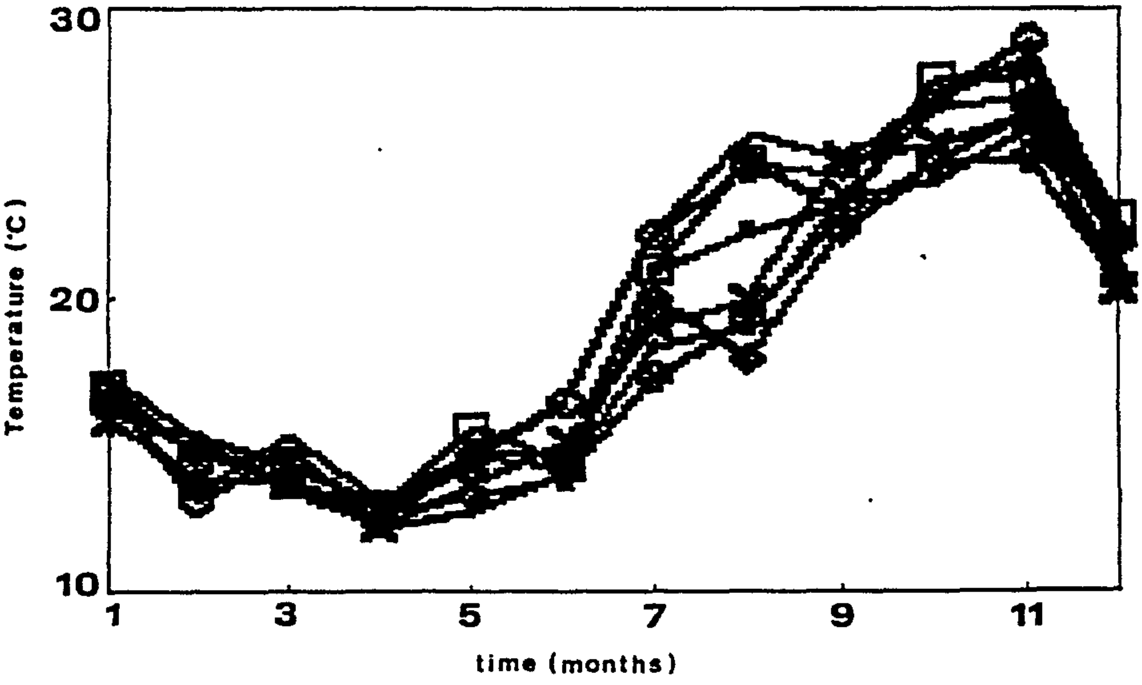

Figure 10

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ABSTRACTS AND EXTENDED ABSTRACTS

RELATIONS ENTRE LES CONTAMINATIONS DES EAUX ET DES SEDIMENTS PAR LES METAUX

par

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EXTENDED ABSTRACT

Sedimentation of metals by fixation on suspended particles in water is schematized by Fig. 1. If we disregard transient phenomena such as "upwelling", "downwelling", or immobilization by thermocline, it is manifest that the speed of sedimentation grows with the weight (or size) of the particles, its duration in the water column growing with the depth to the bottom. It is manifest, too, that there is generally no correlation between the instantaneous concentration of a certain metal in the water and the average concentration of the same metal in a layer of a few centimeters of the sediment on the same column, except if the instantaneous concentration in the water happens to be, by chance, nearly equal to its average concentration. In any case it is normal for the relationship water-sediment to be, other things being equal, poorer when the duration of sedimentation (hence the horizontal distance covered) is greater, which can be due to a deeper bottom or/and to a lesser speed of sedimentation (smaller particles).

The relevance of these general reflexions is experimentally demonstrated by the analysis of Hg, Cd, Pb and Cu water and sediment concentrations both in the Mediterranean (in front of the Rhône delta and of the industrial complex of Fos-Lavera-Port de Bouc) and in the region Channel - North Sea (French coast from Le Havre to Dunkerque and Belgian coast):

1) Mediterranean

a. Metal concentrations have been measured (24-26 nov. 1981) at 21 stations in the sediment and (as well as salinity) at three levels in the water: surface, near the bottom, mid-bottom depth). In addition, owing to many oceanographic cruises at different seasons in the Gulf of Lion, we have determinated salinity and metal concentrations at sea surface with a density sufficient to draw maps giving at least an approximate distribution of their average value.

b. A close scrutiny of these numerous maps and the computation (least squares method) of the interesting possible correlations shows that:

Cadmium appears, to be in solution or fixed on small particles when salinity is low, but when salinity is higher it is precipitated on heavier particles.

Lead seems to fix itself, in seawater, on particules of medium size.

Copper seems to fix itself partly and very quickly on particles of greater size than for Lead, and partly on particles that settle down less rapidly.

Mercury fixes itself essentialy on small particles, but a less important fixation seems to exist on heavier particles.

There is no significant correlation between concentrations in sediment and instaneous concentrations in water, but significant positive correlations exist with the average concentrations in the surface water, in spite of the fact that these average concentrations are only approximate.

The "condensation factors" (concentration in sediment divided by concentration in water) are much less scattered for the average concentration in surface water than for the instantaneous concentrations, but their mean values are of the same order of magnitude for the same metal: thus the instantaneous condensation by sedimentation does not vary much with the instantaneous concentration in water, but chiefly with the conditions of the fixation on the particles, which vary much less.

2) English Channel and North sea

a. Metal concentrations have been measured in sediment and, as well as salinity, only in sea surface at 4 stations in Seine Bay (Aug. 26), 2 stations near Dieppe (Sept. 1 and 2), 1 near Dunkerque (Sept. 8) and 10 along the Belgian coast (Sept. 18, 1984). No average values are available, but plancton identification and counting has been made for each sample of water.

b. The abundance of Hg, Cd, Pb and Cu in surface water and chiefly in the sediment is clearly tied up with the river Seine on the one hand (near Le Havre) and on the other hand with the river Yser and the canals which are connected to it (Belgian Coast), as sources.

c. A close inspection of the data in Seine Bay confirms a fixation of Hg entirely on particles more clearly than for Cd, Pb and Cu which settle down more quickly, while on the other hand Pb seems to fix itself preferably on medium sized particles, less heavy than for Pb and Cu: conclusions very similar to those obtained in front of the Rhône delta. There is, once more, no significant general correlation between concentrations in sediment and instantaneous concentrations in water.

d) Condensation factors (concentration in sediment divided by instantaneous concentration in water) are a little scattered than in front of the Rhône delta, but more interesting is the fact that certain variations of these factors from the Seine Bay to the Dutch border can be explained in relation with the plancton size and the tendancy (that we have brought to light) of such and such metal to fix itself preferably on particles of a given size fraction.

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CONTRIBUTION OF MINERAL AND MAN-MADE AEROSOLS TO THE ACCUMULATION OF TRACE METALS WITHIN THE EASTERN MEDITERRANEAN BASIN

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The contribution of mineral and man-made aerosols to the accumulation of trace metals within the sedimentary load of the Mediterranean Basin through air to sea transfer, either by exchange or sedimentation, has been noticed by various studies during the recent years. However, at our present state of knowledge, we will lack basic data concerning the annual distribution of the atmospheric pollutants as well as the chemical and biogeochemical processes which govern the fractionation of the metallic compounds among the seawater column, marine biomass and solid sediments at bottom. It is the aim of our study to provide analytical results regarding the potential risk of trace metal transportation into the eastern Mediterranean, as derived from the various sources of atmospheric suspended particles of natural and anthropogenic origin.

Migration of dust constituents into the eastern Mediterranean Basin is carried out from Sahara and throughout the arid landmass of Arabia, Jordan and Mesopotamia. Saharan storms might occur over the Levant and eastern Mediterranean any time between September and June, averaging (for the timespan 1968-1987) 15 storms/year. Mineralogical and chemical variations have been established between the different dust trajectories of Ahaggar, Tibesti and Arabia.

Dust particles from urban and industrial atmosphere of low altitude (up to 300 m approximately) are also being transported into the Mediterranean by means of sea and land breeze circulation, which takes place all along the summer as well as through sporadic events during other seasons of the year.

The magnitude of chemical changes of trace metals concentrations, as were observed within the two types of atmospheric particulates of desert and anthropogenic origin, are evaluated for Cu, Co, Cd, Cr, Mn, V, Ni, Zn and Pb.

PARTITIONING OF ORGANIC POLLUTANTS IN THE DISSOLVED AND PARTICULATE PHASES OF COASTAL WATERS AND THEIR OCCURRENCE IN THE SEDIMENTARY RECORD

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In shelf areas the processes in the water column and in the bottom sediment are closely coupled. However, there is some discussion about the suitability of sediments for assessing the area of impact of land-based pollutant sources. In fact, some pollutants occur mainly in dissolved form or associated to colloidal material, thus being transported far from the source and being more available for degradation. Pollutants associated to particulate material may also be transformed during sedimentation. Finally, sediments, depending on their biogeochemical status, may act not only as a sink but as a source of pollutants. Through comparisons, both qualitative and quantitative, of the budget of organic pollutants in the three mentioned compartments it is possible to establish a data base that would be useful in designing monitoring systems as well as in formulating policies for waste discharges into coastal waters.

To this end, we have carried out a broad spectrum analysis of more than 50 samples of dissolved, particulate and sedimentary material collected in different areas of the Spanish Mediterranean coast. The decoupling of organic pollutants among these compartments has been realized and interpreted in terms of the physicochemical properties of the pollutants as well as of the particular nature of input sources.

Petrogenic hydrocarbons occur mainly in the dissolved phase, although the input through particulate material in estuaries is significant and the accumulation in sediment is enhanced in the waters mixing zone. The 2- and 3- ring aromatic hydrocarbons predominate in the dissolved phase whereas the more condensed ones are only found onto particulates. A similar trend is observed for the increasing degree of chlorination in PCBs. Most chlorinated pesticides and particularly the HCH isomers occur in dissolved form. Surfactant components (e.g. linear alkylbenzenesulphonates and etoxylated alkylphenols) also occur in the dissolved phase. The degradation pathways and accumulation of some of these pollutants in sediments and biota will be exemplified.

VERBATIM REPORT OF THE WORKSHOP SUMMARY GROUPS AND DISCUSSIONS

GENERAL DISCUSSIONS ON THE WORKSHOP AND THE FUTURE REQUIREMENTS IN THIS FIELD

The workshop decided to split into three working groups:

(i) Large scale processes -
Chairman: Dr. Francois Nyffler

(ii) Inorganic contaminants -
Chairman: Dr. Michael Krom

(iii) Organic contaminants -
Chairman: Dr. Joan Albaiges.

The conclusions of the working groups were discussed in a general closing session chaired by Dr. Laurence D. Mee who also acted as rapporteur. The verbatum presentations of the working groups and chairmans remarks provide useful background material for future MEDPOL activities and are presented in the following paragraphs:

LDM: Now that we have heard the formal papers we can make some worthwhile conclusions. First we will listen to the general conclusions from the ad-hoc groups and then try to draw out the major conclusions of the meeting.

First we will hear from Dr. Nyffler's group:

FN: We will address the large-scale problems. We think that this was a good way to have some interaction between people working in different related fields who had little or no contact before so we know a little better what people are doing. From this point-of-view the meeting can be considered as a good starting point. If we examine the shortcomings we find that even if the title of the meeting stressed "transport" we have almost no data on fluxes, evaluation of processes, balances and we noticed that the biological component (large scale) was poorly represented. We may thus conclude that we have observed the present state-of-the art with some nice local examples, each addressing the consequences of some primary dilution of specific pollutants. We now have a good description of certain geographical areas but no overview of what happens afterwards. Similarly, most of the measurements were Eulerian, that is they were measurements repeated at one station but there was no possibility to follow, for example, a water mass which is polluted and moves and it seems that the transport is essentially a dynamic concept. We think that the measurements made should be of a more Langragian nature. More backbground information is also needed of the working areas (pluridisciplinary research). IAEA could contribute more to this work using natural or anthropogenic radiotracers as tools for examining these processes.

We will make some suggestions:

(i) Increase the multidisciplinary nature of the research and not to address only specific problems but try to put these approaches in a general framework for all the studied regions. This is in order to avoid dispersion - it is of no use that each group individually develops a similar programme requiring the same background information despite the limited funds available. The task of the agencies could be to define some priorities. We should also receive clarification on how projects are handled once they are received.

(ii) Try, as a priority to define a methodology to have a general framework of the medium/large scale processes involved.

(iii) We think that the limited amount of money available from MEDPOL for research excludes the purchase of instrumentation or start a new research area. Many groups are already equipped from external sources and if the multidisciplinary approach is a desired goal, the funds should be dedicated to favour interaction between the laboratories, especially to encourage the work of younger scientists who are the most dynamic. Older scientists tend to be burdened with administrative work and lose their momentum. Younger workers should have as much scientific contact as possible with one another and they will lead research programmes in the future.

Concerning the meeting itself - we think that it is good to continue with the meetings with a frequency of about 1/year which is a good opportunity to meet each other and to see progress. Only key papers should be presented in future meetings - the work could also be sub-divided. For example on the first day a review could be made of some of the papers giving not fully detailed results but the approach and main features (conclusions, etc.) and the questions addressed to the author could ask, if necessary for a more expanded presentation on the following day - in order to avoid losing much time with papers out of line with the topic of the meeting. Each speaker could be told precisely exactly what is expected of him before the meeting. We think that this constructive criticism should help with future events.

LDM: The "criticism" was well appreciated.

Perhaps I should reply to your request for information before we proceed. Firstly I should explain how research contracts are handled. The MEDPOL programme has a series of research activities (A-L) covering all of the relevant subject matters. Different UN Agencies participating in the Mediterranean Action Plan (FAO, WHO, IAEA, IOC, WMO) have responsibility for handling some of these research activity groups (for example, methodological development is the responsibility of IAEA). When research project proposals are received at MEDU from the national MEDPOL coordinators, they are assigned to one or more agencies for review. This has been the practice in the past. Presently some of the agencies, which incidentally cooperate very closely together, consider that research would be more productive if funding is concentrated on certain priority themes and not distributed in a disperse manner. This is one of the reasons that meetings, such as the present one, have been organized in the past year. This is in order to evaluate what general and specific themes of research need to be conducted in the Mediterranean area and to try to concentrate the limited financial support on subjects which will collectively be most beneficial to the future of the Mediterranean environment. The present subject matter was considered to be an important multidisciplinary research topic and one worthy of considerable collective effort. We hoped (and have succeeded) to obtain feedback on the present level of this work and guidelines now should progress in the future. This is obviously not the only area of research which is being supported but we feel that in medium and long-term, as a multidisciplinary area of research the work should have a large impact on our knowledge of the Mediterranean and contribute towards understanding the environment.

FN: When you have a laboratory interested in research do they tell you their interest or do you suggest to them what lines they should be working along?

LDM: This is now changing. In the past people made requests according to their own "favorite" research topic. What we are now trying to do is to send out some general guidelines. In other words we tell the Scientific community that the Mediterranean Action Plan is particularly interested in a given line of research and if you submit research projects addressing these themes they will have first priority over those which address other matters. In the case of the research on the transport of potential pollutants by sedimentation, this will be one of the positive outcomes of the present meeting.

Also when a research project comes to us, we don't just take a simple decision to accept it or not. There may be quite a lot of scientific dialogue which can of course take some time ... until we think the project can work successfully and fits in to the general guidelines provided ... then we recommend the project for financial support. With these workshops we are trying to provide the feedback that a group of specialists who have successfully carried on research projects have got together and defined this priority and we agree with them and we recommend to the contracting parties that future work be carried on along these lines.

The next group to report will be the "inorganic" group, the conclusions of which will be reported by Dr. Krom.

M.K.: Before I start, I would like to make a comment on something you just said: Defining priorities should come as a result of feedback rather than somebody else telling us what to do. The individual problem often sets the priority and strong feedback is needed to communicate it to all people concerned.

The first formal comments we made were about the important conclusions of the workshop and they are not very different from the first group. We feel that the important thing was getting to know one another and to see what other people are doing and the general discussions that we had both within the meeting and in parallel. Secondly, we got more information on where to go next from the discussions, from talking to people we have ideas on where the best work is being conducted. The organization mechanics of the meeting was very good - and the meeting was isolated from all other distractions.

The idea of cooperation between groups was a further important conclusion. It seems clear that it would be very good to use individual labs and expertise in cooperation with each other in order to avoid duplication of effort and hopefully even sharing equipment, data and personnel. It's a much more efficient way of employing funds instead of having to build up expertise in one's own lab on each individual determination. How this can be achieved is a more complex matter.

In what direction is more research needed? I have to say that the first thing we asked Laurence Mee about was exactly whether he meant "research or monitoring" and he defined for us something which was not clear to me beforehand - that there is a programme and budget for "monitoring" for MEDPOL and that this is not what we are addressing. We are involved here in "applied research" in the true sense of the term. The two are separate. In terms of "applied research" we all agreed that the first priority is to have reliable techniques so that we can believe our own numbers, everyone else's number and compare them. That in itself is not a trivial matter. Methods have changed with this and data may be involved not just due to contamination - some methods even have to be withdrawn.

One of the members of our group pointed out that it's very useful to learn from other peoples mistakes. In particular we discussed that the dynamics of a process is very important, the frequency of sampling. You were talking about the spatial variation of processes but, of course, there are also time variations and there are a lot of different time variations that super-impose upon one another. These are relatively easy to deal with - without necessarily requiring any expensive equipment.

We should point out the need for an adequate inventory of inputs - we have been discussing the "transport of pollutants" but very few people have considered the importance of assessing the input rate of pollutants into a given area. Atmospheric inputs, non-point source inputs and even point source inputs are something that we need to assess the inventory of. Very little of this data is being presented.

In terms of looking at suspended solids in an environmental setting - and there were several workers that discussed this matter; we must have physical, dynamic and hydrological background information together with data on particulate matter in order to interpret the particle distribution.

There was a suggestion that one of the frameworks for looking at the whole ecosystem in the "environmental capacity" approach which defines fluxes, processes and effects. It is worthwhile taking into careful consideration the GESAMP report on this concept.

A number of us within the group were also recommending that we should encourage some pure research on some of the detailed processes involved in contaminant/particle interaction. Aspects such as flocculation of metals, metal speciation, surface processes. Some other members of the group suggested that this work shouldn't be conducted as part of the MEDPOL programme and that this was too complex or detailed a matter for what we are hoping to usefully achieve.

The final point is that the whole idea of multidisciplinary research and getting different types of expertise together is very important and we commented that perhaps there were too few biologists present but that the discussions were beneficial.

LDM: One thing that I would like to mention at this stage are the discussions between Velimir Pravdic and myself (as a "mini fourth working group") about the aspect of "quality assurance" in our work and the comparability of one study with another which is a vital and crucial issue which we should always consider. To be critical, I noticed that of all the presentations, only one person gave specific mention to the use of standard reference materials for checking methodology employed. This is the best way of demonstrating the comparability of data and should be encouraged in future work - even some scientific journals in the marine pollution field are not insisting upon this information. We saw an example today in the sequential extraction technique performed by one researcher. Now, we don't have standard reference materials (SRMs) for the sequential extraction of trace metals but it was very pleasing to see that the researcher took one of our SRMs and did the sequential extraction on it and here are the data. That's a nice way of inviting other scientists who all do sequential extraction to try the same and see how comparable different techniques are (using the same material) - that is an excellent way forward and is something we should be considering in the future.

Internal standards (which were mentioned by our colleague Guerzoni), particularly in the case of trace metals, represent another useful quality control. The idea is to take a constituent which is unlikely to be contaminated in the environment, and compare other elements with it (large variations in ratios may represent contamination). Aluminium is an example of this (it is often used for normalising data to clay fractions of sediment); iron is one which has also been presented at this meeting. Even scandium has been used in some cases but this is more complicated to measure.

If investigators can attempt to find an internal reference in their data, this, in many cases will help them normalize data (for such effects as variable grain size or mineralogy) and give access to more reliable "baseline levels" for environmental applications. These are concepts worth exploring and represent another approach to "quality assurance" in its widest sense.

The next group was that of the organic chemists chaired by Joan Albaiges.

J.A.: I will start with general comments on the workshop. We believe that the workshop has been very useful to promote interaction among groups. Future events could be improved by shorter presentations, having daily discussions (at the end of each session) to identify common topics of interest and enabling people to develop some common ideas for future progress. Of course, workshops are not the only means of enabling scientists to interact. It would be useful, for instance, if the agencies could distribute a newsletter showing all holders of research contracts what is going on in each area and to circulate information about the contracts awarded. This would also help to identify topics of future interests to the programme.

Now, going to the specific topic of organic chemistry, we have identified three main directions for future research activities:

(1) We believe that we should accommodate our research to what is really "pollution". This is not just a static problem but a dynamic one and we must realize that work done at present on organic pollutants has been mainly based only on chlorinated compounds and petroleum hydrocarbons (to a lesser extent) but most of the countries surrounding the Mediterranean are in the process of industrialization and many other compounds are discharged into its environment. Some of these may not have been present ten years ago. Indeed, some of the pollutants that have been found in the North Sea or the Rhine can now, or in the near future, be a problem in the Mediterranean, so we need much more information about them. I think we need to encourage research on this problem, using a broad spectrum of analyses (incorporating information on levels and effects). The organometallic compounds represent another area which requires considerable attention in this respect. There should also be a closer link between "monitoring" and "research" activities on these "new" pollutants.

(2) There is very little known about fluxes, balances and transport processes of organic contaminants and transformations (a particularly pertinent aspect in this field). Insufficient is known about accumulation and also transformation at the interfaces (including the freshwater/seawater boundary).

In this context, I think there are two main lines of activity in this topic, to implement the development of both methodologies and concepts. There is a need for new strategies for flux studies - often to transfer existing methodologies to the Mediterranean area (for sampling interfaces for example - or the use of historical records in sediments - or better instrumental and analytical methodologies). Also in the realm of concepts, there are a large number of conceptual developments in the area of organics, for instance developing the "marker" concept - biomarkers, isotopic markers, etc.

(3) Bearing in mind the difficulty in doing research in the region in the field of the organics (because, in itself, the methodology is rather expensive), there should be some increased effort in promoting interaction between groups and funding could be made more productive by stimulating (as does the EEC) programmes which have been submitted by multinational groups using a multidisciplinary approach. This may be difficult to organize but would make optimum use of scattered good facilities (it is difficult to obtain all the facilities in any one country). By joining the efforts of research groups, many specific important topics could be covered and investigated.

LDM: Thank you for your excellent contribution. We have not heard the overall view of each of three groups formed ad-hoc and it is remarkable to observe how similar some of the conclusions are and how well they compliment each other.

One important point which was expressed by all three groups was the need to interact and how that research could become somewhat more productive if groups are encouraged to work together and funding is directed towards helping scientists toward this goal by overcoming some technical problems. For example, the problem of not having the right basic equipment to do a specific analysis but being aware that a colleague in another country has the right equipment (which is underused) and would be willing to give time to use it if seed funds were available to permit travel with his samples and provide reagents, etc. Identifying individual requirements is very difficult - but with patience it can be done and there are some good examples of this in the region. Joint proposals from scientists in two or more countries would be unusual but should be well received.

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