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ACTION INTERUNIVERSITAIRE

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INTERUNIVERSITAIRE ACTIE

OCEANOLOGIE

Rapport final

Volume 2

Eindverslag

Boekdeel 2

DISTRIBUTION, TRANSPORT AND FATE OF HEAVY METALS IN THE BELGIAN COASTAL MARINE ENVIRONMENT

edited by

A. DISTECHE and I. ELSKENS

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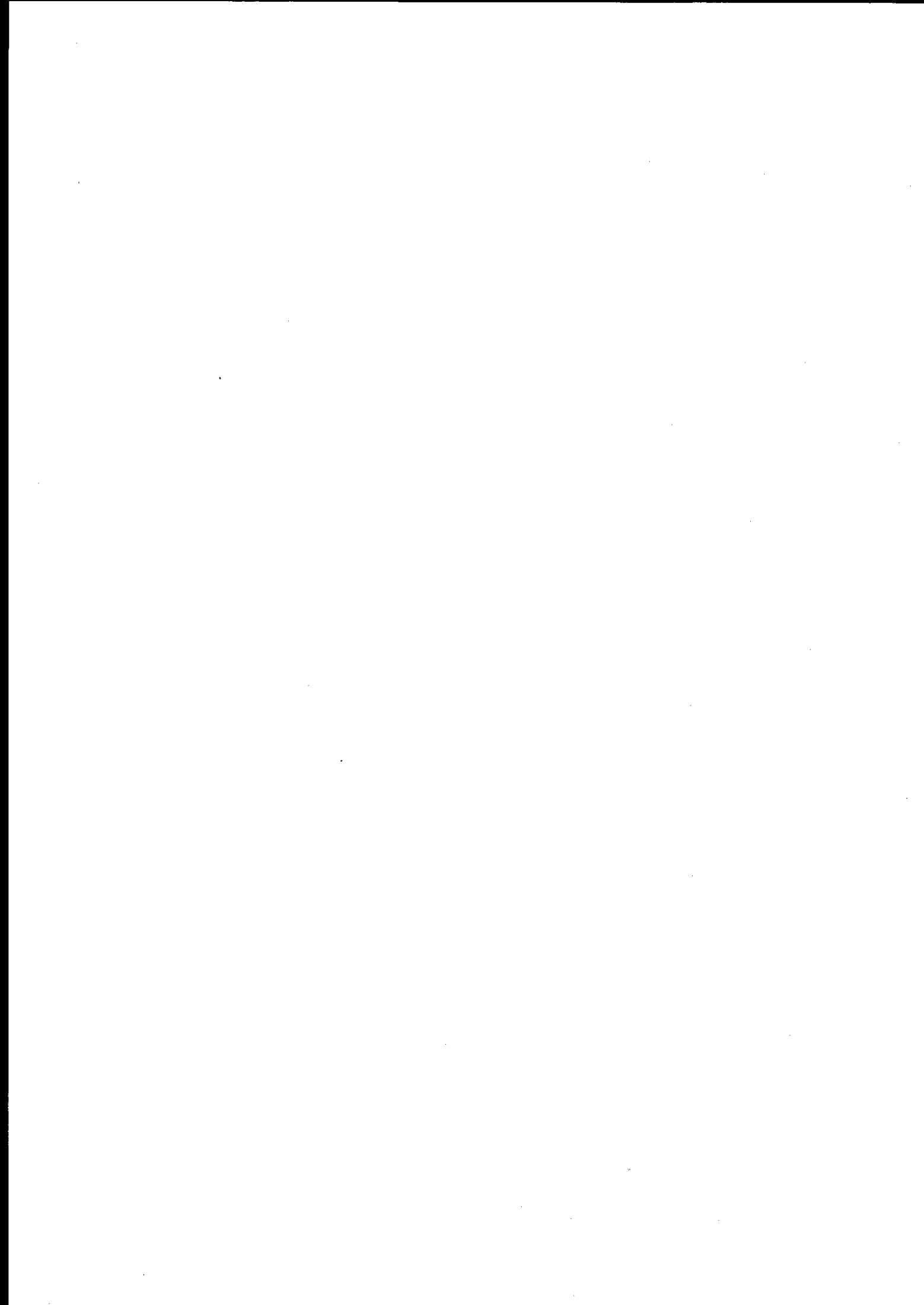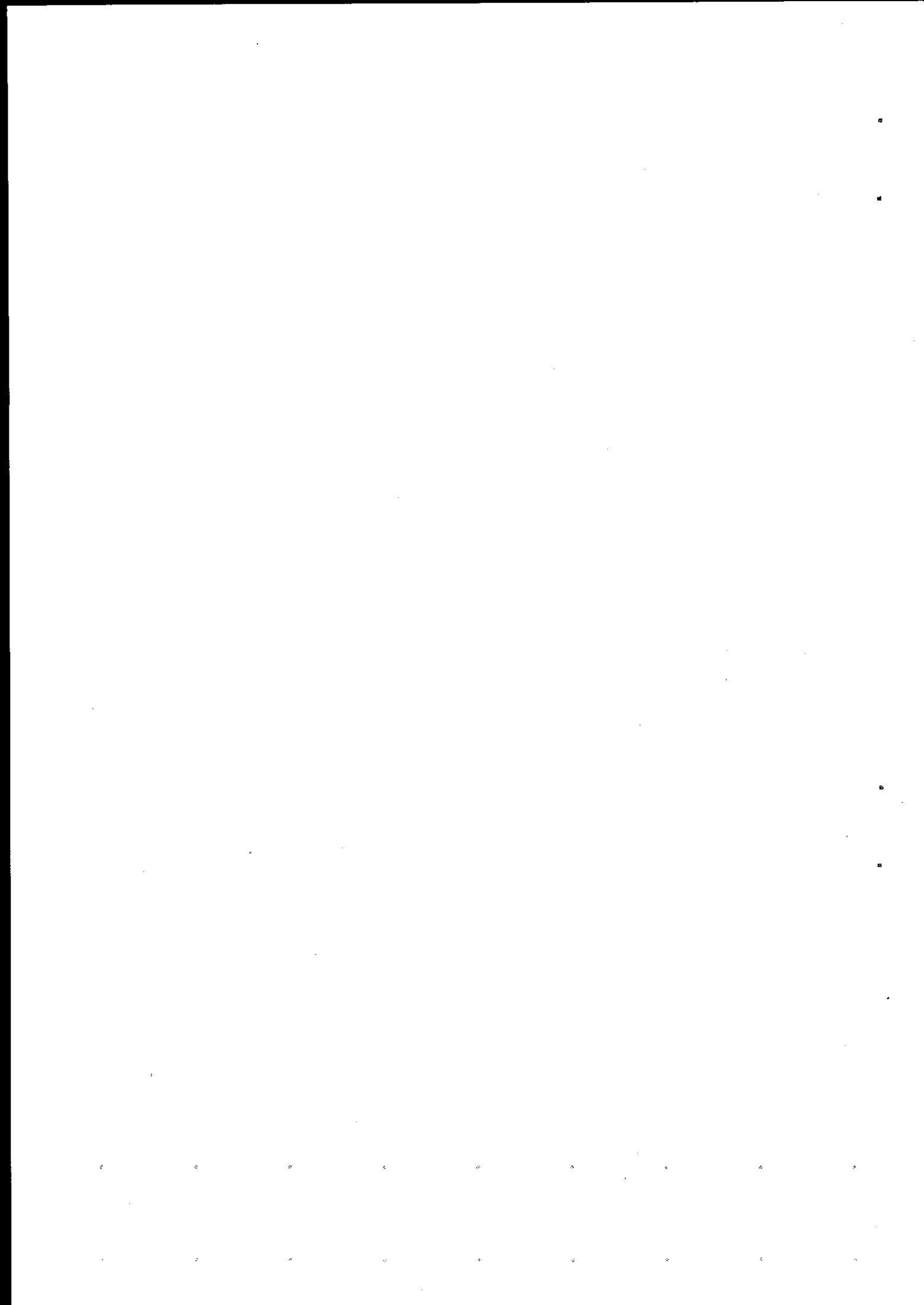## INTERUNIVERSITAIRE ACTIE

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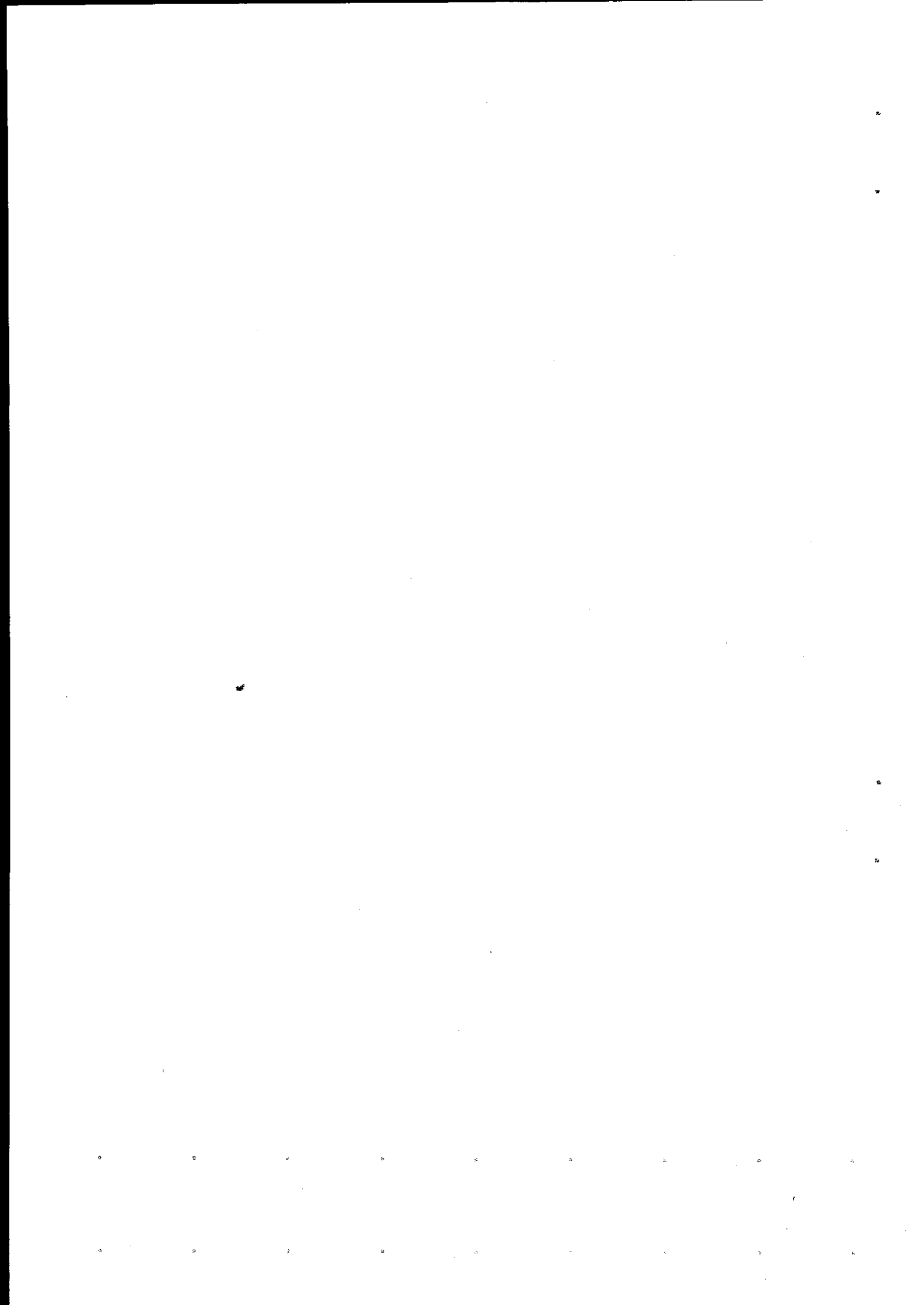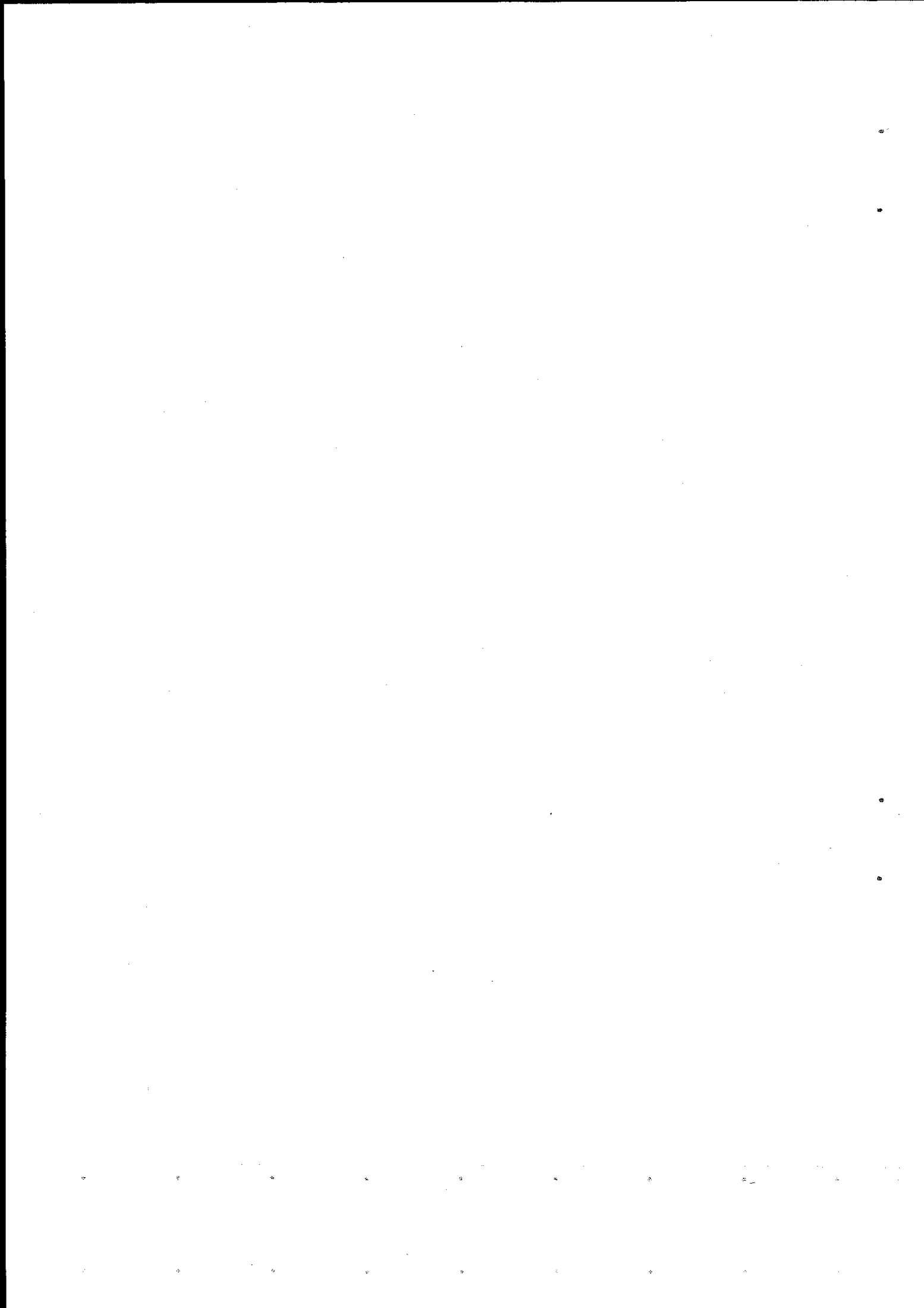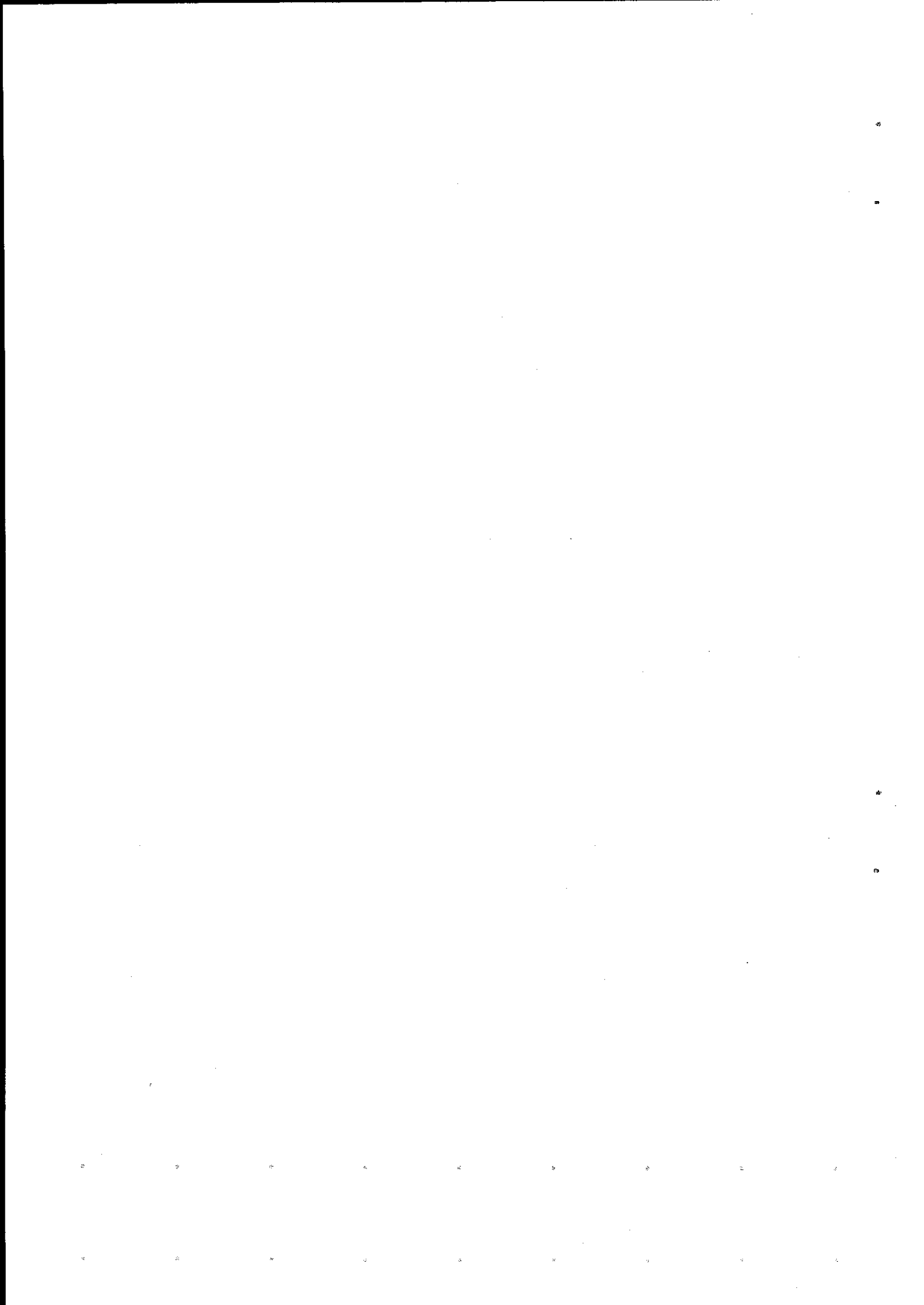
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DISTRIBUTION, TRANSPORT AND FATE

of Bi, Cd, Cu, Hg, Pb, Sb and Zn

IN THE BELGIAN COASTAL MARINE ENVIRONMENT

SUMMARY

INTRODUCTION

General aspects of the distribution, transport and fate
of heavy metals in the Belgian coastal marine environment

The transport of heavy metals by the surrounding fluid as well as their transfer through the different compartments of the marine environment are very important from a toxicological, ecological, oceanographical (e.g. watermass tracing) and management point of view.

In this study, the general aims to achieve or to consider are the characteristics of heavy metals in the marine environment (soluble, colloïdal and particulate species) and, further, any factor capable to change their speciation (pH, redox condition, temperature, ...) with special attention at the level of the lithosphere, atmosphere, biosphere, aqueous solutions interfaces.

The next step is to consider the essential physical parameters involved in the dispersion of heavy metals (advection, eddy diffusion) which can be obtained from a good hydrodynamical model.

It is well known that in a marine region the behavior of any substance can formally be described by equation (1) (given here in its most simplified form) which opens the way to further to modelling :

$$(1) \qquad \frac{\partial C_i}{\partial t} + \nabla.(\mathbf{V}\,C_i) - \nabla.(D\;\nabla C_i) = S_i + I_i$$

where $\frac{\partial C_i}{\partial t}$ is the local change of the concentration C_i of the constituent i with time, $\mathbf{V}$ the velocity of the water mass, D the eddy diffusion coefficient. The terms of the left side of the

equation represent the transport (advection, eddy diffusion) of the element. The terms on the right side of the equation express the output-input S_i and the chemical transformations I_i.

For the description of the spatio-temporal behavior of a conservative element such as sodium, the halogens, the equation (1) is simplified through the disappearance of the I_i term. However, for non-conservative elements such as trace metals, we must take this term into account. In that case, the numerous interactions between metals and any other constituent, necessitate the simultaneous resolution of a set of differential equations.

It is useful at first to make a careful choice of a reduced system. The choice of its constituents is critical since the model has to be sufficiently realistic to start with and be of use for more sophisticated ones.

The understanding of the transport mode and the compartmental distribution of metallic elements in the aquatic environment implies that the rate of interactions between constituents must be known in order to quantify the term I_i (equation 1).

Finally, in order to be able to predict the evolution of the heavy metals in the selected marine systems, we have tried to assess the term S_i (equation 1) at the boundaries with adjacent systems.

Part 1

SAMPLING TECHNIQUES AND ANALYTICAL METHODS

G. GILLAIN[1], G. DECADT[2], F. DEHAIRS[2], H. DEDEURWAERDER[2], L. GOEYENS[2], W. BAEYENS[2]

1.— Introduction.

Trace metals in the marine environment have become a signifi-
cant topic of concern to scientists because of the potential dan-
ger for man resulting from direct or indirect pathways of accumu-
lation of metals in marine food.

Chemical analysis is the basis for studies of the diffusion,
dilution, transport and sedimentation mechanisms of trace elements
in the hydrosphere. But in order to better understand the exact
forms, mechanisms of transport and residence times of the ultra
micro amounts of metals in the marine environment, one is forced
to develop improved technologies for the measurement of the con-
centrations of trace metals in environmental samples of sediment,
plant and animal material, sea water (dissolved and particulate
species), aerosols and volatile elements (especially Hg).

Continuing efforts have been made to increase the sensibility
and the selectivity of methods, the precision and the accuracy of
results and to simplify the procedures in order to avoid contami-
nation especially during sampling and filtration.

In order to check the reliability of the adopted analytical
methods, several intercalibration exercices at the international
level have been performed. We have applied these validated ana-
lytical methods for routine determination of traces of Bi, Cd, Cu,
Hg, Pb, Sb and Zn in the various environmental samples.

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2.— Sampling.

2.1.— *Generalities.*

In principle all stages in the preparation of a sample for the trace metal analysis should be submitted to a severe assessment of occasional or permanent sources of error, whatever the type of sample.

Sampling is one of the most important steps in marine heavy metals studies. If the sampling procedure is biased, the results of analysis will have little or no meaning and the interpretation will suffer as much. This is especially true in the case of trace heavy metals where the concentrations can go down to the sub-ppb levels.

One of the most serious problems in sampling is the choice of the appropriate type of sampler. It is essential that sampling should be performed with an awareness of all possible sources of contamination and preferably under the direction of an analytical chemist.

2.2.— *Sea water, samples (bulk water column) for the determination of dissolved and particulate heavy metals.*

Present knowledge in the distribution of metallic elements in water suggests that trace metals may exist in any or all of the following physicochemical forms :

true solution (< 0.001 µm)

    as inorganic complexes such as chloro-complexes, hydroxides, carbonates ; as complexes with dissolved organic matter such as amino acids, humic material ; in organometallic compounds.

colloïdal (0.001 - 0.10 µm)

    adsorbed on colloïdal matter and/or occluded within colloïdal species.

particulate (0.1 - 50 µm)

    adsorbed on fine mineral material or organic detritus or bound within plankton material or co-precipitated with the hydrated oxides of iron and manganese.

Metal analyses are generally reported both on suspended particulate matter and on the "soluble" metal fraction of sea water samples.

In unfiltered samples, trace metals ions can be liberated rapidly from, or taken up by, particulate matter. High bacterial concentrations associated with sedimentary material will also lead to changes in the distribution of chemical forms of metallic elements in solution. It is advisable to separate the suspended matter as soon as possible after sampling.

The heavy metals content of suspended matter can be determined in a sample collected after filtration.

According to a widely accepted convention in marine chemistry, filtration is defined as separation by a 0.45 μm filter into a filter residue and a filtrate, which contains of course still the colloïds and the fraction of very small particles of mineralogical and biological origin that have passed the pores of the 0.45 μm filter if not clogged.

The two problems confronting the analyst are the representativity of the samples and their possible contamination. Besides the sampler, research ships reveal to be a main cause of trouble if not some other ships leaving behind themself a cloud of Zn, Cu, Pb, ..., from propellers, zinc anodes, paint, engine exhausts among other sources. Airborne material, careless handling by unskilled experimenters, the depth at which the sample is taken versus the ship's draught, the location on board of sampling system, atmospheric conditions, inhomogeneity of the water, etc. are all possible sources of difficulties.

To make sampling more reliable we have designed a sampler adequate to work at moderate depth from a large or small research vessel, even in rough conditions (Gillain et al, 1980). The principle of this system is to continuously collect small samples of sea water from a very large volume screened from atmospheric pollution. A peristaltic pump draws continuously 6 $\ell.min^{-1}$ at 5 meters depth through a PVC tube previously soaked for several days in 6N HCl, rinsed with ultra-pure water.

When sampling, it is necessary to avoid ship's discharges, antifouling paints, etc., in close proximity to the sampling point. The ship is best, left adrift and the tube is on the lee side so that it meets water masses not polluted by the vessel. A second peristaltic pump draws 0.5 $\ell.min^{-1}$ from the main flow which is returned to the sea. The unfiltered sea water is kept in a 5 ℓ polyethylene bottle and continuously stirred magnetically for the next operation : filtration.

The problem of representativity becomes more acute in the suspended matter matrix. This is especially true with the conventional separating system where the amount of suspended matter collected on the filter before clogging is generally very small. In this case, the heavy metal content of particulate matter collected on the filter will be lower than the filter blank. Consequently, the error introduced by filtration is then significantly larger than the bias arising from the dissolution of adsorbed material and from the analysis itself.

On the other hand, filtration is a slow process and the characteristics of the filter will change after the deposition of the first layer of particulate matter. To overcome all these problems and to minimize all possible external interference (dust-free conditions), we have employed a shipboard stirred pressure system in a purified nitrogen atmosphere.

The type of filtration apparatus used is made from a pyrex glass tube 120 mm long and 47 mm diameter fitted in between two PVC lids with silicone seals. A magnetic rod is suspended a few millimeters above the filter to accelerate filtration, retard clogging by vigorous stirring and collect the greatest possible amount of material.

The filtration apparatus is connected directly to the water sampler. The water drained from the sampler is replaced by pure nitrogen and filtered sea water is continuously collected in a polyethylene flask which is used to store the sea water sample.

There is practically no risk of contamination of the sample during transfer from sampler to storage bottle.

More detailed description and cleaning procedure can be found in a recent paper (Gillain et al, 1980). They are summarized below.

In samples containing zoo- and phytoplankton, we use a low constant pressure (0.3 kg/cm^2) in order to avoid desintegration of delicate organisms. This may lead to increase heavy metals concentrations in the filtrate and change heavy metal speciation.

Objections which can be raised against this sampling and filtration system are the adsorption and/or the contamination of samples by the PVC suction tube, filter unit, membrane filter, etc.

The contamination is prevented by cleaning the filters with 100 mℓ of a 10^{-2} DTPA solution and washing them with highly purified water before filtering the sea water.

On the other hand, the sampling and filtration kit is treated during one week with 6N HCl and large amounts of ultra-pure water is used for rinsing.

In any case there is little time for possible interaction between wall and water, since filtration is started immediately after collection and is usually completed within one hour.

The first 200 mℓ are needed to condition the membrane filter ; they are rejected.

Laboratory experiments performed on Reagent Grade NaCl 0.5 M solution (loss test) and on suprapure NaCl 0.5 M solution (contamination test) indicate that it is possible, in our conditions, to apply the described sampling and filtration system for the determination of Bi, Cd, Cu, Sb and Zn dissolved in sea water, without significant changes of their initial concentrations.

The concentrations of the elements were :

(1) Reagent Grade Quality
    NaCl 0.5 M solution (spiked)
            Zn : 5 µg/ℓ ;
            Cd : 0.1 µg/ℓ ;
            Pb : 1 µg/ℓ ;
            Cu : 1 µg/ℓ ;
            Sb : 0.05 µg/ℓ ;
            Bi : 0.05 µg/ℓ .

(2) Suprapure Quality
    NaCl   0.5 M   solution
            Zn : < 0.1 µg/ℓ ;
            Cd* : 0.009 µg/ℓ ;
            Pb* : 0.012 µg/ℓ ;
            Cu* : 0.012 µg/ℓ ;
            Sb* : < 0.005 µg/ℓ ;
            Bi* : < 0.005 µg/ℓ .

This sampling and filtration system has been tested and shown to give far more better results in our survey areas Belgian coast than usual systems which get easily out of control.

Better results   (Zn : 0.70 - 5.00 µg/ℓ ; Cd : 0.020 - 0.180 µg/ℓ ; Pb : 0.20 - 2.00 µg/ℓ   and   Cu : 0.10 - 1.5 µg/ℓ)   mean that in some cases the trace metals concentrations are one order of magnitude lower than with the conventional sampling (Niskin bottle) and filtration methods (open air shipboard suction filtration).

The concentrations of the metals (Cd, Cu, Hg, Pb and Zn) in our sampling area are high compared with other oceanic zones (Bruland, 1980 ; Boyle et al, 1981). However, at the present time, our trace elements data are believed to represent as truthfully as possible the situation in the Belgian coastal area (Southern Bight).

The performance of our sampling and filtration system was tested on the Mediterranean sea in an area considered as uncontaminated (Corsica, Calvi). Our own study on trace metal in this region has revealed dissolved levels for Cd* in the range from 0.02 - 0.005 µg/ℓ,, for Pb* from 0.08 - 0.015 µg/ℓ , for Cu* from 0.10 - 0.04 µg/ℓ and for Zn from 0.18 - 0.05 µg/ℓ . All these data are in sharp contrast to those measured in Belgian coastal water and reinforce our confidence in the sampling and filtration system designed to minimize contaminations.

2.3.– Sea water microlayer samples for the determination of dissolved and particulate heavy metals.

The sea surface microlayer is often characterized by anormalously high concentrations of heavy metals (Wallace et al, 1975 ; Duce et al, 1972b ; Hoffman et al, 1974 ; Baier et al, 1974 ; Wade et al, 1975) and other trace substances thought to be associated with particulate matter and surface-active organic material.

As for the water column, metal analyses are generally reported both for particulate matter and for the "soluble" metal fraction.

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* Determined by ASV on ring-disk glassy carbon electrode.

The methods used to collect the surface microlayer are extremely varied (Garrett, 1965 ; Harvey, 1966 ; Harvey & Burzell, 1972). In our case, the sea surface microlayer samples were collected using the Garrett-screen technique (Garrett, 1965). The sampler consists of a nylon screen with openings of 400 by 400 µm and a fabric thickness of 440 µm stretched in a plexiglas frame. The principal difficulty with the microlayer sampling is the airborne contamination resulting from the research vessel (smoke stacks, corrosion products, dirt and dust particles,...).

The only possibility to avoid this problem is to reach, by a small rubber boat, an uncontaminated zone for sampling. This sampling site is chosen upstream, several hundred meter from the research vessel. Under such circumstances we can effectively work only in calm weather conditions.

To prevent also the contamination by the small boat itself, we move it up-wind and sample water in front of the boat continuously moving into uncontaminated water. The operator, wearing polyethylene gloves, touches the sea surface with the screen in horizontal position. Because of surface tension a film of water is captured between the meshes of the screen and we collect approximately 50 mℓ of surface water, representing a water film of 0.200 mm. Sea water is then transferred from the collecting screen to prewashed polyethylene bottles. At each microlayer sampling site the water column is sampled by immersion of polyethylene bottles at -30 cm.

In the future, we intend to compare different sampling techniques with in view 1) efficiency (recovering any surface film and associated matter present), 2) representativity of microlayer (heterogeneous distribution of physical, chemical and biological constituents), 3) deficiency (time of sampling, deterioration and dilution of microlayer with bulk sea water).

After collection, the samples were transported aboard the ship. Particulate matter in the microlayer surface was then immediately isolated by the filtration processes using the same nitrogen pressurized system and precautions as described for the water column.

2.4.— *Plankton samples.*

The plankton was collected from the sea with a 100 µm mesh nylon net (Hecq, 1981). Contact with metal was avoided at all stages of the sampling ; the net employed and other parts of the sampling gear were constructed of plastic materials.

However, in our case, the magnitude and the extent of the sampling problems for heavy metals determination are not all resolved. These include 1) the difficulty to collect sufficient material for elemental analyses, 2) the difficulty to separate phytoplankton from zooplankton and the inherent difficulty to determine which group contains which element, 3) the contamination

due to ship paint and fall out of rust chips from almost all research vessels, 4) the contamination by mineral materials ; in shallow water, the resuspension of bottom sediments often contaminate the plankton samples, 5) the representativity of the sample, depending on the natural variability (varying with place, depth and time of sampling, species distribution).

In addition to the sampling problems the establishment of general elemental levels for phytoplankton and zooplankton is made difficult because of the complexity of the relationships between the metals and the organisms.

In order to collect and analyze plankton samples for a better estimate of their importance in the biogeochemical cycling of elements in the North Sea (Belgian coastal zone), it seems obvious that future work will be essentially directed to improve sampling techniques.

2.5.– *Air samples.*

The most practical way for a detailed study of atmospheric concentrations and possibly fluxes of pollutants at ocean level is to have a stationary sampling site in operation over a relatively extended period of time.

In our case, sampling of marine aerosols is performed aboard a light vessel anchored on the West-Hinder bank, at 20 miles from the Belgian coast.

The collection of atmospheric particles from the ship presents many problems : 1) contamination by the ship (chips of rust and paint, smoke), 2) contamination by the collecting equipment such as tube, pump, filter, etc., 3) difficulty of collecting a sufficient number of air samples to obtain any meaningful statistics at a given location.

The aerosol samples were collected as follows :

samples of total atmospheric particulate matter were collected by air filtration (200 to 300 m^3) on Whatman 41 filters. Filters were mounted in all plastic filter holders and the sampling PVC head was separated from the Hi-vol sampler (GMW - 2000H) by 15m of supple PVC tubing to avoid contamination by the pump itself. Volumes filtered were determined by use of a calibrated gas volume counter.

Size fractionated aerosol samples were collected by 6 stages Hi-vol Sierra model 235 Cascade Impactors operating with a flow rate of about 55 m^3.hour^{-1}. The particles were deposited on 5 consecutive Whatman 41 filter papers and finally filtered on a Whatman 41 back-up filter.

According to the manufacturer, the equivalent aerodynamic diameter (EAD) cut-offs at 50% collection efficiency for particles with a density of 1g cm^{-3} at the flow rate used,are as follows :

stage 1 : > 7,2 pm ; stage 2 : 7,2 - 3,0 pm ; stage 3 : 3,0 - 1,5 pm ; stage 4 : 1,5 - 0,95 pm ; stage 5 : 0,95 - 0,49 pm and back-up filters : < 0,49 pm.

A specific sampling device using Lo-Vol pumps is used for Hg which is present mainly in the gaseous phase (Fitzgerald et al, 1979). Gaseous Hg is collected by amalgamation on a gold column and up to 1 m³ of air is sampled.

Particulate Hg is collected on Whatman GF/C glass fiber filters by sampling up to 15 m³ of air.

All samplings were performed under controlled conditions of wind-direction and wind-velocity. Filter holders were positioned 5m ahead from the flying bridge at 8m above sea level and also on the bow of the ship.

2.6.— *Sediment samples.*

Sampling meets great problems at the level of contamination and maintaining the "in situ" conditions.

To avoid contamination of samples from the main frame of the apparatus we use a PVC core-liner tube (6.35 cm diam.).

Penetration of the core-line tube was restricted to the first 40 cm. Great care was taken in handling cores : all cores were sealed in situ by two PVC-caps to minimize disturbance and compaction and brought aboard ship in a vertical position.

Two cores were collected at each site.

3.— Sample storage.

3.1.— *Generalities.*

Problems of sample interaction with storage container material will be most evident and most severe because of the longer contact time (day or months) compared to the conditions discussed above concerning the sampling itself which implies times only of the order of minutes or hours.

At this step, we must consider two aspects : 1) container heavy metal content and sample contamination by different kinds of container materials, 2) losses by surface adsorption and bacterial activities.

The contamination risks have induced several authors to analyse a large number of container material for heavy metal content

(Robertson, 1968 ; Montiel et al, 1981 ; Robertson, 1972). On the other hand, the adsorption effects have also received considerable attention (Jenne, 1975 ; Batley et al, 1977 ; Eichholz et al, 1965 ; Issaq et al, 1974). The results depend on a variety of factors such as the characteristics of the solution (pH, salinity, complexing agents, dissolved gases,...), presence of suspended matter, microorganisms ; wall geometry, temperature, contact time, etc).

In addition, most of the results from storage experiments are often based on the addition of ionic metal or radiotracers detectable as spikes which will drastically disturb the solution equilibrium. This possibly explains the wide variation in the results and the data from stored material should therefore be interpreted with caution.

The most reliable experiments are those which attempt to directly measure metal concentrations as a function of time under different conditions (Mart, 1979).

Results generally support the conclusion that PTFE and high density polyethylene show little tendency to adsorb and release the above metals and consequently, these are preferred materials for storage containers.

These problems are of particular importance for mercury (Jenne et al, 1975). In addition to adsorptive losses of ionic mercury both on container walls and on colloïdal and particulate matter, there are also 1) the large adsorption capacity of particulate matter for several organic mercury components, 2) losses to the atmosphere, 3) diffusion through the container surface (Baeyens et al, 1979), 4) the increase of dissolved mercury content stored in polyethylene bottles in areas of high atmospheric mercury content (Robertson, 1972).

3.2.— Cleaning of storage bottles.

In our experiments, 1000 mℓ high density polyethylene bottles have been used. New bottles were used exclusively. Polyethylene bottles are rinsed with pure water (deionized) to remove particles. They are then filled with a 6N HCl solution, analytical reagent grade, for 8 days. The acid is changed and the containers are rinsed several times with pure water. The acid procedure is repeated once again for another 8 days, but at this time, the acid is suprapure Merck (1N HCl). Some days before use the bottles are rinsed with ultra-pure water (Millipore-Milli-Q) and conditioned with sea water which has a very low level of heavy metals.

As we have discussed (Baeyens et al, 1979), the container cleaning procedure for mercury analysis is totally different. Some specific tests have shown that a pretreatment of the polyethylene container with a solution of $KMnO_4$ (2%) in H_2SO_4 (50%)

during 24 hours make a storage bottle completely mercury-free.
Pyrex bottles (BOD type) soaked in boiling 3N HNO₃ and rinsed se-
veral times with Milli-Q water, can also be used.

It needs to be quoted that the efficiency of mostly used sto-
rage procedures for Hg is not subject to an unanimous quality
judgement (Feldman, 1974 ; Fitzgerald et al, 1975).

3.3.— *Storage of samples.*

3.3.1.— *Sea water (water column).*

Our analyses (Zn, Cd, Pb, Cu) of natural filtered sea water
samples stored over a long time period (6 months) in cleaned po-
lyethylene bottles at pH 1 or unacidified at - 20°C in a deep-
freezer showed no significant changes (total metal concentrations)
within experimental error. However, at pH 8 and at room tempera-
ture, significant changes, depending on the element, occur after
a few days. It is difficult to draw a conclusion about Sb and Bi
because their concentrations in natural sea water often approach
the determination limits.

Similar results depending on the storage pH and temperature
conditions were also observed by other investigators (Mart,
1979 ; Batley et al, 1976).

When only a total dissolved metal analysis is required, it
is usual to prevent changes by acidification of the sample after
filtration to pH 1 with either HCl or HNO₃. Since we are inte-
rested in speciation studies, the samples were deep-frozen (-20°C),
immediately after collection and filtration, without any additi-
ve.

With freezing, however, it should be noted that changes in
metal speciation do occur, although the total metal concentra-
tions remain unchanged (Florence, 1976).

Fabricant et al (1966), Batley (1976) and Fukaî (1976) recommend
refrigerator storage at 4°C, but this appears to be hazardous as
a general practice for long time storage (Mart, 1979).

For determination of total mercury, we opted for a sample
storage at -20°C after acidification to pH 1 (Decadt, 1980).
This procedure is not recommended for speciation of mercury forms
(e.g. inorganic mercury, methylmercury and alkylmercury compounds).
In that case, mercury analysis aboard the ship immediately after
sampling and filtration seems necessary.

From what precedes, it looks advisable to choose storage me-
thods selected for a particular research programme and we intend,
in the future, to consider this problem in connection with specia-
tion studies.

3.3.2.– *Suspende matter (water column).*

Suspended matter samples collected on precleaned Millipore membranes for either Hg or other metals such as Bi, Cd, Cu, Pb, Sb and Zn are stored in cleaned Petri dishes and maintained at -20°C prior to analysis.

3.3.3.– *Microlayer samples.*

Immediately after collection and filtration the solution and particulate samples are stored in the same conditions as described above for water column samples.

3.3.4.– *Plankton samples.*

Short term storage is made under conventional refrigeration at 4°C, but freezing at -20°C is the best method for long term sample conservation.

3.3.5.– *Sediment samples.*

The cores are best immediately deep-frozen to minimize alterations during storage and transport.

3.3.6.– *Aerosol samples.*

The aerosol samples are kept in acid cleaned plastic containers at low temperature (-30°C).

4.– Pretreatments and analytical methods.

4.1.– *Prevention of contamination in the laboratory.*

In addition to the sampling operation and sample containers, local laboratory dust, reagents and common laboratory equipment (glassware, cells, pipette, etc) all represent potential sources of contamination.

All materials whenever possible are precleaned by soaking in 6N HCl for several days before use. Only ultra-high purity reagents are used (suprapure Merck H_2O_2, HF, HCl, HNO_3, NaCl, ...). High purity water is prepared by using the Milli-Q system which consists of a prefilter and a charcoal absorption column followed by two mixed-bed ion exchange columns. After deionisation, water

passes through a microfilter (0.22 μm) to remove particulates. A typical analysis of this water yields the following results :

Zn < 0.05 μg/ℓ ;
Cd : 0.006 μg/ℓ ;
Pb : 0.008 μg/ℓ ;
Cu : 0.005 μg/ℓ .

4.2.— Analytical methods used for accurate determination of trace heavy metals in environmental samples.

Atomic absorption spectroscopy (AAS) and anodic stripping voltammetry (ASV) are two of the most widely used method for trace metal analysis. The selection of the most appropriate technique is not always a simple matter. Such factors as specific element, the chemical forms of the metal to be determined (e.g., ionic as opposed to total), sensitivity, accuracy, ease and rapidity of analysis, potential run (ASV) for multi-element analysis, availability of instrumentation, cost, support the decision.

4.2.1.— Atomic absorption spectrophotometry (AAS).

a) The determination of Cd , Cu and Pb.

The principle of AAS is easily described. The wavelength of light from a cathode lamp is characteristic of the element being analyzed and the energy absorbed in the flame is related to the concentration of the element in the sample.

This technique can be used for the determination of most of the metallic elements.

When using the flame method, the detection limits are often unsuitable to make directly quantitative determinations of low level heavy metals in some environmental samples.

Recent developments of flameless atomizers such as the graphite furnace (GFAAS) have increased sensitivity by several orders of magnitude and therefore can 1) eliminate the need for prior concentration, 2) reduce possible contamination and 3) blank lower values.

However, matrix effects of concentrated salt solutions such as sea water are especially serious and preliminary treatments are unavoidable in most cases.

In addition, in sea water with very low trace element concentrations, separation techniques may serve to concentrate the element to be analysed. However, the great number of operations and reactives used in manipulations such as complexation with APDC or DDDC, extraction with MIBK or chloroform, separation by centrifugation, wet digestion, evaporation to dryness, redissolution, etc. are not desirable steps for they greatly increase the possibility of loss, contamination and extend the analysis time.

For these reasons conventional methods were reviewed. We used the complexation-extraction method of Bruland et al (1979). Its main advantages, stated by Bruland et al are : 1) the combined use of the dithiocarbamates APDC and DDDC as chelating reagents for metals which was shown to work well over a wide pH range and allowed a good discrimination against the major cations in sea water, 2) the chelated metals are extracted with chloroform, since only small volumes of this solvent are required and since re-extraction of the metals in HNO_3 is possible, 3) the buffering of the solution is done with ammonium acetate, since it has a good buffering capacity at the optimum pH for extraction (pH 4) and since it was shown that for Cu and Zn no interference of acetate ion-metal complexes occurred.

Furthermore, contamination problems are minimized by a more rigorous pre-cleaning of the commercial reagents, utilization of pre-cleaned PTFE vessels and handling the samples in a controlled dust-free atmosphere.

In our experiments a Varian AA 275 spectrometer equipped with a graphite furnace was used for the determination of Cd and Cu in sea water after preconcentration and following the method of Bruland et al (1979). The overall recovery factor using the prescribed method for sea water spiked with Cd and Cu was 110% and 105% respectively.

The average blanks were 1,8 µg/ℓ for Cd and 4,8 µg/ℓ for Cu. After a 50:1 preconcentration by the described extraction methodology, the detection limits, based on 3 times the standard deviation of the blanks, were 0,6 µg/ℓ for Cd and 0,73 µg/ℓ for Cu.

The reproducibility of the solvent extraction method was observed to be 6% for Cd and 10% for Cu, as based on five replicate extractions performed on the same sample.

Determination of Cd, Pb and Cu in particulate matter (air, sea water, biota and sediments) are carried out with a JARRELL ASH 810 spectrometer using an air-acetylene flame after a wet digestion of the sample.

In general, atomic absorption techniques require a solution for analysis, but there have been some attempts to analyse solid samples directly by flameless atomic absorption. For example, Lord et al (1975) and Machiroux et al (1976) have determined a variety of metals in freeze-dried fresh water mollusks and in dried plankton samples. Two problems occur particularly with solid samples. One is the difficulty of obtaining a representative sample, since only milligram amounts are analysed. The other problem concerns the availability of an adequate calibration procedure which takes into account the solid matrix composition.

Of considerable current interest is the form in which a metal exists in solution. In the case of atomic absorption it is assumed that the high temperatures involved eliminate the direct possibility of discriminating between species ; only total metal is determined. However, speciation is eventually possible in some cases by coupling the atomic absorption spectrometer with a gas chromatograph which serves to separate various volatile metal species.

b) The determination of mercury

The mercury ion is usually determined by flameless (cold vapour) atomic absorption spectrophotometry with or without a preconcentration process.

This technique is rapid and simple to use and has the advantage of very high sensitivity and in many cases complete freedom from interference due to other elements.

In a coastal marine environment, an important part of the mercury components is associated with the particulate matter.

For the total mercury (particulate and dissolved) in sea water, we use a method based on the complete conversion of all mercury components present to $Hg^{(II)}$ and subsequent reduction of this form to $Hg^{(0)}$ aeration of the solution and spectrophotometric determination with the MAS-50 (Baeyens et al, 1979). It is, therefore, important to choose an appropriate digestion method for the complete oxidation to $Hg^{(II)}$ such as $KMnO_4$ + acid or the H_2O_2 method (see below).

We compared both digestion methods, but no systematic difference could be shown. For the dissolved mercury concentration in sea water which is in most cases close to the detection limit, a preconcentration step is necessary. An adapted method such as a reduction-aeration Au-amalgamation procedure, or a preconcentration on an exchange column has been tested in order to obtain a better estimate of the concentration of dissolved mercury.

After modification of the single-beam standard apparatus type MAS-50 into a double-beam and the operating conditions being optimized, a detection limit of 5 ng Hg ℓ^{-1} is obtained.

The relative standard deviation obtained in replicate determinations of standard solutions is about 5% at mercury levels of 20 ng Hg ℓ^{-1}.

In order to evaluate our method, we participated in an intercalibration exercise of Hg in sea water, organized by Olaffson (1979).

From these results we deduce that 1) the precision of our method for the measurement of very low mercury levels (5 ng Hg ℓ^{-1}) is approximately 15%, 2) the recovery of the added quantity of Hg is 102% for 21 ng ℓ^{-1}.

The mercury content in solid matrixes such as particulate matter (air, sea water), biota and sediments were determined by the same method after digestion (see analysis procedure).

A certain number of supplementary studies such as speciation will be carried out in the future ; it has been found possible to distinguish more species of mercury compounds (inorganic mercury, arylmercury compounds, alkylmercury compounds) by changing the chemical reduction system (Goulden et al, 1980).

4.2.2.— *Anodic stripping voltammetry (ASV).*

The determination of Bi, Cu, Pb, Sb and Zn.

Numerous anodic stripping voltammetry procedures have been reported with direct current (DCASV) applied to a mercury film electrode (TFE) or a hanging mercury drop electrode (HMDE).

Essentially, ASV is a two-step technique, the first step of which involves the electrolytic deposition of a portion of the metal ions in solution into the HMDE or TFE, to preconcentrate the metals in the form of a dilute amalgam. In the second step, the metal in the amalgam is reoxidized to the corresponding ion by the application of a fast linear potential sweep. Current and potential measurements are made during the second step. The position and height of stripping peaks are characteristic of the type and concentration of the metal ion in solution.

In order to increase the signal to background ratio, various voltammetric techniques have been developed. The differential pulse anodic stripping voltammetry method (DPASV) has extended downwards the limits of detection compared to direct current anodic stripping voltammetry (DCASV) and thereby has made this technique very practical.

The voltammetric techniques are only applicable to a relatively small group of metals compared to AAS.

However, it has recently received considerable attention from analytical chemists specialized in water analysis because of the following advantages : 1) the direct determination of heavy metals in natural sea water without the complication of the presence of matrix components (alkaline salts), since they are rather welcome in this case, as the sample contains the necessary supporting electrolyte, 2) for all sorts of aqueous samples (sea water, estuarine, river, lake, rain,...) and other solid matrixes (particulate matter, biota, sediments, ...) stripping voltammetry enables simultaneous determination of several toxic trace metals such as Bi, Cd, Cu, Pb, Sb and Zn after a minimum of sample pretreatment and pH adjustement. The amount of acid required to do this is small and with the ready availability of highly purified acids (suprapure Merck), the need to acidify is not a significant source of contamination, 3) the possibility to discriminate between various oxidation states or such categories as "free" and "bound" metals without modifying the medium, 4) the relative simple and inexpensive instrumentation and its very high sensitivity without preconcentration, 5) the possibility to study the interactions between heavy metals and organic matter (stability constants) and it might be used to determine the concentrations and surface active properties of some organic compounds (e.g. humic substances) in water.

However, some remarks may be made about the interference effects. The most common type of interference is the overlapping stripping peaks (e.g. Sb-Bi). The next most common interference obscures DPASV results because inter-element compound formation

on/in the electrode (e.g. Zn-Cu). The third type of interference encountered is the formation of an organic film over the electrode surface which inhibits the metal deposition and/or stripping processes.

In our experiments a Bruker E 310 modular polarographic analyser with a Hewlett-Packard 7040 A X-Y recorder was used for differential pulse anodic stripping voltammetry on a hanging mercury drop electrode (DPASV-HMDE). A three electrode system was employed. A Metrohm E 410 hanging drop mercury electrode (HMDE) was used as the working electrode. Potentials were measured in reference to a saturated calomel electrode (SCE). An auxiliary platinum electrode was used to minimize I.R. drop effects across the electrolysis cell.

We overcome the overlapping stripping peaks problem by changing the supporting electrolyte and the stripping conditions. An example of that is clearly demonstrated in the simultaneous determination of Bi, Cd, Cu, Pb, Sb and Zn (Gillain et al, 1979). On the other hand, we use the HMDE because this type of electrode is less susceptible to inter-element compound formation then the mercury film electrode (MFE). In our experimental conditions, no intermetallic formation between Zn-Cu and Cu-Sb was found. However, Zn can be expected to interfere with Cu (Cu = 80 µg/ℓ) if it is present at a level exceeding 500 µg/ℓ (f.e. in some plankton samples). In that case, to achieve the independent determination of Zn and Cu, it is necessary to add gallium ions to the solution.

Finally, natural water contain tensio-active substances which have a strong tendency to be adsorbed at the electrode surface. This may lead to various effects depending on the voltammetric technique, the type of electrode used and the nature of adsorbed species. Very strong effects have been observed in our simultaneous determination of Bi, Cd, Cu, Pb, Sb and Zn in sea water such as depression of stripping peaks as a result of film formation on the electrode and appearance of anomalous stripping peaks in the vicinity of Pb, Sb and Bi peaks.

However, despite these difficulties, the DPASV technique proves to be a valuable tool for studying metal species dissolved in filtered sea water since some forms are not reductible at the electrode (Florence et al, 1977 ; Gillain et al, 1977 ; Figura, 1980) whereas other forms are. Under in situ (neutral) conditions, the DPASV results include ionic as well as some easily dissociable organic and inorganic metal complexes. By changing experimental conditions such as decreasing the pH, we obtain more metal available to the electrode during the reduction step. The metals are apparently made available through a number of processes : 1) protonation of inorganic complexing anions such as carbonate, sulfate, bicarbonate and hydroxide, 2) dissolution of hydrous iron oxide which adsorbs metals, 3) protonation of organic complexing agents (e.g. weak-organic acids such as amino acids) for which complexation strength increases with pH.

With the ultra-violet irradiation step, we destroy organic matter and analyse the "total" dissolved heavy metal content.

The limit of detection, arbitrarily defined as three times the standard deviation of the noise level for the simultaneous determination of Bi , Cd , Cu , Pb , Sb and Zn are 0.02 , 0.05 , 0.10 , 0.03 , 0.02 and 0.01 µg/ℓ respectively under the following conditions : electrolysis time 60 min , stirring 450 r/min and electrode diameter 0.760 mm .

The precision is estimated to be 5 % for 5.2 µg/ℓ Zn ; 10 % for 0.6 µg/ℓ Cd ; 11 % for 6.2 µg/ℓ Pb ; 9 % for 4.3 µg/ℓ Cu ; 15 % for 0.4 µg/ℓ Sb and 13 % for 0.3 µg/ℓ Bi .

4.3.— *Drying, homogenization and ashing of samples with solid matrixes samples (particulate matter, biota, sediments).*

The determination of chemical trace elements in solid matrixes such as suspended matter, plankton and sediment presents many methodological difficulties : drying, homogenization and ashing.

4.3.1.— *Drying.*

A freeze drying method, when carried out close to dry ice temperature, under high vacuum and with cold traps is used (lyophyliser Leybold-Heraeus GT2).

The freeze drying process has the advantage to minimize environmental contamination and involves much less risks of loss of constituents than oven drying.

Prior to drying the sample is frozen but this is not always required for solid material containing not much water (sediments, suspended matter).

The procedure for relatively rapid drying of sample, depending on the nature of product to be dried, is established by trial and error. The total time for complete drying is determined by pressure control.

4.3.2.— *Homogenization.*

The dry residue is very heterogeneous. When small quantities are used for each analysis (plankton, sediment), we reduce the particle size by grinding the sample in a cleaned mechanical agate mortar.

We have tested the homogeneity of the samples and the conclusion is that the gross sample obtained by our method of preparation can be considered as homogeneous (Gillain et al, 1977).

4.3.3.– *Ashing.*

a) Low temperature ashing (LTA) [Gillain et al., 1982].

A stream of low pressure oxygen excited by a radio frequency discharge is used to decompose organic substances prior to trace element analysis.

The sample is inserted in a closed borosilicate glass reaction chamber. Variable power (0-400 watts) is supplied by a conventional radio frequency oscillator.

Low temperatures (70°C - 100°C) can be maintained by using a low excitation power.

This LTA method minimizes sample handling, is easier to perform as it avoids the use of reagents and gives very low blank values : Zn : 0.030 ; Cd : 0.003 ; Pb : 0.020 ; Cu : 0.020 µg/g° (Sb and Bi not detected).

We have shown that the LTA method does not introduce any noticeable losses of Cd, Cu, Pb and Zn. The ashing was conducted under the following conditions : power 200 watts, pressure 1 mmHg, oxygen flow 40 mℓ/min and time 10-15 hours.

Nevertheless, under these conditions the mineralization of a standard sample (NBS, n° 1571) has shown that losses of Sb can appear (recovery 25-35%) chiefly in the presence of chlorides.

Because of the dependence of temperature and oxydation rate at the applied power, different powers and ashing times have been tested on a standard solution of Sb^{III}. The results show that quantitative recuperation of Sb is obtained only for a low power (< 150 watts) and very short lapses of times (< 1 hr).

The conclusion is that the volatilisation losses cannot be prevented in the conditions previously cited necessary to a complete mineralization of marine samples (power 200 watts, time 10-15 hours).

Consequently, the low temperature ashing appears to be an acceptable method, except when dealing with volatile compounds.

b) Digestion bomb.

We use a home-made PTFE digestion bomb as described in a recent paper (Gillain, 1982).

We have determined the volume of acids (HNO_3 or $HNO_3 - H_2 SO_4$ 1:1) necessary to dissolve completely 300 mg samples (ASV) or 1 g samples (AAS) at a temperature such as to obtain in the bomb an internal pressure lower than 10 atmospheres with a heating time of 6 hrs.

From the experiments it was concluded that the samples with a high organic content were easily decomposed but not completely mineralized when these acids were used. Consequently, we decided to use the $HNO_3 - H_2 O_2$ 1:1 mixture (biological samples) + concentrated HF (geological, mineralogical samples).

The efficiency of the digestion has been checked with a NBS sample (Orchard Leaves, 1971).

We also use a commercial PTFE digestion bomb (Techni-Verre, Paris) with a larger inner volume of about 100 mℓ. The bomb should be heated above 80°C and the internal pressure must not exceed 2-3 atmospheres.

A definite advantage of the wet ashing in a PTFE bomb is that no significant loss of volatile metals such as Hg and Sb was observed (Decadt et al, 1980 ; Gillain, 1982).

Nevertheless the blank values are somewhat higher than those obtained by LTA ashing

Zn : 0.12 μg/g * ;
Cd : 0.01 μg/g * ;
Pb : 0.12 μg/g * ;
Cu : 0.06 μg/g * ;
Sb and Bi : not detected.

4.4.— *Procedure for analysis.*

4.4.1.— *Sea water samples (water column, microlayer).*

a) Direct and simultaneous determination of Zn , Cd , Pb , Cu or Zn , Cd , Pb , Cu , Sb , Bi dissolved in sea water by differential pulse anodic stripping voltammetry with a hanging mercury drop electrode. An approach to speciation.

Direct and simultaneous determination of Zn , Cd , Pb and Cu .

30 mℓ of sea water previously filtered through a membrane (0.45 μm) is placed in the electrolysis cell. The sample is stirred magnetically (450 rpm) and oxygen is removed by bubbling pure nitrogen for 30-40 min. Electrolysis is carried out at a potential of -1.200 V (V.S. SCE) for 10-20 min while nitrogen is introduced into the space above the surface of the solution. One minute before the end of the electrolysis, the stirrer is stopped and the current-potential curve is then recorded from -- 1.200 to 0 V with an appropriate current sensivity with scan rate 2 mV.s^{-1} and pulse 35 mV .

Direct and simultaneous determination of Zn , Cd , Pb , Cu , Sb and Bi .

30 mℓ of filtered sea water are introduced into the electrolysis cell and adjusted to a 2M NaCl concentration with suprapure NaCl. Reagents blanks subjected to this procedure gave no problems.

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* Dry weight ashed.

The solution is stirred, purged and deposition of six elements was made at -1.200 V (V.S. SCE) for 15-20 min in the same conditions as described above.

One minute before the end of the electrolysis, the stirrer is stopped and the current-potential curve is then recorded from - 1.200 to - 0.350 V with scan rate 2 mV.s^{-1} and pulse 35 mV.

The potential is held at - 0.350 V with stirring for 15-20 min. At the end of this plating time, the stirring is stopped again and the resulting current-potential curve is recorded down to a potential of 0 V with scan rate 0.5 mV.s^{-1} and pulse 10 mV.

b) Speciation of Bi, Cu, Pb, Cd and Zn.

Determination of free and "very labile" metals.

Ionic and "very labile" metals were determined in sea water at its natural pH (pH = 8).

Determination of "moderately labile" metal.

Direct analysis is performed immediately after addition of suprapure concentrated HCl to about pH 1.

"Moderately labile" metal concentration is defined as the difference in concentration under acidic conditions (pH 1) and under in situ (neutral) conditions.

Determination of total metal and "very weak labile" + "inert" fractions.

Total metal concentrations were determined after exposing acidified sea water (containing 0.05 mℓ of 30 % H_2O_2 per 30 mℓ) in quartz tubes to UV light with rotative stirring for one night (Gillain 1980).

The difference between the total concentration and concentration under acidic (pH 1) conditions represents the amount of "very weak labile" + "inert" metal.

c) Speciation of Sb.

Determination of Sb^{III}.

Direct analysis of acidified (pH 1) sea water are performed immediately after adjusting to a 2 M NaCl concentration.

In these conditions, we determine free metal ions + ASV "very labile" and ASV "weakly labile" organic and inorganic complexes of Sb^{III}. Sb^{V} gave no stripping peak in our experimental conditions ([Cl^{-}] = 2 M, pH = 1).

Determination of $Sb^{III} + Sb^{V}$

The determination of $Sb^{III} + Sb^{V}$ is performed on acidified sea water (pH 1) after reduction of Sb^{V} to Sb^{III} by bubbling SO_2 through the solution.

Excess of SO_2 was removed from the solution by bubbling pure nitrogen through the cell (Brihaye, 1979).

The efficiency of the reduction procedure was tested on a standard solution and it was found that total Sb^{V} could be completely reduced by this technique (Brihaye, 1979).

Determination of total Sb.

Total antimony can be determined on a sea water aliquot after acidification to pH 1, UV irradiation and reduction of Sb^{V} to Sb^{III} are carried out by the same procedure as described above.

The flow chart for the speciation method is presented in figure 1.

d) Determination of Cd and Cu dissolved in sea water by atomic absorption spectrophotometry with graphite furnace.

The metals were determined after using an organic extraction technique. In this particular case it involves chelation with ammonium 1-pyrrolidine-dithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC), an extraction with chloroform and back-extraction with nitric acid (Bruland et al, 1979).

About 250 ml of sea water (filtered through a 0.45 µm membrane) was buffered to pH 4 with 2-4 mℓ of ammonium acetate ; 1 mℓ of a solution containing 1% (w/v) each of APDC and DDDC (stabilized in 1% ammonium hydroxide solution and purified by chloroform extraction) and 8 ml of chloroform were added. The mixture was then shaken vigorously for 2 min in a separation funnel.

After 5 min to allow phase separation, the chloroform fraction was drained into a 125 mℓ separation funnel, and 4 mℓ of 7.5 M HNO_3 were added to initiate degradation of the dithiocarbamates.

The original sea water sample was then re-extracted with an additional 6 mℓ chloroform and the chloroform fractions were combined. The funnel containing the chloroform and the acid phases was then shaken for 2 min. After phase separation, the chloroform fraction was discarded and the acid fraction collected in a PTFE container.

The separation funnel was rinsed with another 2.5 mℓ of 7.5 M HNO_3 and the acid fractions were combined. The acid extract was then evaporated to dryness and the residue was redissolved in 5 mℓ of 1% HNO_3 for analysis by graphite furnace atomic absorption spectrophotometry.

The procedure yields a 50 : 1 concentration increase.

Sea-water

Sampling and filtration on treated Millipore 0.45 μm filters

Solution

DPASV at in situ pH (I)

Zn, Cd, Pb, Cu free ions and very labile complexes

DPASV at pH 1 (II$_a$)

DPASV at pH 1 after reduction of Sb^V into Sb^{III} with SO$_2$ (II$_b$)

Zn, Cd, Pb, Cu, Sb, Bi free ions + weak organic and inorganic complexes
II$_a$ = Sb^{III}
II$_b$ = Sb^V

DPASV at pH 1 after reduction of Sb^V into Sb^{III} with SO$_2$ and overnight UV irradiation (III)

Zn, Cd, Pb, Cu, Sb, Bi total concentration

Suspended matter and plankton

Mineralization LTA 600 200 watts

Dissolution of the residue in 1 mℓ concentrated supra-pure HCl

Analysis by DPASV (pH 1, Cl$^-$ = 2 M) Zn, Cd, Pb, Cu

Mineralization Teflon bomb HNO$_3$ + H$_2$O$_2$ 1:1

Evaporation of reactants at 50°C

Dissolution of the residue in 1 mℓ concentrated supra-pure HCl

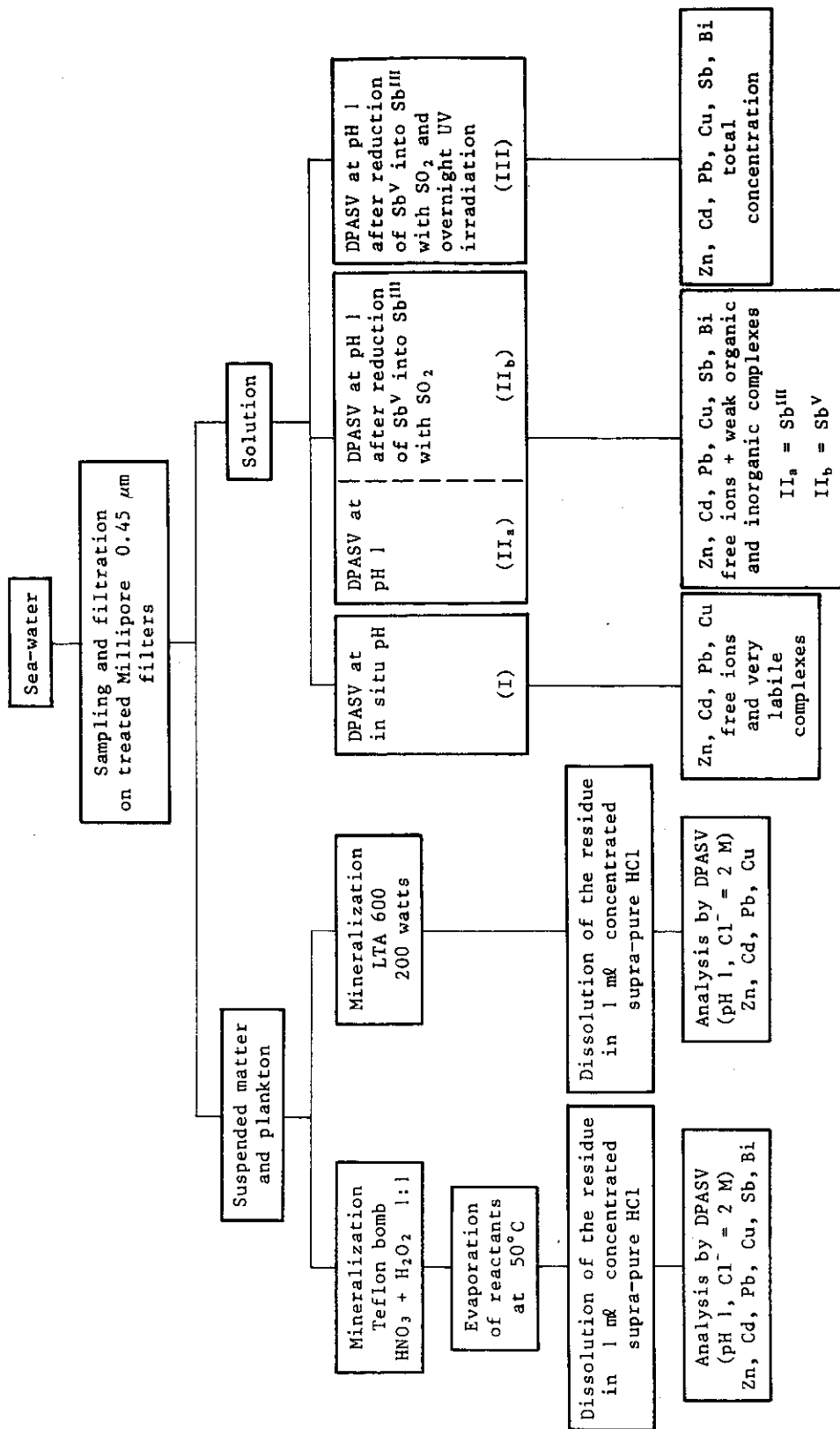Analysis by DPASV (pH 1, Cl$^-$ = 2 M) Zn, Cd, Pb, Cu, Sb, Bi

fig. 1.

Analytical protocol to analyse Zn, Cd, Pb, Cu, Sb and Bi in suspended matter, plankton and to study speciation of metals in solution in the water column.
LTA = low temperature ashing (activated O$_2$).

e) Determination of total and dissolved Hg in sea water by cold vapour atomic absorption spectrophotometry.

To 150 mℓ of sea water sample one adds 5 mℓ of $KMnO_4$ (5 %) + 5 mℓ of H_2SO_4 (1:1) + 5 mℓ of HNO_3 (1:2).

The digestion lasts 16 hours at 60 °C. The excess $KMnO_4$ is reduced with 1 mℓ hydroxylamine (5 %) and the volume in the BOD-bottle is brought to 180 mℓ. After reduction by 1 mℓ of $NaBH_4$ (1 %), mercury determination is carried out with a MAS-50.

The results obtained will be defined as dissolved Hg for the filtered and total Hg for the unfiltered samples.

4.4.2.– Solid matrixes (particulate matter in sea water and air, biological samples and sediment samples).

a) Direct and simultaneous determination of Zn, Cd, Pb, Cu or Zn, Cd, Pb, Cu, Sb and Bi present in particulate matter (sea water, air), sediments and biological samples by differential pulse anodic stripping voltammetry.

Wet digestion procedure.

The Millipore membrane filters or 300 mg of lyophilized material are, in a laminar flow clean box, inserted into a PTFE vessel. 4 mℓ of concentrated HNO_3 , 4 mℓ of H_2O_2 (30 %) and 1 mℓ of concentrated HF were added to the bomb which was then closed and heated to approximatively 160 °C for 6 hours.

The digested material was subsequently evaporated to dryness and a further 1 mℓ of suprapure concentrated HCl was added. The digestion was allowed to proceed overnight and the digest was then brought to pH 1 . The final volume was 100 mℓ of which 30 mℓ were transferred to the polarographic cell for DPASV analysis by the same procedure as for sea water samples.

A blank solution containing 4 mℓ concentrated HNO_3 , 4 mℓ H_2O_2 (30 %) and 1 mℓ concentrated HF was evaporated in the same way.

LTA procedure.

The Millipore membrane filter samples or 300 mg of solids are, with precautions against airborne contamination (clean box), introduced into a quartz beaker. The filter or the samples are then destroyed either by low temperature ashing in an oxygen plasma (< 200 °C) with the following conditions :
O_2 flow   50 mℓ/min ,
RF power   200 watts ,
Time   24 hours .

After dissolution of the ashed sample in 1 mℓ suprapure concentrated HCl during a night, the solution was quantitatively transferred to 100 mℓ volumetric flasks (final acid concentration : 0.1 N HCl) for DPASV analysis

b) Cd, Pb and Cu determination in particulate suspended matter, aerosol and sediment by atomic absorption spectrophotometry.

Particulate matter and sediment.

The membrane filter or 1g of finely ground sample are transferred into the PTFE bomb with concentrated HNO_3 + HCl + HF 4:1:1. The bomb is sealed and heated to 80°C for 24 hours.

The bomb is then cooled in a deep-freezer and its content is evaporated to dryness. Purified nitrogen was passed over the acid to accelerate the evaporation and to avoid contamination by dust. The residue was redissolved in 25 mℓ of 1% HNO_3.

Depending on the concentration, the measurements of Cd, Pb and Cu are carried out using air-acetylene flame (FAAS) or graphite furnace atomic absorption spectrophotometry (GFAAS).

Aerosols.

Whatman filter samples are cut into quarters and inserted into the PTFE bomb with 10 mℓ concentrated HNO_3, 5 mℓ concentrated HCl and 2.5 mℓ concentrated $HClO_4$.

The digestion is carried out at 80°C for 4 hours. After cooling in a deep-freezer, the bomb is opened and 5 mℓ concentrated HNO_3 is added. Then the bomb is recapped and allowed to stand for 5 hours at 80°C. After cooling, the sample is evaporated to 1 mℓ and quantitatively transferred in 25 mℓ containers using ultra-pure water. The samples can then be analysed directly for the element of interest by flame atomic absorption spectrophotometry (FAAS).

c) Determination of mercury content in particulate suspended matter, sediments and biological materials.

Pyrolysis procedure.

10 mg of weighed lyophilized material are pyrolyzed under H_2 flux at 800°C. Complete reduction of pyrolysis products was ensured by passage through a tube packed with a catalyst (Ni) and the mercury set free was fixed on a Au-column.

By heating in an electric mini-oven (500°C), the amalgam formed is then decomposed and the released mercury is swept by the transporting gas at a flow rate of 750 mℓ.min^{-1} into the MAS-50 measuring cell at 253.7 nm into 75 s.

Aerosols collected on a GF/C-filter preheated at 500°C prior to the sampling, can be inserted directly into the pyrolysis tube.

The calibration curve is obtained by injections of known amounts of mercury saturated nitrogen. The coefficient of variation is about 1%.

Blanks were run frequently and consisted in the ultra-pure water and acids and unused, decontaminated GF/C-filters. No signal above analytical noise was detected.

Wet digestion procedure.

Sediments.

1 g of lyophilized material is weighed directly into the PTFE digestion bomb. 5 mℓ mercury-free (less than $5 \cdot 10^{-7}$ %) concentrated nitric acid and 5 mℓ concentrated fluohydric acid are added.

The digestion is carried out at 110 °C during 16 hours. After cooling the volume is brought to 180 mℓ with ultra-pure water. After addition of 1 mℓ of $NaBH_4$ (1 %), to reduce the oxidized mercury to its atomic state, mercury concentrations were determined using a Coleman MAS-50 mercury analyser.

Biological material.

1 g of undried or lyophilized material is weighed into a 250 mℓ Erlenmeyer flask with ground neck. 2 mg vanadium pentoxide, 10 mℓ concentrated nitric acid and 4 mℓ sulfuric acid are successively added.

The sample is gently refluxed at 80 °C during about 10 minutes. 20 mℓ of $KMnO_4$ (5 %) are added dropwise while the reflux is continued during 15 minutes. After cooling, 15 mℓ of hydroxylamine (5 %) is added and the cooler is washed down. The sample is quantitatively transferred to a 250 mℓ volumetric flask and the mercury content of this solution is determined using a MAS-50.

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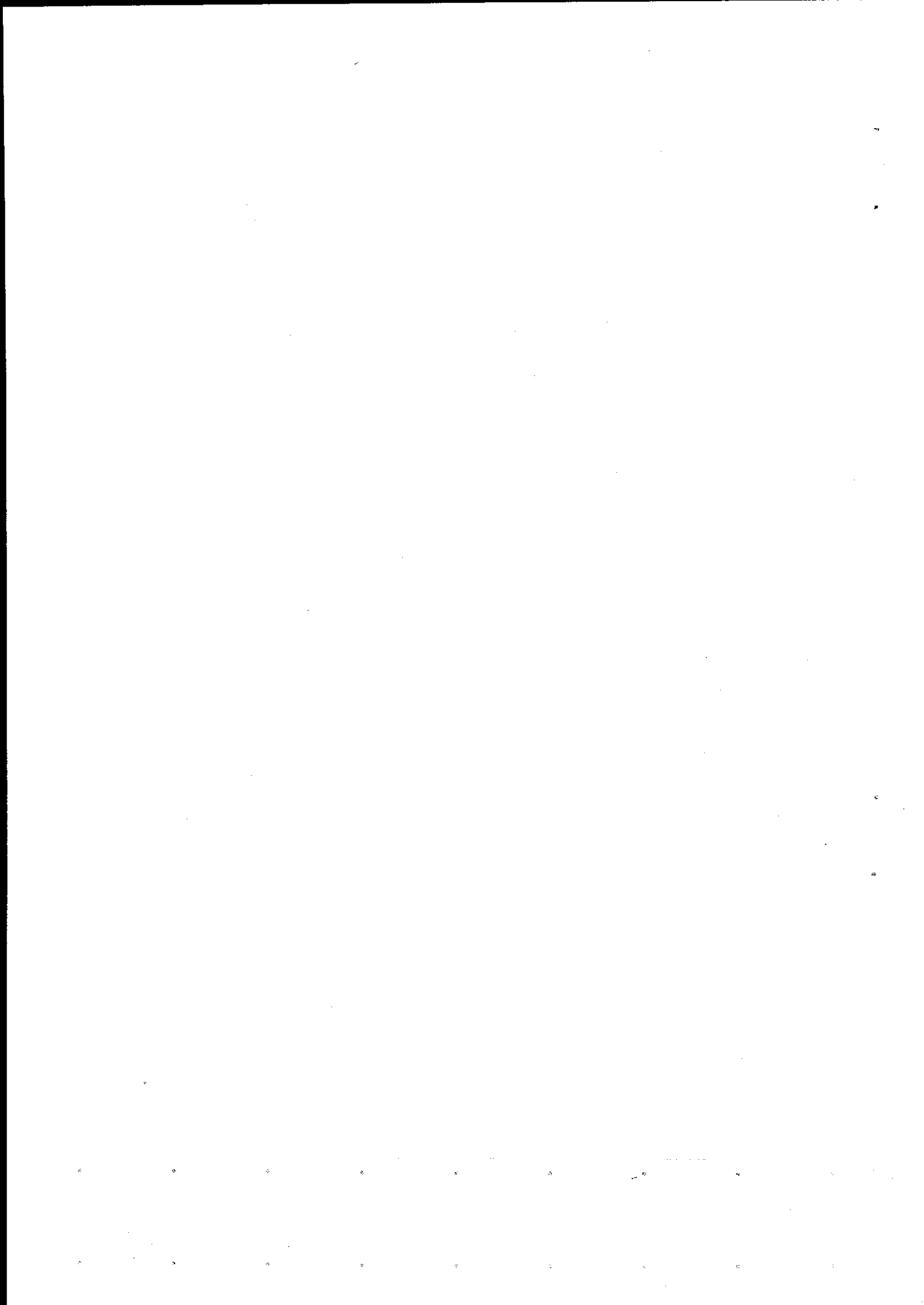
Part 2

SPATIAL, TEMPORAL AND COMPARTMENTAL DISTRIBUTION IN THE WATER COLUMN

G. DECADT[1], G. GILLAIN[2], F. DEHAIRS[1]*, H. DEDEURWAERDER[1],
L. GOEYENS[1] and W. BAEYENS[1]

Abstract.

The concentrations of dissolved and particulate Bi , Cd , Cu , Hg , Pb , Sb and Zn have been measured during surveying cruises along the Belgian coast (1979-1981) to determine the distribution of these heavy metals and to determine how this distribution is effected by coastal discharges, dumping and river discharges (mainly the Scheldt estuary).

Dissolved Cd , Cu , Hg , Pb and Zn concentrations average respectively 0.11 µg/ℓ , 2.2 µg/ℓ , 12 ng/ℓ , 3.9 µg/ℓ and 6.6 µg/ℓ .

The large scattering of the results do not allow to observe a clear spatial distribution pattern. On the other hand, dissolved mercury concentrations clearly decrease with the distance from the coast.

Mean particulate Cd , Cu , Hg , Pb and Zn concentrations are respectively 20 ng/ℓ , 0.24 µg/ℓ , 35 ng/ℓ , 0.36 µg/ℓ and 1.3 µg/ℓ . Particulate metal concentrations are highest in the zone near the Scheldt estuary and diminish progressively with distance from both the coast and the mouth of the Scheldt estuary.

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1.– Introduction.

Increasing awareness of the potential hazards of large scale contamination of the ecosystem by heavy metals from urban and industrial sources, has led to the need of regularly monitoring the levels of these substances (Dutton et al, 1973 ; Duinker and Nolting, 1977, 1982 ; Baeyens et al, 1979a, 1979b ; Decadt et al, 1980 ; Gillain et al, 1979, 1980) and to attempts of modelisation of the heavy metal circulation in the Southern Bight of the North Sea (Duinker & Nolting, 1976 ; Elskens, 1976).

A basic requirement to describe the circulation pattern of a heavy metal is the knowledge of its distribution among the different compartments of the ecosystem and its spatial-temporal fluctuation in each of these compartments.

Although the heavy metals considered in this study (except perhaps Zn and Cu) do not play an essential function in the food chain, they may become accumulate into the higher organisms either through direct uptake from the dissolved phase (Bouquegneau et al, 1977) or indirectly after adsorption on detrital matter, nanoplankton, etc. and ingestion by organisms of the higher trophic levels. As a consequence, base line studies on the levels of these heavy metals (dissolved and particulate) in the water column are not only important for pollution control, but can also provide valuable information on the biogeochemistry of trace metals.

This paper deals with the relative importance of heavy metal concentrations in the dissolved and particulate phases of the water column and their spatial distribution patterns. An attempt has been made to discuss them in terms of external inputs.

2.– Materials and methods.

Sampling and analytical methods are described by Gillain et al. in part 1 (pp. 13-39).

3.– Presentation of the results.

Results described in this paper refer to samples collected during surveillance cruises along the Belgian coast. The stations are located along grid lines perpendicular to the coast (fig.1).

$\overline{s} = 32\,88 \pm 0\,809$

$\overline{s} = 31.57 \pm 1.087$

$\overline{s} = 33.82 \pm 0.785$

$\overline{s} = 34.24 \pm 0.589$

45

25

15

44

34

24

14

IV

III

Zeebrugge

Oostende

Nieuwpoort

WH

II

I

42

41

31

21

11

12

22

32

33

23

13

43

51°30'

51°20'

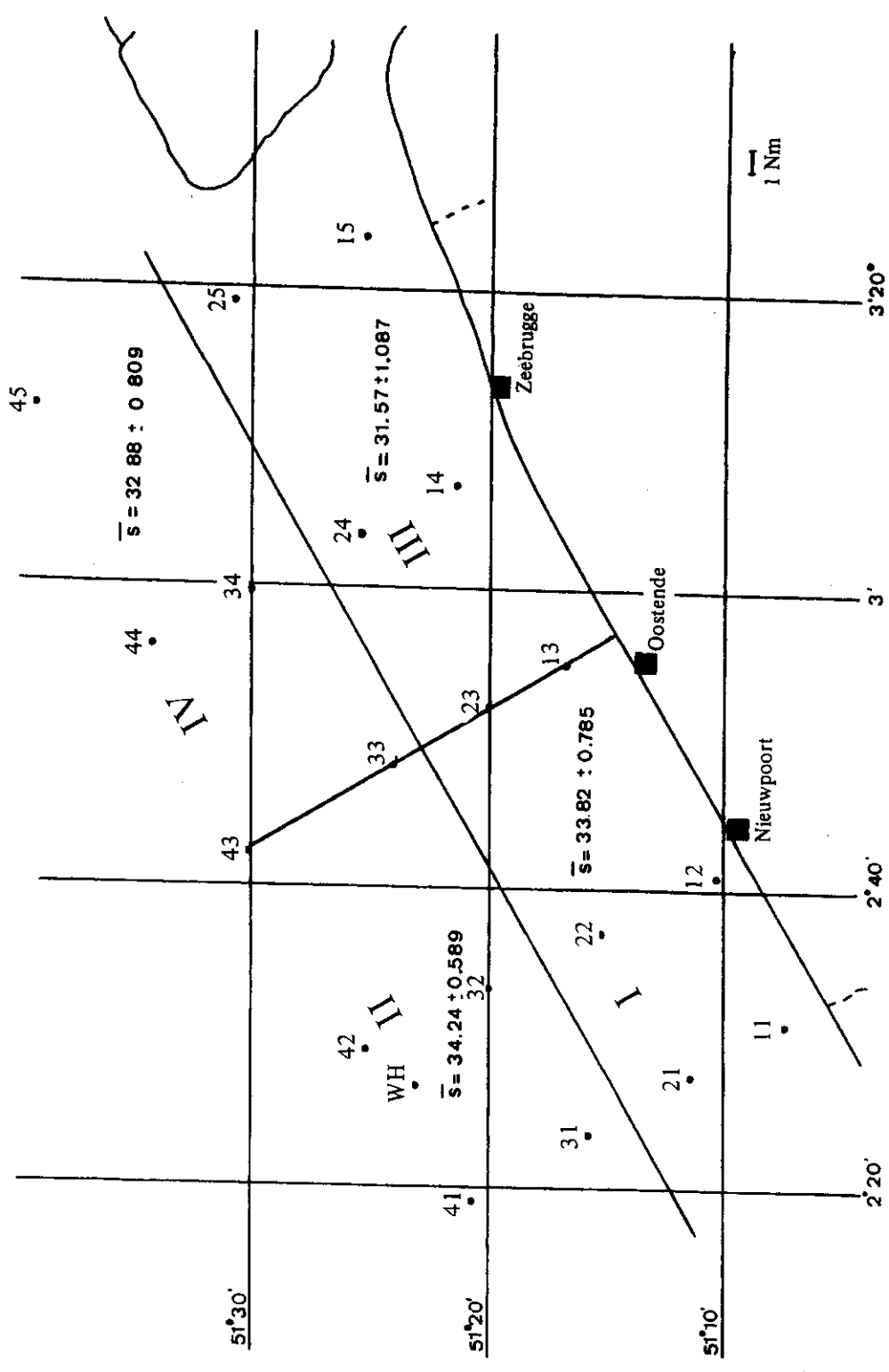51°10'

2°20'

2°40'

3'

3'20"

1 Nm

fig. 1.

Mean salinity during the period 1977-1981 (Unité de Gestion, Ministry of Public Health, personal communication)
$\overline{s}$ = mean salinity

Table 1

Mean heavy metal concentration in the Belgian coastal zone

Metal	Zone	Nb	Range (μg/ℓ)	Arithmetic mean		Geometric mean		Median
				$\overline{x}$	σ	$\overline{x}g$	σg	
Total dissolved Zn	B.C.	83	1.7 −23.20	8.19	5.52	6.66	1.91	6.60
	I	18	2.35 −21.37	7.22	5.04	5.92	1.90	6.10
	II	17	2.4 −19.8	9.21	5.98	7.50	1.96	6.92
	III	15	1.7 −23.20	10.37	5.91	8.85	1.87	8.82
	IV	15	2.6 −20.40	6.98	4.73	5.96	1.73	5.70
Part. Zn	B.C.	46	0.15 −14.7	2.48	3.37	1.29	3.03	1.07
	I	11	0.56 −14.7	3.08	4.61	1.53	3.00	1.12
	II	12	0.15 − 1.24	0.52	0.31	0.44	1.83	0.45
	III	5	0.56 − 6.10	3.22	2.15	2.46	3.30	3.30
	IV	7	0.46 − 1.60	1.10	0.38	1.03	1.51	1.10
Total dissolved Cd	B.C.	84	0.025−0.980	0.151	0.133	0.118	1.98	0.116
	I	18	0.025−0.480	0.160	0.112	0.127	2.07	0.129
	II	17	0.040−0.530	0.161	0.130	0.124	2.07	0.100
	III	15	0.074−0.980	0.205	0.224	0.156	1.91	0.140
	IV	16	0.035−0.330	0.106	0.070	0.091	1.71	0.083
Part. Cd	B.C.	45	0.005−0.095	0.026	0.019	0.020	2.07	0.021
	I	11	0.007−0.067	0.027	0.018	0.022	1.97	0.024
	II	12	0.005−0.040	0.014	0.011	0.011	1.87	0.010
	III	5	0.016−0.041	0.026	0.010	0.025	1.44	0.022
	IV	7	0.009−0.050	0.026	0.014	0.023	1.75	0.022
Total dissolved Pb	B.C.	82	0.90 −13.87	4.61	2.75	3.86	1.86	3.97
	I	18	1.4 −13.87	5.00	3.22	4.19	1.83	3.99
	II	16	1.0 −10.95	5.15	2.99	4.13	2.15	4.73
	III	15	1.2 −13.80	4.79	3.08	4.06	1.82	4.00
	IV	15	0.9 − 8.30	3.86	1.89	3.40	1.73	3.40
Part. Pb	B.C.	46	0.033−5.8	0.781	1.105	0.365	3.61	0.370
	I	11	0.059−1.7	0.564	0.460	0.407	2.54	0.500
	II	12	0.033−0.44	0.172	0.121	0.133	2.19	0.160
	III	5	0.470−1.33	0.958	0.385	0.888	1.57	1.000
	IV	7	0.050−1.30	0.363	0.431	0.223	2.86	0.190

B.C.: Belgian coast.

Table 1

Mean heavy metal concentration in the Belgian coastal zone
(continued)

Metal	Zone	Nb	Range (μg/ℓ)	Arithmetic mean		Geometric mean		Median
				$\bar{x}$	σ	$\bar{x}g$	σg	
Total dis-solved Cu	B.C.	84	0.50 -21.8	2.82	2.66	2.21	1.96	2.30
	I	18	1.10 - 5.15	2.43	1.13	2.21	1.57	2.08
	II	17	0.50 - 8.50	3.01	2.57	2.12	2.44	2.44
	III	15	1.20 -21.80	3.63	5.10	2.54	2.02	2.10
	IV	16	0.80 - 6.00	2.37	1.32	2.08	1.69	2.30
Part. Cu	B.C.	46	0.039-1.900	0.371	0.382	0.241	2.57	0.210
	I	11	0.118-0.780	0.301	0.212	0.248	1.88	0.200
	II	12	0.039-0.210	0.117	0.055	0.104	1.71	0.108
	III	5	0.386-0.790	0.614	0.200	0.586	1.43	0.710
	IV	7	0.075-0.450	0.224	0.121	0.195	1.80	0.220
Total Hg	B.C.	253	0.002-0.787	0.074	0.073	0.050	2.63	0.059
	I	55	0.004-0.255	0.062	0.061	0.037	3.02	0.046
	II	43	0.002-0.180	0.051	0.040	0.036	2.63	0.047
	III	58	0.020-0.787	0.120	0.112	0.095	1.95	0.092
	IV	47	0.009-0.234	0.061	0.041	0.049	2.09	0.052
Part. Hg	B.C.	69	0.003-0.570	0.060	0.081	0.035	2.75	0.040
	I	11	0.009-0.050	0.028	0.014	0.025	1.78	0.030
	II	11	0.003-0.054	0.026	0.020	0.018	2.57	0.014
	III	18	0.029-0.570	0.126	0.132	0.087	2.34	0.095
	IV	16	0.009-0.080	0.033	0.025	0.025	2.34	0.024
Suspended matter	B.C.	47	6 -100	24.1	18.9	19	1.97	18.2
	I	11	12.2 -31.7	21.1	6.0	20.3	1.35	20.2
	II	12	6.1 -13.9	9.1	2.3	8.9	1.28	8.4
	III	5	23.4 -50	42.7	11.2	41.2	1.38	48.8
	IV	7	9.3 -30.9	17.9	6.7	16.9	1.44	17.6

B.C.: Belgian Coast.

Duinker & Nolting (1976) suggest that a number of distinct regions can be characterized by their values for the particulate Fe:Mn ratio. In the Southern Bight, they found a total particulate Fe:Mn ratio of 30 to 40 for inshore samples and of 60 to 85 for offshore samples. Fig.2 shows the relation between total iron and manganese for samples obtained in the Belgian coastal zone, during three cruises (May 1980, May and June 1981).

Fe and Mn were strongly correlated (r = 0.98). The mean Fe : Mn ratio of 32 indicates that we are most probably dealing with inshore samples. To be able to observe any possible influence of estuarine (Scheldt estuary) and coastal inputs on the heavy metal concentrations in the Belgian coastal zone, the monitoring network was divided into four sections (fig.1). This subdivision can be justified if one looks at the mean salinities observed in that area during the period 1977-1981 (fig.1), although salinity might not be correlated with heavy metal distribution.

Table 1 summarizes the mean values (arithmetic and geometric means) for Zn, Cd, Cu, Pb (dissolved and particulate) and Hg (total and particulate). Extremely high values, sporadically measured in our coastal zone, were not excluded.

3.1.— *Spatial distribution of Bi, Cu, Cd, Hg, Pb, Sb and Zn in the Belgian coastal zone.*

3.1.1.— *Dissolved Zn, Cd, Pb and Cu.*

Data obtained by Jones (1972) and Duinker & Nolting (1982) for the Southern Bight, show a clear smooth dependence (concentration gradient similar but opposite to the salinity gradient) on the distance of the sampling site from the coast. Although zone III (zone under the influence of the river runoff) generally shows somewhat higher concentration levels than the other zones (table I), concentration gradients are not obvious. Several facts have to be taken into account. First, the wide scattering of the results in each of the individual subareas will mask largely the possible existence of smooth concentration gradients. Secondly, since our sampling area is too reduced (the maximum distance from the coast is about 30 km) the region of maximum salinity (35 ‰), occuring in the central part of the Southern Bight, is not included in our sampling network (fig. 1). The fact that we are greatly dealing with an inshore watermass, is corroborated by the remarkable constant particulate Fe : Mn ratio of 32 (fig. 2, Duinker et al., 1976). Thirdly, the existence of a gyre off the Belgian coast (Nihoul & Ronday, 1976) can also be a reason for a somewhat different and perhaps more homogenized system compared to other regions of the Southern Bight (Jones, 1972 ; Duinker et al, 1976).

The mean freshwater content in section I, II, III and IV is respectively 3.5, 2 , 10 and 6 % relative to the maximum salinity observed in the Southern Bight (35 %). The mean concentrations in box III are increased over the overall mean for the Belgian coastal area respectively about 2 µg/ℓ for Zn (30 %), 0.04 µg/ℓ for Cd (17 %), 0.2 µg/ℓ for Pb (5 %) and 0.33 µg/ℓ for Cu (15 %).

According to Baeyens et al. (1982a), the annual dissolved heavy metals supply of the Scheldt estuary amounts to 28.2 t/year for Zn , 6.6 t/year for Cu , 2.3 t/year for Pb and 0.98 t/year for Cd . If we accept a conservative character for the dissolved element, as suggested by Duinker & Nolting (1976) in the case of
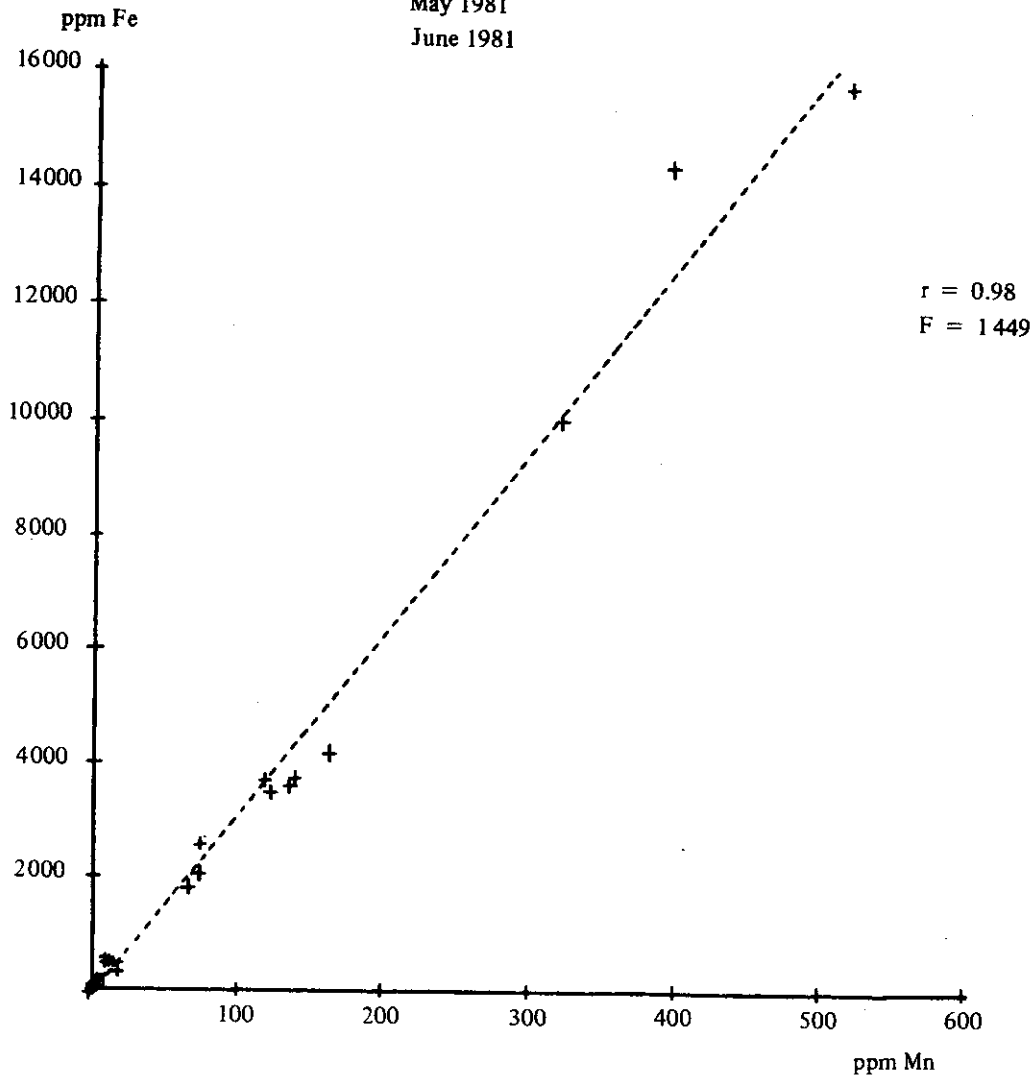
ppm Fe $= -138 + 32$ ppm Mn

May 1980
May 1981
June 1981

fig. 2.

Zn and using a mean residual outflow of 6 km³/year , calculated on the basis of the spatial distribution of the salinity, an adequate conservative parameter (Decadt et al., 1982), the Scheldt estuary supply would give a concentration increment of 1.5 µg/ℓ for Zn , non detectable for Cu , non detectable for Pb and 0.12 µg/ℓ for Cd .

The observed increments for Zn and Cd in box III can therefore be explained by the Scheldt estuary input while this is not

the case for Pb and Cu. However, one has to keep in mind that the analytical techniques actually in use have a relative error of about 10 %.

The sensitivity of the Belgian coast to the input from the Scheldt estuary can also be tested by a model suggested by Yeats et al (1978). The change in concentration of a particular dissolved metal m in the estuary, required to significant alter the metal concentration in coastal receiving waters $\Delta m_{estuary}$ can be expressed as

$$\Delta m_{estuary} = \Delta m_{coastal} \frac{D}{1 - S_m} \frac{F_t}{F_{est}}$$

where $\Delta m_{coastal}$ is the minimum detectable change in metal concentration in coastal water, its value is based upon the confidence limit for all the samples at the 90 % level; D is the size of the mixing ratio between fresh water and sea water (about 9 in our area); F_t is the total fresh water flux $(4 \text{ km}^3 \cdot \text{y}^{-1})$; $F_{estuary}$ is the estuary flux $(3.3 \text{ km}^3 \cdot \text{y}^{-1})$; S_m is the sources and sinks of the dissolved metal during transit through the coastal water body (we consider here the dissolved element, displays a conservative property and, as a consequence, $S_m = 0$).

The results of the calculations are shown in table 2.

Although these calculations are very crude, they prove that a very small concentration increase in the Belgian coastal area corresponds to a much larger increase in the estuarine heavy metal input corroborating the conclusions of Yeats et al (1978) that the precision with which trace metal levels in a coastal water body can be determined, is generally not high enough to detect increased levels of these trace metals due to anthropogenic activity.

In table 3, we make a comparison of our data with trace metal concentrations measured in adjacent regions. The levels in the Belgian coastal zone are increased over the minimum values in the central part of the Bight (maximum salinity area) by a factor 9 for Cu, 20 for Zn and 6 for Cd. The question arises whether we can expect an increased input from the atmosphere in our coastal area or not. Considering the data obtained at a marine platform (West-Hinder, situated at the border of our monitoring network), the global atmospheric fall-out (dry and wet) is even smaller or equal to those observed for other regions in the North Sea (Dehairs et al, 1982a). On the other hand, observations suggest an increased emission with continental wind directions and a gradual dry fall-out from land to sea (Dehairs et al, 1982b). It might be that the real fall-out in the Belgian coastal zone is underestimated comparing the measured fall-out at the West-Hinder with that on a landstation (De Blanckaert).

We found indeed differences in dry and wet fall-out, although, the total atmospheric fall-out on land is not quite different from that at sea.

Consequently, other factors should be taken into account to explain the increased concentrations in the Belgian coastal zone.

Table 2

Compositional changes required in the Scheldt estuary
to produce detectable changes in the Belgian coastal waters

		Zn	Cd	Pb	Cu
Mean concentration at the mouth of the Scheldt Estuary (Baeyens et al, 1982a)	$\mu g.l^{-1}$	11	0.39	0.93	2.6
Maximum concentration in the Scheldt Estuary (Baeyens et al, 1982a)	$\mu g.l^{-1}$	135	1.9	5	12.9
Minimal detectable change in the Belgian Coast (Δm, coastal)	$\mu g.l^{-1}$ %	1 15	0.03 25	0.51 13	0.48 22
Corresponding change in the Scheldt Estuary concentration (Δm, estuary)	$\mu g.l^{-1}$ % min–max	11 8–100	0.32 17–82	5.6 112–602	5.3 41–204
Change in estuarine metal flux	T/j	36.3	1.06	18.5	17.5

Table 3

Mean and range of dissolved concentrations of Cu, Zn, Cd and Pb for the North Sea and adjacent regions ($\mu g/\ell$)

Area	Cu	Zn	Cd	Pb	References	Anal. method
Min. values in the Southern Bight	0.2-0.3 0.5-1	0.3-0.4 2 - 4	0.02-0.03 0.1 -0.3	- -	Duinker & Nolting (1982) Dutton et al (1973)	GFAAS AAS
English East Coast (inhore)	1.4 (1.2-2.8)	6.3 (3.0-15.6)	0.5 (0.1-6.2)	-	Dutton et al (1973)	AAS
Straits of Dover	1.0 0.86 (0.06-3.6)	6-8 -	1.2 -1.6 0.14 (0.02-0.26)	- -	Dutton et al (1973) Dehairs et al (1982)	AAS AAS
British Channel	0.34(±0.27) 0.22 (0.1 -0.4) 0.46 0.23-1.29	0.78(±0.28) 0.6 (0.3-0.9) 2.0 (1.2-3.8)	0.041(±0.19) 0.01 (0.01-0.02) 0.06 <0.01-0.38	- - 0.17 <0.05-1.1	Duinker & Nolting (1982) Jones in Topping et al (1979) Preston (1973)	AAS AAS AAS
North-East Atlantic	0.26 0.05-0.80	3.0 1.4-7.0	0.04 <0.01-0.41	-	Preston (1973)	AAS
Bristol Channel	2.07 1.02-4.74	9.98 3.57-21.42	1.13 0.28-4.20	1.18 0.35-5.00	Abdullah (1972)	ASV

Area	Cu	Zn	Cd	Pb	References	Anal. method
Belgian Coastal Area	2.21 (0.5-21.8)	6.66 (1.7-23.2)	0.118 (0.025-0.98)	3.86 (0.9-13.87)	This study	DPASV pH=1 + U.V.
	0.34-2.00	-	0.024-0.11	0.1-2.6	Mart (1976)	DPASV pH=2
	0.6-2.4	-	0.1-0.4	-	Duinker & Nolting (1977)	AAS
Dutch Coastal Area	1.7 (1-2.5)	9.9 (3-20)	0.2 (0.1-0.3)		Duinker & Kramer (1977)	DPASV pH=2.7
Northern North Sea	1.0 (0.8-1.2)	1.0 (0.8-1.2)	0.03 (0.02-0.03)	-	Duinker & Nolting (1982)	AAS
	0.26 (0.1-0.9)	2.7 (1.4-4.2)	0.07 (0.01-0.17)	-	Jones in Topping (1979)	AAS
	2.7	5.7	-	1.2	Burda (1978)	X-Ray fluorescence
Western Atlantic shelfwaters	0.26	0.16	0.023	-	Bruland (1981)	AAS

The main source of water supply to the Belgian coastal zone is the Straits of Dover. However, due to the lack of sufficient reliable data in the Straits of Dover and to the rather wide scattering of the results, possible local effects such as dumping, remobilization from the sediments or effects related to increased biological activities are not evident.

From a restricted chemical point of view, extended intercalibration exercises for sampling might help to elucidate the origin and fate of trace metal levels found in the Belgian coastal waters, simply to increase the reliability of the data given by different teams.

3.1.2.– *Particulate Zn, Cd, Pb, Cu and Hg.*

The distribution of the particulate trace metal concentrations ($\mu g/\ell$) is similar to the distribution of suspended matter :

- a zone with relatively high concentrations situated near the mouth of the Scheldt estuary,
- a progressive diminution with the distance from the coast and the mouth of the Scheldt estuary outlet.

The trace metal concentrations in terms of particulate matter (dry weight ($\mu g/g$)) are distributed in a more complex way ; the results are shown in table 4. No differences between the four sectors are observed for Cu. The relative abundances of Pb and Zn are higher in sector I and III than in sector II and IV. Hg (table 5) and Cd show an inverse distribution pattern. More mercury or cadmium is adsorbed per weight-unit of suspended matter at low turbidity (zone II, most similar to an open-sea situation) than at high turbidity (zone III, zone under the influence of the Scheldt estuary). Each of these elements shows its proper behaviour. Therefore, to explain the observed distribution patterns, one must also study the characteristics of the suspended matter such as grain size, chemical and mineralogical composition as well as specific interactions between the metal and the suspended material in function of these characteristics (see e.g. the study of mercury interactions with suspended matter from the Scheldt estuary by Baeyens et al (1982).

3.1.3.– *Total and dissolved mercury.*

The spatial distribution of total mercury is completely analogous to the distribution of particulate mercury. The mean observed particulate and total mercury concentrations indicate that an important fraction of the mercury is attributed to the particulate phase and that dissolved mercury concentrations must be very low.

Table 6 shows results obtained during a cruise in May 1981.

Table 4

Mean relative abundances of trace metals in particulate matter ($\mu g/g$)

Metal	Zone	Nb	Range	Arithmetic mean		Geometric mean		Median
				$\bar{x}$	σ	$\bar{x}g$	σg	
Zn	Belgian Coast	35	5.7 – 735	94	166	55	2.5	52
	I	11	5.7 – 735	169	280	61	2.4	53
	II	12	23 – 155	57	35	49	1.7	57
	III	5	11 – 141	82	55	59	2.8	88
	IV	7	26 – 80	59	20	55	1.5	58
Cd	Belgian Coast	36	0.10–3.90	1.27	0.85	1.00	2.1	1.03
	I	11	0.65–3.15	1.32	0.88	1.08	1.9	0.95
	II	12	0.10–3.90	1.31	1.01	0.93	2.7	1.29
	III	6	0.32–1.55	0.80	0.43	0.71	1.7	0.74
	IV	7	0.50–2.45	1.55	0.76	1.35	1.8	1.80
Pb	Belgian Coast	36	3.6 –57.3	21.6	14.2	17.0	2.1	18.6
	I	11	3.6 –41.0	23.0	12.8	18.5	2.2	23.8
	II	12	4.1 –43.3	18.0	10.6	15.0	2.0	17.2
	III	6	9.4 –55.0	29.6	16.9	25.3	1.9	27.1
	IV	7	5.5 –57.3	18.4	18.5	13.2	2.3	10.5
Cu	Belgian Coast	36	4.8 –31.6	13.8	6.5	12.3	1.6	14.2
	I	11	4.8 –31.6	14.5	8.6	12.3	1.8	15.8
	II	12	6.2 –25.6	13.1	6.3	11.7	1.6	11.6
	III	6	7.7 –18.7	15.4	4.0	14.8	1.4	16.7
	IV	7	6.3 –22.1	12.4	5.4	11.4	1.5	13.6

Table 5

Relative abundances of mercury in particulate matter $(\mu g/g)$

Period	Zone III – Scheldt Estuary zone – high turbidity (A)	Zone II – open sea zone – low turbidity (B)	B/A
November 1978	2.1	4.6	2.2
October 1979	0.7	1.5	2.0
May 1980	1.0	–	–
June 1980	0.5	1.2	2.4

Measured values of dissolved mercury range between 6.2 and 24.4 ng Hg/ℓ. These results agree fairly well with those observed by Burton & Leetherland (1971) in British coastal waters ranging from 11 to 21 ng/ℓ.

3.1.4.— *Bismuth and Antimony.*

Total concentrations range between 0.08 µg/ℓ and 0.3 µg/ℓ for Sb and between non detectable amounts to 0.1 µg/ℓ for Bi (table 7). Data on Sb and Bi are scarce and comparison can only be made with results obtained with other analytical techniques and in very different geographic localities. Nevertheless, the same order of magnitude was found by Schutz (1965) in the Atlantic Ocean and by Portmann (1966) in the Irish Sea.

The data for Bi show concentrations often below detection limit (< 0.05 µg/ℓ) ; few results have been obtained on samples close to the coast and in the vicinity of the mouth of the Scheldt estuary. They might indicate that Bi diffuses from the coast and is rapidly diluted or removed by unknown processes from the water column offshore.

Table 6

Dissolved mercury concentrations in the Belgian Coastal Zone
(May 1981)

Station	ng Hg / ℓ	Salinity (‰)
15.05.120581.0950	13.5 ± 1	30.27
25.05.120581.1120	8.5 ± 0.4	31.26
35.05.120581.1210	13.3 ± 0.2	31.30
45.05.120581.1255	10.7 ± 0.3	31.62
54.05.120581.1435	6.2 ± 0.6	33.64
44.05.120581.1444	5.9 ± 1.8	32.59
34.05.120581.1650	7.9 ± 1	31.07
24.05.120581.1740	10.9 ± 0.9	30.07
14.05.120581.1830	16.9 ± 0.7	29.64
12.05.130581.0920	19.3 ± 0.1	32.99
22.05.130581.1010	20.7 ± 0.2	33.52
32.05.130581.1050	15.1 ± 0.3	33.36
42.05.130581.1140	14.4 ± 0.2	33.76
43.05.130581.1235	16.9 ± 0.4	33.52
33.05.130581.1345	24.4 ± 0.4	32.39
23.05.130581.1440	21.7 ± 0.2	31.38
13.05.130581.1500	19.5 ± 0.5	31.18
11.05.140581.0850	13.4 ± 0.1	33.20
21.05.140581.1220	6.6 ± 0.4	33.52
31.05.140581.1310	–	–
41.05.140581.1400	–	–

3.2.– Metal speciation (Zn, Cd, Pb, Cu, Sb and Bi).

Besides its very high sensibility, DPASV has another advantage (see part 1) as it allows an approach to speciation. As an illustration of this speciation approach, we provide some results obtained during a cruise in October 1979, in table 7.

Table 7

Speciation of dissolved heavy metals in sea-water (μg/ℓ)

(October 1979)

Stations	Zn			Cd			Pb		
	pH in situ I	pH acid IIa	UV III	pH in situ I	pH acid IIa	UV III	pH in situ I	pH acid II	UV III
11	0.15	0.95	2.97	0.12	0.18	0.30	0.05	1.10	2.21
21	0.21	2.70	4.15	0.03	0.08	0.14	0.22	1.00	2.20
31	0.10	1.10	3.37	0.02	0.14	0.25	0.07	0.40	1.13
41	0.10	0.70	6.37	0.02	0.05	0.27	0.05	0.61	1.03
12	0.50	1.10	6.10	0.05	0.05	0.20	0.10	0.30	3.15
22	0.75	1.90	3.40	0.08	0.08	0.16	0.05	0.30	1.40
32	0.36	1.30	2.40	0.04	0.05	0.10	0.05	0.35	1.00
42	0.10	2.25	4.16	0.02	0.06	0.13	0.05	0.36	3.02
13	0.50	1.23	2.38	0.06	0.10	0.26	0.14	0.75	1.31
23	0.30	1.50	2.05	0.04	0.04	0.06	0.11	0.80	1.22
33	0.50	2.12	3.10	0.05	0.10	0.15	0.16	0.80	1.80
43	0.20	1.20	3.50	0.05	0.08	0.18	0.08	0.20	1.60
14	0.54	1.42	1.70	0.08	0.08	0.10	0.16	0.44	1.20
44	0.30	2.00	4.30	0.03	0.03	0.06	0.05	0.30	1.80
15	0.80	4.50	7.90	0.02	0.08	0.18	0.05	1.20	1.80
25	0.30	5.08	5.80	0.05	0.06	0.13	0.07	1.54	3.90
35	0.50	3.65	6.70	0.02	0.10	0.16	0.08	1.23	3.40
45	0.30	2.25	7.18	0.02	0.05	0.14	0.08	1.88	3.23

I   = free ions + very labile complexes
IIa = free ions + weak organic and inorganic complexes (for Sb, IIa = Sb^{III})
IIb = Sb^V + Sb^{III}
III = total concentration

Table 7

Speciation of dissolved heavy metals in sea-water (μg/ℓ)

(October 1979)

(continued)

Stations	Cu			Sb			Bi	
	pH in situ I	pH acid IIa	UV III	pH acid IIa	pH acid+SO₂ IIb	UV + SO₂ III	pH acid IIa	UV III
11	0.11	1.05	1.30	N.D.	0.17	0.17	N.D.	N.D.
21	0.20	1.14	1.85	N.D.	0.08	0.10	0.14	0.20
31	0.10	0.25	0.82	N.D.	0.12	0.14	N.D.	N.D.
41	0.06	0.12	0.70	N.D.	0.12	0.12	N.D.	N.D.
12	0.15	0.40	1.65	N.D.	0.10	0.15	N.D.	N.D.
22	0.25	0.60	1.20	N.D.	0.14	0.20	N.D.	0.08
32	0.10	0.40	0.80	N.D.	0.10	0.15	N.D.	N.D.
42	0.10	0.10	0.50	N.D.	0.12	0.15	N.D.	0.07
13	0.20	0.40	0.80	N.D.	0.17	0.25	N.D.	0.05
23	0.60	0.90	1.20	N.D.	0.12	0.18	N.D.	N.D.
33	0.30	0.80	1.60	N.D.	0.05	0.08	N.D.	N.D.
43	0.06	0.20	0.60	N.D.	0.15	0.25	N.D.	N.D.
14	0.30	0.84	1.32	N.D.	0.26	0.30	N.D.	0.05
44	0.10	0.30	1.20	N.D.	0.18	0.28	N.D.	N.D.
15	0.12	1.50	2.90	N.D.	0.20	0.23	N.D.	0.10
25	0.54	1.12	1.90	N.D.	0.25	0.26	N.D.	0.08
35	0.15	0.80	0.80	N.D.	0.16	0.20	N.D.	N.D.
45	0.15	0.80	1.42	N.D.	0.10	0.25	N.D.	N.D.

I = free ions + very labile complexes

IIa = free ions + weak organic and inorganic complexes (for Sb, IIa = Sb^III)

IIb = Sb^V + Sb^III

III = total concentration

The fraction detected in step I at in situ pH refers rather arbitrarily to ionic species since very labile complexes (probably inorganic) can also be involved. The difference between the results obtained in step IIa (acid pH) and I corresponds to weak complexes. Finally, step III gives us the total concentrations. The difference between III and IIa corresponds to strong complexes. This concerns Zn, Cd, Pb and Cu. The content of Zn, Cd, Pb and Cu involved in organic complexes represents frequently an important fraction of the total concentration but shows strong variations from one sampling site to another : 12 to 87 % for Zn, 20 to 80 % for Cd, 33 to 87 % for Pb and 20 to 83 % for Cu. More results are necessary to look at possible links with other important water quality parameters such as nutrients, DOC, Chl.A and processes such as primary production, grazing, etc.

Sb and Bi cannot be measured at in situ pH because of hydrolysis of their salts under these conditions. As a consequence, the ionic form cannot be dissociated from weak complexes and step IIa of table 7 gives the sum of the two forms. The IIb data for Sb corresponds to the sum of Sb^{III} and Sb^{V}. The results for Sb lead to the conclusion that Sb^{V} is the main dissolved form of this metal. The percentage of Sb complexed by organic matter can be estimated to vary between 20 and 40 % of the total concentration.

3.3.— *Compartmental distribution of Zn, Cd, Pb, Cu and Hg.*

Up to 90 % of the total content of Zn, Cd, Pb, and Cu is found in the dissolved phase (table 1). This may suggest that the largest part of these metals are transported out of the Belgian coastal area and that only a minor fraction is involved in the sedimentation cycle. The behaviour of mercury however is completely different : the dissolved phase represents only about 30 % of the total content in the Belgian coastal waters. Practically all the mercury is associated with the suspended matter in the Scheldt estuary zone (zone III). The dissolved mercury-particulate mercury ratio increases with the distance from the coast. This seems quite acceptable since in the very turbid Belgian coastal waters, dissolved mercury has been scavenged by particulate suspended matter (Reimers, 1974 ; Baeyens et al, 1977, 1979a, 1979b and 1982) while mercury data for open ocean regions reveal that, due to the very low particulate matter content, the dissolved phase is the major compartment.

4.– Discussion.

Little information is available about the distribution of Bi in the explored zone. But, the present results indicate that the distribution of Bi along the coast is primarily a coastal problem. The Bi is possibly derived entirely from domestic effluent (including the estuary), as there are no known large natural and industrial Bi sources in the region.

Dissolved mercury shows a smooth decreasing dependence on the distance from the coast.

The spatial distribution patterns of total dissolved Zn, Cd, Pb, Cu and Sb exhibit no analogy with those of salinity. It is most probably determined by the intensity of life processes and the cumulative effect of many small or large sources of contamination (ship traffic, industrial dumping, estuarine area, Dover straits inputs as well as outputs depending on residual currents).

Data on "organically bound" metal ions (representing up to 80 % of the total dissolved metal content) show effectively that organic binding may play a major role in "controlling" the concentrations of these elements, at least in this zone characterized by high biological productivity. It must however be clear that the survey described here are limited in time and space and that different patterns might appear if long time averages (many years) are taken (see part 6).

The availability of the metals to living cells or adsorption by particulate matter obviously affect the ratio of the different metal species (ionic, inorganic and organic fractions).

Further evidence for this hypothesis is the observed correlation of the different fractions of metal concentrations with an indicator of productivity e.g. chlorophyll concentrations and ^{14}C uptake.

Particulate metal distributions are similar but opposite to the salinity gradient and follow clearly the turbidity distribution.

The dissolved phase (free metals, inorganic and organic soluble species) seems to be the main compartment for heavy metals in the explored region, except for mercury.

Our results seem to be comparable with those found in other coastal areas.

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Part 3

THE ATMOSPHERE AS A TRANSPORT ROUTE OF HEAVY METALS
TO THE SEA

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Abstract.

   The Cu, Zn, Cd, Pb, Hg, Fe and Mn contents of the marine aerosols and also the volatile Hg fraction over the Southern Bight of the North Sea were studied from a maritime platform in the Belgian coastal area. Observed average annual concentrations of Cu, Zn, Cd, Pb, Mn and Fe are similar to those found by others in the North Sea area during different periods indicating a state of homogeneity of the aerosol burden in this area.

   However, significant month to month variations in concentrations were observed and could be related to the prevailing winddirections and the magnitude of the precipitations.

   Winddirections within the continental sector (< 280°, > 5°) viewing Belgium and France, resulted in higher concentrations at sea (from 1.9 for Cu to 4.3 for Mn) than during marine conditions (winddirection within sector > 280°, < 5°). Furthermore, within this continental sector a positive relationship of the concentration of Zn and Cu with the windvelocity is observed, while for volatile Hg the inverse is true.

   A more efficient transport of the larger anthropogenic aerosol and a dilution of the volatile fraction with increasing windvelocities are respectively invoked to explain these observations.

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Sea surface microlayer concentrations of particulate and dissolved Cu, Cd, Zn, Pb and Hg in screen samples are observed to be systematically higher than watercolumn concentrations.

However, enrichments are relatively small and remain within one order of magnitude, excepted for particulate Pb and Cd for which enrichment factors of approx. 30 are observed.

In this area of the North Sea, microlayer enrichments of particulate trace metals can almost entirely be explained by dry deposition, as is indicated by the similarity between the dry deposition flux onto the sea surface and the flux of settling particles leaving the microlayer. For the microlayer excess of the dissolved phase, concentration from the watercolumn of heavy metals complexed to humic material is invoked. This assumption is supported, at least for Cd, by the observed seasonal covariation of dissolved Cd and DOM in the microlayer.

1.– Introduction.

For several anthropogenic and terrigenic elements in the open ocean, the atmosphere is an important if not a main route of transport.
For the North Atlantic Ocean it was observed that Pb (Buat-Menard and Chesselet, 1979; Schaule and Patterson, 1981) and Se, Al, Sc, Th concentrations (Buat-Ménard and Chesselet, 1979) in the watercolumn, can be mostly explained by fall-out from the atmosphere.
For semi-enclosed basins such as the Mediterranean Sea and the North Sea under direct impact of river run-off, atmospheric input must still be regarded as a main source of heavy metals. (Chesselet et al., 1978;   Cambray et al., 1975 and 1979; Dehairs et al., 1982).

During the past decade aerosols have been studied in the North Sea area, from land-based stations surrounding the North Sea Basin and from a single maritime platform (Peirson et al., 1974; Cambray et al., 1975 and 1979; Kretzschmar and Cosemans, 1979). For the southernmost section of the North Sea, including the Belgian coastal area, no data exist concerning marine aerosols sampled at sea. Therefore a sampling campaign was started in the framework of the National R.D. program "AIR" (Dedeur-waerder et al., 1981) in order to study (1) the heavy metal load in the marine atmosphere above the Southern Bight and the impact of the surrounding countries; (2) the importance of the atmosphere as a transport route of heavy metals to the sea; (3) the impact of atmospheric fall-out on the watercolumn and the sea-surface microlayer composition and (4) the importance of the enriched sea-surface microlayer as a source of material-output to the atmsophere. The discussions pertaining to the impact of atmospheric fall-out on the watercolumn composition and of point (4) are given in Dehairs et al. (1982).
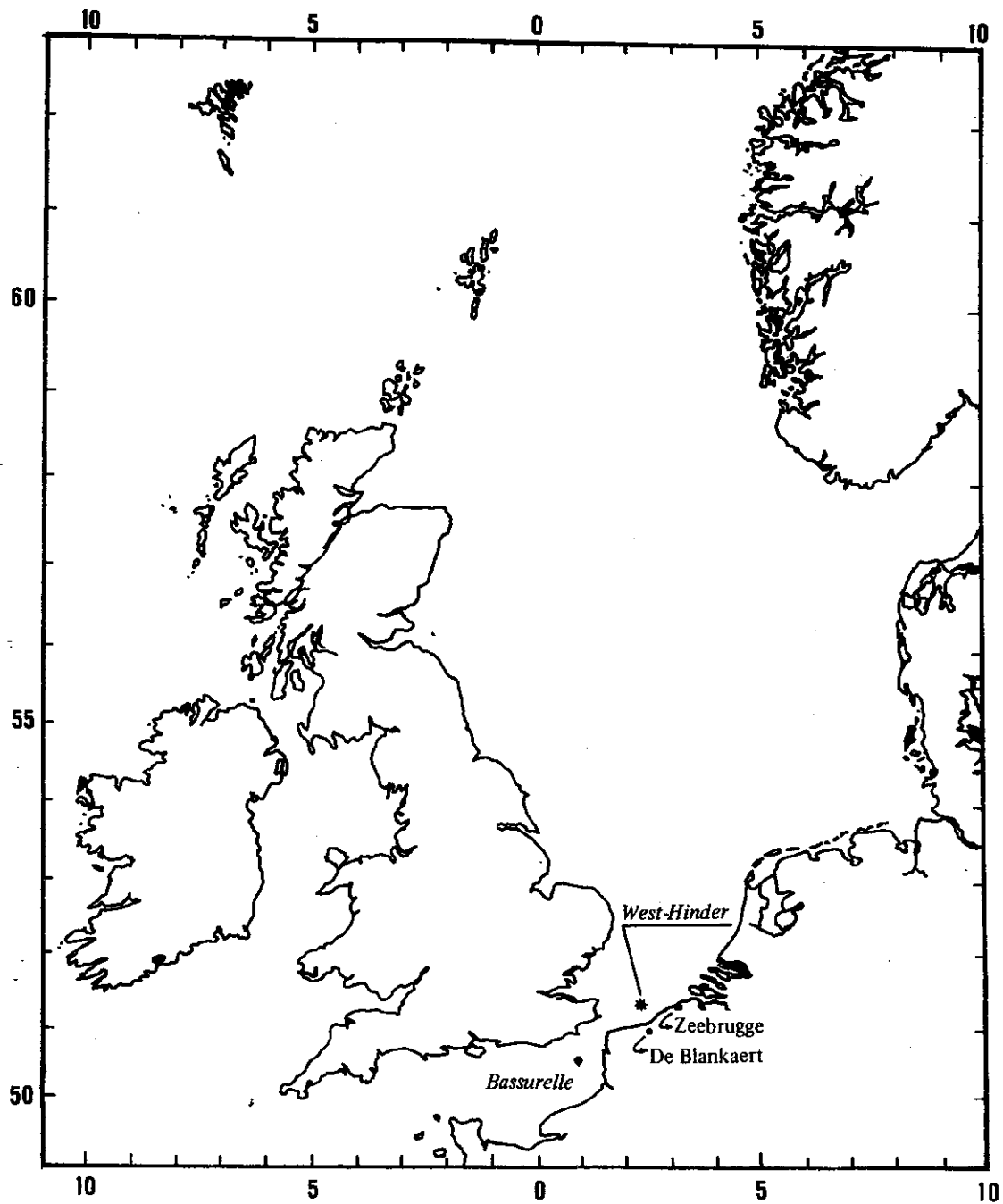
fig. 1.

Position of both maritime sampling platforms.
West-Hinder (51° 23' 30" N — 2° 21' 30" E)
Bassurelle (50° 33' 24" N · 0° 54' E)

On from January 1980 the atmosphere above the Southern Bight was sampled on an intermittent basis for the study of several heavy metals (Cd, Cu, Hg, Pb, Zn, Mn, Fe). Besides these heavy metals, aerosol-concentrations of Na and Al were also studied. The sampling was done mainly from the Light-Vessel "West-Hinder" (position: 51° 23:5N - 02° 21:5 E; see Figure 1). On a few occasions during 1981, samplings were done from the R.V. "Mechelen", anchored in the vicinity of the Light-Vessel and also off Boulogne in the Straits of Dover (Bassurelle light-buoy, position: 50° 33:4 N - 00° 54:E; Figure 1).

Both, total aerosol samples and size fractionated aerosol samples were taken. As concerns Hg, both the particulate and the gaseous phases were sampled. The sea-surface microlayer was sampled with the Garrett-screen technique. The complete description of the sampling and the analysis methods is given in Gillain et al., (1982, this volume).

2.- Results.

2.1.- *The atmosphere.*

2.1.1.- *Comparison of our heavy metal data with those obtained during other studies in the North Sea area.*

In table 1 our heavy metal data are compared with those obtained by others. (Peirson et al., 1974; Cambray et al., 1975; Kretzschmar and Cosemans, 1978).

Although our data show systematically lower values, it is seen that all values agree well within an order of magnitude with each other (largest discrepancy =factor 3) and this despite differences in geographical locations, sampling period and sampling methodology. This reflects a state of homogeneity, both in time and space of the aerosol burden in the North Sea troposphere.

Our data are closer to those of Cambray et al. (1975), than of Peirson et al. (1974), although it is only the latter authors who present data which were also collected at sea. Despite the fact that the West-Hinder sampling station is close (about 40 km) to the sampling platform of Kretzschmar and Cosemans. (1978) on the pier in Ostend, differences in concentrations are the largest, excepted for Cu. An impact of local sources, due to the proximity of the city of Ostend, is thought to induce the systematically higher values found by the latter authors.

This is emphasized by the fact that a good agreement exists between their data and ours for Cu, Cd, Pb and Zn in the marine sector (> 280°, < 5°), as shown in table 2 (see point 2.1.2 below).

Table 1

Comparison of our mean aerosol values (geometric means) for the West-Hinder site
with literature data
All values in ng/m^3

Work	Cu	Zn	Pb	Cd	Fe	Mn
This study	6.5	87	83	2.7	250	14.6
(1) Peirson et al. (1974)	21	156	150	-	337	22
(2) Cambray et al. (1975)	9.4	101	121	-	312	18
(3) Kretzschmar and Cosemans (1978)	13.7	182	176	4.1	802	42.6

(1) Data for a gas platform in the North Sea.

(2) Arithmetic mean values of the data for four land-based stations, surrounding the North Sea (1972-1973).

(3) Mean values of the data obtained for a five-year sampling period on the Ostend pier (1972-1977); geometric means of the data in their table 2.

(-) No data.

Table 2

Geometric mean elemental concentrations for aerosols
sampled during marine and continental wind conditions
Concentrations in ng/m^3
West-Hinder station

Conditions	Na	Al	Cu	Zn	Pb	Cd	Fe	Mn	Hg gaseous (15 samples) [*]	Hg part. (8 samples) [*]
"Marine" sector (> 280°, < 5°)	2039	89	3.9 (5.9)	36 (58)	53 (57)	1.8 (1.9)	98.6 (266)	5.2 (11.2)	5.4	0.07
"Continental" sector (< 280°, > 5°)	1734	141	7.4 (17.5)	107 (253)	121 (243)	3.4	349 (1099)	22.2 (62.4)		

[*] For Hg no distinction was observed between the concentrations for samples taken during "marine" and "continental" conditions.

( ) Kretzschmar and Cosemans (1978) values; see text.

2.1.2.— *Element concentrations in marine aerosols : variable influence of wind direction and precipitation.*

Table 2 demonstrates the dependency of the element concentrations from the prevailing conditions of wind direction. With the exception of Na, the concentrations measured in conditions of wind blowing from the continent (arbitrary sector < 280° and > 5°) are higher by a factor 1.9 (Cu) to 4.3 (Mn), than the concentrations measured in conditions of wind blowing from the marine sector (arbitrary sector > 280° and < 5°). This situation reflects the direct impact of the land-based anthropogenic pollution upon the aerosol composition of the marine atmosphere.

In figure 2 are plotted the month to month variations we observed for the year 1980. It appears that for all elements the highest concentrations are observed in February. Concentrations decrease from February to April, are still low in July and increase slightly during August and October.
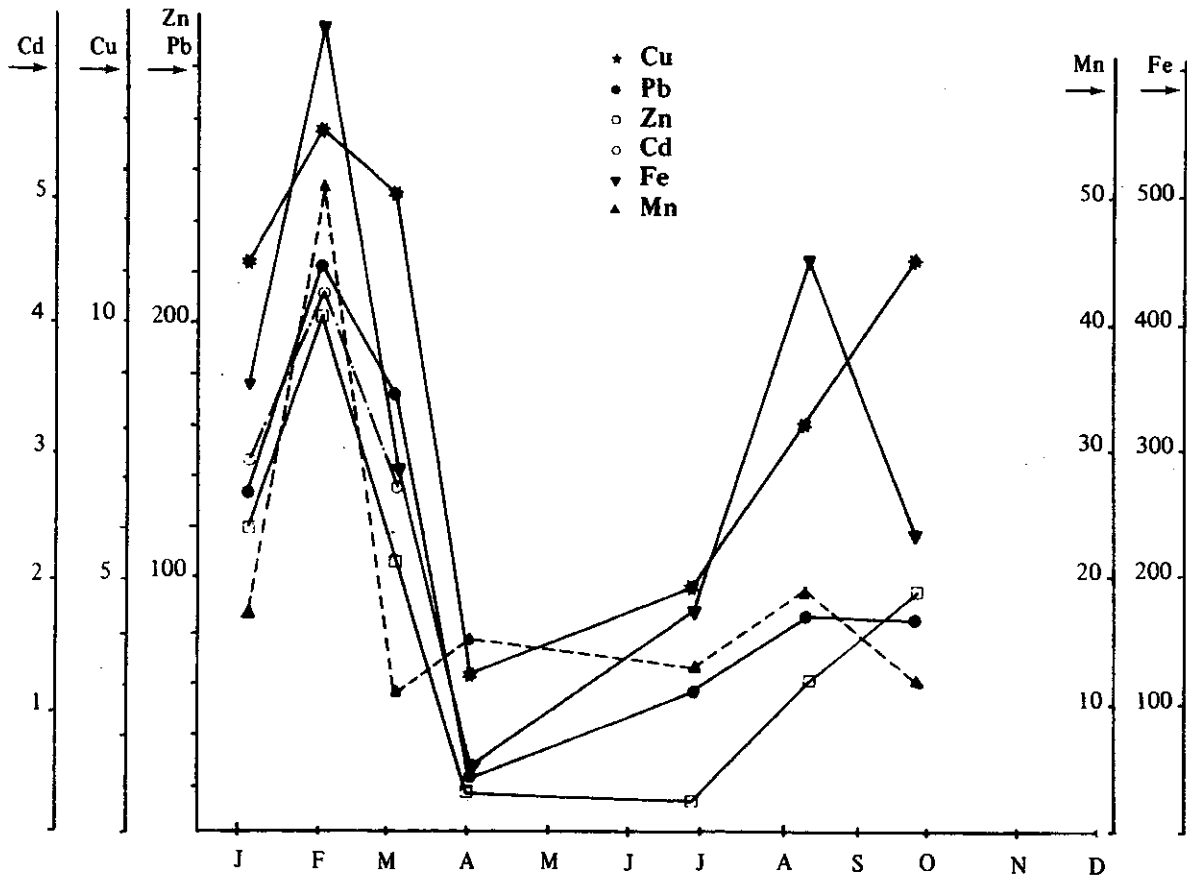
fig. 2.

Monthly concentrations for Cu, Pb, Zn, Cd, Fe and Mn in aerosols at the West-Hinder site.
All values in ng/m³   (1980 data)

In figure 3, we have plotted the time-weighed average wind-directions for each month recorded during sampling. Assuming a constant rate of aerosol production, it then appears that the low concentrations in April can be explained by the presence of "clean" air masses, coming from polar regions (mean sector : 359°).
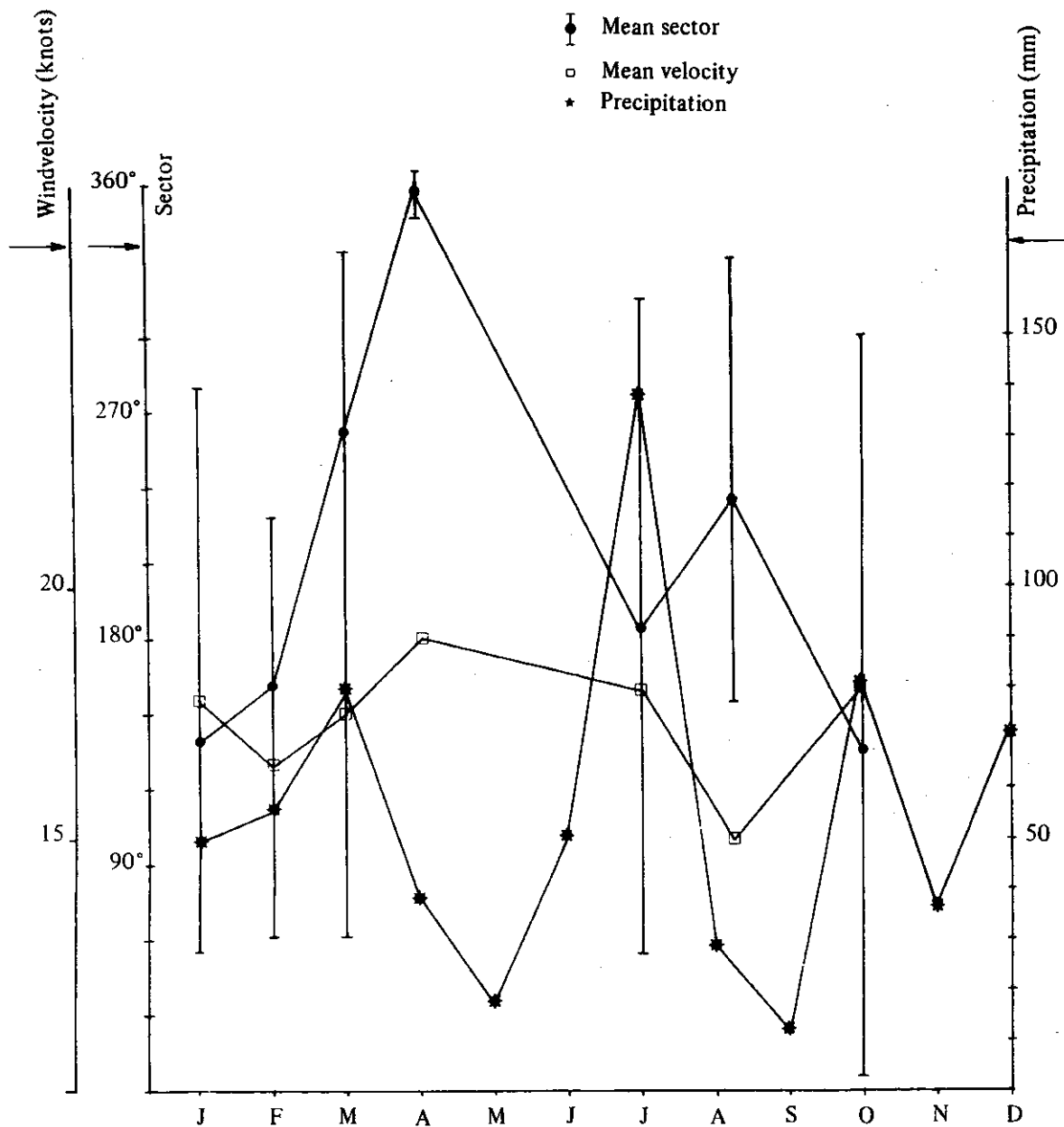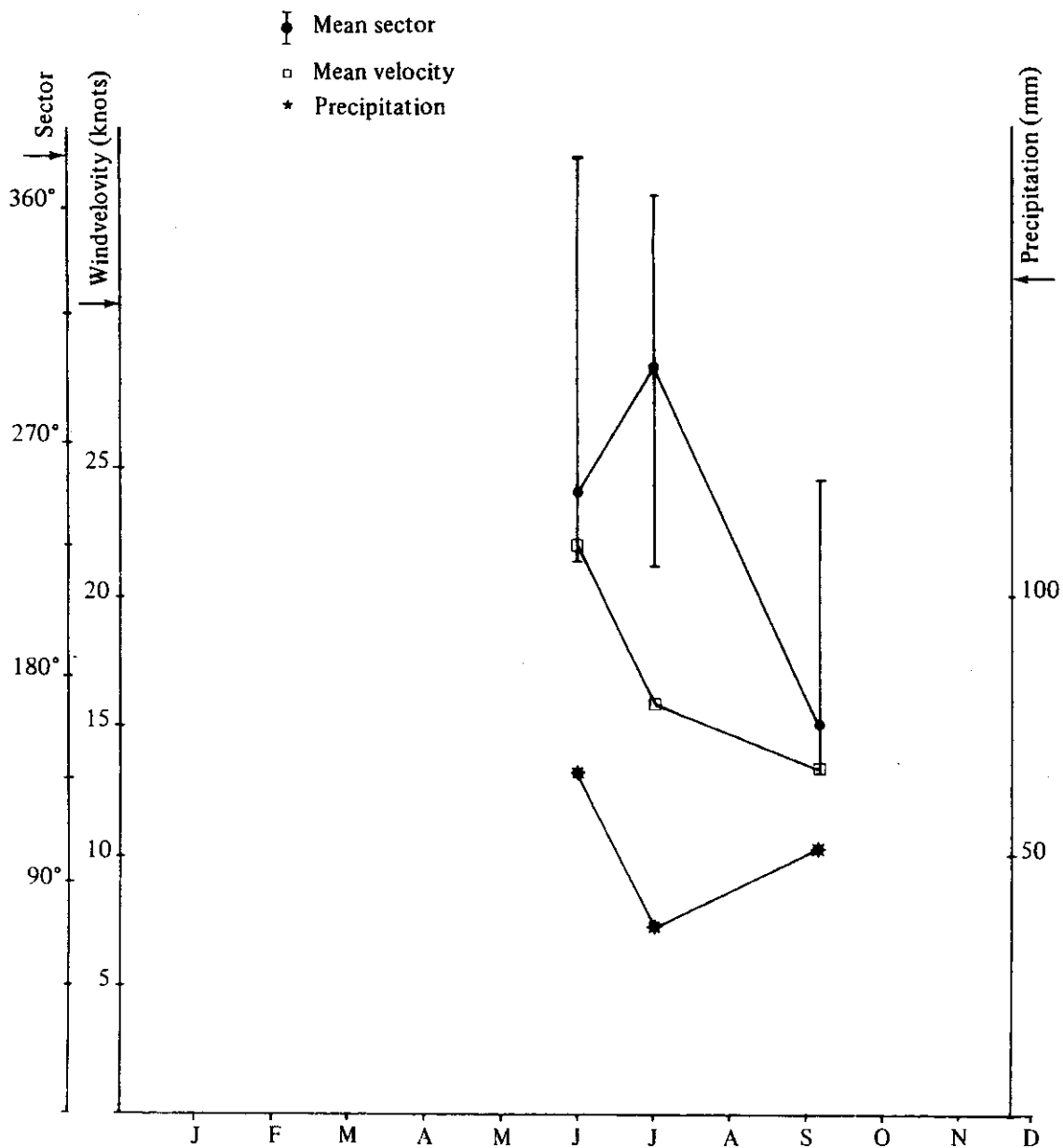

fig. 3.

Monthly average winddirections, windvelocities and precipitation at the West-Hinder site.
(1980 data)

The high concentrations of January and especially of February coincide with winddirections in the continental sector. For July, August and October, winddirections must be considered as continental too. Although for these months concentrations tend to increase again, they do not reach the values of January.

In figure 3, we also have plotted the monthly precipitations recorded for 1980 on the pier of Zeebrugge (data from "Regie der Luchtwegen"). This pier extends several hundred meter into the sea and therefore, the observed precipitation values should be the closest to the real values at sea. It then appears that the high precipitation during July (the highest observed for 1980) and the resulting frequent washout of the atmosphere, can explain the relatively low heavy metal concentrations which are observed, despite a prevailing continental winddirection.
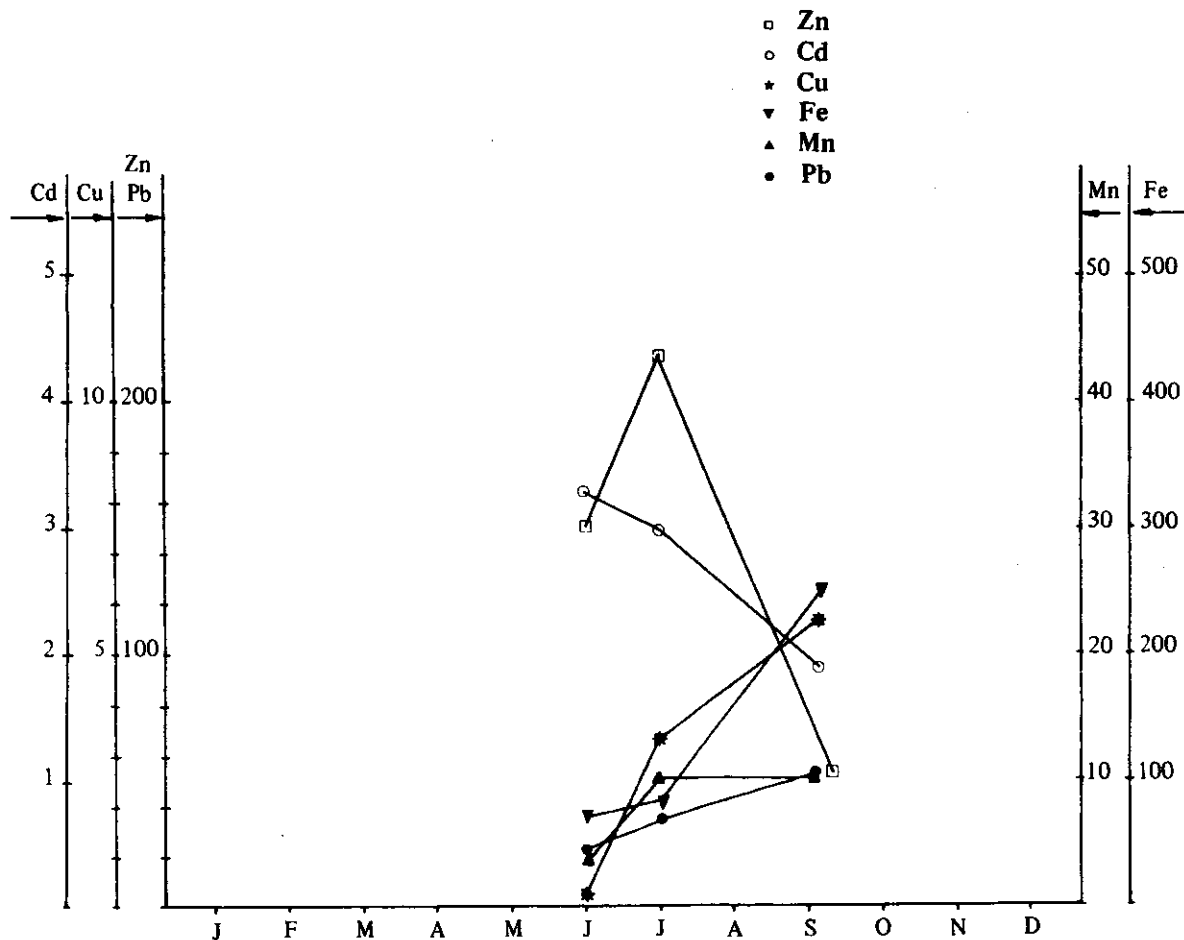
fig. 4.

Monthly concentrations for Cu, Pb, Zn, Cd, Fe and Mn in aerosols at the West-Hinder site.
All values in ng/m³   (1981 data)

In figure 4 are given the average monthly heavy metal values we observed for 1981. In figure 5 are given the corresponding average monthly winddirections and windvelocities observed on board and the precipitation observed in Zeebrugge. Heavy metal concentrations are similar (Fe, Mn, Zn) or lower (Pb and Cu) than the 1980 concentrations for the same period (figure 2).

fig. 5.

Monthly average winddirections, windvelocities and precipitation at the West-Hinder site.
(1981 data)

Although less clear than for the 1980 data, the impact of winddirection and precipitation on the heavy metal content of the atmosphere can also be discerned here. It is seen from Figures 4 and 5 that the increases of Pb, Cu, Mn and Fe from June, over July to September, coincide either with a reduction of the precipitation and a resulting reduction of atmosphere washouts, or a prevailing continental winddirection. However, in none of the cases are these factors acting in concert. For Zn a maximum concentration is observed for July, while Cd decreases from June to September. The latter events can not directly be related with the prevailing meteorological conditions.

2.1.3.— Effect of wind velocity on local aerosol composition.

When considering only those 1980 samples we collected with winddirections within the sector Gravelines (France) to Nieuw-poort (Belgium) (sector <230° and >130°), which covers the important industrial center of Dunkirk, we observed a linear relationship between some heavy metal pollutants and the wind-velocity.

Indeed, for this sector higher windvelocities result in higher Zn and Cu concentrations at the West-Hinder site (figures 6 and 7). This specific relationship of heavy metal content and wind-velocity is not observed for Pb, which shows no significant relationship between concentration and windvelocity.

For Hg in the gas-phase we observed an inverse relation-ship between windvelocity and concentration. For *all* samples taken, (the sampled sector was ≤293° and ≥45°) concentrations of gaseous mercury tend to decrease with increasing windvelocity (figure 8). No such dependency from the windvelocity exists for particulate mercury.

For Cu and Zn, a plausible explanation is that these pol-lutants are emitted by relatively nearby pointsources. High windvelocities can result in a more efficient transport of the H.M. pollutants away from the emission source by delaying the fall-out of the larger particles. Some evidence for this is given by the data for 3 impactor samples taken in the same continental sector (<230° and >130°), during the same period as the TPM samples.
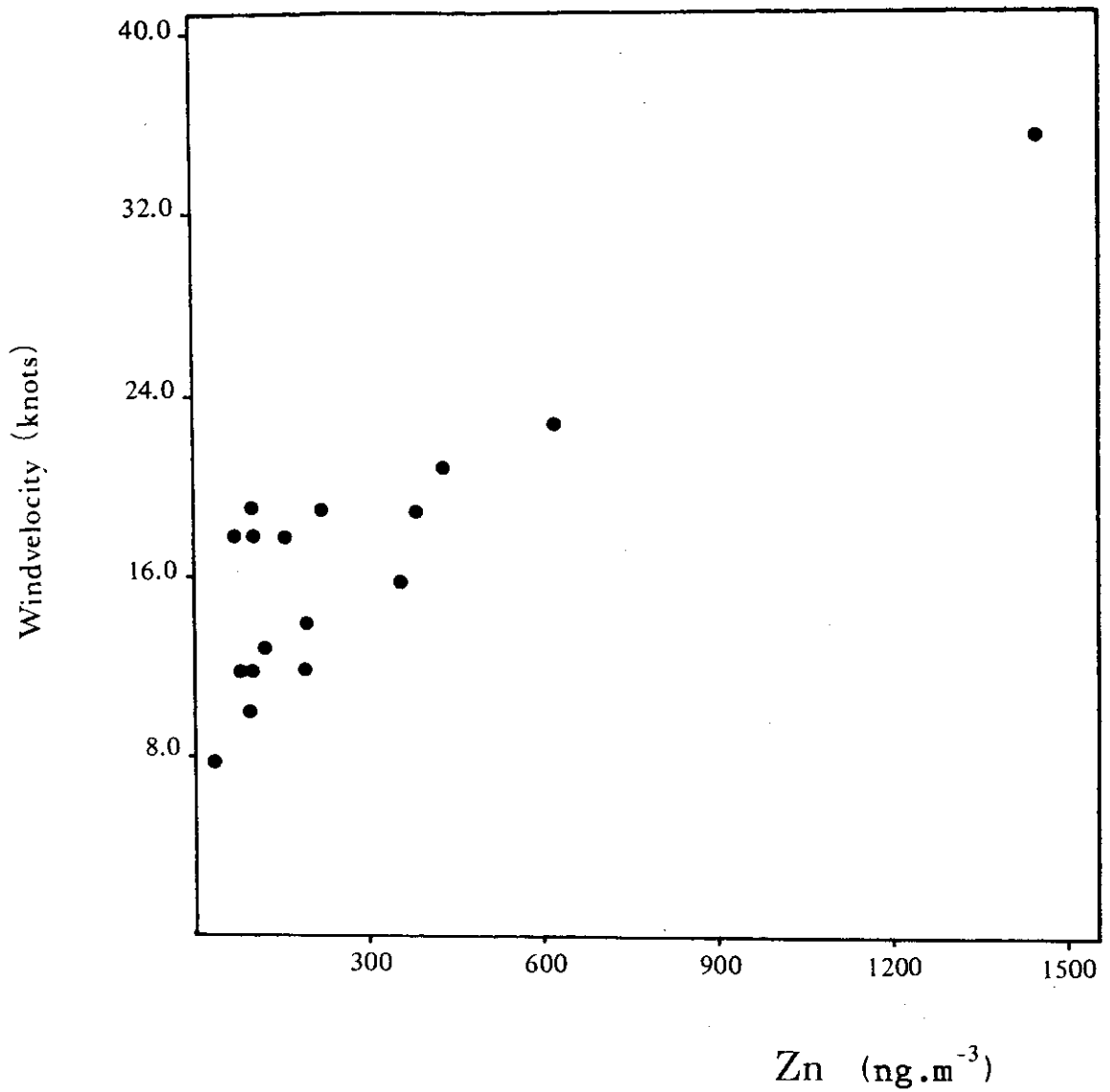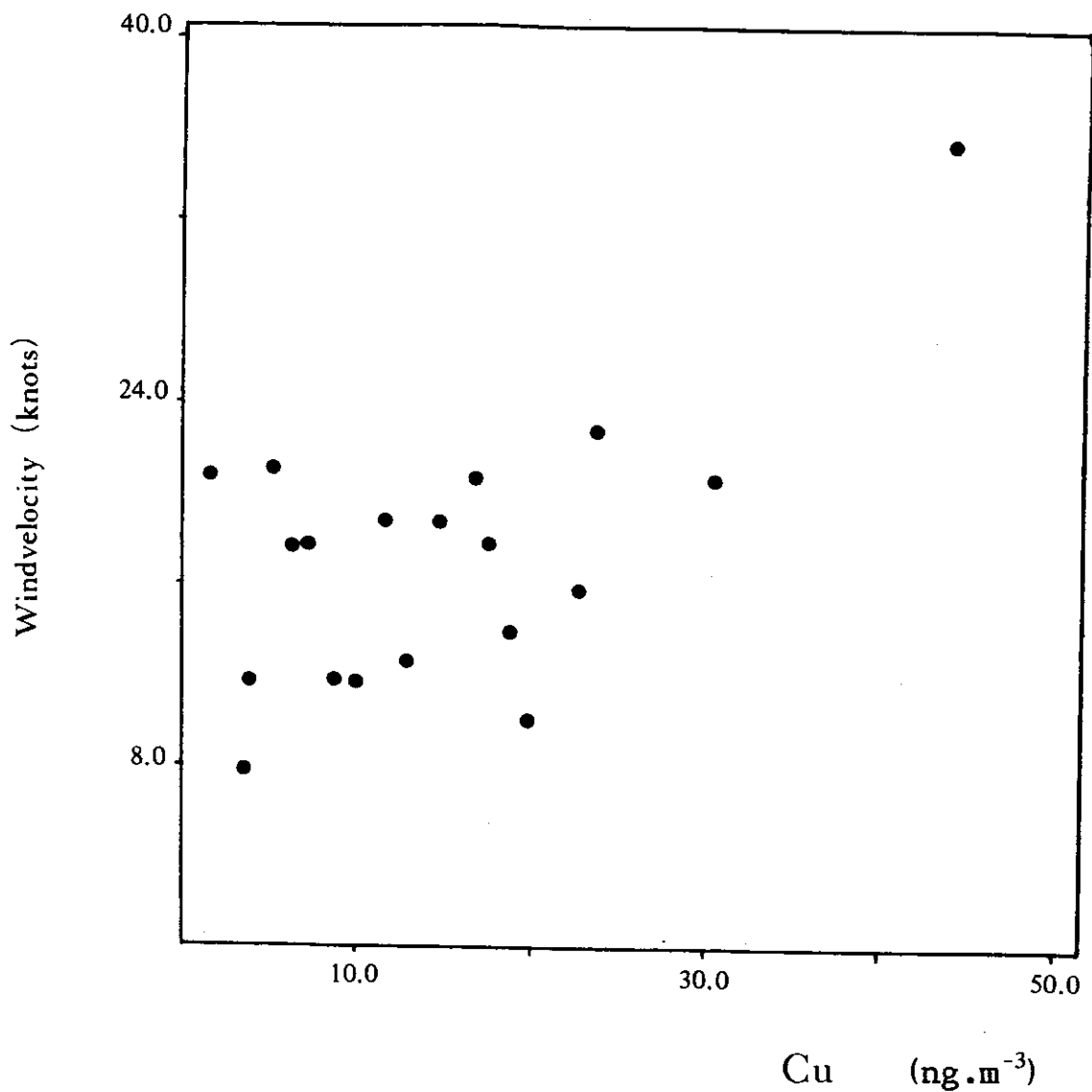
fig. 6.

West-Hinder site : dependency of the zinc concentrations on windvelocity
for winds blowing from the continent (sector $< 230°$; $> 30°$)

For Cu a small but continuous increase of the M.M.D. value
is observed for windvelocities increasing from 10 to 19 knots
(Table 3). For Zn the increase is much more abrupt and coincides
with a windvelocity increase from 10 to 15 knots (Table 3).
M.M.D. values of Pb on the contrary show no change between 10
and 15 knots, and a small decrease between 15 and 19 knots.

fig. 7.

West-Hinder site : dependency of the copper concentration on windvelocity
for winds blowing from the continent (sector $< 230°$; $> 30°$)

For Cu and Zn a sharp fall-out gradient from the land to the sea is then to be expected in the very coastal area. For Pb , its production by a great number of sources on land, such as fuel combustion by cars, can preclude the sensing at sea of local point sources.

For gaseous Hg , the inverse relationship with windvelocity is believed to reflect the effect of dilution.
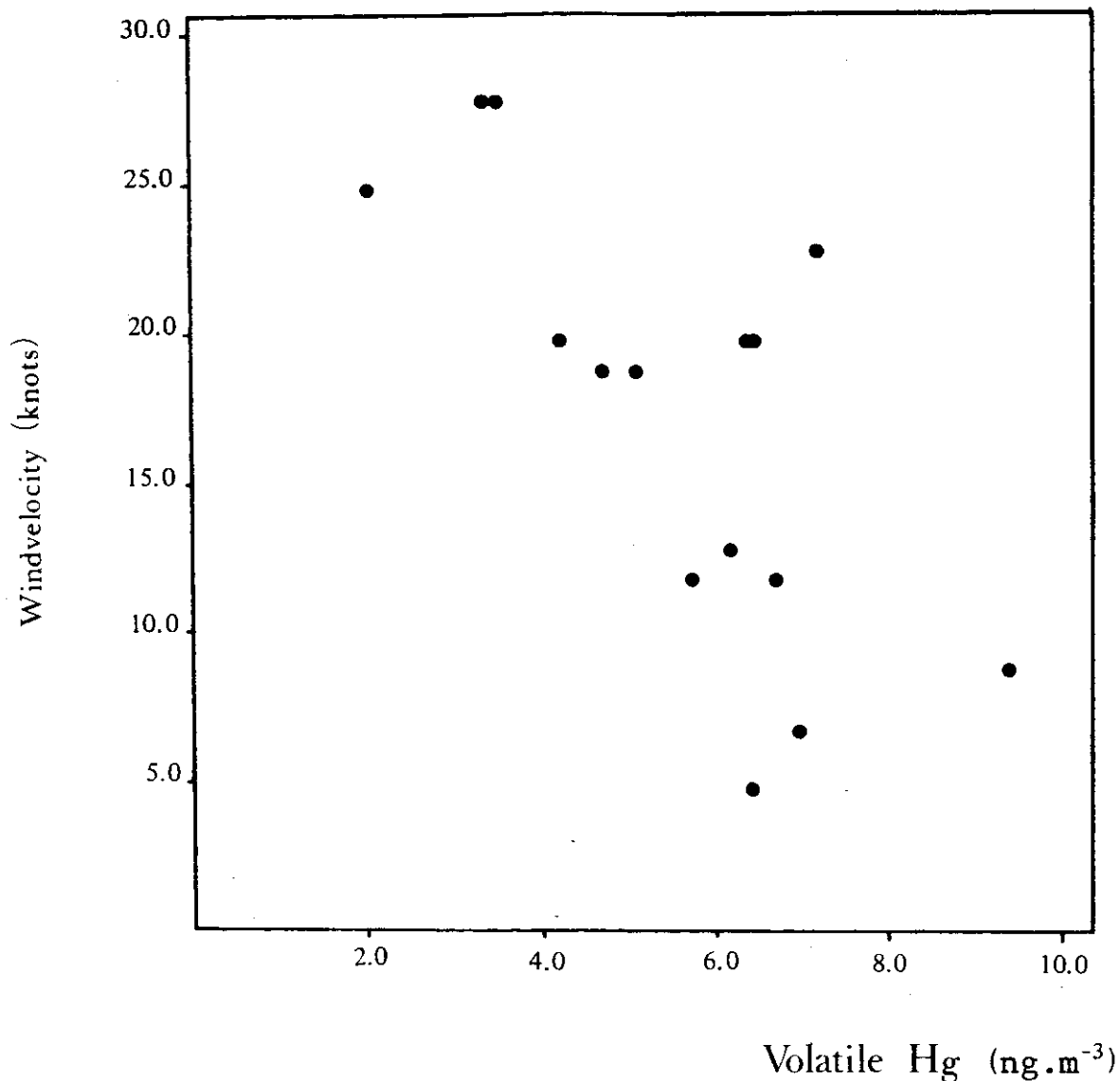
fig. 8.

West-Hinder site : dependency of the volatile Hg concentration on the windvelocity.
(Sampled sector : < 293° ; > 45°)

It thus appears that high windvelocities can result in increased concentrations of some heavy metals in the particulate phase by favoring the long range transport of the larger particles (the case of Zn and Cu), while for the gaseous phase (Hg) and most probably the smaller aerosols, high windvelocities result in smaller concentrations by the effect of dilution.

Table 3

Mass median diameter (M.M.D.) in function of wind velocities
for winds blowing from the continent (sector < 230° ; > 130°)
Cascade impactor samples (1980)
West-Hinder station

Sector (mean)	Velocity (mean) [knots]	M.M.D. in μm		
		Cu	Zn	Pb
154°	10	0.85	0.40	0.69
135°	15	0.90	0.95	0.68
175°	19	1.00	0.85	0.58

M.M.D.: Mass Median Diameter.

2.2.— *The sea-surface microlayer.*

2.2.1.— *The heavy metal enrichment in the sea-surface microlayer.*

The mean values (geometric means) for the microlayer (ML) and bulk sea-water (BSW) concentrations at the West-Hinder and Bassurelle sites are given in table 4. Enrichments in the microlayer are expressed as fractionation factors, being the ratios of the microlayer over the watercolumn concentrations. For the dissolved phase, enrichments remain within one order of magnitude. Enrichment is highest for Cu (FF = 8.1) and lowest for Hg (FF = 1.6).

For the particulate phase enrichments are highest for Pb (FF = 24) and Cd (FF = 30) as a result of the very low values we observed in bulk seawater. Indeed, particulate Pb and Cd in the watercolumn are lower by a factor 10 and 100 than the values observed in more coastal regions (Decadt et al., 1982). With exception of the particulate Pb and Cd cases our micro-layer enrichment values for the dissolved and particulate phases are similar to those observed by Hunter (1977) in the North Sea.

Table 4

Mean heavy metal concentrations in the microlayer and the bulk seawater
for samples taken during 1980 and 1981 at the West-Hinder and Bassurelle sites (fig. 1)

Enrichments are given by the fractionation factors (FF) being the ratios of
the concentrations in the microlayer (ML) over those in bulk seawater
(BSW); BSW data concern only samples taken during the ML-sampling
campaigns.

Element (number of samples)	Dissolved phase $\mu g. \ell^{-1}$		Particulate phase $\mu g. \ell^{-1}$		FF Dissolved	FF Particulate
	ML	BSW	ML	BSW		
Cu (17)	2.99	0.37	0.61	0.09	8.1	6.8
Zn (2)	17.31	3.65	8.65	1.29	4.7	6.7
Pb (Ndiss.=2) (Npart.=17)	2.22	0.59	0.99	0.04	3.8	25.0
Cd (17)	0.38	0.10	0.120	0.0004	3.8	30.0
Hg (12)	0.040	0.025	0.009	0.004	1.6	2.2

2.2.2.– *A possible relationship between heavy metal enrichment in the microlayer and biological activity.*

In order to verify if heavy metal enrichments in the micro-layer are due to the biological activity, we have compared the dissolved heavy metal distributions in the microlayer with the one of dissolved organic carbon (DOC).

DOC was measured on the same samples analyzed for heavy metal content. This was done by coulometric determination of CO_2, after combustion of the dissolved organic matter (DOM) at 900 °C in an oxygen flow.

Prior to this, the DOM was preconcentrated by ultrafiltration of 1 to 2 ℓ sea-water through a 500 dalton membrane. The preconcentrated samples were acidified and bubbled with Ar to eliminate the alkalinity.

The spring and the summer samples are characterized by the presence of a volatile component detected during the evaporation of the sample at 120°C. At 900°C these samples contained a minor fraction of non-volatile DOM. The autumn samples contained only this non-volatile DOM fraction.

It was observed that for most microlayer samples (13/14), dissolved Cd and the non-volatile DOC fraction defined above are positively related (figure 9).

Figure 9 shows that the highest DOC and dissolved Cd concentrations are found in the spring (April) and also in the summer (June), while the smallest values are observed for the autumn (September) samples. While for Pb and Zn no sufficient data have been obtained up to now to check a possible relationship with the DOC content, for dissolved Cu this relationship does not exist.

Evidence thus exists at least for Cd, that the microlayer enrichment is sustained by the biological activity and therefore is subject to seasonal fluctuations.

Up to now, not much is known about the nature of this non-volatile DOM component. However, it is believed that it consists of humic material (i.e. fulvic acid + humic acid). Evidence for this is given by: 1) the yellowish color of the ultra-filtration concentrate, pointing towards the presence of "gelbstoffe" (see f.i. Hunter and Liss, 1981); 2) the high correlation between absorption at 254 nm and the DOC content.

It was furthermore observed that the near totality of the absorption at 254 nm is due to the presence of an acid soluble fraction, such as fulvic acid. This acid soluble fraction was separated from the acid insoluble humic acids, by passing the ultra-filtration concentrate over a Dowex 50 X 12 (20-50 mesh size) resin in the acid form and eluting with aq. dest.; the acid insoluble fraction was thereafter eluted with 0.5 N NaOH (Schmidt et al., 1980).
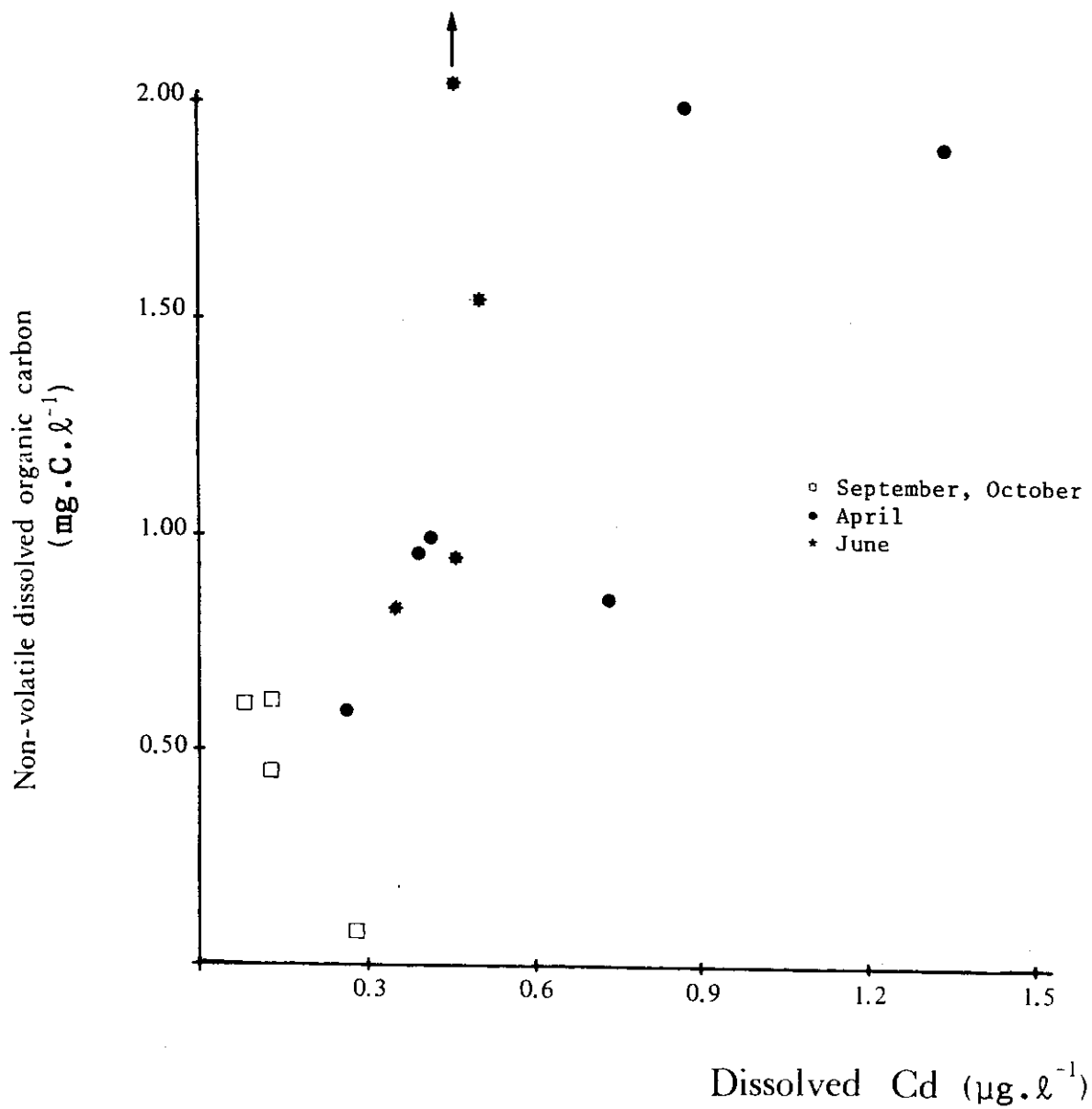
fig. 9.

Covariation of the dissolved Cd and the "non-volatile" DOC fraction
in the microlayer; seasonal effect.

2.2.3.— *The sea-surface heavy metal enrichment : maintained by deposition of atmospheric material or by concentration of the metals from the watercolumn ?*

In Table 5 we have compared for Cu, Zn, Pb and Cd in the dissolved plus particulate phases, the element ratios in bulk seawater and atmospheric wet and dry fall-out with the ratios of element excesses in the microlayer. Microlayer excess is given by the difference between the microlayer and the bulk seawater concentrations.

Table 5

Comparison between element ratios in bulk seawater (BSW), atmospheric fall-out (AFO) and the ratios of element excesses in the microlayer (ΔML = [ML] - [BSW])

Phase	Cd/Pb	Cd/Zn	Cd/Cu
BSW	0.159	0.020	0.219
ΔML	0.113	0.014	0.092
AFO	0.118	0.015	0.075
Phase	Pb/Zn	Pb/Cu	Zn/Cu
BSW	0.128	1.38	10.79
ΔML	0.123	0.82	6.69
AFO	0.129	0.63	4.91

The data for atmospheric fall-out are discussed in Dehairs et al. (1982) [see table 1].

The element ratios for the microlayer excess the bulk seawater are based on the values in table 4 above.

From table 5, it is apparent that the element ratios for the microlayer excess are closer to those of atmospheric fall-out than the ratios for the bulk sea-water. This suggests a predominant impact of atmospheric fall-out on the microlayer composition.

The particulate phase.

In Table 6, we have compared the atmospheric dry fall-out onto the sea surface with the output from the microlayer due to gravitational sedimentation.

The latter flux was calculated using a stokes settling velocity based upon observed aerosol particle diameter values [i.e. the Mass Median Diameter values in Dehairs et al (1982) {table 2}] and the observed microlayer excess of particulate trace metals (PTM).

Table 6

Comparison between atmospheric dry fall-out onto the sea-surface
and sedimentation from sea-surface microlayer due to stokes settling
Residence times of PTM's in the microlayer

Element	MMD μm (1)	Atmospheric dry fall-out g/cm².s × 10⁻¹⁵ (2)	Microlayer PTM excess g/cm³ × 10⁻⁹ (3)	Sedimentation output from ML g/cm².s × 10⁻¹⁵ (4)	Residence time in ML (min) (5) (a) dry fall-out	(b) stokes settling
Cu	.59	2.35	0.52	6.4	74	27
Zn	.28	13	7.36	20	213	138
Pb	.71	16	0.95	17	20	19
Cd	.53	0.14	0.012	0.12	280	332

(1)(2) : resp. from tables 2 and 1 in Dehairs et al. (1982); MMD, Mass Median Diameter.

(3) : from table 4, p. 78; PTM, Particulate Trace Metal.

(4) : flux due to stokes settling; the settling velocity is $\dfrac{g(\rho_p - \rho_w)}{18\,\eta} D^2$ where
$g = 981$ cm/s² ; $\rho_p = 2$ g/cm³ is the particle density; D is the particle diameter;
$\rho_w = 1.024$ g/cm³ is the sea-water density; $\eta = 0.015$ g/cm.s is the sea-water viscosity.

(5) : the residence times of PTM's in ML is given by $\tau = \dfrac{(C_{ML} - C_{BSW})\,d}{\text{flux}}$
where C_{ML}, C_{BSW} are the respective PTM concentration
in microlayer and bulk sea-water; d is the microlayer thickness,
observed to be 200 μm with the screen device used here; the flux is either
the dry atmospheric fall-out (a) or the sedimentation flux (b).

A particle density of 2 g/cm^3 was assumed. This calculation implicity assumes (1) that the PTM excess in the microlayer is entirely of atmospheric origin and (2) that deposited aerosols do not change their particle diameter by processes such as dissolution or aggregation. For Pb and Cd both fluxes are nearly the same, while for Zn and Cu gravitational settling produces vertical fluxes which are in excess of the atmospheric flux by a factor 1.5 to 2.7 respectively.

This indicates that gravitational settling is the major removal process for the atmospheric PTMs from the microlayer and that both fluxes are in balance.

For Pb and Cu , the residence times in the microlayer range from 20 to 70 min depending on which flux is considered. For Zn and Cd , they range from 140 to 330 min .

For Zn and Cu an additional PTM input to the microlayer should exist in order to balance the output by gravitational settling. Such an additional supply can be the transport of particles by bubble flotation (Hunter, 1980).

As concerns the bulk sea-water, steady state of the vertical PTM flux requires an increased PTM settling velocity, since the PTM content of BSW is smaller than in the microlayer. This increased settling velocity in the bulk phase can be achieved by aggregating or sequestering the PTM's into larger particles. Such a process can be the result of biological activity.

The dissolved phase.

Wet fall-out of Cu , Zn and Cd is at least one order of magnitude larger than dry fall-out, while they are of similar magnitude for Pb. However, wet fall-out is unlikely to represent a direct source for the dissolved phase heavy metal microlayer excess. Indeed raindrop impaction is likely to disrupt any layered structure at the sea surface.

Therefore, microlayer enrichment of heavy metals in the dissolved phase could essentially be the result of a concentration from the watercolumn. A likely enrichment mechanism is the transport of humic material-heavy metal complexes to the air-sea interface.

As this humic material can be authigenic in origin (Sieburth and Jensen, 1968 and 1969; Nissembaum and Kaplan, 1972; Hunter and Liss, 1981), this would result in seasonal fluctuations of the dissolved heavy metal content of the microlayer. For Cd at least, this was effectively observed.

3.— Conclusions.

The levels of particulate Cu , Zn , Pb , Cd , Fe , Mn and of gaseous Hg above the Southern Bight were observed to be controlled mainly by the prevailing meteorological conditions, such as winddirection, windvelocity and precipitation.

However, despite significant short term fluctuations, average annual concentrations are of similar magnitude as observed by others for the North Sea at different locations, during different periods. This reflects a state of homogeneity in time and space of the tropospheric aerosol load over the North Sea.

The sea surface microlayer is shown to be enriched in dissolved and particulate Cu , Cd , Pb , Zn and Hg , with respect to bulk sea-water. The similarity between element ratios in total atmospheric fall-out and microlayer excess, points towards the important impact of atmospheric fall-out upon the microlayer composition.

For the particulate phases of Cu , Cd , Pb and Zn a good agreement exists between dry atmospheric fall-out onto the sea surface and particle sedimentation from the microlayer, indicating that the excess particulate trace metals in the microlayer can be mostly attributed to tropospheric input.

Although for most trace metals atmospheric wet fall-out exceeds by far the dry fall-out this former supply process is unlikely to affect directly the microlayer excess for the dissolved phases.

Indeed, the positive relationship observed between dissolved Cd and the humic material fraction of DOM, suggests that it is rather by extraction of the metals· from the watercolumn that the enrichments of the dissolved phase is build up.

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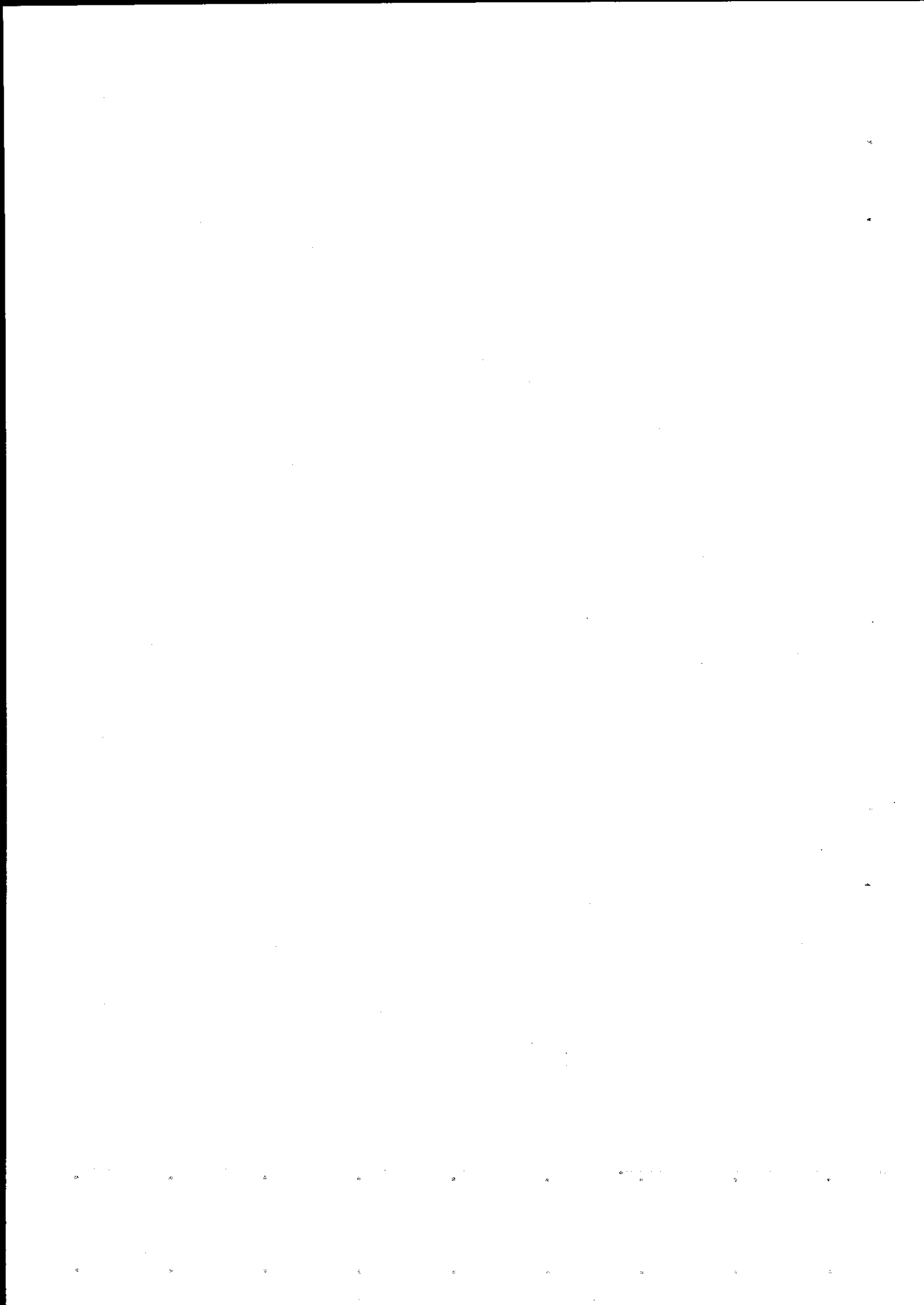
Part 4

THE RIVER SCHELDT AS A TRANSPORT ROUTE
FOR HEAVY METALS IN THE SEA

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Abstract.

Cd , Cu , Fe , Hg , Mn , Pb and Zn have been analyzed in sediment cores, suspended matter and water samples from the Scheldt estuary with high performance analytical techniques.

During early stages of mixing, most dissolved heavy metals concentrations show a maximum. Owing to real time analyses of dissolved mercury in function of a number of physicochemical parameters, we found evidence that, at least for Hg , the concentration maximum was correlated with the upstream decrease of the pH (from 7.83 on) to its estuarine minimum (7.50). Dissolution of upstream transported iron and manganese oxides and hydroxides rich in trace metals, due to a pH decrease, can be a possible explanation of the heavy metals increase.

Particulate trace metals concentrations decrease strongly in the central estuarine area, due to mixing with large amounts of resuspended bottom deposits. The particles which escape the area of turbidity maximum are in the downstream estuary diluted with sea-borne suspended matter in a more or less conservative manner.

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The overall longitudinal decrease of heavy metals concentrations corrected for grain size differences in a seaward direction, in the top layer as well as deeper sediment layers, is tightly related to the decrease in heavy metals of the suspended material. At the bottom, the finer sediments are abundantly mixed with a coarse, recent sand fraction. An important fraction of this recent sand population seems to consist of reworked subbottom deposits.

1.– Introduction.

To understand the transport of heavy metals in an estuary, it is essential to understand the physical behaviour of the estuary, and the way in which the individual parts of the system react with each other and how each affects, or is affected by, the others.

Estuaries are governed by tidal action at the sea face and by river flow. In the mixing zone of salt and fresh water, strong longitudinal gradients in physico-chemical parameters such as salinity, pH, temperature, ... are created. They have an influence on internal processes such as precipitation of solutes (Spencer and Brewer, 1971; Gibbs, 1973; Duinker et al., 1979), coprecipitation of solutes (Sridharan and Lee, 1972; Gibbs, 1973; Inoue and Munemori, 1979), flocculation and net sedimentation of fine suspended matter, associated metals included (Wartel, 1971; Sholkovitz, 1976; Baeyens et al., 1981), removal of trace elements from the dissolved phase by adsorption (Reimers and Krenkel, 1974; Gadde and Laitinen, 1974; Frenet–Robin and Ottmann, 1978; Baeyens et al., 1982), desorption and solubilization of particulate metals (Kharkar et al., 1968; De Groot et al., 1971; De Groot, 1973; Martin and Salvadori, 1974; Hanor and Chan, 1977; Etcheber, 1979), suspension of sediments and subsequent release of their metals (Windom, 1975; Lindberg and Harriss, 1977; Gambrell et al., 1980), and transformation and migration of trace metals species in interfaces of seawater and sediments (Spangler et al., 1973; Olsen and Cooper, 1974; Kudo et al., 1975; Bartlett et al., 1977; Lu and Chen, 1977; Bothner et al., 1980).

These processes as well as external effects mainly anthropogenic activities such as discharging of pollutants or cooling water, dredging of the channels and in some cases subsequent disposal of the spoil on the shoals or on the river bank, may modify the conservative mixing of river-borne and sea-borne solutes and particulates (Muller and Förstner, 1975; Duinker and Nolting, 1978; Salomons and Eysink, 1979; Etcheber, 1979).

The overall effect of the internal and external processes is an often unexpected and complex distribution pattern, which differs from element to element and from estuary to estuary.

In this study heavy metals were analyzed in solution, suspended matter and sediment cores sampled in the Scheldt (Scheldt) estuary. Concomitantly related variables such as physico-chemical parameters, grain-size distribution, organic matter content were measured in order (1) to understand better the role plaid by external and internal processes, (2) to distinguish between the effects of physical mixing and physico-chemical processes and (3) to obtain an estimate of the heavy metals input to the North Sea via the river Scheldt.

2.— Sampling, methods and materials.

At seven estuarine stations (2, 7, 12, 15, 22, 25, 29 see figure 1) and two stations a few kilometer off the mouth, samples have been taken at slack water of the ebb in 1981 between March 16 and 20. During one hour water samples were collected with a peristaltic pump and conducted to a closed pressure filtration system (G. Gillain et al., 1982), a teflon coated centrifuge and physico-chemical measuring devices (turbidity, temperature, salinity).

Sediment cores were sampled by divers of the Belgian Navy in 6 cm plexiglass tubes. The coring locations were selected by examining in situ recorded high resolution subbottom profiles made with a system (Wartel, 1980), capable of resolving sedimentary layers about 30 cm thick.

The cores were segmented according to textural variations with depth shown by X-radiographs, using an X-ray tube (W-anticathode and Be-window) at an excitation potential of 90 KeV; see for example figure 7. Analyses of heavy metals in solution, suspended matter and bottom sediments were carried out as described by Gillain et al. (1982). On several liquid and solid samples, cross determinations of heavy metals with two independent analytical methods (DPASV and AAS) were performed to ensure that analytical results were exact.

Particulate organic matter was determined with a Perkin-Elmer C, H, N-analyzer, Model 240. The amount of carbonate was determined using a Scheibler-Dietrich calcimeter. On a few samples inorganic and organic particulate carbon were also measured by coulommetry and particulate nitrogen by Kjeldahlisation and colorimetry

Grain size analyses were performed on dry samples. Salts, organic compounds and carbonates were previously eliminated with a H_2O_2 (1 : 2) solution and HCl (1 : 10).

THE NETHERLANDS

BELGIUM

North Sea

Flushing

Breskens

Zeebrugge

Hansweert

Terneuzen

Bath

Doel

Antwerp

Rupelmonde
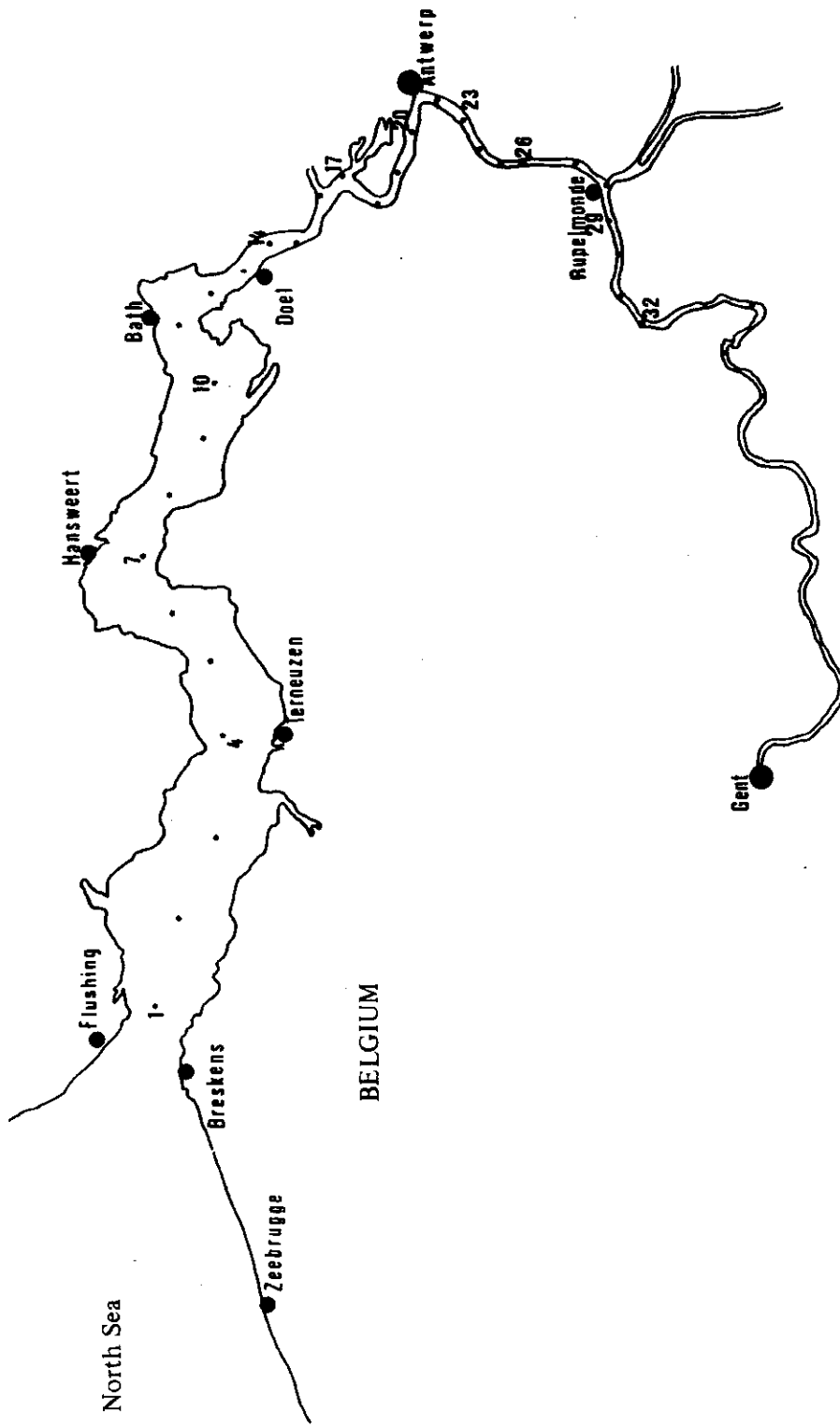
Gent

17

23

26

29

32

10

7

1

fig. 1.

Sampling stations in the Scheldt estuary

The sample was suspended by adding 500 mℓ of distilled water and 50 mℓ of a solution of 8.93 g Na-oxalate and 1.33 g Na-carbonate per liter solution. The suspended sample was then poured on a 5 ϕ sieve. The finer particles ($< 5 \phi$) were analyzed using a sedimentation procedure and the coarser particles by dry sieving using A.S.T.M. sieves with a 1/4 ϕ interval.

3.-- Hydrographical and physicochemical characteristics.

The Scheldt estuary extends from Ghent (Gent) to Flushing (Vlissingen). The average tidal differences are 3.8 m at Flushing, 5 m at Antwerp (Antwerpen) and 2 m at Ghent were the tide is stopped by a sluice. The average total fresh water supply at Schelle (89.5 km from the mouth) is about 80 m^3/s (Valcke, 1966).

Daily values vary from a few m^3/s to 600 m^3/s. These values are small compared to the flood discharge of 2 590 m^3/s at the same place. As a result large tidal velocities (up to 1.4 m/s) occur in the Scheldt estuary but the residual transport is very small. The residual current is of the order of 1 cm/s in the upstream area, and decreases to 0.1 cm/s at the mouth.

The salinity distribution in the estuary mainly depends on the fresh water supply and can easily be calculated in function of the latter variable with a one-dimensional stationary model (figure 2). Vertical stratification is limited (it never exceeds 0.25 g Cl$^-$.ℓ^{-1}.m^{-1}) and only occurs over short periods of the tide.

Downstream from km 55 to the mouth, the redox potential has the normal value of an aerated water. Upstream, an anaerobic zone exists, except under high fresh water supply conditions.

In the central area Antwerp to Doel the finest bottom sediments, fine sands to clayey silts, occur (Wartel, 1977). Most of these sediments are transported either as a uniform or as a graded suspension. Flocculation and local hydrodynamic conditions govern the settling down of this material in the central area (Baeyens et al., 1982).

A large part of these sediments are resuspended after deposition when the bottom shear stress exceeds the critical erosion shear stress and contribute to the observed high suspended sediment concentration indicating the turbidity maximum of the estuary. From this central area towards both the up- and downstream area, a marked increase in grain size of bottom sediments (gravels and medium to coarse sands) occurs. About 10 to 30 % of the sediment here is transported by rolling and the rest as a graded suspension, and to a lesser extent as a uniform suspension.
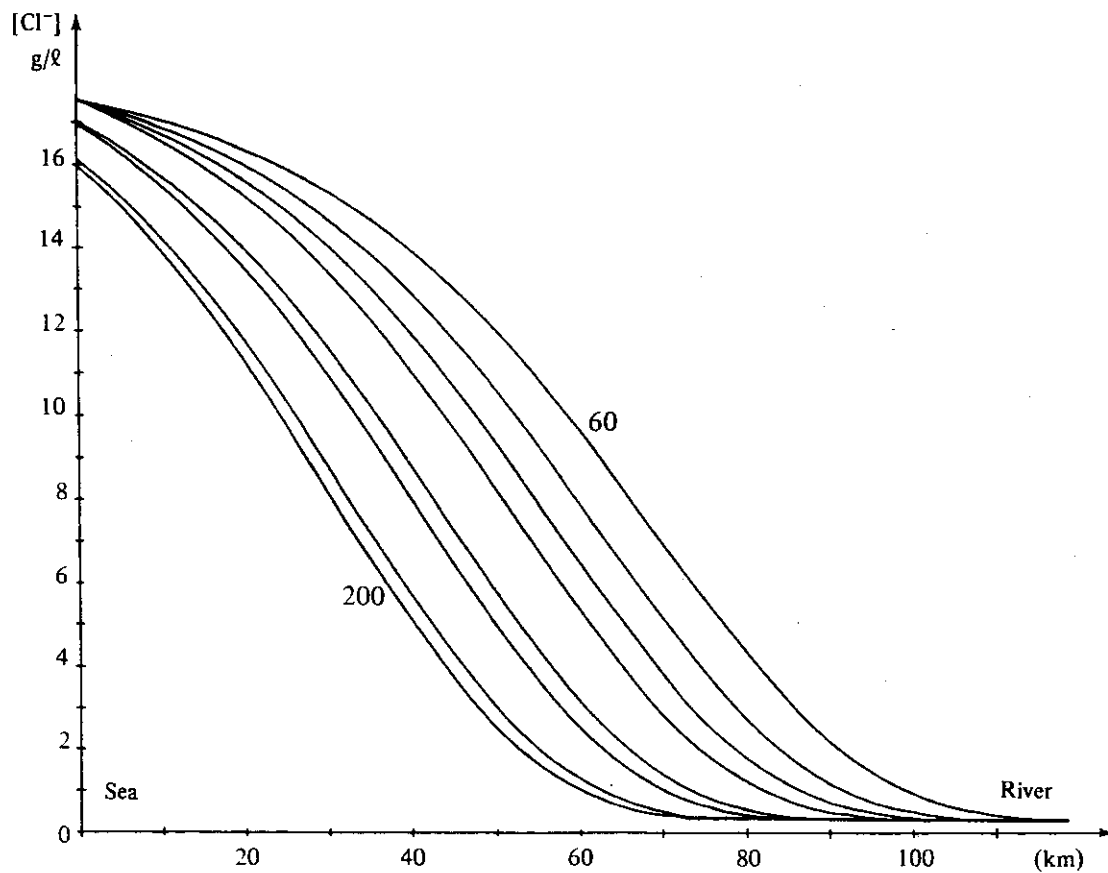
fig. 2.

Longitudinal chloronity profiles in the Scheldt estuary
as a function of the river flow (60 to 200 m³/s)

4.— Results and discussion.

None of the heavy metals considered in this study appear to behave in a conservative way. The dissolved concentration profiles of mercury, copper, zinc and cadmium observed in March 1981 are very similar: a rather constant concentration level in the fresh water area, an almost symmetrically sharp increase and decrease during early stages of mixing and again a rather constant concentration towards the mouth (figure 3).

The lead, manganese and iron profiles differ however (figure 4) : lead and manganese show an irregular but definite overall decrease, suggesting removal processes are predominant in the estuary, while iron shows a sudden increase at the mouth.
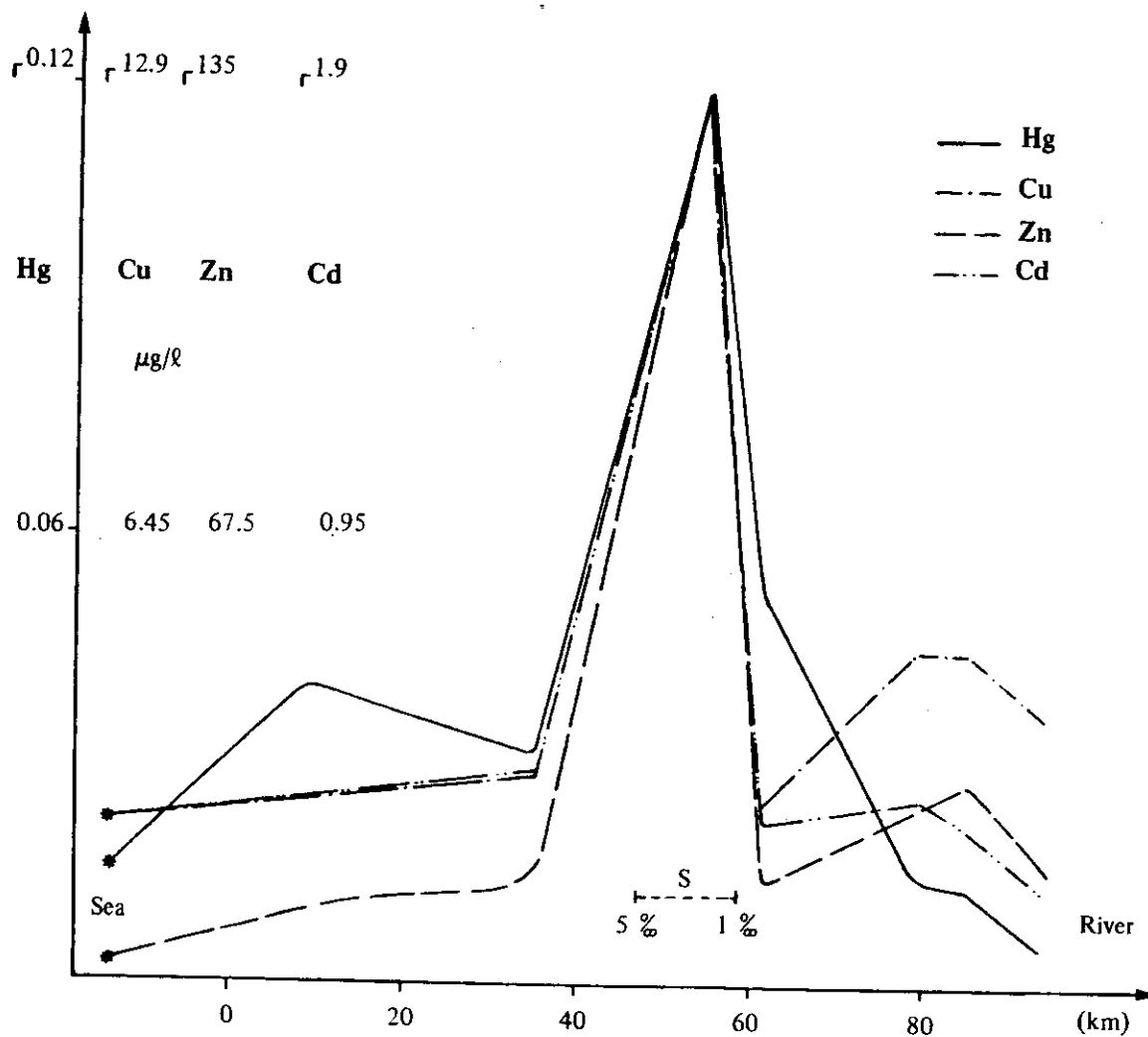
fig. 3.

Longitudinal profiles of dissolved Hg, Cu, Zn and Cd concentrations in the Scheldt estuary

The plots of these heavy metals against salinity all show de-
viations from the ideal dilution line. Provided the fresh and
salt water end member concentrations observed, reflect correct
boundary conditions, mercury, zinc, copper and cadmium are pro-
duced and removed from solution in a rather narrow (1 - 5 ‰)
salinity range, lead and manganese are removed in a broader
salinity range, except, a small production during early stages
of mixing, and iron is besides a small production during early
stages of mixing too, strongly produced at the mouth (24 ‰ S)
taking into account that dissolved iron concentrations in our
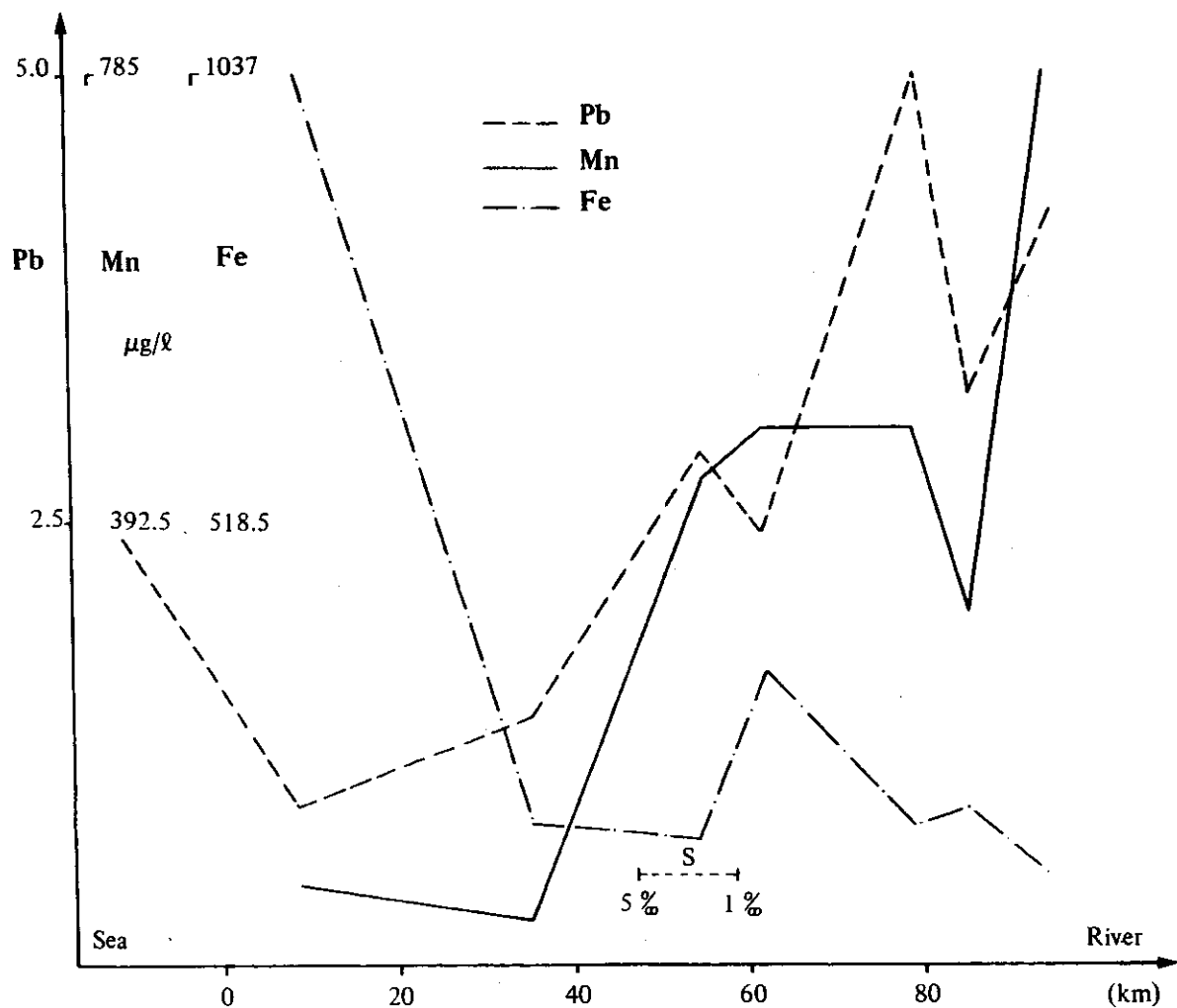
fig. 4.

Longitudinal profiles of dissolved Pb, Mn and Fe concentrations in the Scheldt estuary

coastal zone never exceed 100 ppb . Etcheber (1979) also observed maxima for Cu, Zn and Pb in the Gironde estuary especially in periods of low fresh water supply and in the middle area of the estuary. In the Rhine estuary, dissolved metal-salinity plots show that Cu, Zn, Fe and Mn are removed from solution during estuarine mixing (Duinker and Nolting, 1978).

Unless a very important and simultaneous discharge of Hg , Cu , Zn and Cd took place at station 12, four mechanisms may be responsible for their sudden increase in concentration :
(1) desorption from suspended sediments,
(2) dissolution of iron and manganese oxides and hydroxides as well as their associated metals,

(3) diffusion and migration of interstitially dissolved metals to the overlying water,

(4) degradation of organic matter and mobilisation of the associated metals.

In a very recent cruise up and down the estuary, dissolved mercury concentrations (filtered and centrifuged) were measured in real time on board the ship. Samples were taken in function of conductivity, pH, dissolved oxygen and temperature values which were recorded continuously.

The most striking correlation observed (twice since we went up and down the estuary), was the upstream increase of dissolved mercury when the pH felt below 7.83, and the subsequent mercury decrease once the pH estuarine minimum (7.50) was passed. Changes of other physicochemical parameters such as (in the upstream direction) a 25 % dissolved oxygen drop, the decrease of the conductivity down to 7.6 mS or the temperature raise, appeared in a first approximation, not to be linked to a substantial change in the dissolved mercury concentration.

Assuming the observations made during this cruise do not reflect a particular situation — the pH minimum is in any way according to Mook and Koene (1975) a normal phenomenon when the pH of the river water is lower than that of seawater- and assuming adsorption-desorption characteristics of river-borne and sea-borne particulates are similar, desorption from suspended sediments seems not to be a major cause for the dissolved metals increase. Indeed, river-borne particles contain much more heavy metals than sea-borne particles, but when the river pH decreases to the estuarine minimum, no dissolved mercury increase is observed.

Dissolution of upstream transported iron and manganese oxides and hydroxides, due to a pH decrease, can however explain the heavy metals increase. For a better understanding of this phenomenon, it is worthwile to discuss the general estuarine behaviour of manganese and iron.

In the early stages of mixing, a production of about 130 and 40 μg/ℓ of dissolved Fe and Mn respectively has been observed compared to their ideal dilution curves, but when the pH and dissolved oxygen concentration increases in the downstream area, both metals and also several other trace metals are removed from solution by (co) precipitation. This corresponds to the trace metals decrease once entering the middle part of the estuary and has also been observed by Duinker and Nolting (1978) in the Rhine estuary. These freshly precipitated particles, enriched in most trace metals, progressively settle down in the downstream estuary; part of them are, however, reintroduced into the upper estuarine zone by the upstream current. Arriving in the upstream area, they meet suddenly a much lower pH which favours their dissolution and a concomitant release of the associated metals. Continental derived manganese and iron particles probably are more reluctant to pH changes or contain less heavy metals.

In an area where the bottom shear stress is large, one may expect a contribution from interstitially dissolved compounds to the overlying water. Since a turbidity maximum was observed at station 12, great evidence exists that this condition was fulfilled there (Wartel, 1977; Baeyens et al., 1981). In one core, at point 22, interstitial metal concentration were determined. Zn, Pb and Cu were approximately 10 times, Cd 25 times larger than in the bulk water at the same station. Assuming the same interstitial to bulk water ratios at point 12, one can calculate that only a slight increase of the bulk water concentrations may be expected.

The degradation of organic matter may be accompanied by a release of heavy metals to the solution. But despite that the heterotrophic activity observed in the upper estuary is indeed very high, it drops rapidly when the salinity reaches a value of 2 to 4 g Cl^-/ℓ (Billen et al., 1976) and can thus not explain the sudden dissolved metals increase.

An additional remark concerning the very high dissolved iron concentration at the mouth has to be made. This excessive concentration is probably due to regular dumping of TiO_2-waste, containing large quantities of dissolved iron. Evidence was found by examining the particulate material at the same station; the Fe:Ti ratio corresponded to that in the waste material itself.

Almost all particulate heavy metals concentrations drop abruptly (figures 5 and 6) between km 60 (station 15) and km 40 (station 7). In this area dissolved trace metals are also produced and removed from the solution. Besides conservative mixing of highly polluted upstream suspension with suspended matter of marine origin which is far less contaminated, two other mechanisms are involved. On the one hand dissolution of upstream transported manganese and iron oxides and hydroxides as explained above, on the other hand in the area of the turbidity maximum, a strong dilution of the suspended material by mixing with locally eroded, less contaminated bottom sediments. Due to flocculation and a decrease of the turbulence at the bottom, a subsequent sedimentation of the suspended material occurs. The remaining particles are in the downstream area in a more or less conservative manner diluted with marine suspension. As mentioned before, manganese and iron oxides and hydroxides will precipitate when the pH and oxygen concentration increase.

The longitudinal profiles of heavy metals, total and organic carbon, percentage of grain size smaller than 16 μm, etc. in the upper, superficial sediments, acting as an interface between the water flow and underlying sediments, are very erratic. Two distinct areas, however, can be distinguished: an upstream area (stations 12 to 25) showing, organic carbon : nitrogen ratios in the range 10.2 to 12.8 and higher trace metals concentrations corrected for grain size differences (similar results were obtained if not the grain size but organic carbon or total carbon
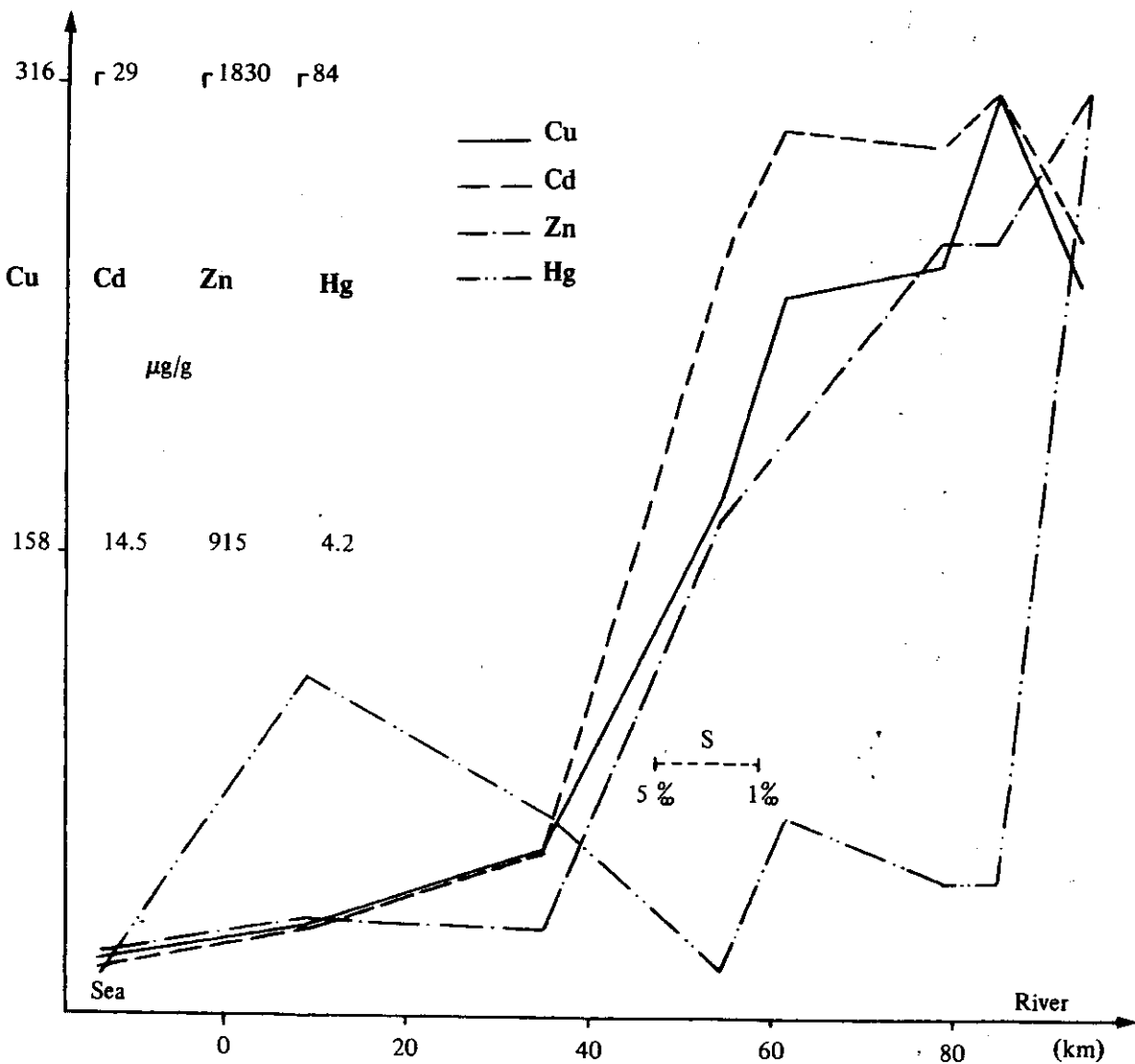
fig. 5.

Longitudinal profiles of particulate Cu, Cd, Zn and Hg concentrations in the Scheldt estuary

was used as the correcting parameter) and a downstream area (stations 2 to 7) showing organic carbon: nitrogen ratios in the range 6.2 to 7.4 and lower trace metals concentrations corrected for grain size or carbon (organic or total) differences.

The overall longitudinal decrease in a seaward direction of heavy metals concentrations corrected for grain size differences, in the sediments, is tightly related to the decrease of heavy metals in the suspended material. The metal-fine
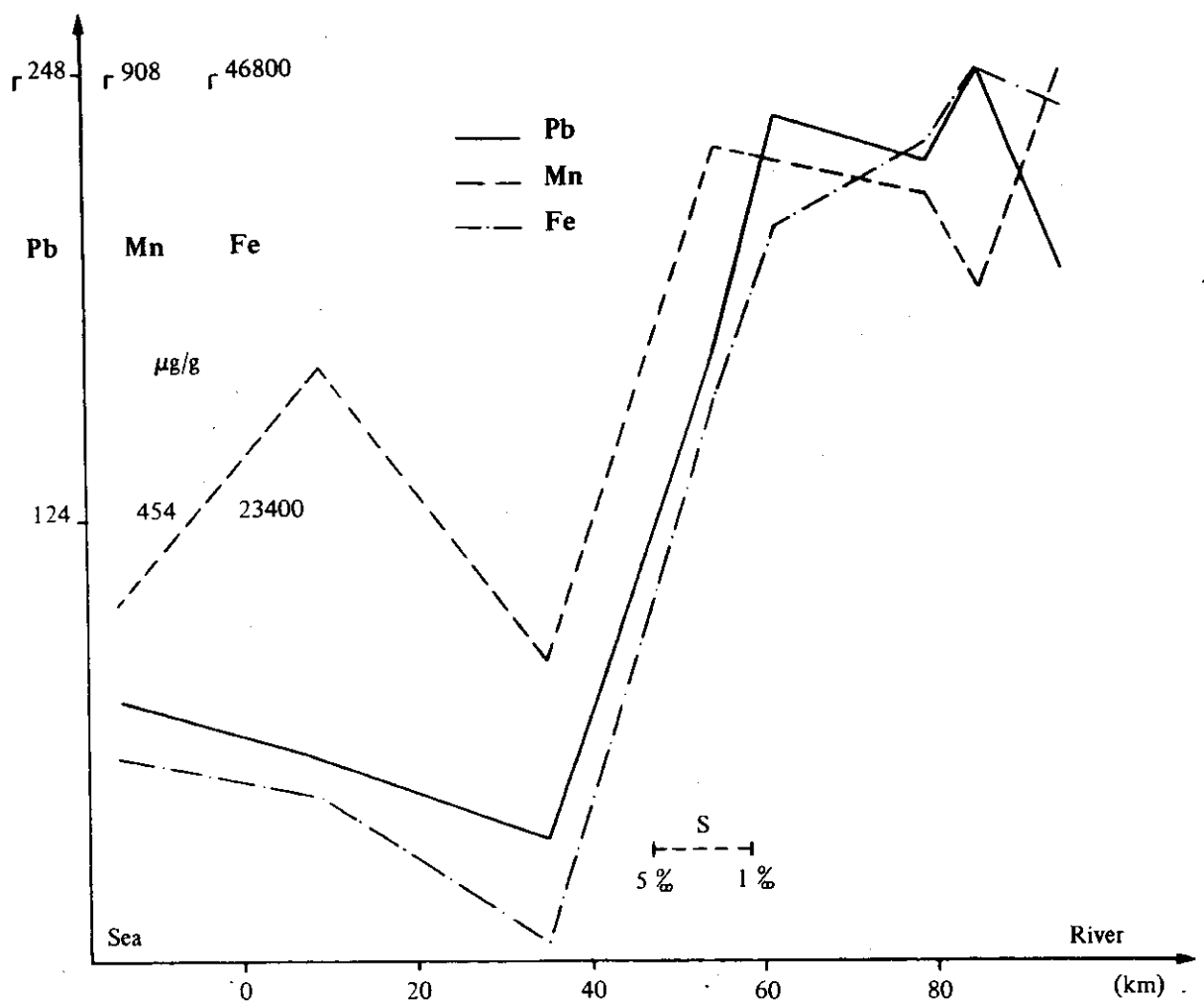
fig. 6.

Longitudinal profiles of particulate Pb, Mn and Fe concentrations in the Scheldt estuary

sediments (< 16 μm) correlation, found in the suspended matter is, however, modified in the sediments due to the fact that
(1) an ultrafine, metal rich fraction will probably not settle down, and
(2) in the sediments mobilisation and precipitation processes can occur.

During a tidal cycle, an important fraction of the suspended particles obeys an almost cyclic movement; sedimentation when the tidal energy in the watercolumn falls beneath a critical sedimentation treshold, resuspension when it exceeds a second critical erosion value. To increase the probability to find on top of the cores freshly deposited suspended matter,

coring was carried out at slack low water. However, only the top layer of cores 12 (Ballastplaat) and to a lesser extent 15 (Doel) showed concentrations of the same order as the suspended particles. This is not surprising, since these stations were in the area of turbidity maximum, where the magnitude of sedimentation and resuspension phenomena is strongly enhanced due to local hydrodynamic conditions and flocculation processes.

The cyclic sedimentation-erosion pattern is, however, definitively disturbed when the freshly sedimentated, fine particles are mixed with or covered by a much coarser sand fraction. According to Wartel et al., (1979), it can be assumed that at least an important part of the recent sand population, abundantly present in all our sediment cores, consists of reworked subbottom deposits. Horizontal transport of the sand fraction as far as it could be deduced from the foraminifera analyses, is limited and has a prevailing downstream component between the river Rupel and Kallo and a downstream as well as upstream component in the Western Scheldt (downstream area). The mixing of the finer sediments (< 16 µm), rich in metals, with a much less contaminated sand fraction diminishes the absolute metal content of the sediments.

The vertical texture of the sediment cores varied from almost homogeneous to very heterogeous. Therefore two coring sites — Hansweert (station 7) and Ballastplaat (station 12) — are described in more detail.

4.1.— *Subbottom profilings.*

Hansweert.

Down to a depth of 2 to 5 m below the actual bottom surface and concordant with it, several (maximum 5) reflecting horizons exist. They show regular layering consisting of beds 0.4 to 1 m thick and composed of subrecent Scheldt sediments.

Ballastplaat.

Near the sampling station an old gully, crossing the actual valley and filled with layered sediments exists. The deepest point of it occurs at approximately 5 m below the actual surface.
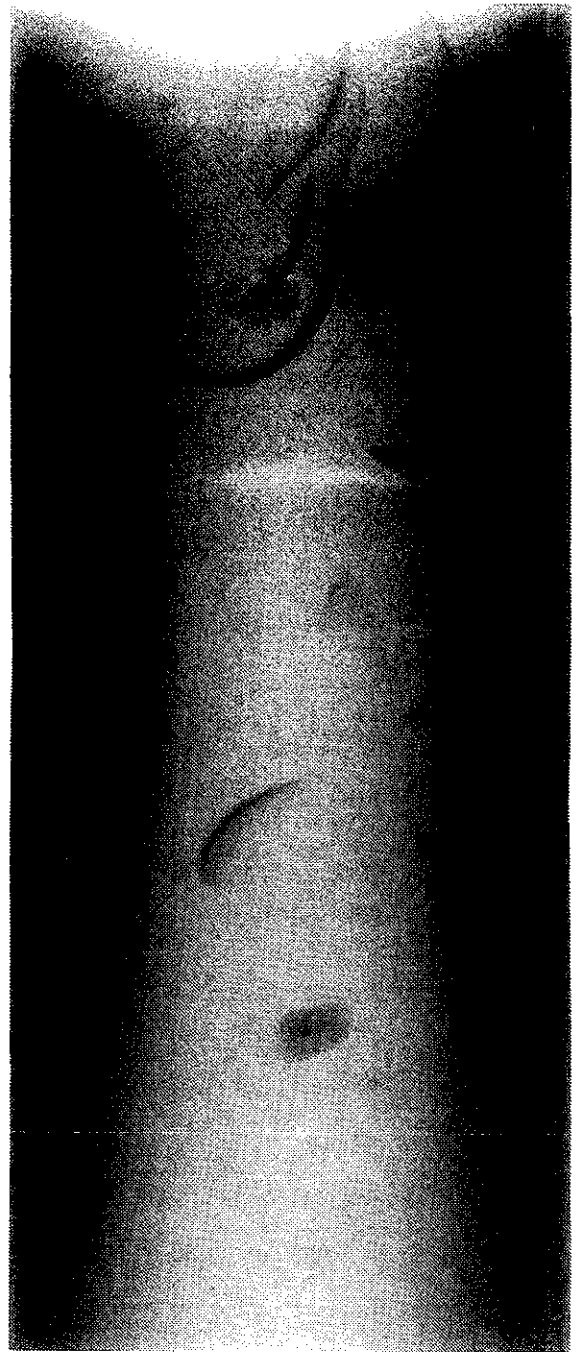
4.2.— *X-ray photography.*

Hansweert.

The X-ray photographs of both cores (figure 7) show over their whole length a rather homogeneous structure. In core 7A a gravel and shells, in core 7B a few gravels and shells occur. Apart from that, no substantial differences between both cores were observed.
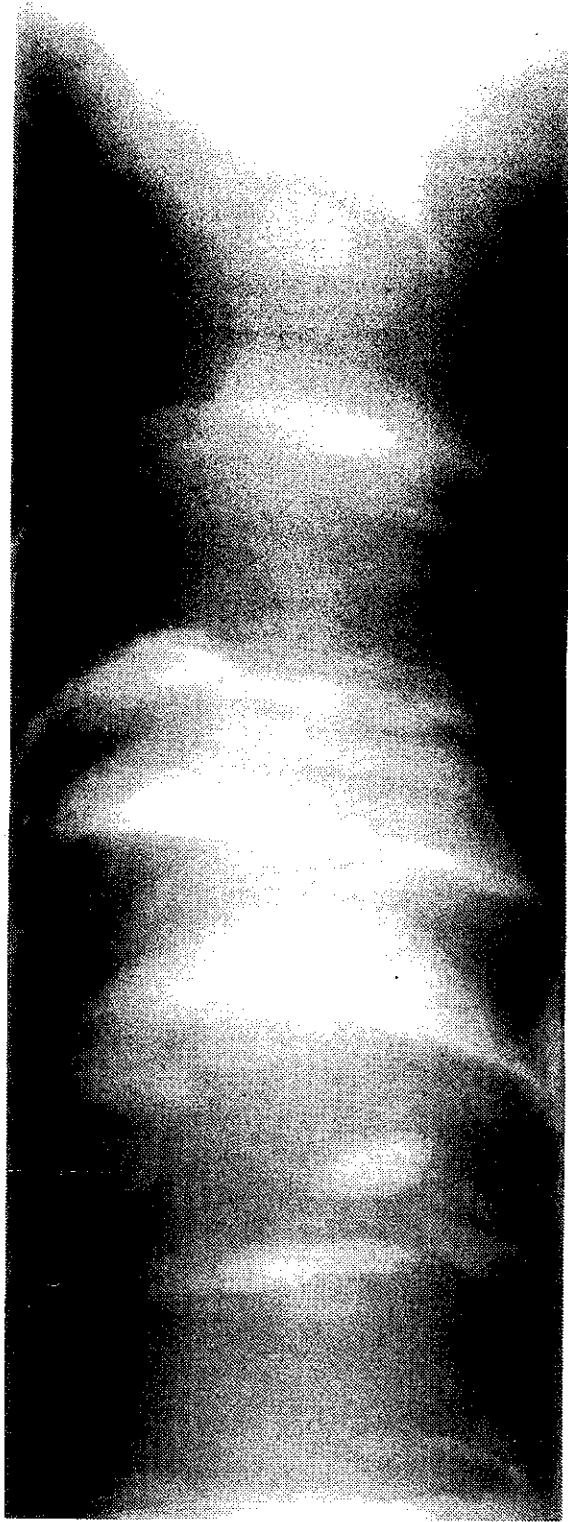
7 A   7 B

fig. 7.

X-ray photographs of the top of cores 7A and 7B collected at Hansweert

12 A   12 B

fig. 8.

X-ray photographs of the top of cores 12A and 12B collected at Ballastplaat

Table 1

Grain size distribution of bottom sediments
at Hansweert (station 7) and Ballastplaat (station 12)

Sample	Depth cm	Sand %	Silt %	Clay %	Md μm	Sorting
7A-1	0-2	97	1	2	191	WS
7A-2	5-8	97	1	2	212	WS
7B-1	0-2	97	1	2	235	WS
7B-2	2-4	99	0.5	0.5	224	WS
12A-3	0-2	62	23	15	21	VPS
12A-1	2-6	93	4	3	150	MWS
12A-2	6-7	93	4	3	150	MWS
12A-4	15-16.5	96	1	3	179	MWS
12A-5	17-20	92	6	2	180	MWS
12A-7	28.5-29.5	83	13	4	100	PS
12B-1	0-3	43	36	21	12	VPS
12B-2	20-22	95	2	3	160	WS
12B-4	38.5-40.5	94	3	3	153	MWS
12B-5	44.5-46.5	76	16	8	68	PS

```
Sand : 2 mm - 0.063 mm        Silt : 0.063 mm - 0.002 mm
Clay : < 0.002 mm             Md   : median grain-size
VPS  : very poorly sorted     PS   : poorly sorted
MWS  : moderately well sorted WS   : well sorted
```

Ballastplaat.

Both cores 12A and 12B are structurally identical (figure 8). Irregular beds, 1 to 4 cm thick and composed of alternating silt and sand laminae 1 to 2 cm thick, alternate with sand beds of similar size. In the sand beds mud pebbles occur.

4.3.— *Grain size.*

Hansweert.

According to the very homogeneous structure shown by the X-ray photography, only two samples of the top of the core were analyzed. In both cases the sediment appeared to be composed of a well sorted fine sand (Table 1).

Ballastplaat.

Both cores yield similar results. The sand fraction is high (76 to 96 %), except for the 2 to 3 cm thick top layer (43 to 62 %). In all subsamples the silt fraction is higher than the clay fraction. Sorting varies from very poorly for the finer sediments (median between 12 and 21 µm) to moderately well for the coarser ones (median between 150 and 180 µm). The coarsest sand fraction is approximately 300 µm .

4.4.— *Heavy metals and total carbon.*

Hansweert.

The absolute amounts in this sandy sediment are very low (Table 2).

Ballastplaat.

The silt laminae contain much higher metal and carbon levels than the sand laminae (Table 2).

From these results, as well as those from the other stations, it appears that in two layers belonging to one core, and with comparable grain size and total carbon content, the highest metal concentration can be found either in the upper or lower layer. Varying contamination levels of the sedimentating material in former years can be one of the main reasons.

Similar to the top layers, higher metals concentrations corrected for grain size (or for total carbon) occur in the upper estuary.

Finally, zinc and copper levels observed in the Scheldt are compared to those prevailing in other estuaries and to a global mean value (Table 3).

The pollution level in the Scheldt estuary seems to be comparable to that in the Gironde. Only the particulate metals concentrations in the Scheldt are somewhat higher, owing to its lower load of suspended matter, which is about 100 mg/ℓ compared to the 1 200 mg/ℓ in the Gironde (Etcheber, 1979).

Table 2

Heavy metal concentrations (μg/g)
in bottom cores 7A (Hansweert) and 12B (Ballastplaat)

Depth (cm)	[Cu]	[Pb]	[Cd]	[Hg]	[Fe]	[Mn]	[Zn]	[TPC] (mg/g)
Core 7A								
0–1	2.82	10.0	1.075	0.10	6,828	61.1	23.0	5.4
14–16	2.125	8.25	0.70	0.08	6,693	62.9	17.0	3.2
26–28	1.80	7.75	0.575	0.02	6,020	54.3	15.0	2.9
Core 12B								
0–3	111.75	174.0	18.75	2.60	30,462	1017.9	788.8	67.3
20–22	9.25	21.5	2.15	0.20	11,875	123.6	70.3	8.5
25–26	45.00	65.5	8.50	1.09	19,028	511.0	348.2	27.4
38.5–40	7.57	16.75	1.46	0.11	11,042	99.3	60.4	7.1
44.5–46.5	35.25	46.0	6.0	0.69	18,394	372.2	188.2	21.4

Table 3

Comparison of heavy metals levels in the Scheldt estuary
with these of other estuaries (from Etcheber, 1979)

	Global mean		Gironde		Ems		Rhine		Scheldt	
	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu
Water (ppb)	10	5	50	5			150	10	38	5
Suspension (ppm)	300	50	600	30	1000	70	3000	400	1060	190
Sediments (ppm)	100	50	300	25	600	50	900	200	218	28

The input of heavy metals to the sea via the river Scheldt has been estimated. Annual amounts of dissolved and particulate Cd , Cu , Fe , Hg , Mn , Pb and Zn supplied to the North Sea by the Scheldt .98 and .48 , 6.6 and 5.3 , 420 and 1 500 , .10 and .50 , 180 and 100 , 2.3 and 9.9 , 28 and 32 tons/year respectively.

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Part 5

INTERACTION KINETICS BETWEEN DISSOLVED INORGANIC MERCURY AND ESTUARINE SUSPENDED MATTER

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Abstract.

The adsorption kinetics (adsorption capacity and adsorption rate) of mercury on natural suspended matter of the Scheldt estuary were studied. The results indicated that up to 2 ppm, the particulate matter adsorbed all the mercury added (24 hours experiments) independently of salinity and redox potential.

At higher mercury concentrations the ratio Hg-adsorbed/Hg-dissolved was inversely proportional to the salinity except at low redox potential; in that case the salinity showed no influence. Great evidence exists that organic matter is a major mercury scavenger.

Accurate mercury adsorption rates were obtained with a continuous filtration system connected to a mercury auto-analyzer. The adsorption rate increased with increasing temperature, turbidity and dissolved mercury, but decreased with increasing salinity and adsorbed mercury. As a consequence the adsorption rate in the upstream area of the estuary appeared to be about ten times faster than in the downstream area.

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1.- Introduction.

The fate of a pollutant discharged into the marine environment depends on the hydrodynamical conditions of the area and the possible interactions with other chemical and biological constituents. If the pollutant is a conservative element, its concentration is only influenced by external inputs and outputs. This is, however, not the case for heavy metals. Indeed, calculations based on atmospheric and telluric inputs provide theoretical concentrations of copper, nickel, silver, gold, lead and other metals in the oceans, which are many orders of magnitude higher than the best currently measured values (Turekian, 1977). Mercury concentrations measured in the Southern Bight of the North Sea also appear much lower than those permitted by thermodynamical solid-dissolved equilibrium calculations (Baeyens et al, 1979).

The mean residence time of the dissolved radionuclides ^{210}Pb, ^{210}Po, ^{234}Th, ^{228}Th, relative to particle removal, have all been shown to be between a half-a-year and a year-and-a-half in the open ocean, according to Turekian (1977). As the coastal areas are approached the residence time for these nuclides in the water column drops sharply to tens of days and in coastal mixing basins with a heavy load of resuspended bottom sediments it drops to one day. To the extent that a trace metal follows the pattern of all of these radionuclides, they also can be expected to be effectively sequestered by particles for transport out of the surface layers. This is indeed the case for mercury, since only 0.1 to 0.07 % of the amount of mercury entering into the oceans remains in the water column (Krauskopf, 1956).

Laboratory and field studies suggest that among the various constituents of natural particulate matter, organic matter (Lindberg & Harriss, 1974 ; Reimers & Krenkel, 1974) hydrous manganese oxides (Harriss, 1968 ; Lockwood & Chen, 1973) and clays (Reimers & Krenkel, 1974 ; Frenet-Robin & Ottmann, 1977 and 1978) seem to be the most effective mercury scavengers.
Until now most of the adsorption studies concerning mercury aimed only at the determination of (1) the maximum adsorption capacity of this metal on a particular solid and (2) the ratio dissolved mercury : adsorbed mercury at equilibrium.

Few attempts have been made to measure the rates of adsorption. This is probably due to the difficulties encountered in finding an appropriate solid-liquid separation method capable of assessing in a sufficiently accurate way the rapid decrease of the dissolved mercury concentration. In general, it has only been possible to determine the time necessary to reach the equilibrium state (Reimers & Krenkel, 1974 ; Lockwood & Chen, 1973).

Therefore we have developed an automated method allowing the continuous assessment of adsorption rates of mercury on particulate suspended matter (Baeyens et al, 1982).

In this paper, the adsorption capacities of mercury on particulate suspended matter of the Scheldt estuary as well as the ratios dissolved mercury : adsorbed mercury at equilibrium are

discussed. In addition adsorption rates including the influence of some important water-quality parameters, such as temperature, salinity and redox potential are presented.

2.– Experimental.

2.1.– *Characterisation of the natural samples.*

The particle size distribution has been determined with a Coulter Counter (Coulter Electronics Ltd). The redispersion of coagulated particulate matter has been carried out with a Branson Sonifier (Model S-75), until the particle size distribution corresponded again to the original one. The heavy metal content of the suspended matter has been determined as described by Gillain et al (1982), while organic matter has been quantified by the dichromate oxydation method. Determination of the weight loss between 550 °C - 1 100 °C, which is correlated with the carbonate content and the weight loss between 100 - 1 100 °C, which is anti-correlated with the SiO_2 content, have been carried out on the particulate matter too.

In the solution the pH (Tacussel pH-meter), Eh (Pt and calomel electrodes), chlorinity (by gravimetry) and the organic matter content (by dichromate oxydation) were measured. Particulate and dissolved mercury concentrations were manually determined as described by Gillain et al (1982).

2.2.– *Adsorption capacity determinations.*

Twenty four hours after the injection of a known amount of dissolved mercury, particulate and dissolved mercury concentrations were measured manually. To avoid sedimentation of the particulate material, we used flasks with a screw-cap attached to a continuous rotating system (10 rpm).

2.3.– *The mercury auto-analyzer.*

The concept of the auto-analyzer (figure 1) is based on the manual method of Hatch & Ott (1968) and on the semi-automatic method as reported by Goulden & Afghan (1970) and Agemian & Chau (1975).
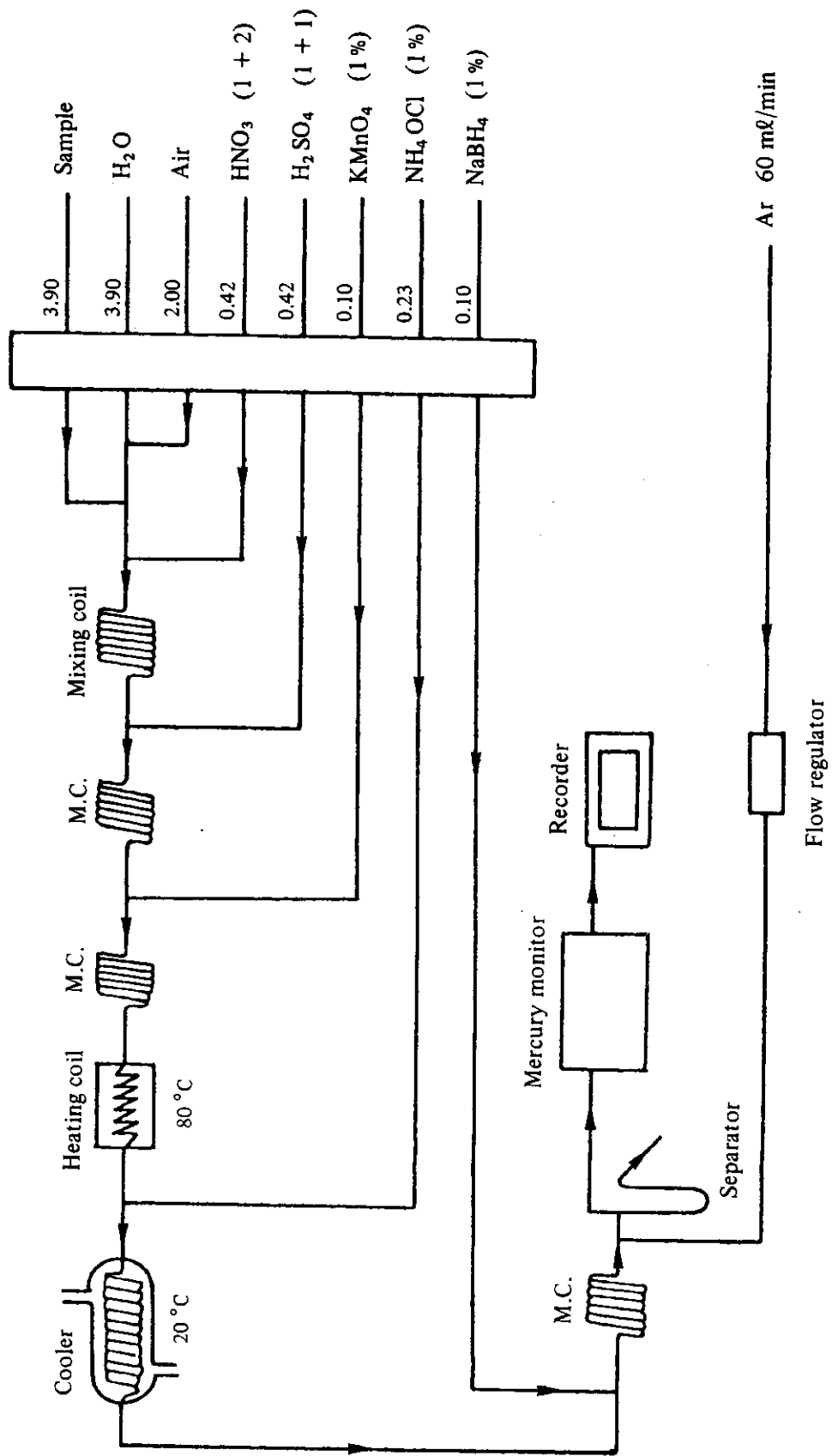
fig. 1.

Mercury Manifold

The sample is successively acidified with nitric acid (1 + 2) and sulphuric acid (1 + 1), oxidized at 80°C with potassium permanganate (1 %) and cooled to 20°C. The excess potassium permanganate is eliminated with hydroxylamine (1 %) and mercury (II) is reduced to metallic mercury with sodium borohydride (1 %). In the gas separator metallic mercury is swept from the solution by a current of argon. The argon gas flow rate is kept as constant as possible with a Brooks gas flow regulator ((60 mℓ/min). The gasstream was dried over magnesium perchlorate. All mercury detections were made on a Coleman Instruments Hg Analyzer (MAS-50). The sampling tube of the mercury manifold is connected to an automatic switching valve, which conducts sample from the reaction vessel to the mercury manifold and a 2 percent nitric acid washsolution to the waste or the inverse. For our experimental condition, a wash solution-reactor solution time ratio of 2:1 appeared to be sufficient for a complete return to the baseline.

2.4.— *The reaction vessel.*

The adsorption vessel is a double-wall plexiglass (345 mℓ) or pyrex glass (325 mℓ) container, fitted with a filtering device, an injection system, a thermometer and Eh-probes.

Two kinds of materials (plexiglass and pyrex glass) have been used, in order to verify if the nature of the wall had any influence on the adsorption kinetics. The double wall, which almost entirely surrounds the inner container, serves as a thermostatic mantle. In this way a constant sample temperature is ensured.

The sample is continously pumped out of the vessel by a Technicon pump, but is alternatively conducted to the manifold and to the waste, according to the position of the switching valve. A Millipore filter with a pore-size of 0.8 µm, fitted in an airtight filter head at the outlet of the vessel, prevents losses of particulate material. Although a partial clogging of the filter could not be avoided, it appeared (1) that the outlet flow rate remained constant during the time of the experiment and (2) that the amount of suspended material in the vessel did not substantially decrease. The solution leaving the reactor is automatically replaced by a filtered sample. Changes in the volume of the reactor sample were avoided by using identical in and outflow rates.

Through the injection system known amounts of mercury were added to the sample. These injections were made with an automatic Hamilton syringe (5-20 µℓ). Insertion of the thermometer and the Eh-probes into the sample is possible through air-tight silicone joints.

As the whole analyzing device forms a closed system, vaporization or atmospheric contamination of mercury is negligible.

2.5.— Estuarine samples.

Sample characteristics had to fulfil the following requirements : low salinity and high turbidity. Indeed this allows us to vary salinity or turbidity in an easy way, respectively by adding salt or diluting with filtered water ; this procedure, we believe, does not disturb the initial characteristics of the sample. The samples were collected in the Scheldt estuary at 90 km from the mouth ; at this site typical values of salinity and turbidity are respectively 1 % NaCl and 300 mg/ℓ particulate matter.

In each case, thirty litres of natural estuarine water were returned to the laboratory in a polyethylene container, and subdivided in 2.5 ℓ polyethylene bottles. One bottle served for the characterisation of the sample. These characteristics are summarized in table 1. The remaining bottles were rapidly deep frozen and maintained at - 20 °C.

Table 1

Sample characteristics

	Unit	Sample 1 2.09.76	Sample 2 22.10.76	Sample 3 18.04.77
pH		7.4	7.5	7.4
Eh	mV	300	300	280
Turbidity	g/ℓ	320	520	200
Chlorinity	gCl$^-$/ℓ	0.15	0.8	0.3
DOM	mg CH_2O /ℓ	30.8	36.7	
POM	mg CH_2O /ℓ	47.3	66.1	
Dissolved Mercury	µg Hg /ℓ	< 0.05	< 0.05	< 0.05
Particulate Mercury	µg Hg /ℓ	0.15	0.26	0.12
Particulate Calcium	% Ca	7.9	3.0	
Particulate Iron	% Fe	3.8	4.2	
Particulate Magnesium	% Mg	0.40	0.31	
Particulate Manganese	% Mn	0.07	0.07	
Weight loss 100–550°C	%	13		
Weight loss 550–1100°C	%	8.7		

2.6.– *Operational procedure for the determination of the adsorption rates.*

A differential procedure has been adopted for the determination of the adsorption rates. Such a method has the advantage that as long as processes other than adsorption on particulate matter (mainly losses of mercury to the reactor wall) are not competitive, their effects are negligible. The first experiment, hereafter called the dilution experiment, is carried out on the filtered sample (pore-size of 0.8 μm). The same filtered sample is also used as inlet solution. After injection of a known amount of mercury (II) chloride or metallic mercury, the evolution of the mercury concentration in the vessel sample is followed during 30 to 40 minutes ; the dissolved concentration in real time, the particulate concentration from the law of mass conservation as well as from a control measurement at the end of the experiments. As the mercury concentration in the vessel sample was always a few orders of magnitude higher than in the inlet solution, the former one is continuously diluted.

The second experiment, hereafter called the adsorption-dilution experiment, is similar to the dilution experiment except that in this case the reaction vessel contains natural, unfiltered sample. The dissolved mercury concentration decreases much faster in this experiment as a result of the combined effect of dilution by the inlet solution and adsorption on the particulate matter.

2.7.– *Dilution constants.*

Injections of dye in distilled water showed that the vessel solution is sufficiently homogeneous to admit that the internal and the outflowing concentrations are equal. Moreover the inflowing mercury concentration was always negligible compared to that in the vessel.

Under such conditions the law of mass conservation reduces to the following equation :

$$(1) \qquad \frac{dC}{dt} = - kC \qquad \text{or} \qquad C = C_s \ e^{-kt}$$

However, since in the experiments k was of the order of 10^{-2} min^{-1} , the dilution curve equation approximated a linear relation.

The dilution experiments also showed a definite functional relationship between temperature and k , and salinity and k .

Hence, for each set of physicochemical conditions, the adsorption rate has been computed using the mean k-value obtained under the same conditions.

2.8.— *Adsorption rates.*

Since the decrease in mercury in the vessel during the adsorption/dilution experiment equals the sum of the decreases due to adsorption and to dilution, one can write at time t :

$$(2) \qquad \left(\frac{dC}{dt}\right)_{vessel} = -kC + \left(\frac{dC}{dt}\right)_{adsorption}$$

The left handside of equation (2) represents the derivative of the adsorption-dilution curve equation ; it has been determined by a least squares polynomal fitting through the set of data-points.

It appeared that a cubic curve satisfied very well.

3.— Results.

Figure 2 shows the dissolved and particulate mercury concentrations measured 24 hours after a mercury injection varying between 0.1 and 50 ppm. The assumption that after one day both mercury forms are at equilibrium is justifiable. Indeed, Reimers and Krenkel (1974) found that illite, montmorillonite, octadecylamine and dodecanethiol adsorbed all of their inorganic mercury in 10 minutes, kaolinite and stearic acid attained maximum capacity in approximately 1 hour, and sand required 3 to 4 hours to reach maximum capacity. Frenet-Robin and Ottmann (1978) on the other hand found that the clays involved in their studies attained maximum capacity in 4 hours.

Our results indicate that up to 2 ppm, almost all mercury injected in samples 1 and 2 is scavenged by the particulate suspended matter, at low as well as at high salinity. For higher mercury level injections, however, different dissolved to particulate ratios are observed, depending on the salinity and the redox potential. At a redox potential of approximately 360 - 440 mV, 70 % of a 10 ppm mercury injection disappears on the particulate matter at low salinity, while at a salinity of 20 g NaCl/ℓ only 30 % is adsorbed. A high salinity seems to prevent the adsorption of Hg^{++} ions at certain sites or on a certain fraction of the suspended material. At a low potential, when metallic mercury is the stable species, this salt effect seems not to exist. Indeed, for a redox potential of 100 mV, 70 % of a 20 ppm injection disappears on the particulate matter at low as well as at high salinity. These results suggest that the particle charge is modified by the salt increase, so that the Hg^{++} ions are more strongly repelled while the neutral metallic mercury compound seems not to be affected. In the study of the adsorption kinetics, the mercury concentrations varied between
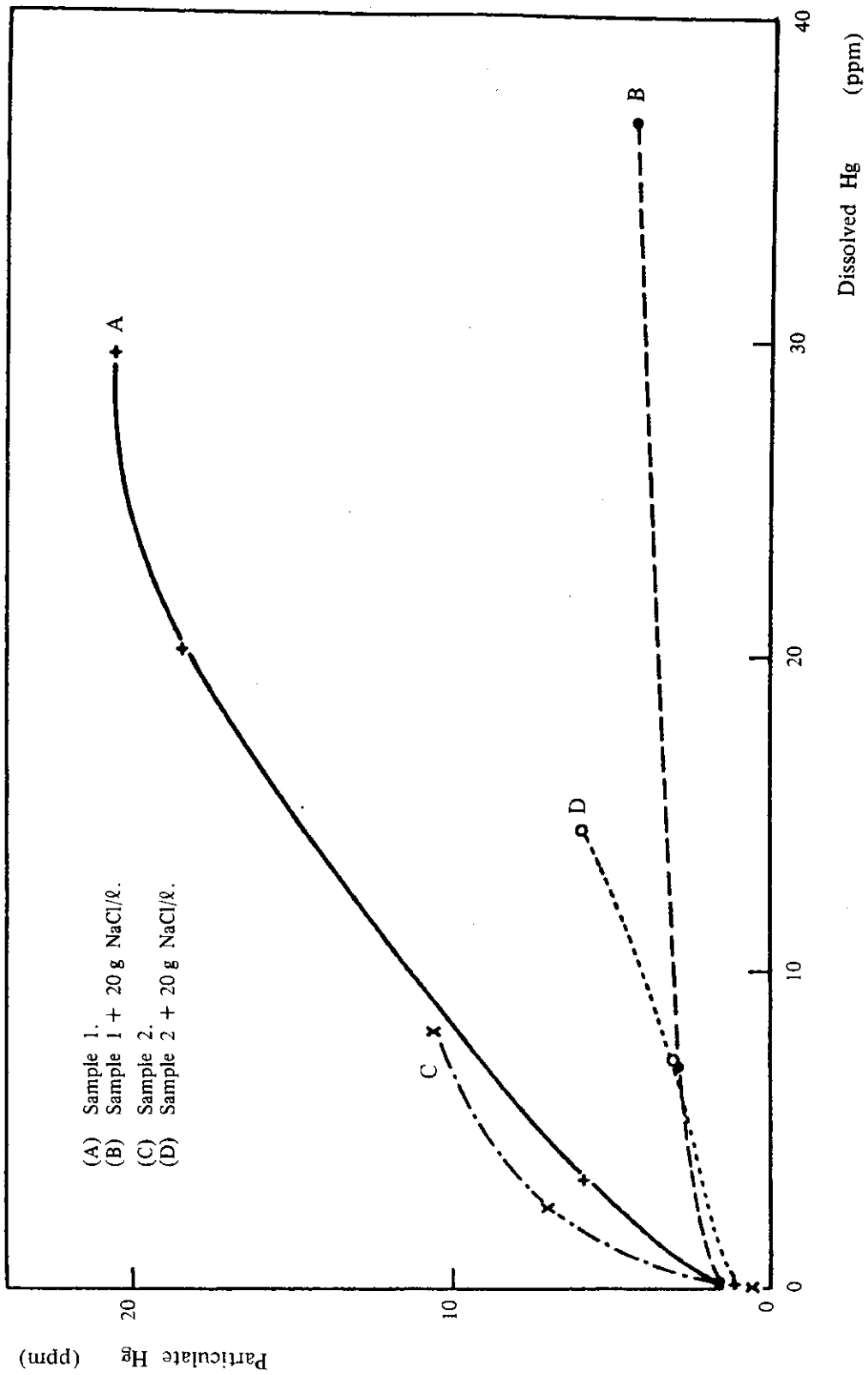
Equilibrium profiles of dissolved and particulate mercury

fig. 2.

(A) Sample 1.
(B) Sample 1 + 20 g NaCl/ℓ.
(C) Sample 2.
(D) Sample 2 + 20 g NaCl/ℓ.

Dissolved Hg   (ppm)

Particulate Hg   (ppm)

10 and 50 µg Hg/ℓ . It is obvious that in this concentration range, desorption effects have not to be taken into account.

The coefficient of variation for the initial adsorption rates resulting from duplicate dilution and adsorption-dilution experiments ranged, according to the physicochemical conditions, from 1 to 6 %. The variation on the dilution constant k contributed only slightly to this overall variation. A sensitivity test indicated that a 10 % increase of k, which is beyond the observed range of variation, modified the adsorption rate by no more than 0.3 % .

The applied differential method theoretically eliminates any contribution to the adsorption rate resulting from possible interactions with the vessel wall. In order to prove this, we compared adsorption rate data obtained with a plexiglass and a pyrexglass vessel under similar physicochemical conditions (see table 2). In view of the different nature of the two materials it is unlikely that they react with mercury in an identical way. But this also means that if the mean difference between the two data sets equals zero, the nature of the vessel wall has no influence on the adsorption rate determinations. A paired T-test (Dagnelie, 1970) allowed us to accept the hypothesis of equality of both data sets on the 0.05 level.

The influence of the various parameters on the initial adsorption rate (the initial amount of adsorbed mercury is negligible), which is fairly well illustrated in table 2, can be expressed as follows :

$$(3) \qquad V_{t=0} = 1.48 \ 10^{-3} (2.63 + 0.17 \ [Hg])[SM](TE)(27.01 - 0.43 \ [SA])$$

where $V_{t=0}$ is the initial adsorption rate in µg Hg/ℓ.min , [Hg] is the dissolved mercury concentration in µg Hg/ℓ , [SM] is the suspended matter concentration in g solid/ℓ , TE is the temperature in °C , [SA] is the salinity in g NaCl/ℓ .

The influence of the redox potential and hence of the mercury speciation on the adsorption rate was not unequivocal. With the pyrexglass vessel the adsorption rate slightly decreased for a decreasing potential, while the inverse occurred with the plexiglass vessel. Therefore this parameter is not included in the equation.

Although the adsorption capacity of the suspended material exceeds by far the amounts of mercury added to the samples, the adsorption rate normalized with respect to the prevailing dissolved mercury concentration decreased initially rather fast. As soon as R , the ratio Hg-adsorbed/Hg-dissolved , approached however a value of 0.3 , the rate became constant (figure 3). Taking into account that in our experiments $V_{R=0}$ equals $V_{t=0}$ in equation (3), the decrease of the adsorption rate in function of R can be expressed as follows :

Table 2

Mercury adsorption rates obtained with a pyrex glass and a plexiglass reaction vessel,
under similar physico-chemical conditions

Parameter conditions[b]	Plexiglass vessel		Pyrex glass vessel		Differences
	Initial adsorption rate[c] (10^{-2} ℓ.min^{-1}.g^{-1})	Initial Hg-concentration ($\mu g/\ell$)	Initial adsorption rate[c] (10^{-2} ℓ.min^{-1}.g^{-1})	Initial Hg-concentration ($\mu g/\ell$)	
Reference			31	18.0	
Reference	27	20.0	29.8[a]	20.0[a]	− 2.8
Reference	26.7[a]	22.9[a]	28	22.9	− 1.3
Reference	26.3[a]	26.2[a]	28	26.2	− 1.7
Reference	26	28.3	27.4[a]	28.3[a]	− 1.4
Reference	25	29.0	27.1[a]	29.0[a]	− 2.1
Reference	22	42.9	23	42.3	− 1
T = 40°C	31	29.3	40	24.9	− 9
T = 14°C	13	29.5	12	34.8	1
+ 20 g NaCl ℓ^{-1}	15	29.2	15	28.5	0
Eh = 150 mV	29	26.3	24	26.4	5

a. These values are linear interpolated values.

b. Reference : T = 25 °C; Eh > 300 mV; salinity < 1.3 g NaCl/ℓ ;
   (sample 2), turbidity = 260 mg solid/ℓ ,
   (sample 3), turbidity = 100 mg solid/ℓ .

c. The adsorption rate is normalized with respect to turbidity and dissolved-Hg concentration.
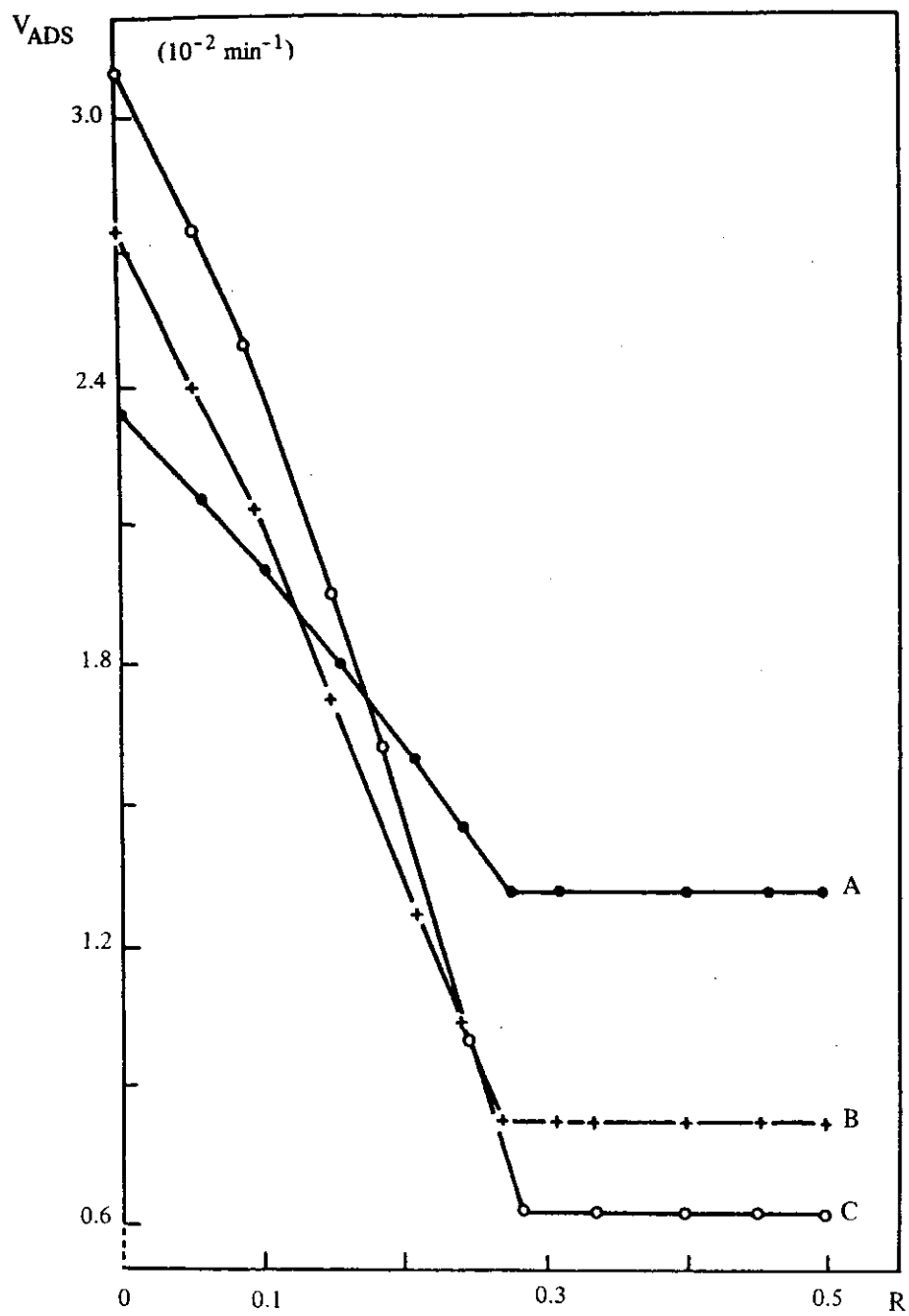
fig. 3.

The decrease of the adsorption rate with respect to the ratio Hg-adsorbed : Hg-dissolved.
(A), (B), (C) : initial Hg-dissolved concentration of 42.3 , 26.2 and 17.9 μg Hg/ℓ respectively.
R : ratio Hg-adsorbed/Hg-dissolved.
V_{ADS} : adsorption rate normalized with respect to the dissolved Hg-concentration.

$$(4) \qquad \overline{V} = \overline{V}_{t=0} + (0.017 - 1.477 \, \overline{V}_{t=0} - 3.949 \, \overline{V}_{t=0}^2) \times R \qquad R < 0.27$$

$$(5) \qquad \overline{V} = \overline{V}_{R=0.27} \qquad\qquad\qquad\qquad R > 0.27$$

where $\overline{V}$ is the adsorption rate normalized with respect to turbidity and dissolved mercury concentration.

As an example, the short-term behaviour of dissolved and particulate mercury (initially respectively 10 and 0 µg Hg/ℓ) in the upstream area (2 g NaCl/ℓ , 160 mg solid/ℓ , 15 °C) respectively downstream area (25 g NaCl/ℓ , 20 mg solid/ℓ , 15 °C) has been calculated by introducing in equations (4) and (5) the right parameter. This computation yields the following results :

Upstream			Downstream		
Time (min)	Hg-diss. (µg/ℓ)	Hg-ads. (µg/ℓ)	Time (min)	Hg-diss. (µg/ℓ)	Hg-ads. (µg/ℓ)
0	10	0	0	10	0
6	8.24	1.76	41	8.92	1.08
28	5.84	4.16	311	5.84	4.16
58	3.68	6.32	641	3.60	6.40
148	0.93	9.07	1391	1.20	8.80

Apparently, the adsorption of mercury in the upper part of the estuary proceeds about ten times faster than in the downstream part. As a consequence only a small fraction of the total amount of mercury discharged into the upstream area of the estuary will reach the sea, due to the adsorption process and an intensive sedimentation of the particulate suspended matter in the area of 1 to 5 % salinity, estimated to 90.6 kg/m^2.year (Baeyens et al., 1981), and corresponding to about 60 mg Hg/m^2.year .

In several studies e.g. Klein (1973), Lindberg and Harris (1974),strong correlations between the mercury and organic matter content of suspended sediments or bottom sediments have been found. Hence, the suggestion has been made, that the particulate organic matter is the most important mercury scavenger in the aquatic environment. In the Scheldt estuary the particulate suspended matter is composed of quartz, clays, carbonates, hydroxydes of iron and manganese and organic matter. Heating this material two or three times up to 550 °C yields us a residue free of organic material.

This residue has than been redispersed in filtered estuarine water sample (0.8 µm filter) using ultra-sounds, until the particle size distribution corresponded to the natural one (see table 3). The mercury adsorption capacity of this inorganic suspended

Table 3

Particle size distributions

Diameter		Number of particles		
			Suspension free of organic matter	
Limits μm	Mean μm	Natural sample	redispersed (ultra-sounds)	not redispersed
22.05 - 27.79	24.92	80	122	84
17.51 - 22.05	19.78	266	454	269
13.89 - 17.51	15.70	570	1250	482
11.03 - 13.89	12.46	952	2475	763
8.75 - 11.03	9.89	1817	4730	1194
6.95 - 8.75	7.85	3665	9193	1789
5.51 - 6.95	6.23	7105	16913	2871
4.37 - 5.51	4.94	12326	26480	3963
3.47 - 4.37	3.92	21133	37187	5334
2.76 - 3.47	3.11	34723	48428	7379
2.19 - 2.76	2.47	54884	60554	11096

matter was however significantly lower than the capacity of the natural material; in fact it was inferior to 1 ppm for Hg^{++} and inferior to 2.5 ppm for metallic mercury when an amount of 10 ppm Hg was added.

These results seem to corroborate the important role played by the organic matter. However, there are two facts we do not have verified yet : (1) could the heating of the suspended matter up to 550°C, modify the surface characteristics of the inorganic compounds ? (2) is coprecipitation especially with iron and manganese hydroxydes, an important process of mercury removal in the Scheldt ?

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Part 6

AN APPROACH TO ELABORATE A PASSIVE TRANSPORT MODEL

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1.– Introduction.

The evolution of a marine constituent results from the advection by the currents, the dispersion by molecular diffusion, turbulence at scales in time and space compatible with the studied environment, the vertical migration movements of for example of sediment particles due to gravity and buyoncy, the chemical and biological interactions with the other constituents.

If the space and time variations of the concentration of a given constituent are depending only on the velocity field, the dispersion flux and possible inputs-outputs, its behaviour can be described by a single evolution equation called a passive dispersion model (Nihoul, 1975). It is clear that even in the case a non-passive constituent it is preferable to base the prediction of its evolution on a passive dispersion model when the interaction processes are not entirely understood or cannot be formulated with sufficient accuracy and if one disposes of long time averages (several years). Indeed, such models always provide valuable estimates of (1) the distribution of non-passive constituents by, at least,appraising their possible transport by the sea motions and (2) the relative importance of possible unknown interaction processes when compared to the distribution of a real passive constituent as NaCl.

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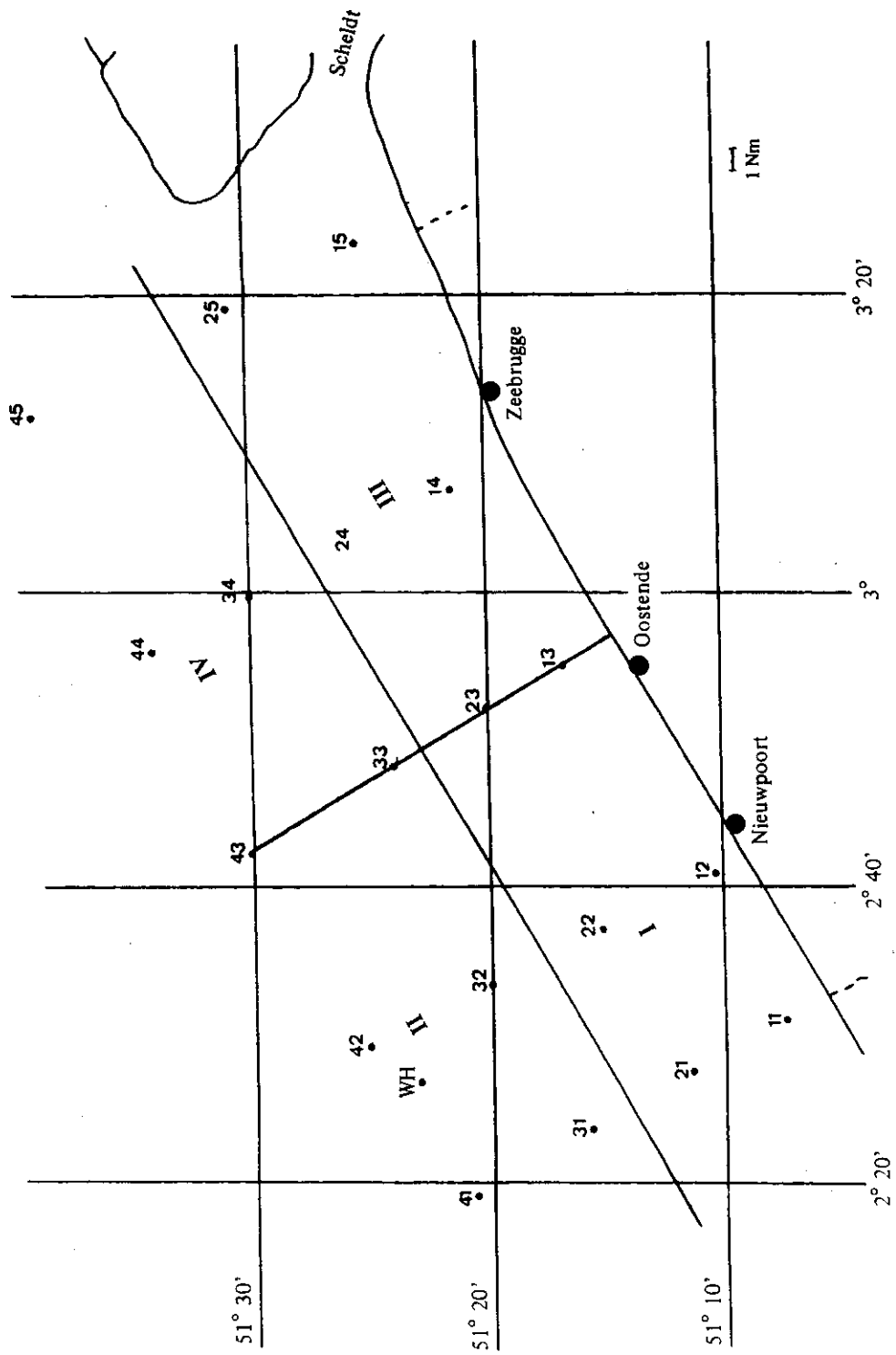
fig. 1.

Location of sampling stations in the North Sea (Belgian coast)

In previous papers, bulk concentrations of heavy metals in the Belgian coastal waters (Decadt et al, 1982), as well as boundary conditions at the air-sea interface (Dehairs et al, 1982a, 1982b) and at the sea-land interface such as the Scheldt estuary (Baeyens et al, 1982) are discussed together with the hydrodynamical data. They make it possible to calculate passive circulation patterns of dissolved Cd, Cu, Pb and Zn as well as total Hg through the four subareas defined on our sampling grid (fig.1).

Relying upon the carbon cycle (mean phytoplankyon productivity and grazing of zooplankton) and the mean cadmium content of zooplankton, Elskens (1973) inferred that in the offshore area, adjacent to our coastal zone, the maximum quantity of cadmium involved in the plankton box is about 4.3 tons.year^{-1}. Compared to the several hundred tons of cadmium transported in and out that area, these fluxes too and from the food web are negligible. Unfortunately, we do not have sufficient data on the heavy metal content in zooplankton consequently we are not able to carry out the same calculations for our area.

Nevertheless, it is not obvious that the heavy metal flow related to biological activity is also negligible in our area since Decadt et al (1982) showed that the organo-complexed fraction may represent up to 80% of the total dissolved content (see part 2). Other processes such as for example adsorption, desorption, mobilisation, precipitation,... may appear also important ; in that case the passive dispersion model will show a production or disappearance of the given metal inside the considered box.

2.- Hydrodynamical characteristics.

Since we are mainly interested in the overall transport patterns of the selected trace metals (Cd, Cu, Hg, Pb and Zn), residual currents should be specified. Unfortunately, on the scale of the boxes defined within our sampling grid (15-30 km), no such residual flow lines are available. Only at some lateral boundaries are these flows known from measurements (3.3 km^3.year^{-1} from the Scheldt estuary to box III and 0.3 km^3.year^{-1} from the coast to both boxes I and II) and computations (642 and 962 km^3.year^{-1} inflow to boxes I and II respectively,according to Nihoul & Ronday (1976)). However, the mean salinity distribution in the area (fig.2) is well known (Unité de Gestion du Modèle Mer du Nord, pers.comm.).

Applying the law of mass conservation on this conservative parameter yields the residual flow pattern shown in fig.3. The overall diffusion coefficient deduced from the computations equals

32.76 45
32.49
32.22 35
31.86 25
31.38
30.89 15
Scheldt estuary

33.59 44
33.26
32.92 34
32.58
32.24 24
31.78
31.31 14
Zeebrugge

33.99 43
33.59
33.19 33
32.69 23
32.67
32.65 13
Oostende

34.32 42
34.16
34.00 32
33.92
33.84 22
33.69
33.54 12
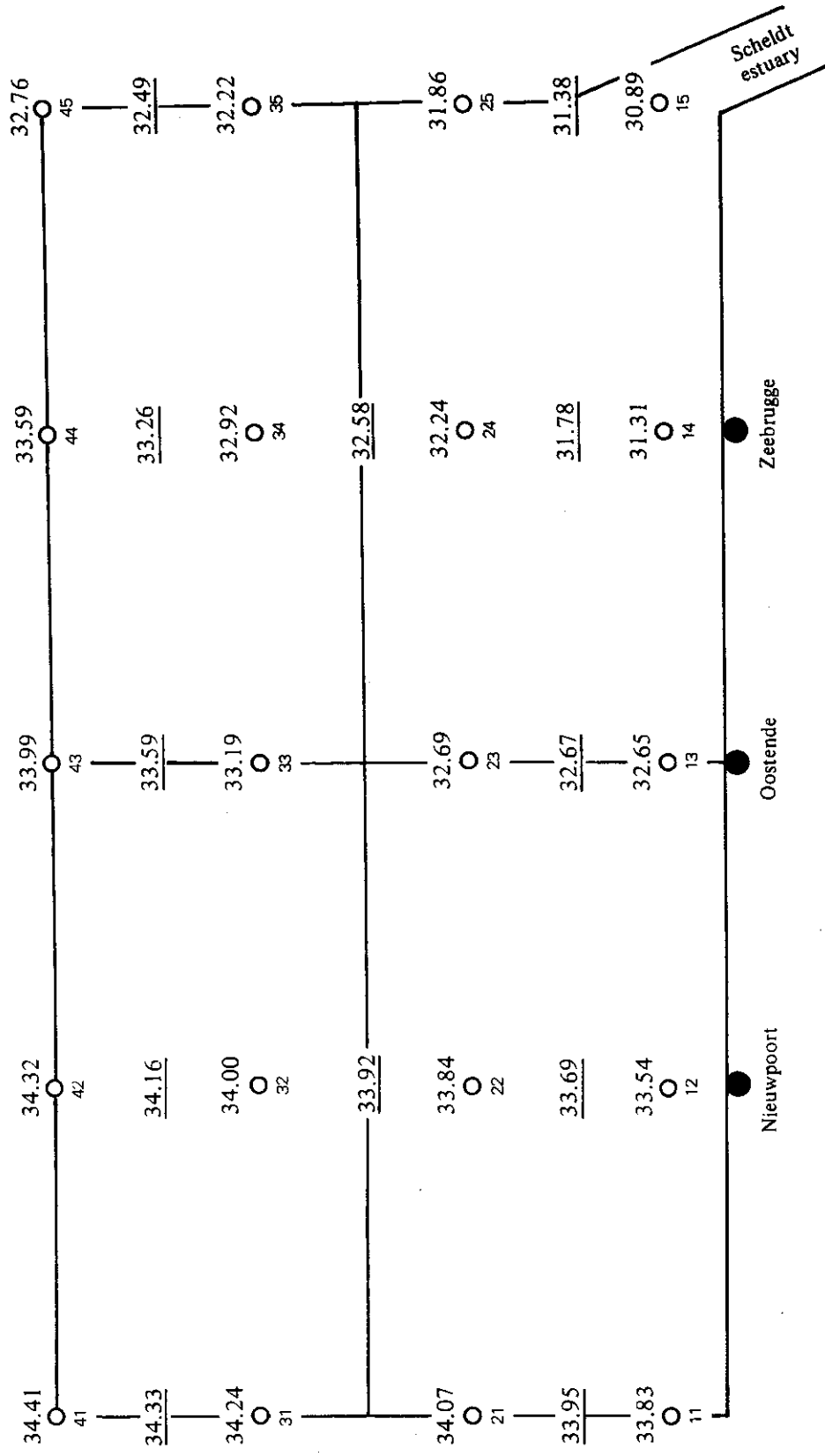Nieuwpoort

34.41 41
34.33
34.24 31
34.07 21
33.95
33.83 11

fig. 2.

Schematic salinity distribution in the Belgian Coastal Area
Mean observed values (1977-1981) in ‰
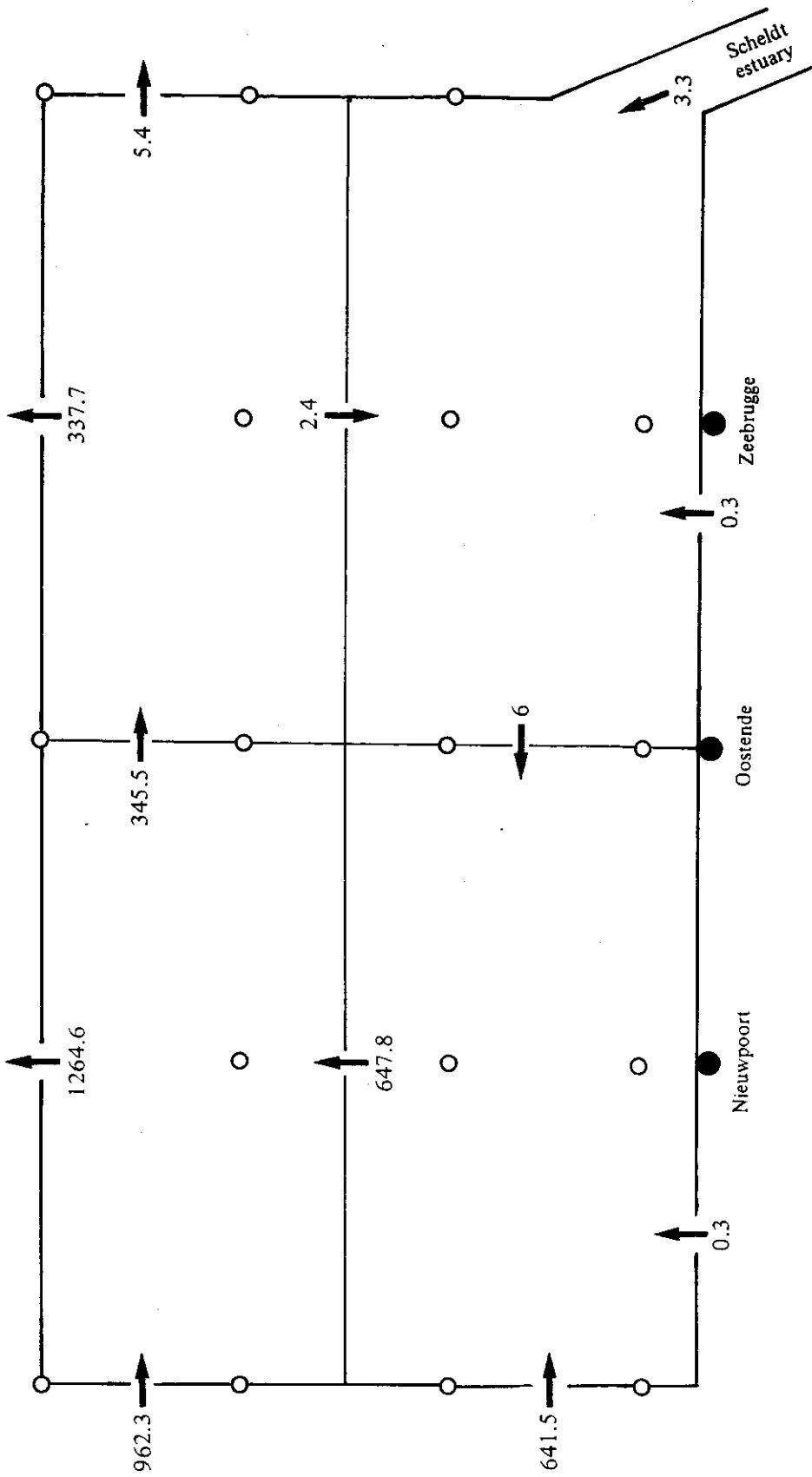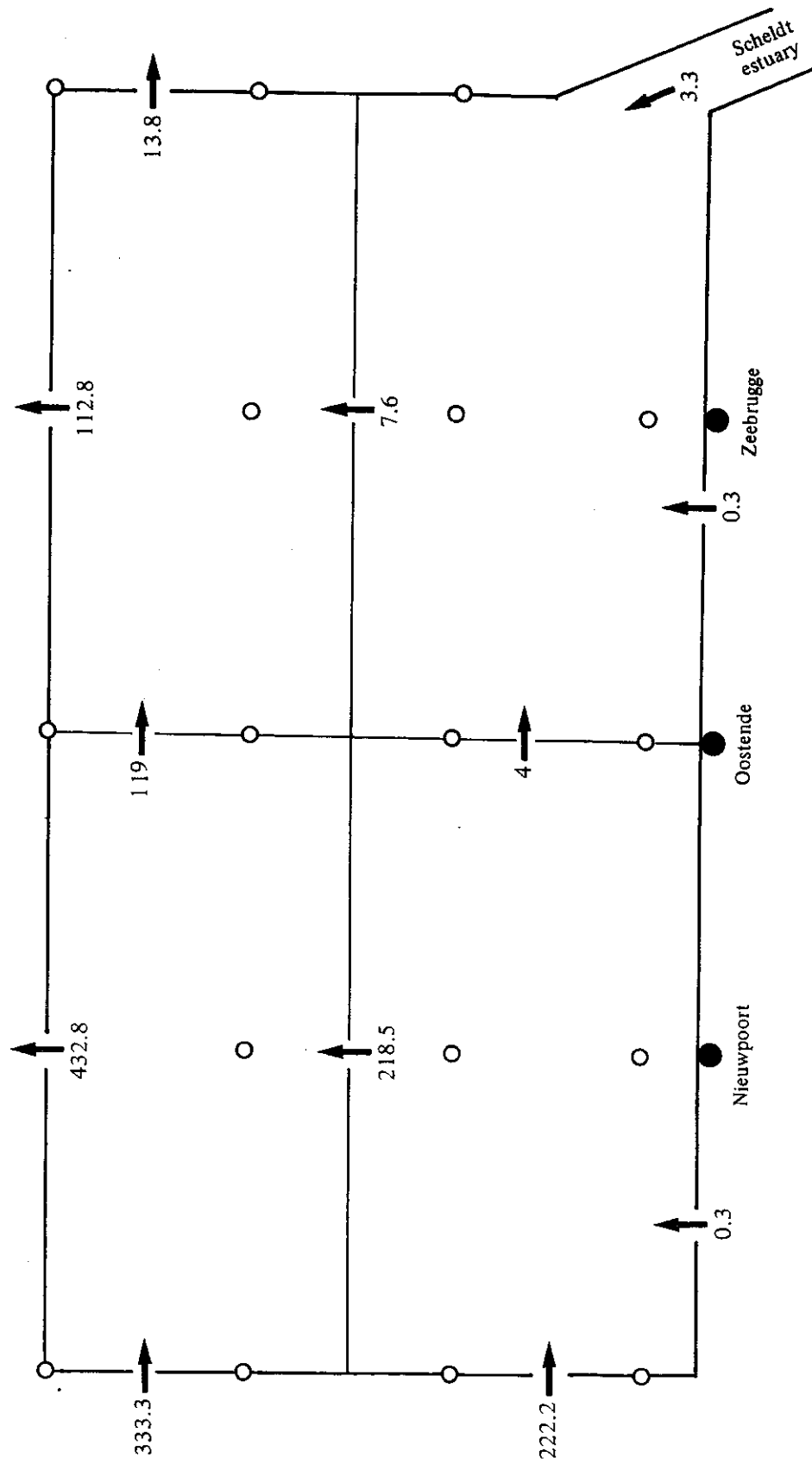— values calculated as the mean of the two adjacent values
○ sampling stations

fig. 3.

Residual circulation in the Belgian Coastal Zone

(Flows in km³/year; overall diffusion coefficient : 466 km³/year)

466 km^3.year^{-1}. Under the given boundary conditions, these results corroborate the existence of a gyre (cyclic residual circulation) off the Belgian coast, as predicted by mathematical models based on the mechanical variables describing the system's hydrodynamics (Nihoul & Ronday, 1976).

However, the possible existence of such a gyre must be considered with care. Indeed a decrease of the inflow at the lateral boundaries of boxes I and II to 222 and 333 km^3.year^{-1} respectively, changes the circulation pattern to a non-cyclic one as is indicated by fig.4. In that case the overall dispersion coefficient amounts to 436 km^3.year^{-1}.

3.– Trace metals circulation patterns.

The residual trace metals circulation patterns shown in fig. 5 to 9 are based on the residual currents illustrated in fig.3 and the mean metal concentrations determined in each of the twenty sampling stations (Decadt et al, 1982). Since no data were available for the coastal trace metal inputs, we considered them, arbitrarily, as negligible.The input from the atmosphere to the sea has been calculated by Dehairs et al (1982a) but since the atmospheric fall-out in each box may be considered as similar, this flux does not affect the residual trace metal flow patterns.

Results obtained for dissolved cadmium (fig.5) indicate that there may be a net production in box III and a net consumption in boxes I, II and IV. Even, when taking into account a variation of at least 10% on the greatest flow in or out the box (this variation is acceptable from the point of view of errors still involved in the used analytical techniques (Gillain et al, 1982), there is still a reasonable probability that under the given flow conditions, production of dissolved Cd occurs in box III and disappearance in boxes I and IV. Following the same method for the other metals, one may suggest that :

- for dissolved Zn (fig.6), there is production in box IV and consumption in boxes II and III,

- for dissolved Pb (fig.8), there is production in boxes I and IV and consumption in boxes II and III,

- for dissolved Cu (fig.7), there is production in box III and consumption in boxes I and II,

- for total Hg (fig.9), there is production in boxes II, III and IV.

fig. 4.

Residual circulation in the Belgian Coastal Zone
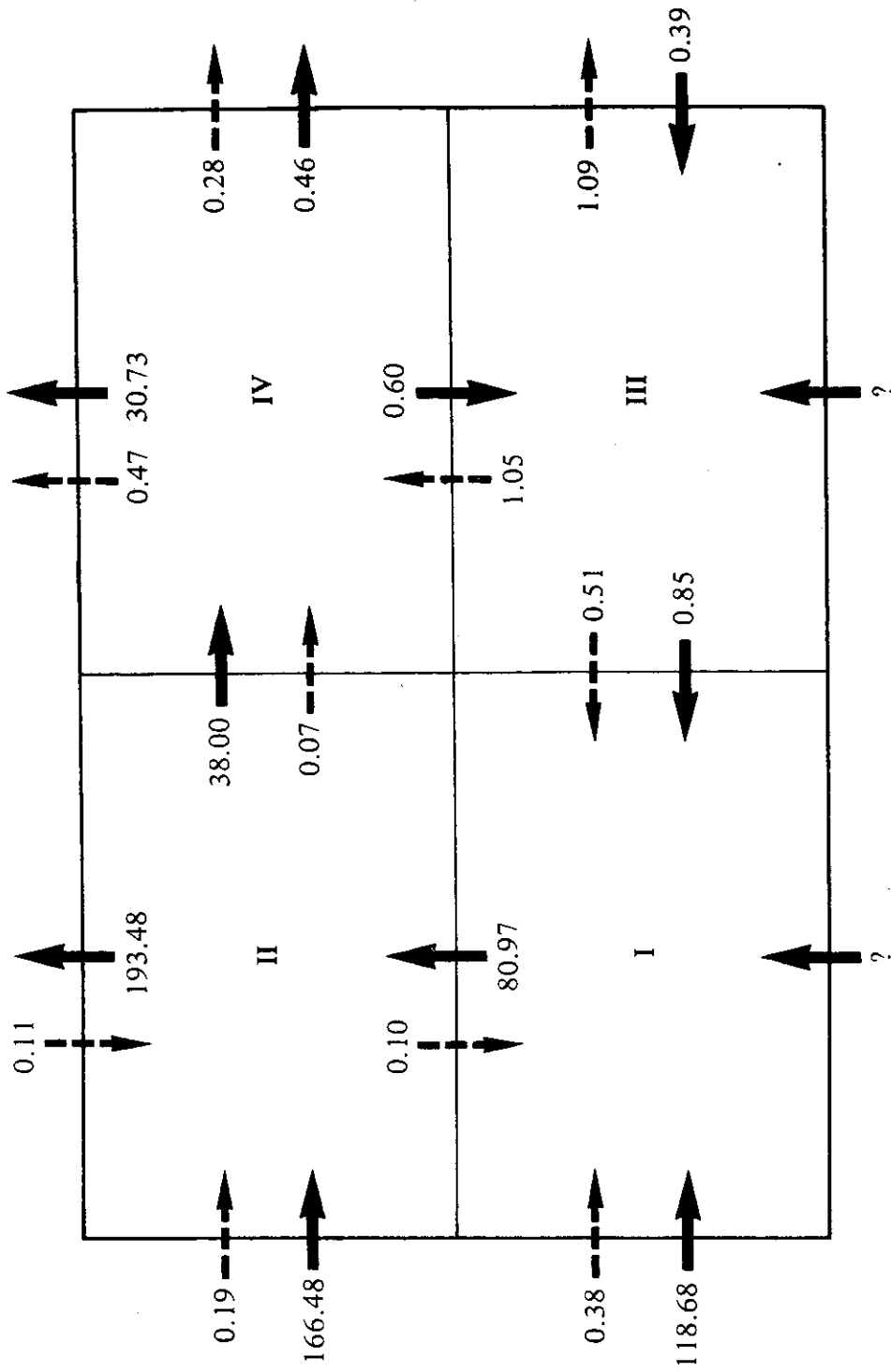(Flows in km³/year; overall diffusion coefficient : 436 km³/year)

Passive dispersion patterns for Cd (flows in t Cd/year)
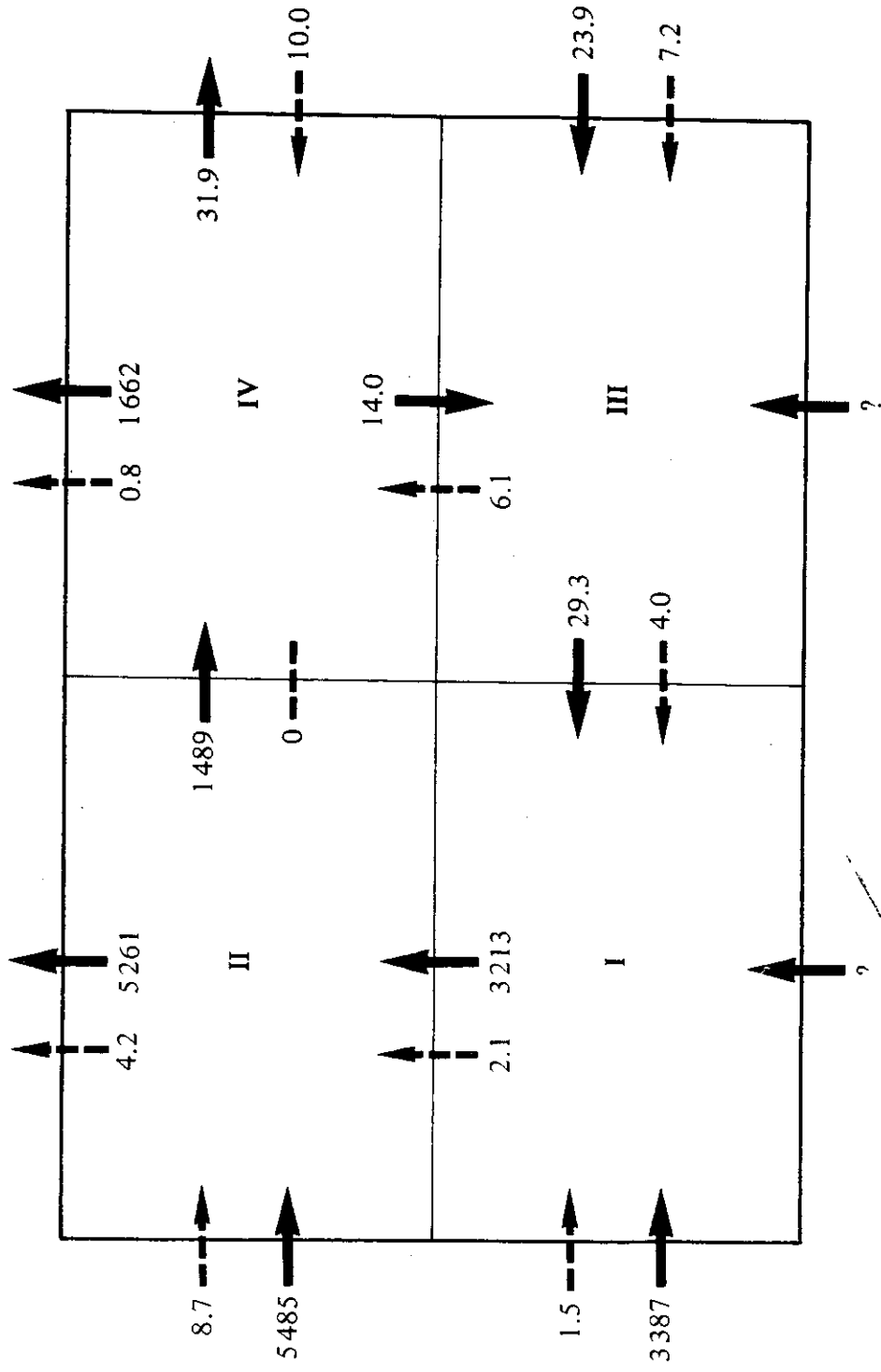Arrow : advection; broken arrow : diffusion

fig. 5.

Passive dispersion patterns for Zn (flows in t Zn/year)
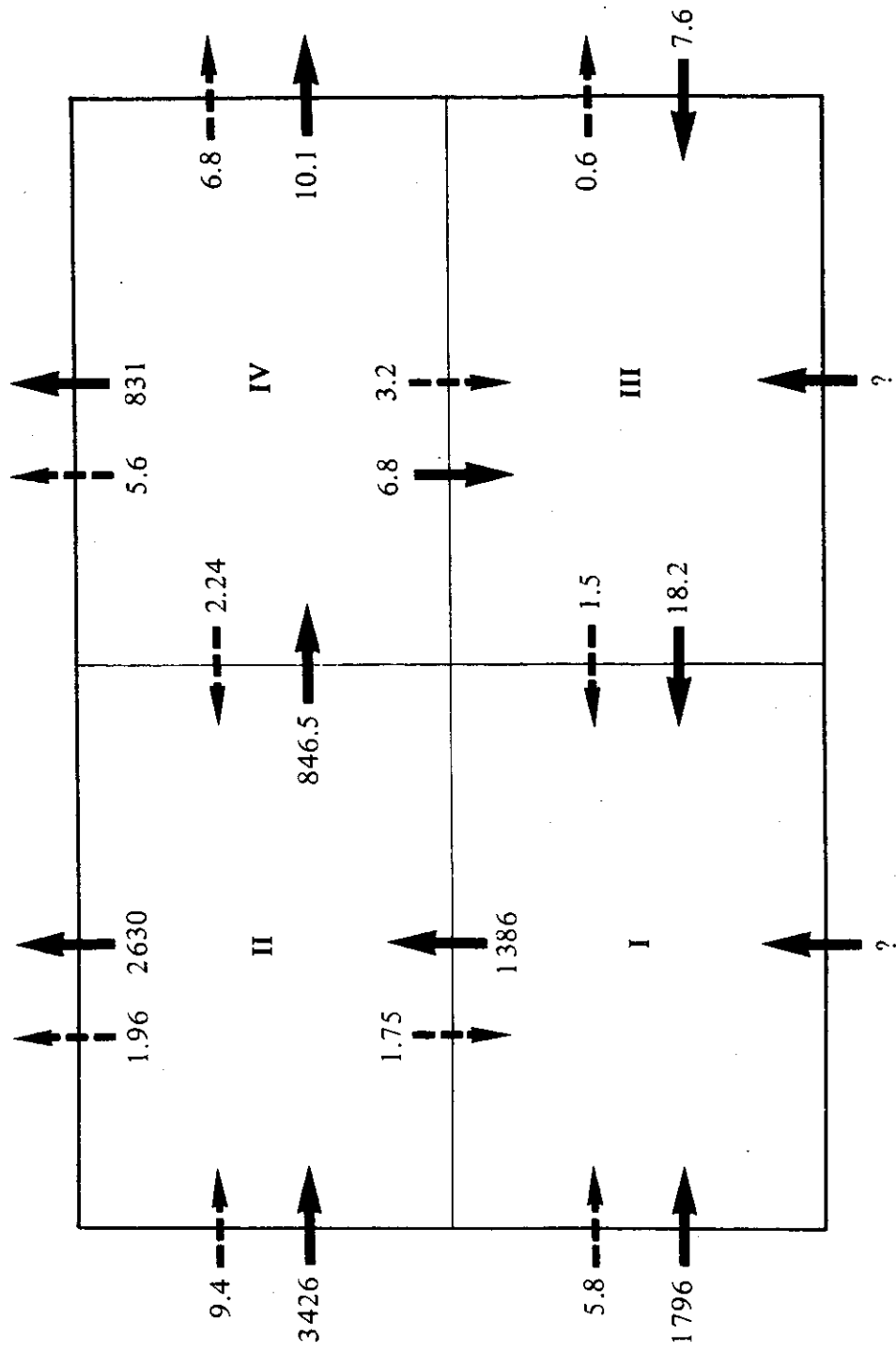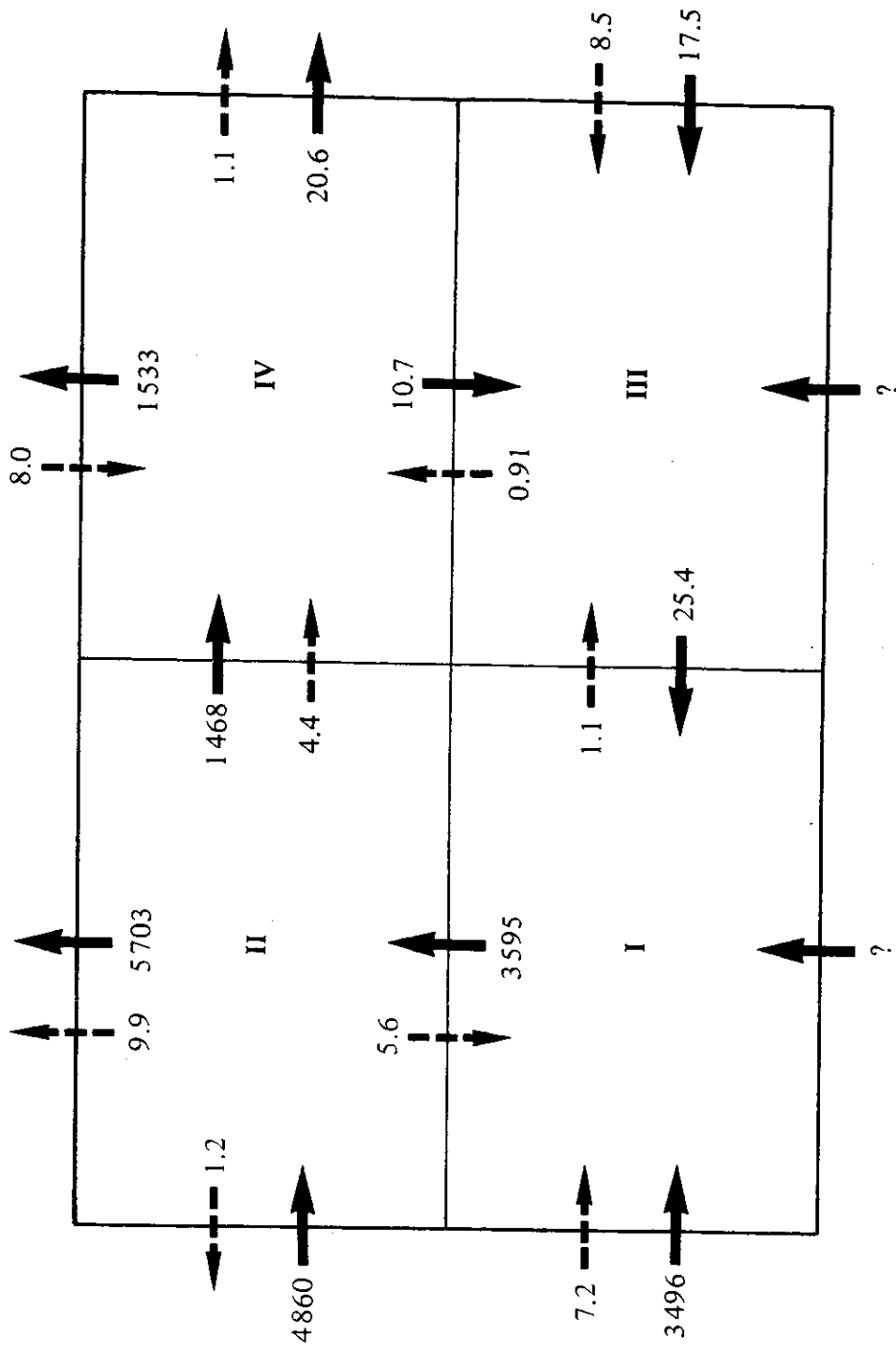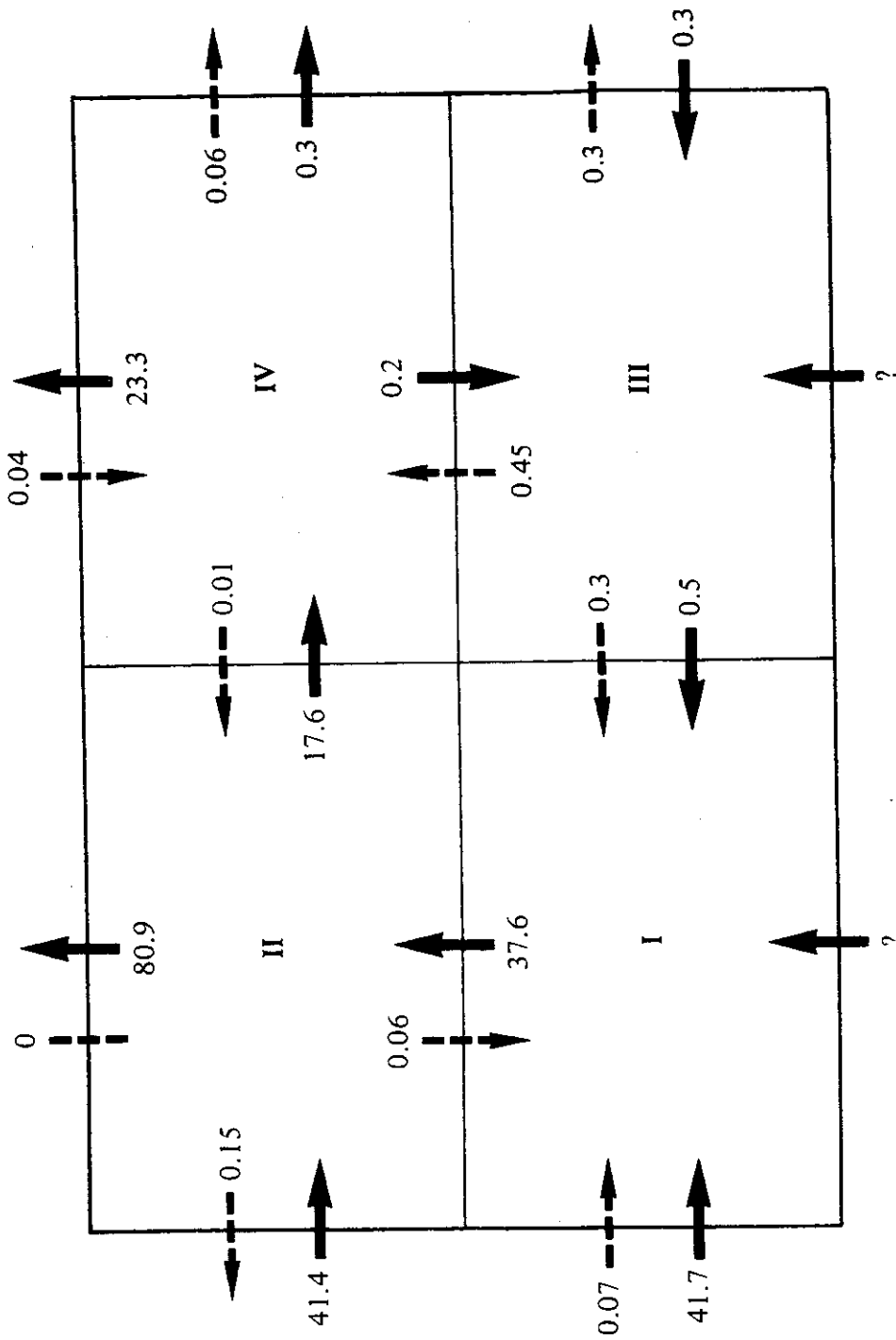Arrow : advection; broken arrow : diffusion

fig. 6.

Passive dispersion patterns for Cu (flows in t Cu/year)
Arrow : advection; broken arrow : diffusion

fig. 7.

Passive dispersion patterns for Pb (flows in t Pb/year)

Arrow : advection; broken arrow : diffusion

fig. 8.

fig. 9.

Passive dispersion patterns for total mercury
Arrow : advection; broken arrow : diffusion

Until now, we are not able to evaluate and to give a clear explanation for these trace metal flow patterns, but we have to keep in mind that this is only a first attempt to built up a passive dispersion model - with the hope to later produce interactive ones - and that with the great uncertainty of the used residual currents values these trace metal flow patterns can only be used as an indication. It looks clear however that the dissolved trace elements we have determined do not have a conservative character and that more elaborate interactions will have be taken into account.

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THE ACCUMULATION OF HEAVY METALS
IN MARINE ORGANISMS

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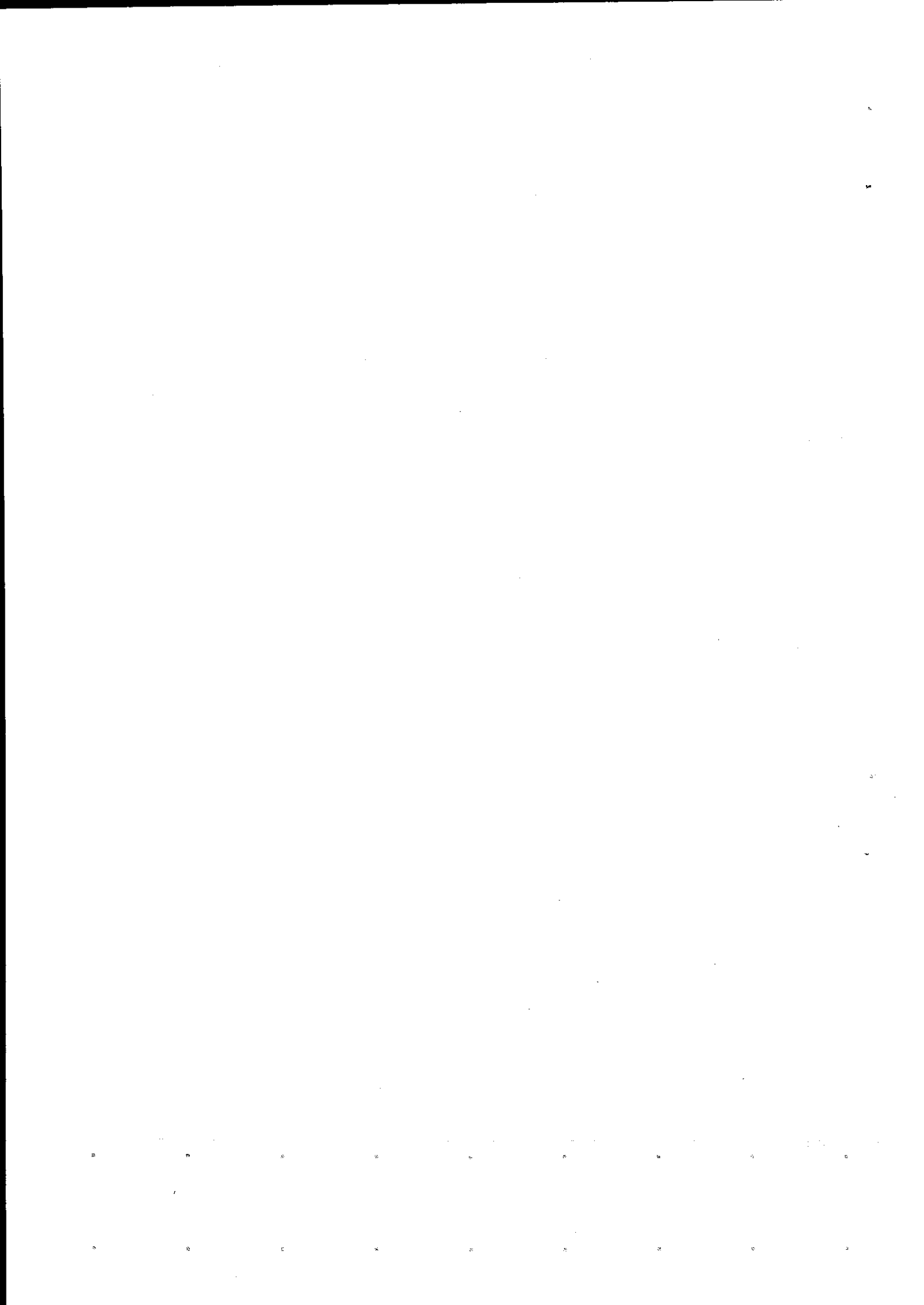
The understanding of the heavy metal contamination of aquatic organisms is rather difficult because it depends not only on the nature and concentration of the pollutant but also on many physico-chemical and biological characteristics of the ecosystem. Moreover a high concentration of metal present in an organism is not necessarily correlated with a high degree of pollution of the medium. Indeed, in contrast to the non-essential trace metals such as mercury and cadmium, the essential ones such as copper and zinc have important biological functions in the organisms and can therefore be found in important amounts in some of their organs in unpolluted as well as in polluted media.

On another hand, several species are able to develop physiological mechanisms of storage, under a detoxified form, of heavy metals present in excess in the organism.

So, from an ecotoxicological point of view, the occurrence of high heavy metal concentrations in marine organisms is to be carefully studied considering at one time environmental factors influencing their accumulation and toxicity, and at another time the physiology as well as the adaptative ability of the organism to stand unusual concentrations of trace metals in their environment.

1.– Occurrence of high heavy metal concentrations in marine organisms.

Table 1 presents the exceptionally high heavy metal concentrations we could observe in some tissues from marine organisms together with some relevant bibliographic data. These high values are compared in this table with the concentration of the same metal in other samples from the same area. Animals were collected in natural environments with relatively little or no pollution except for samples coming from the Bristol Channel where Cd concentration in water lies around 5 ppb (Abdullah et al, 1972 ;

Table 1

	Locality	n	Mean metal concentration of the tissue compared with that of other organs or organisms from the same locality (ppm wet weight/ppm dry weight)		
CADMIUM					
Pecten maximus digestive gland	Roscoff	8	99 ppm w.wt/ 502 ppm dr.wt	versus	0.5 ppm w.wt/ 2.5 ppm dr.wt in muscle
Spondylus gaederopus kidneys	Monaco	1	61 ppm w.wt/ 315 ppm dr.wt	versus	0.5 ppm w.wt/ 3.7 ppm dr.wt in gills
Pinna nobilis kidneys	Corsica	1	52 ppm w.wt/ 114 ppm dr.wt	versus	2 ppm w.wt/ 12 ppm dr.wt in digestive gland
Patella vulgata soft parts	Bristol Channel*	40	54 ppm w.wt/ 351 ppm dr.wt	versus	0.7 ppm w.wt/ in *Actinia equina*
Nucella lapillus soft parts	Bristol Channel*	22	93 ppm w.wt/	versus	8 ppm w.wt/ in *Littorina littorea*
Sepia officinalis digestive gland	Bristol Channel*	1	43 ppm w.wt/	versus	0.2 ppm w.wt/ in muscles and skin
ZINC					
Pecten maximus kidneys	Roscoff	4	1995 ppm w.wt/11602 ppm dr.wt	versus	8 ppm w.wt/ 57 ppm dr.wt in mantle
Pinna nobilis digestive gland	Corsica	2	825 ppm w.wt/ 4040 ppm dr.wt	versus	104 ppm w.wt/683 ppm dr.wt in mantle
Spondylus gaederopus kidneys	Monaco	1	540 ppm w.wt/ 2769 ppm dr.wt	versus	17 ppm w.wt/ 73 ppm dr.wt in muscles
Crassostrea gigas soft parts	Bristol Channel*		9860–35120 ppm dr.wt		BOYDEN & ROMERIL (1974)
Nucella lapillus soft parts	Bristol Channel*	22	719 ppm w.wt/	versus	35 ppm w.wt/ in *Littorina littorea*
Sepia officinalis digestive gland	Bristol Channel*	1	897 ppm w.wt/	versus	14 ppm w.wt/ in muscles
Balanus balanoides soft parts	Cardigan Bay*		1770–3438 ppm w.wt/		WALKER et al. (1975)

Mean metal concentration of the tissue compared with that of other organs or organisms from the same locality (ppm wet weight/ppm dry weight)

	Locality	n	Mean metal concentration	Reference / organ
COPPER				
Nucella lapillus soft parts	Bristol Channel*	22	131,6 ppm w.wt/ versus 5 ppm w.wt/	in *Arenicola marina*
Crassostrea gigas soft parts	Bristol Channel*		/1760-6480 ppm dr.wt	BOYDEN & ROMERIL (1974)
Sepia officinalis digestive gland	Bristol Channel*	1	1175 ppm w.wt/ versus 1.6 ppm w.wt/	in muscles
IRON				
Porphyra spp. red alga	Irish Sea		/104-3800 ppm dr.wt	PRESTON et al. (1972)
Spondylus gaederopus digestive gland	Monaco	1	425 ppm w.wt/1446 ppm dr.wt versus 0.4 ppm w.wt/ 3.2 ppm dr.wt	in mantle
Pecten maximus digestive gland	Roscoff	8	327 ppm w.wt/1319 ppm dr.wt versus 7 ppm w.wt/ 30 ppm dr.wt	in mantle
Pecten novae-zelandiae unspecified	New-Zealand		/2915 ppm dr.wt	BROOKS & RUMSBY (1965)
Mytilus edulis	New-Zealand		/1960 ppm dr.wt	BROOKS & RUMSBY (1965)
Mercenaria mercenaria	Irish Sea		/5400 ppm dr.wt	SEGAR et al. (1971)
Patella vulgata	Irish Sea		/2060 ppm dr.wt	PRESTON et al. (1972)
MANGANESE				
Pecten maximus kidneys	Roscoff	4	2516 ppm w.wt/14620 ppm dr.wt versus 0.2 ppm w.wt/ 1 ppm dr.wt	in muscles
Pinna nobilis kidneys	Corsica	1	13730 ppm w.wt/30227 ppm dr.wt versus 4 ppm w.wt/ 20 ppm dr.wt	in digestive gland
Tridacna maxima kidneys	Polynesia	3	247 ppm w.wt/ 1130 ppm dr.wt versus 3 ppm w.wt/	in digestive gland
LEAD				
Pinna nobilis kidneys	Corsica	1	432 ppm w.wt/ 951 ppm dr.wt versus < 3 ppp w.wt/	in gills

* Polluted area.

Peden et al, 1973). After dissection, tissues were directly fro-
zen. Wet or dry samples were analysed by atomic absorption spec-
trophotometry (Perkin-Elmer, model 370A) after mineralization for
8 hrs at 80°C in HNO_3 65% (2.5 ml g^{-1} fresh tissue) and twenty-
fold dilution.

It is of importance to note that, except for the case of sam-
ples coming from the Bristol Channel (Noël-Lambot et al, 1978,
1980b) and Cardigan Bay (Walker et al, 1975), the high metal con-
centrations observed in the tissues are not associated with envi-
ronments known as polluted and thus may correspond to normal va-
lues. It thus appears that some tissues are able to specifically
accumulate very high amounts of some metals occurring in trace
concentration in their environment. This property is very wide-
spread in molluscs particularly in the kidneys and digestive
gland as shown in table 1. It should be observed that, in verte-
brates, kidneys and liver are also the principal organs involved
in heavy metal storage.

Metal distribution in the organs is thus very heterogeneous.
This distribution is quite different from a species to another
and it varies depending on the metal considered. Moreover indi-
vidual variations are important. In some cases, as in *Patella
vulgata* and *Nucella lapillus*, a correlation between age and the
Cd, Zn and Cu concentration could be established (Noël-Lambot et
al, 1980a & b) but this observation cannot be generalized.

It is well known that molluscs have a particular accumulation
capacity for heavy metals ; though some of the results presented
in table 1 are probably the highest values ever reported.

Heavy metals tend to accumulate in living matter because of
their high affinity for cellular components. Binding sites are
provided by practically all normal cell constituents but there
also exist more specific storage mechanisms which contributes
largely to the existence of high heavy metal loads in some orga-
nisms.

2.— Factors controlling the accumulation of heavy metals by aquatic organisms and importance of storage mechanisms.

As far as the pollutant concentration and the physico-chemical
characteristics of the surrounding medium remain constant, the
direct uptake of metals from water can often be described by the
following equation (see for example Bouquegneau et al, 1979) :

$$C_t = C_{ss} (1 - e^{-Kt})$$

where C_t is the concentration of the metal at time t ; C_{ss} the steady-state concentration;

$$K = \frac{0.693}{t_{b_{1/2}}} ,$$

$t_{b_{1/2}}$ being the biological half-time.

The shape of the curve depends both on the initial rate of uptake of the pollutant and on its rate of elimination (biological half-time).

The rate of uptake of metals may depend on several physiological mechanisms such as passive diffusion, facilitated diffusion, active transport and, in the case of colloïdal metal species, endocytosis (for a review, see Coombs, 1980).

Working with the teleost *Serranus cabrilla*, we have shown that the effect of mercury concentration on the metal uptake by the gills revealed the existence of a mercury carrier at the gill epithelium level (Bouquegneau et al, 1982).

On the other hand, the biological half-time should be theoretically equal to the half-time of elimination of the pollutant when the animal is put back in clean water. Sometimes it is effectively the case, but in many species such as *Serranus cabrilla*, we have found that the steady-state could be reached very quickly even when the half-times of elimination of the pollutant were very long (Radoux & Bouquegneau, 1979).

Thus, it appears that other factors are able to modify the uptake kinetics of the pollutants.

Table 2 shows the different factors affecting the heavy metal load of an organism exposed to a polluted environment. Those factors are numerous and can influence each other as shown by the arrows in the table. The concentration of the pollutant in water or in sediment of course but also its chemical form can affect the uptake significantly.

For example, it is now well known that the more hydrophobic alkyl and aryl mercury compounds are more readily taken up and are more toxic to phytoplankton or to fish than inorganic mercuric chloride. Moreover, mercury as sulphide in sediments is made unavailable and become immobilized. Many environmental factors are able to affect too the uptake of heavy metals. The main factors are salinity and temperature, and they influence both the chemical form of the pollutant and the physiology of exposed organism (see table 2).
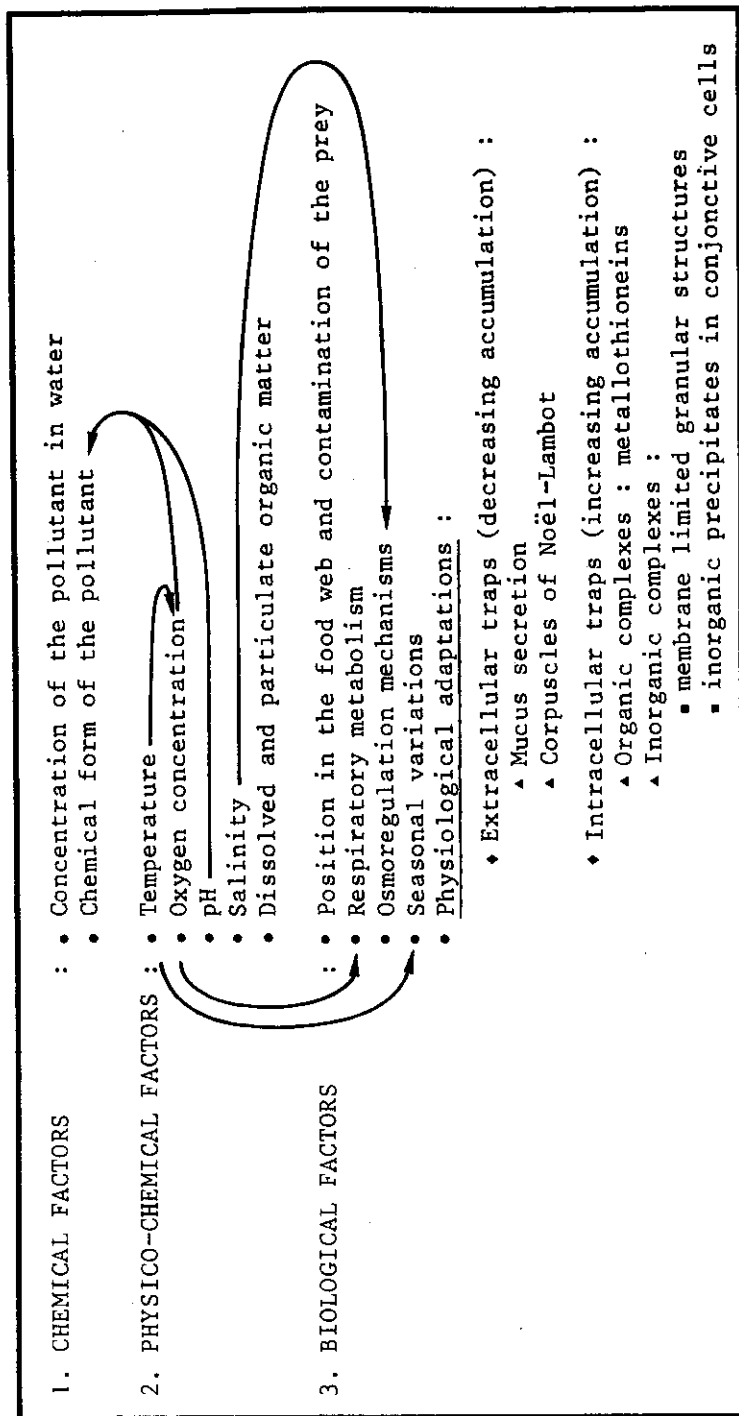
Reduction in salinity generally results in an increase in heavy metal uptake. For example, the rate of mercury accumulation of the chinese crab *Eriocheir sinensis* is much more important in

Table 2

Factors affecting the heavy metal load of an organism exposed to a polluted marine environment.
Arrows show some interactions between these factors.
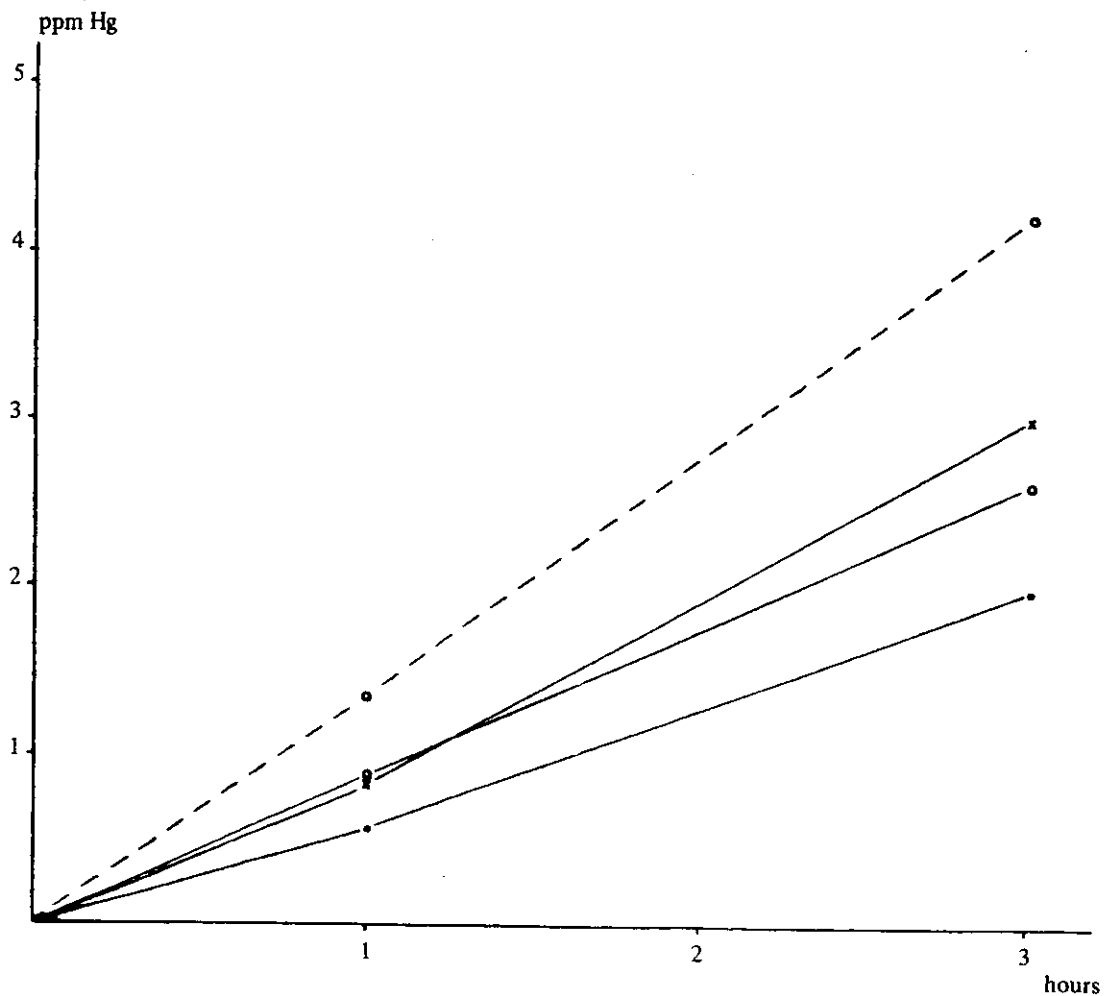(Adapted from Bouquegneau & Verthé, 1981)

1. CHEMICAL FACTORS : • Concentration of the pollutant in water
                        • Chemical form of the pollutant

2. PHYSICO-CHEMICAL FACTORS : • Temperature
                               • Oxygen concentration
                               • pH
                               • Salinity
                               • Dissolved and particulate organic matter

3. BIOLOGICAL FACTORS : • Position in the food web and contamination of the prey
                         • Respiratory metabolism
                         • Osmoregulation mechanisms
                         • Seasonal variations
                         • Physiological adaptations :

                           ◆ Extracellular traps (decreasing accumulation) :
                             ▲ Mucus secretion
                             ▲ Corpuscles of Noël-Lambot

                           ◆ Intracellular traps (increasing accumulation) :
                             ▲ Organic complexes : metallothioneins
                             ▲ Inorganic complexes :
                               ■ membrane limited granular structures
                               ■ inorganic precipitates in conjonctive cells

fig. 1.

Accumulation of mercury by *Leptomysis linguura* in filtered sea-water (Millipore 0.22 μ --o - -) and in sea-water containing complexing agents as : cystein (—•—), citrate (—x—) and EDTA (—o—). Each point is the mean of the results obtained for 10 specimens (from Verthé et al., 1982).

fresh water than in sea water (Bouquegneau et al, 1979). Generally, increase in temperature results in an increase in uptake until lethal effects begin to take effect.

A possible important environmental factor which is often neglected is the presence in water of more or less dissolved and particulate organic matter.

Fig.1 (Verthé et al, 1982) shows that the rate of uptake of mercury by *Leptomysis linguura* is decreased by the presence in the medium of some highly concentrated organic complexes such as cystein, citrate and EDTA. However, it seems that such an inhibitory effect cannot be generalized to all natural organic
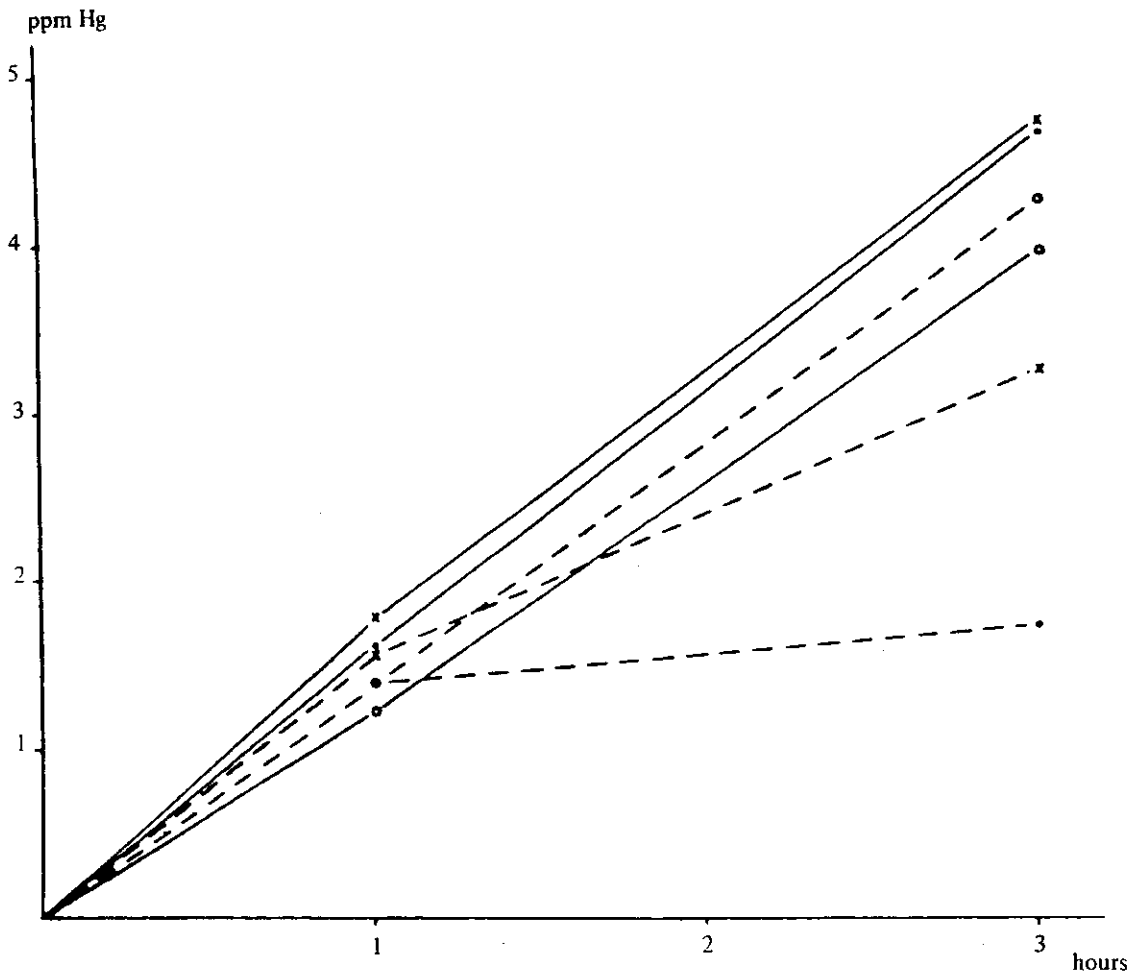
fig. 2.

Mercury accumulation by *Leptomysis linguura* in sea-water filtered on a 0.22 μ Millipore filter (– – o – –), in unfiltered water (– – ● – –), in sea-water containing 2 x (——●——), 5 x (——x——) and 10 x (——o——) times the normal amount of organic matter with molecular weight higher than 10 000 daltons and in ultra-filtered sea-water (– – x – –) [organic matter molecular weight < 10 000 daltons]. Each point is the mean of the concentrations observed in 10 animals (from Verthé et al., 1982).

complexes since no effect on the uptake has been detected when natural high molecular weight dissolved organic matter is added to the medium (fig. 2, Verthé et al., 1982).

Moreover, when considering cadmium complexation, different effects can be observed depending on the highly concentrated organic complex used : EDTA totally inhibits the entry of cadmium in *Leptomysis linguura* and in *Patella caerulea* ; cystein largely increases the rate of entry of Cd in *Leptomysis linguura* but has no short-term effect in *Patella caerulea* ; citrate has no effect in both species (fig.3 & 4, Noël-Lambot et al, 1982).
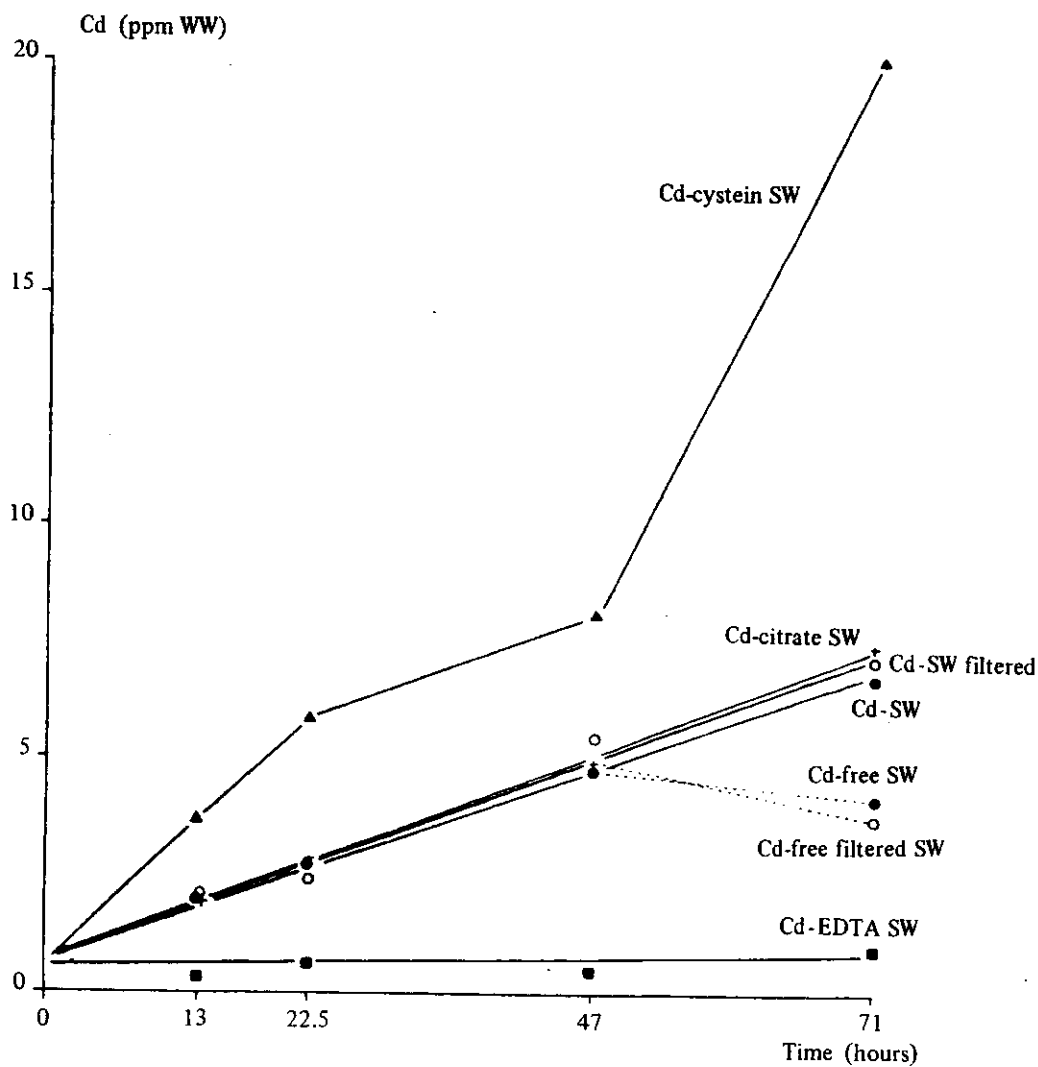
fig. 3.

Effect of different complexing substances on the Cd accumulation kinetics in *Mysidacea* exposed to 0.1 ppm Cd. Each point corresponds to a sample containing about 15 animals (from Noël-Lambot et al., 1982).

So it appears that metal complexation by dissolved organic matter has a variable effect on the rate of accumulation depending on the nature of the organic complex and of the metal, and on the studied species.

On the other hand, particulate organic matter has an important inhibitory effect on the uptake of metals by macroorganisms (Verthé et al, 1982).

Among biological factors responsible for the accumulation of heavy metals, the position of the species in the food web is worth to be discussed.
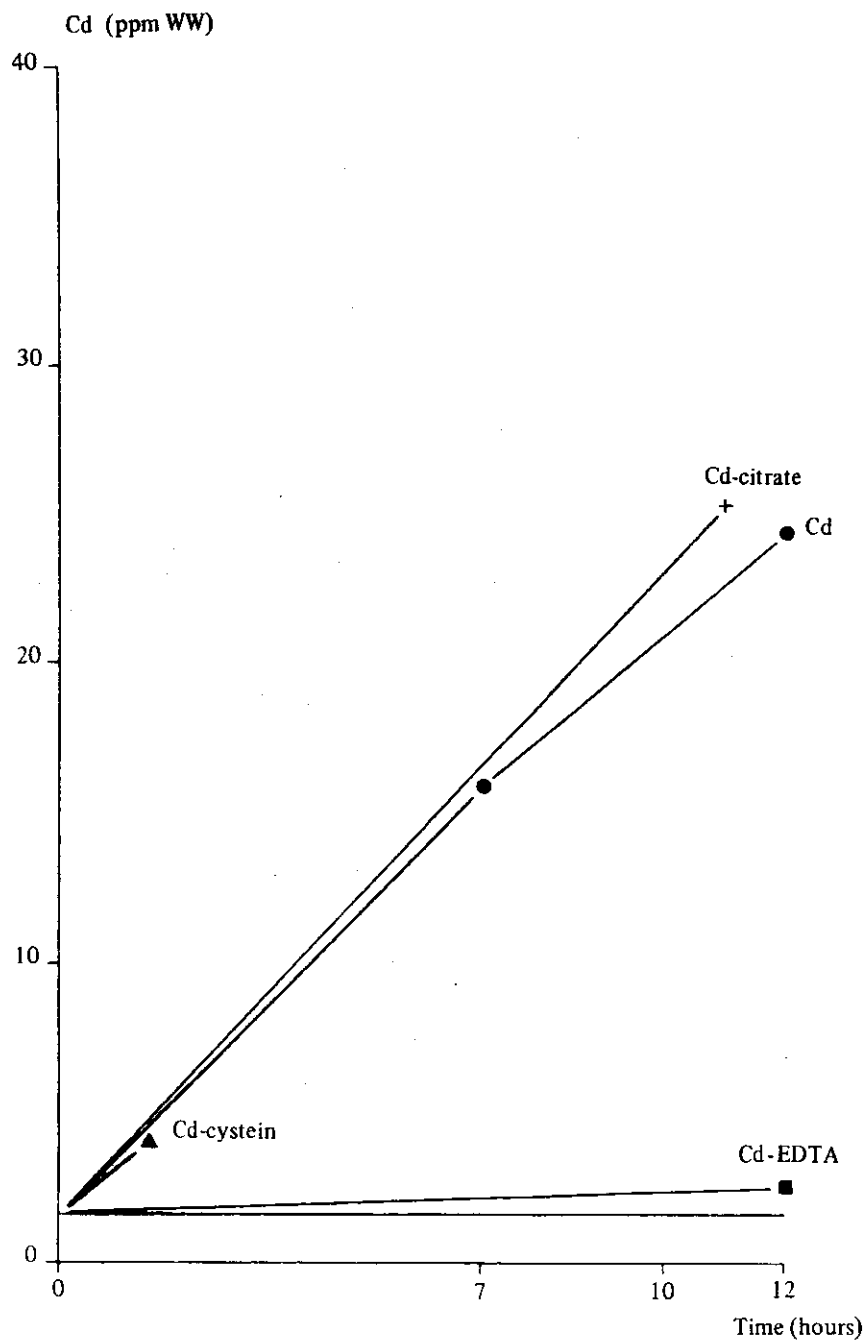
fig. 4.

Effect of different complexing agents on the Cd accumulation kinetics in *Patella caerulea* (Cd water concentration : 0.5 ppm). Each point corresponds to an average of data obtained from 2 to 9 specimens (from Noël-Lambot et al., 1982).

Most of the in situ measurements do not reveal any increase in the metal loads along the marine food chains (for a review, see Bouquegneau et al, 1976 ; Bouquegneau & Noël-Lambot, 1977). On the contrary, the following increasing sequence of heavy metal concentrations is often shown :

$$\text{water} \; < \; \text{fish} \; < \; \text{zooplankton} \; < \; \begin{array}{l}\text{sediments and}\\\text{macroinvertebrates}\end{array}$$

suggesting that the main route of entry of metal pollutants is a direct contamination from water and that the percentage of metal assimilated from food must be small.

Some experiments have been carried out to test this hypothesis (see Bouquegneau et al, 1979). The results show that the percentages of ingested heavy metals assimilated from food are generally low (0.1 - 10.0 %) except in the case of methylmercury intoxicated preys (30 - 50 %), so that probably a difference can be defined between liposoluble and non-liposoluble pollutants in this regard (see also Bouquegneau, 1980).

The presence of heavy metals in abnormal concentrations in water sometimes can be considered as a stress to which the animal may be able to response by developing one or several physiological mechanisms which may lead to either a decrease of the rate of entry of the pollutant by the production of extracellular traps or an increase which is generally accompanied by a tolerance to the pollutant due to a storage under a detoxified form (intracellular traps).

One of the physiological adaptation mechanisms which decreases the rate of accumulation of heavy metals is a high production of mucus.

Radoux & Bouquegneau (1979) and Bouquegneau et al (1979) have shown that $HgCl_2$ intoxication induced an increase of mucus production by gills of *Serranus cabrilla*. This phenomenon and the subsequent mucus delamination limits the rate of entry of the pollutant in the animal.

In several species of sea water fish, other kinds of extracellular traps have been described by Noël-Lambot (1980, 1981). They are white mucous corpuscles and have been observed in the intestinal lumen of unfed teleosts and are regularly evacuated by the anus. In fish intoxicated with $CdCl_2$, $ZnCl_2$ or $CuCl_2$ added to sea water, the corpuscles are found to contain enormous concentrations of these metals and although their weight is small, they carry a very large part of the total metals found in the animals. The presence of intestinal corpuscles, directly accumulating Cd or other metals from the sea water ingested by the animals, seems therefore to greatly limit the entry of heavy metals through the intestine wall, since they decrease the pollutant concentration of the intestinal liquid and thus protect fish against these pollutants.

On the contrary to the mechanisms described above, two other ones lead to important concentrations of heavy metals in animals.

The fact that many aquatic organisms can concentrate metals to very high levels and apparently survive and reproduce normally indicates that they have evolved some forms of tolerance.

The two mechanisms of tolerance described till now consist in a storage of metals inside the cells, either in membrane limited granular structure or bound to metallothioneins.

The capacity of all studied phyla of marine animals to synthetize metallothioneins when exposed to heavy metals such as Cd and Hg accounts for the high heavy metal load of some organs, the long half-time of elimination of those pollutants and the good tolerance of some species against such contaminations. Detailed study on the heavy metal storage as metallothionein by marine animals is described in the next chapter of this volume. It is worth noticing that metallothioneins are quickly degradated after the death of the organisms (fig.5) so that metals stored in that way can be recycled again in the food web.

On another hand, many phyla of marine and terrestrial invertebrates are able to store heavy metals in intracellular granules or vesicles (Coombs, 1980).

Metallothioneins may also be associated with particulate structures within the cell and not be freely available within the cytoplasm (Jeantet et al, 1980 ; Ballan-Dufrançais, Jeantet & Bouquegneau, to be published).

Numerous inorganic precipitates have been now identified. For example, Martoja & Berry (1980) have shown in mediterranean cetaceans the biosynthesis and the storage of pure thiammanite in the liver. Cetaceans are unable to excrete the thiammanite particles. Such a detoxification process leads to the fossilization of mercury under the form of a non-biodegradable component.

A similar study has been performed in our laboratory (in collaboration with M. Martoja, Institut Océanographique, Paris, France) about the storage of copper as copper sulphide by Gastropods (Bouquegneau & Martoja, 1982).

The copper, cadmium and zinc content of four species of Gastropods (*Monodonta crassa*, Archeogastropod ; *Littorina littorea*, Mesogastropod ; *Thais lapillus* and *Murex brandaris*, Neogastropods) collected in non-polluted areas has been investigated.

When considering copper, a mineralization technique has been used which allows to separate the most strongly bound copper identified as CuS from copper complexed to organic matter. There is no correlation between soft tissue weight and copper concentration in *Monodonta crassa* and young *Thais lapillus*. In these animals, no copper sulphide was found either.

On the contrary, in *Littorina littorea*, *Murex brandaris* and aged *Thais lapillus*, there is a significant correlation between copper content and age. Moreover, copper sulphide has been both chemically and histologically detected in their tissues. However, copper sulphide has been detected only at the visceral mass level and is responsible for the increase of the copper content of oldest animals.
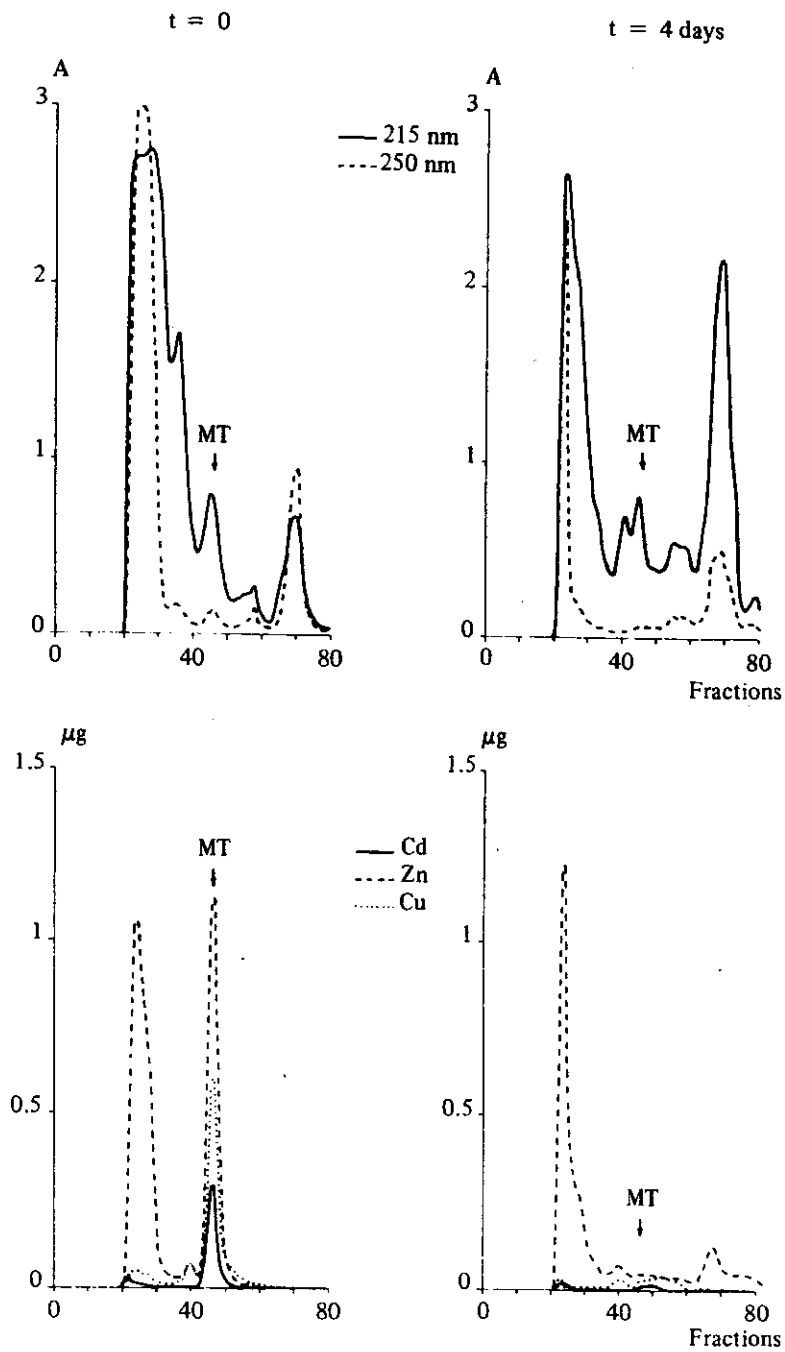
fig. 5.

After death degradation of hepatic metallothioneins in eels.

Eels have been used after decerebration, having been submitted to 50 days intoxication in water containing 1.3 ppm of Cd. Some animals have been used immediately for analysis, others have been kept four days in non contaminated sea-water, aerated and replaced each day. Chromatographic extracts from two livers: AcA 54 (2.6 x 83 cm). Volume of fractions: 7 mℓ. The metal content of the eluted fractions are given in μg per fraction corresponding to 1.5 g of liver.

From those results and from literature data, it appears that copper metabolism in Archaeogastropods is quite different from that in Meso- and Neogastropods. In the two latter, copper from hemocyanin catabolism is stored as copper sulphide in conjonctive cells which are situated in the visceral mass of the animal, and the number of these cells increases with age. In Archaegastropods, copper from hemocyanin catabolism is either used again or excreted out of the soft tissues.

The described phenomenons have two important ecotoxicological implications : 1° Meso- and Neogastropods are to be considered bad copper pollution biological indicators because most of the copper load results of a natural metabolic process ; 2° the ability of predators to assimilate CuS should be studied in order to evaluate the importance of such a storage for the food web contamination. Probably copper sulphide is a non-biodegradable compound which cannot therefore be metabolized by any organism of marine food chains. The final result of such phenomenons is therefore a fossilization of heavy metals and an enrichment of their concentrations in the sediments.

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ONE EXAMPLE OF HEAVY METAL STORAGE AS METALLOPROTEIN :

ACCUMULATION, ELIMINATION AND STORAGE OF CADMIUM

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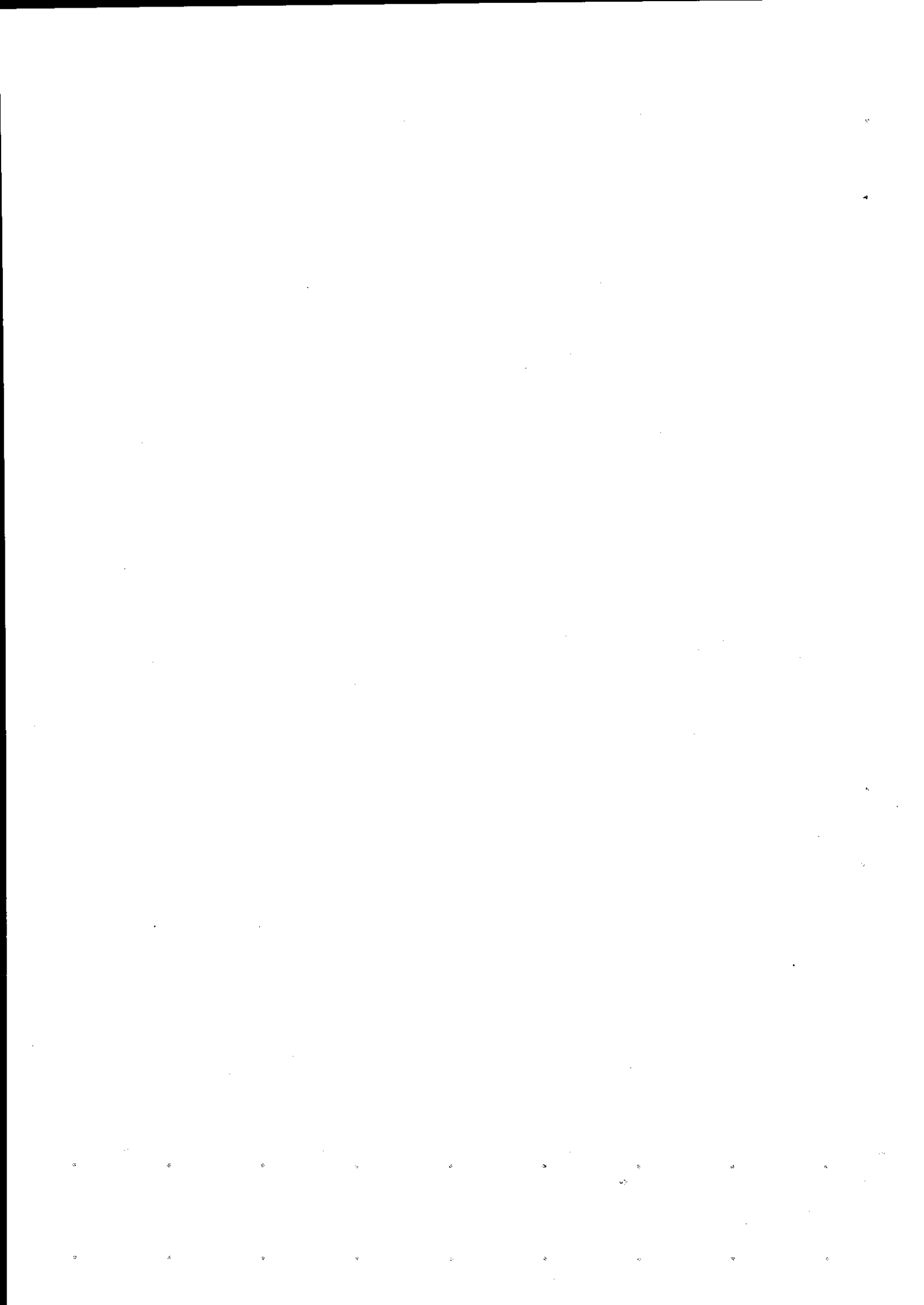
1.— Introduction.

Increasing release of Cd in nearshore waters prompts to study the toxicity and the accumulation of this metal in marine organisms. The natural Cd concentration in seawater is below O.1 ppb (see for example, Nurnberg et al, 1976). However in some polluted coastal regions, concentrations of between 1-10 ppb have been reported (Preston, 1973 ; Chan et al, 1974 ; Zaroogian & Cheer, 1976).

High Cd levels in marine waters often result in an accumulation of this metal in organisms. This is particularly true in the case of some invertebrates such as molluscs but alarming Cd concentrations have never been observed in fish. For recent reviews on this subject, see Coombs (1979) and Noël-Lambot (1980).

Some studies have described the accumulation of Cd by aquatic animals during exposure in the laboratory (Kumada et al, 1972 ; Eisler, 1974 ; Rowe & Massaro, 1974) but these studies are generally of rather short duration.

The aim of this work is to study the accumulation and the elimination of Cd by marine animals which have been naturally or experimentally exposed to this metal for a long time and to define the major sites of Cd binding within cells. In this respect, we more particularly investigated the occurrence of metallothioneins, soluble proteins of low molecular weight, with a high affinity for Cd and whose synthesis is induced by administration of some heavy metals. These proteins, well-known in mammals, were described for fish and molluscs in previous papers (Bouquegneau et al, 1975 ; Noël-Lambot et al, 1978b ; Noël-Lambot et al, 1980 ; Frankenne et al, 1980). Recent reviews on metallothioneins are available (Bouquegneau & Noël-Lambot, 1978 ; Kägi & Nordberg, 1979 ; Webb, 1979).

2.– Material and methods.

In our experiments, Cd was directly added to seawater.

Cd in the tissues was determined by atomic absorption spectrophotometry (Perkin-Elmer 103) after mineralization for 12 hours at 80°C in HNO_3 65 % (2.5 mℓ per g wet weight) and twentyfold dilution.

Some soft tissues with a very low Cd content were analysed by anodic stripping voltammetry (MASA-2014 ESA) after ashing with microwave activated oxygen (Calcinator Tracerlab 600) and dissolution in concentrated HCl.

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                        WHOLE TISSUE

                            │
                     homogenization
                            │

                        HOMOGENATE

                            │
                      centrifugation
                            │
                   ┌────────┴────────┐
               SUPERNATANT        PELLET

                   │
           gel chromatography
                   │
          ┌────────┼────────────────┐
       HMWP       MT          lower molecular
                              weight components*
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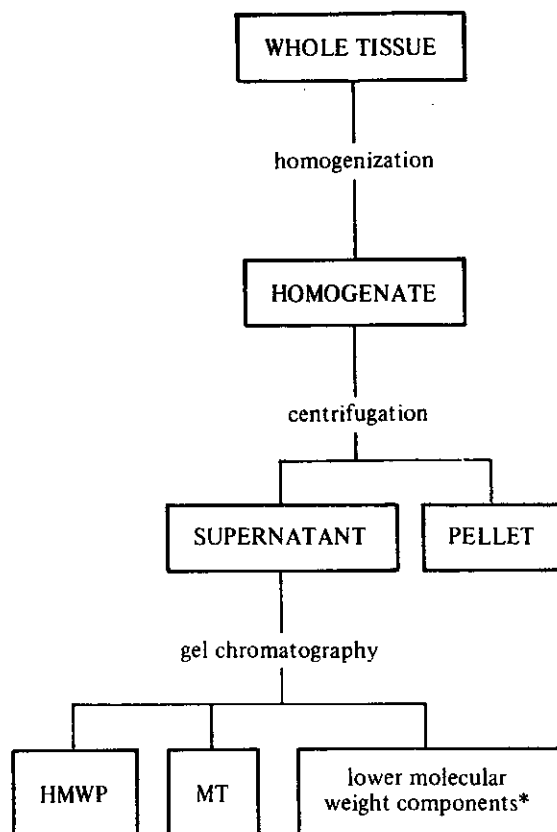
fig. 1.

Schematic diagram of the fractionation procedure
HMWP : high molecular weight proteins
MT : metallothioneins

* Cd in this fraction was always below the detection limit so that

$$Cd_{total} = Cd_{(in\ pellet)} + Cd_{(in\ HMWP)} + Cd_{(in\ MT)}$$

All concentrations are expressed in µg/g (or ppm) on the basis of wet weight.

From the metal concentrations in the different fish organs and from the weight fractions of these organs, the metal load (expressed in µg) of each organ could be calculated for a fish whose weight was reduced to 100 grams. The total body load was then determined by summation of the load of each organ.

Fig.1 summarizes the various steps of the study of Cd intracellular location. Tissues were homogenized in three volumes of 0.5 M sucrose by means of a Polytron Homogenizer. The supernatants obtained by centrifugation of the homogenates at 100 000 g for 1 hour at 4°C were chromatographed on Sephadex G-75 or LKB Ultrogel AcA 54 columns of various sizes, equilibrated in ammonium formate 0.01 M pH 7.4 or ammonium bicarbonate 0.05 M. The elution fractions were measured for U.V. absorbance and directly analysed by atomic absorption spectrophotometry.

The relative metallothioneins concentrations were estimated from the metal content (sum of Cd, Zn and Cu, in g-atoms) of the chromatographic fractions containing them (MT fraction on fig. 5 and 6). This method of estimation of metallothioneins concentration, assuming saturation of the metal-binding sites, was described in detail and discussed in a previous paper (Noël-Lambot et al, 1978b). Other recent results obtained in our laboratory confirm its validity (Noël-Lambot, 1980).

3.— Results.

Fish may be considered as having a low Cd accumulation capacity because muscles which represent the major part of total body weight always contain very low concentrations of this metal, even when exposed for a long time to high Cd concentrations in water (fig.2 and 3, see also Bouquegneau et al, 1979 ; Noël-Lambot, 1980). Cd is predominantly accumulated in the viscera, particularly in kidneys and liver (fig.2 and 3, table 1).

Owing to the very low Cd accumulation capacity of fish muscles, it is very improbable that sea pollution by Cd, to the contrary with Hg pollution, might even lead to metal levels in fish dangerous for man.

μg Cd/g wet weight
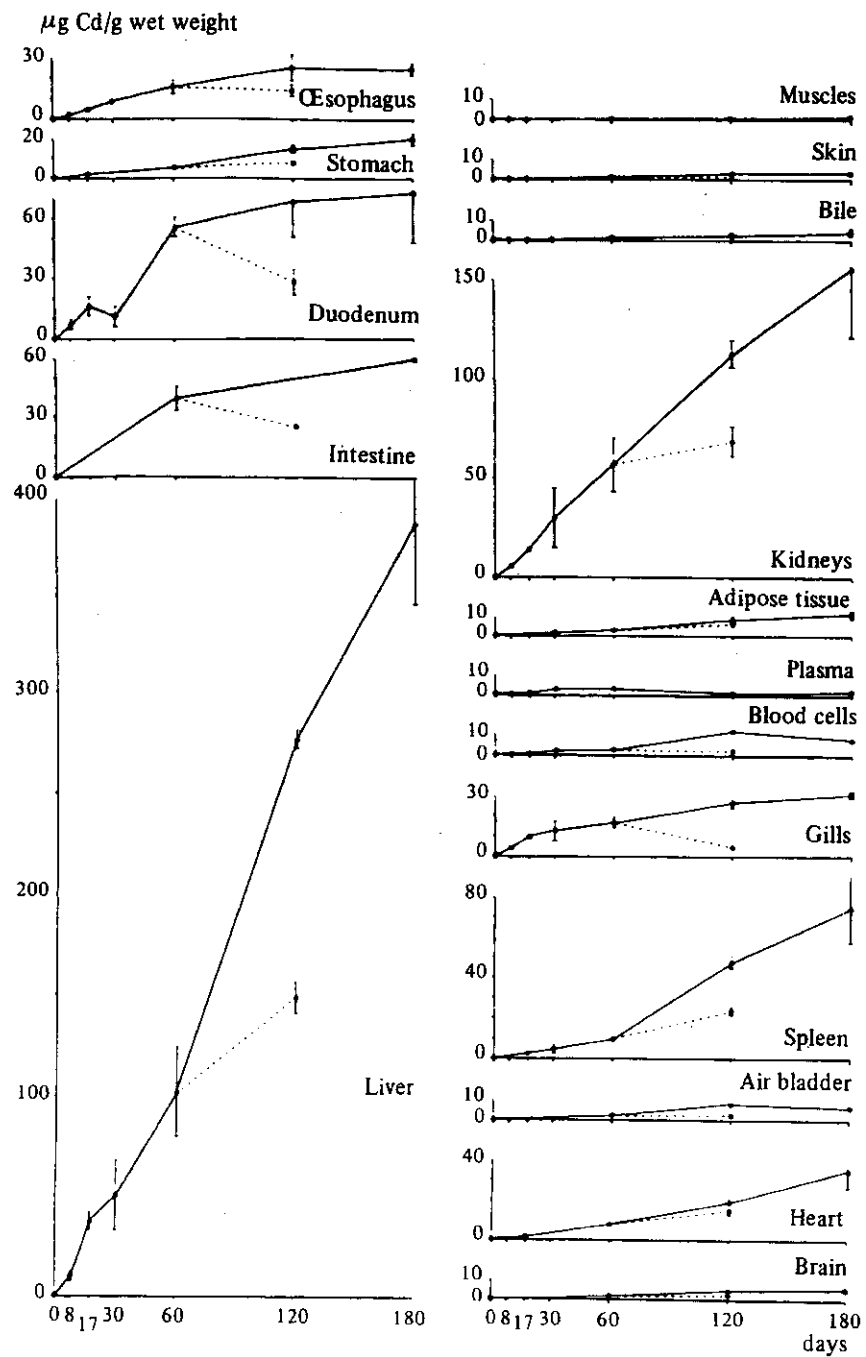
fig. 2.

Accumulation (——) and release (– – – –) of Cd by various organs of eels exposed
to seawater containing 13 ppm Cd (mean on 3 or 5 specimens ± standard error).
Release was studied in animals kept in unpolluted water after 60 days Cd exposure.
[From Bouquegneau et al. (1979)]

Cd concentration
in total body
(mean ± ES)

μg/g wet weight
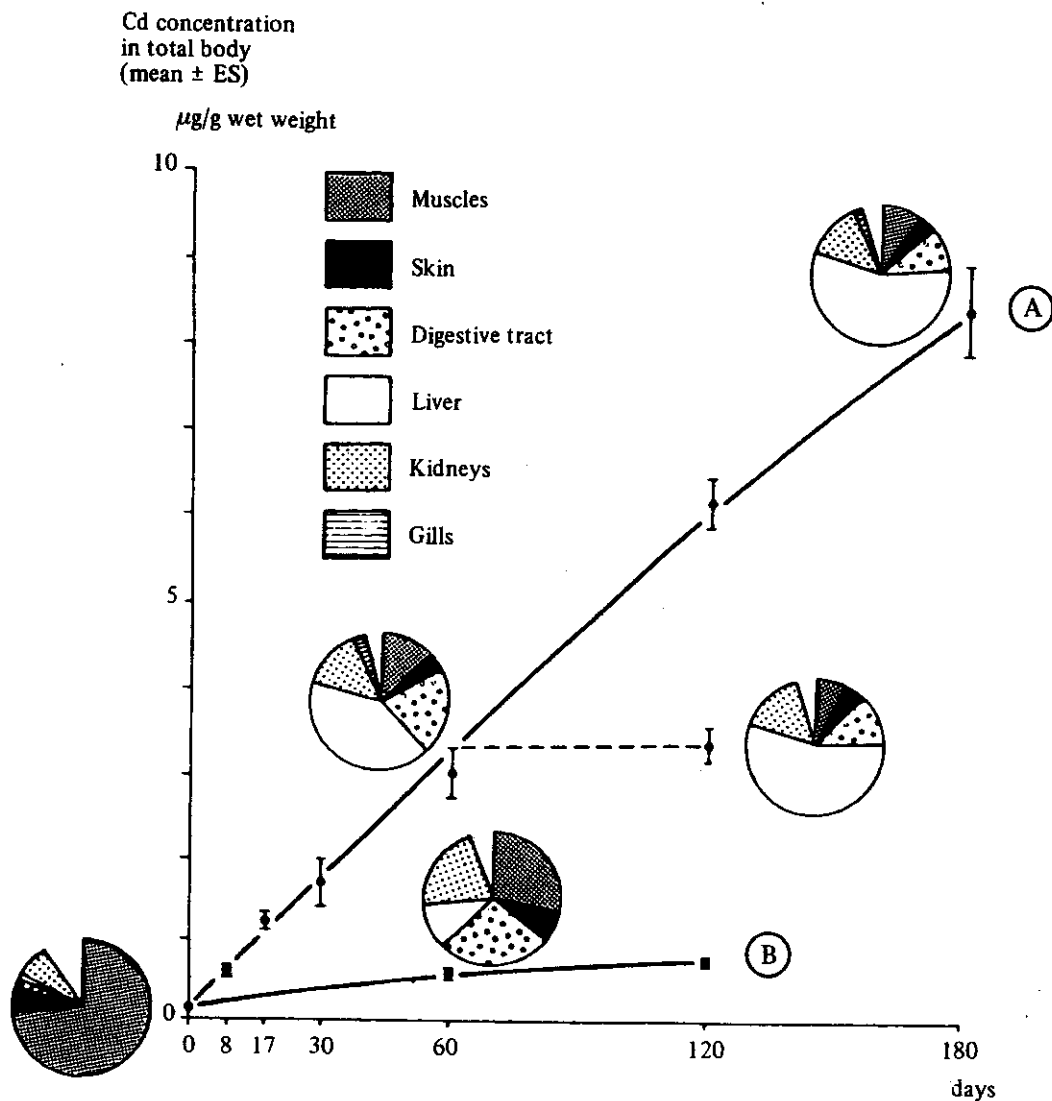
fig. 3.

Accumulation, release and distribution of Cd in the whole body of eels exposed to seawater containing 13 ppm (A) or 0.13 ppm (B). Dashed curve represents Cd concentration in animals kept during 60 days in unpolluted water after initial intoxication. Circles represent the distribution of Cd in the body : the surface assigned to each organ is proportional to its Cd load expressed in percentage of the total body load. [From Noël-Lambot (1980)].

On the other hand, our works confirm that some invertebrates, especially molluscs (both their viscera and their muscles) have a very high Cd accumulation capacity (Noël-Lambot et al, 1978a, 1980, 1981).

In many tissues, both from vertebrates and invertebrates, Cd loading can occur at a constant rate over a very long period of

Table 1

Cd concentration in various organs of one eel bred at the marine farm of Hinkley Point (Bristol Channel, England). This animal, about two years old, spent its whole life in polluted waters of the Bristol Channel (Cd level between 0.001 and 0.005 ppm). [From Noël-Lambot (1980)]

Organs	Cd, µg/g w.wt.
Muscles	0.3
Skin	1.1
Stomach	0.3
Intestine	0.5
Liver	2.9
Bile	0.4
Kidneys	9.5
Gills	0.4
Heart	< 0.2
Brain	0.2
Air bladder	0.2

time. For example, in some experimental intoxications, a steady state is not achieved within 180 days (fig.2 and 3) and in the field, a direct relationship between Cd concentration and age can sometimes be observed. This is the case of *Patella vulgata* living in the polluted water of the Bristol Channel (Noël-Lambot et al, 1980).

Such kinetics suggest a very low rate of metal excretion. This is confirmed by experimental work : in many cases, for example in the organs of the eel where a linear Cd accumulation was observed (fig.2 and 3), binding of Cd in the tissues may be considered as an almost irreversible phenomenon. It can be observed on fig.2 that the gills and the digestive tract are the only tissues from the eel for which the half-life of Cd is rather short. This can be explained by the fact that both are the main routes for metal uptake and thus organs of Cd transit.

Another cause of such a continuous accumulation of Cd with time is the continuous production of metallothioneins in response to Cd exposure : these soluble proteins of low molecular weight are almost inexistant in non-intoxicated animals and their concentration increase with the duration of exposure to Cd (fig.4 for example, see also Noël-Lambot et al, 1981). On the basis of the metal/protein stoechiometry found by us for the eel metallothioneins (16 g-atoms of metals per 11 700 g protein, see Noël-
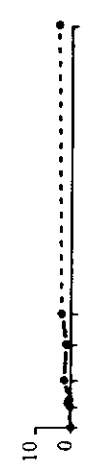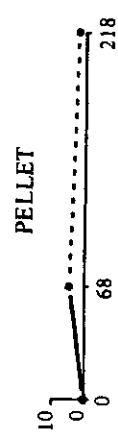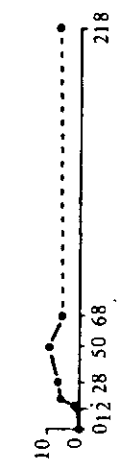
fig. 4.
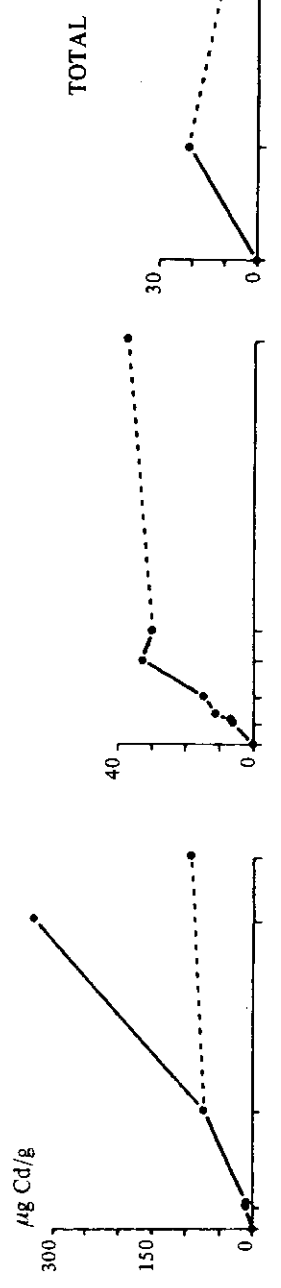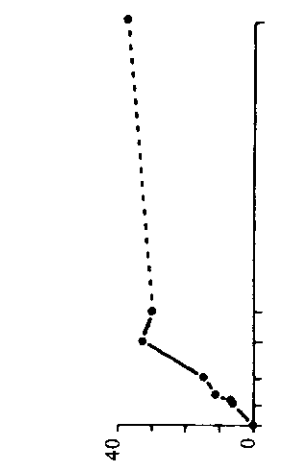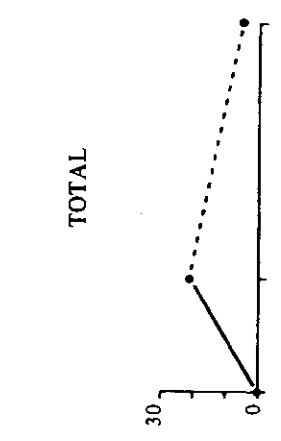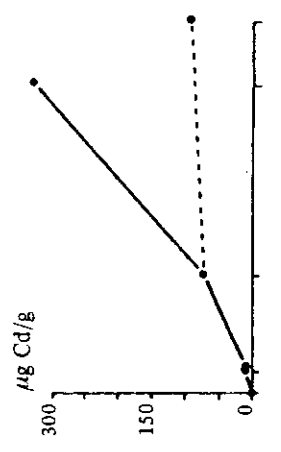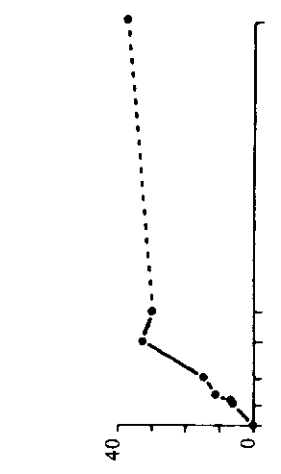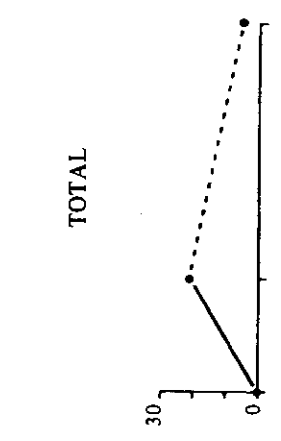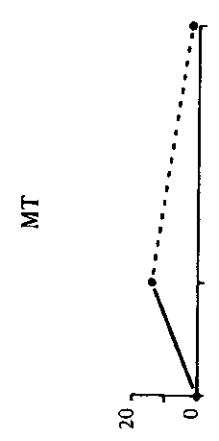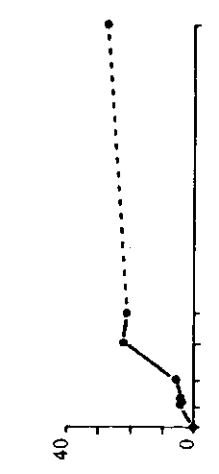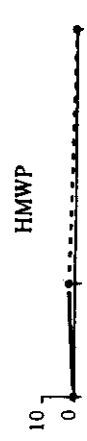
Cd accumulation in the whole liver, kidneys and gills and in their various subcellular fractions
during exposure to seawater containing 13 ppm Cd.
All concentrations are expressed in µg Cd/g whole tissue (means on 2 or 3 eels).
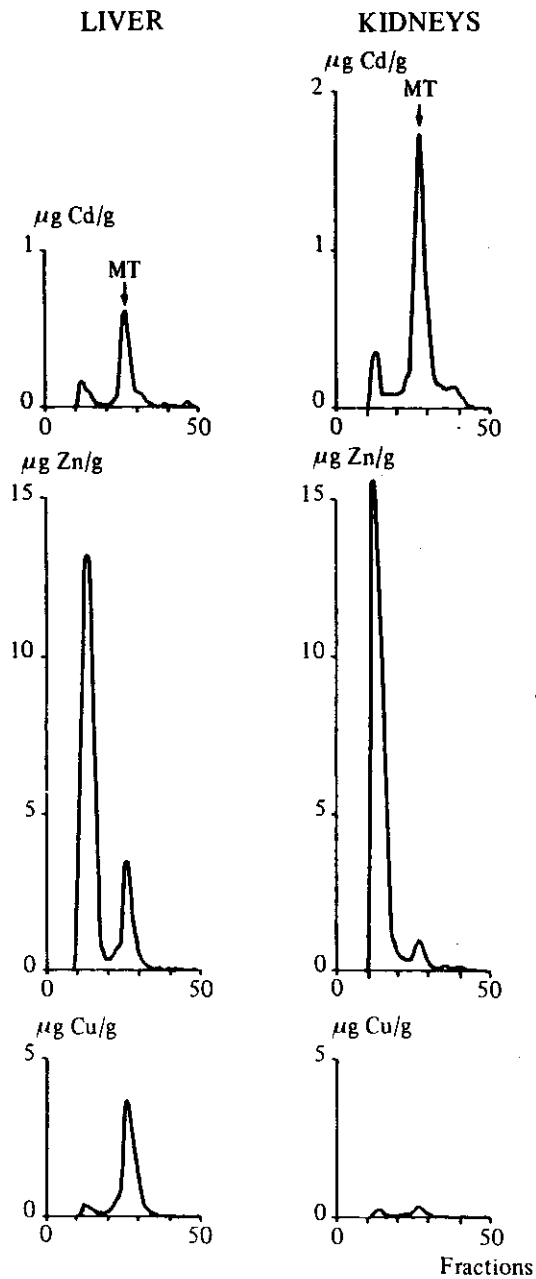– – – : animals returned in clean water. See also fig. 1.

fig. 5.

Elution profiles on AcA-54 column (2.6 × 36 cm; fraction volume : 5mℓ) of water soluble fraction extracted from liver and kidneys of an eel coming from Bristol Channel (Cd polluted area). See also table 1. Metal concentrations in elution fractions expressed in μg per fraction and per gram of tissue. MT : metallothioneins. Metal concentrations in the total organs 2.9 ppm Cd, 42.5 ppm Zn and 20.7 ppm Cu for liver; 9.5 ppm Cd, 68.3 ppm Zn and 3.1 ppm Cu for kidneys.
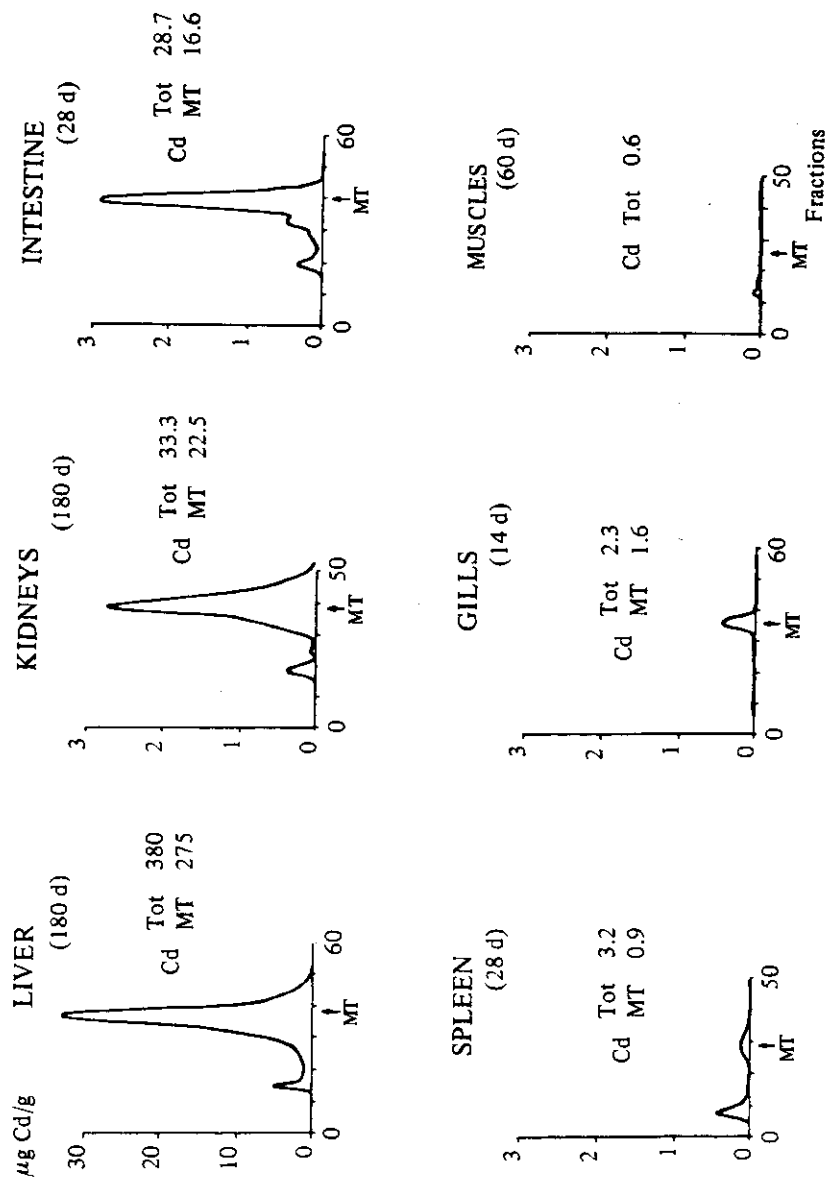
fig. 6.

Gel chromatography of the water soluble fraction of various organs from chronically Cd-exposed eels (13 ppm Cd in water; exposure length given in brackets). Cd concentrations in eluted fractions are expressed in μg per fraction and per gram of tissue. Tot. = Cd concentration (in $\mu g/g$ tissue) in the total organ; MT = Cd concentration (in $\mu g/g$ tissue) in the MT peak (indicated by an arrow), see also fig. 1. For liver, intestine, spleen and gills, a Sephadex G-75 column (76 × 3 cm) was used; fraction volume was 10 mℓ. For kidneys and muscles, an Ultragel AcA-54 column (37 × 2.6 cm) was used; fraction volume was 5 mℓ.

Lambot, 1980), we can calculate that the concentration of metal-
lothioneins in liver (fig.4) rises from about 200 µg protein/g
wet liver to 1852 µg/g after 180 days exposure in seawater con-
taining 13 ppm Cd.

This increase in metallothioneins concentration corresponds
to an increase in the amount of Cd-binding sites. One is faced
with a storage system, the size of which increases the more Cd
there is to be trapped (see also Noël-Lambot et al, 1980, 1981).
Fig.4 also shows that most of Cd accumulated during the chronic
intoxication is associated with metallothioneins.

These proteins were also detected in marine animals not sub-
mitted to laboratory intoxications, for example in molluscs and
fish from the Bristol Channel (F.Noël-Lambot, 1980 ; F. Noël-
Lambot et al, 1978a, 1980, 1981 ; table 1 and fig.5). Fig.5
shows that metallothioneins can bind the major part of Cd as also,
in some cases, of Zn and Cu present in these animals.

When intoxication ends, metallothioneins persist in most of
the tissues although the cause of their formation has disappeared
(fig.4). Metallothioneins thus act as a trap for Cd.

It seems that all tissues are not able to produce metallothio-
neins and there is a correlation between the ability of Cd to en-
hance the level of metallothioneins and to accumulate in the or-
gans. In tissues with a very low Cd accumulation capacity, such
as fish muscles, metallothioneins are not detected (fig.6). A
similar correlation between Cd concentration of an organ and oc-
currence of metallothioneins was also made in mammals by Piotrow-
ski et al (1974) and in invertebrates by Noël-Lambot et al (1978a,
1980,1981).

Another argument for the role of metallothioneins in Cd accu-
mulation is that Cd concentration increases with age only in tis-
sues when metallothioneins are present. In fish liver and kidney
it is possible to detect an increase of Cd concentration with age
(Mears & Eisler, 1977 ; Müller & Prosi, 1978) but this has never
been shown for muscle (Lovett et al, 1972 ; Stevens & Brown,
1974 ; Tong, 1974). A similar relationship also exists in mol-
luscs (Noël-Lambot et al, 1980, 1981).

Binding of Cd to metallothioneins also explains that animals
exposed for a long time to low environmental Cd concentrations
may tolerate very high Cd levels in their tissues : the major
part of Cd is then bound to metallothioneins and thus exists in
a detoxified form. So, chronically intoxicated animals can sur-
vive with Cd concentrations in the tissues much higher than those
attained during a short lethal intoxication (Bouquegneau et al,
1979 ; Noël-Lambot, 1980).

4.- Conclusions.

The understanding of the fate of heavy metals released by natural sources or by man in the sea depends to a large extent on our knowledge of bioaccumulative processes. Our works indicate that the study of Cd accumulation is closely linked to that of metallothioneins.

The induced production of metallothioneins in response to Cd exposure and the persistence of these proteins are considered here as the main mechanisms responsible for the cumulative Cd absorption during long-term intoxication. A practical consequence is that tissues with a high capacity of metallothioneins synthesis must be used in priority for surveillance work. Indeed these tissues, when exposed for a long time to low environmental Cd concentrations, are able to store the metal under a supposedly non-toxic form. So, animals can tolerate very high Cd burdens, thus becoming a potential danger for their predators.
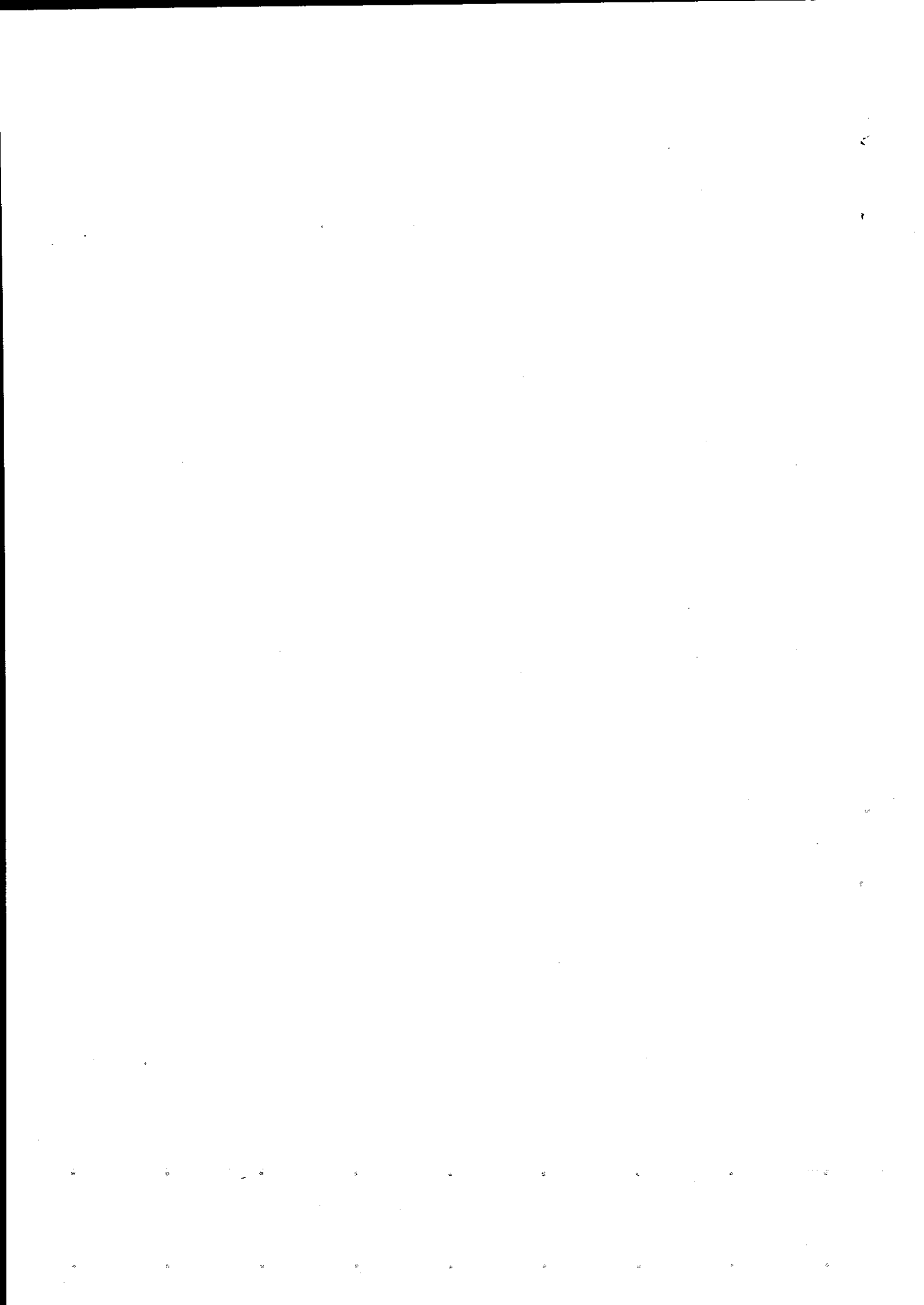
The results reported here principally concern cadmium but it must be kept in mind that metallothioneins can also bind Hg, Cu and Zn. So the existence of these proteins cannot be ignored in heavy metal ecotoxicology.

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D/1982/1191/8