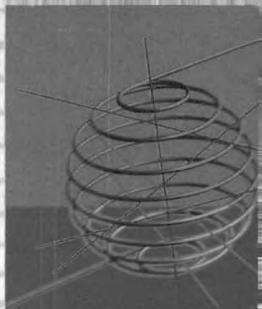


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**Biogeochemistry  
of nutrients, metals and  
organic micropollutants  
in the North Sea**

**SUSTAINABLE  
MANAGEMENT OF  
THE NORTH SEA**

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115566

## BELGIAN SCIENCE POLICY

### SCIENTIFIC SUPPORT PLAN FOR A SUSTAINABLE DEVELOPMENT POLICY (SPSD-I)

#### Programme: "Sustainable management of the North Sea"

VIZ (vzw)  
VLAAMS INSTITUUT VOOR DE ZE  
FLANDERS MARINE INSTITUUT  
Oostende - Belgium

#### Biogeochemistry of nutrients, metals and organic micropollutants in the North Sea

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## ABSTRACT

Trace elements were sampled on various sampling campaigns and averages were calculated compared for a certain amount of metals, such as lead, copper, zinc, nickel and chrome with data found in literature (Hoornaert et al., 1999).

The concentrations measured on the R.V. Belgica have nearly doubled for lead, compared with the measuring campaign at Blankenberge from 1992 until 1994. A possible explanation for this growth is the exclusive sampling of on shore winds at Blankenberge, where direct contamination from land was avoided. This is also demonstrated with the samples from the sampling campaign, organized at Adinkerke, with generally higher concentrations compared with the Blankenberge campaign. The Zn concentrations for the Adinkerke campaigns are elevated probably a result of direct contamination from the neighbourhood such as the influence of the Dunkerque industrial harbour area.

Nutrients were sampled for a period of nearly one year on various sampling points and the measured concentrations were used to validate the Atmospheric Chemistry and DEPosition model (ACDEP)(Hertel et al., 1995).

The importance of phosphate compounds can be stated as very limited, as a result of the general nitrogen limitation of the North Sea and the very low phosphate concentrations in the air. Nitrogen compounds are, however, very important. There clearly can be concluded that the ammonium compounds are responsible for the most important atmospheric nitrogen input over land (yearly average of 2.3 t N /km<sup>2</sup>.yr) and over sea (yearly average of 1.1 t N /km<sup>2</sup>.yr). After that, the wet deposition of the ammonium compounds becomes the most important input source (1.0 t N /km<sup>2</sup>.yr), followed by the wet deposition of the nitrogen oxides (0.8 t N /km<sup>2</sup>.yr), the dry deposition of the nitrogen oxides over land (0.6 t N /km<sup>2</sup>.yr) and over sea (0.1 t N/km<sup>2</sup>.yr). This makes that, generally, the wet deposition of nitrogen compounds to the North Sea is the most important deposition route with a yearly average of 1.8 t N/km<sup>2</sup>.yr (60% of the total deposition).

Main difference between our findings and the earlier results for the entire North Sea (Hertel et al., 2002) was the major importance of the deposition of ammonium compounds for the Belgian coastal zone. The ammonium components were responsible for only 38% of the total deposition for the entire North Sea surface, while this is around 70% for the Belgian coastal zone. The calculated total deposition of nitrogen compounds

amounts 3.0 t/km<sup>2</sup>.yr, which doubles the modelled values for 1999, a direct consequence of the adaptations made to the model. These depositions were however already the highest for the entire North Sea. This is mainly the result of the very high ammonia concentrations above Belgium (De Fré et al., 1999) and the Netherlands (Bouwman et al., 1998), a consequence of agricultural activities and the cattle and pig farms density.

Total budgets have been estimated and there was stated that the atmosphere contributes to a comparable amount to nitrogen components as the riverine inputs do. The dissolved organic nitrogen (DON) part was also investigated. There was indicated that the DON fraction could be responsible for about the same amount of input of nitrogen compounds to the North Sea as the inorganic nitrogen. These data are very important because they give a clear indication about the massive importance of the organic nitrogen fraction and prove again that further research about the identification, concentrations, bio-availability and solubility has to be carried out.

Much effort has been put in the development of the thin-window electron probe micro analysis technique (TW-EPMA) (Szaloki et al., 2001, Osan et al., 2000, Ro et al., 2000, Szaloki et al., 2000, Posfai et al., 1995). This technique offers the determination of the concentration of light elements, such as carbon, nitrogen and oxygen in atmospheric aerosol particles and is therefore very important for the study of atmospheric pollution. North Sea aerosol samples were analysed using the TW-EPMA technique (de Hoog et al., 2002) providing additional useful information to marine aerosol studies, compared to the conventional EPMA studies. The complementarities between conventional IC analysis and the relatively new and promising TW-EPMA was also investigated Eyckmans et al., (2002a). Using both techniques, one gains clearer insights in the contribution of the different aerosol fractions. In the near future, it will be possible to give more precise information about the air mass history (marine and continental), a better definition of the pollution sources (speciation) and a better insight in the different atmospheric interactions of the pollutants (primary, secondary or coagulated particles). The combination of both methods could be most helpful in the study of processes like e.g. sea salt aging.

The distribution and behaviour of particulate trace elements in marine systems has received until now much less attention than the dissolved fraction. The aim of our study was to examine the composition of suspended matter in the Southern Bight of the North Sea and adjacent area, under various climatic conditions. Both major elements (Si, Al,

Fe, Ca, Mn, Corg) and minor elements (Zn, Cu, Co, Ni, Cd, Pb) were analysed. As one may expect the major factor controlling the distribution of particulate elements is the origin of the solid material, either continental and transported to the sea by rivers and by the atmosphere, or biologically produced in-situ essentially by primary production.

It was possible to identify in our case four classes of particles on the basis of a statistical analysis. In the area investigated, the input of suspended material from the Scheldt estuary is dominant along the Belgian coast. Particles of continental origin probably transported by the atmosphere are also the most abundant in the Northern part of the area. In the central part, the detrital continental particles are less abundant and more diluted by authigenic organic carbon.

It is well known that many trace elements are used as oligo-elements by organisms and that phytoplankton consumes efficiently the dissolved trace elements. However, we have shown that the concentration of trace metals in the the particulate organic phase is lower in the organic fraction than is the inorganic detrital fraction, except for Cd. The primary production has thus a diluting effect on the amount of trace elements in the solid phase, except for Cd for which the particulate concentration is almost doubled during the spring bloom.

We have furthermore used radionuclides of Zn, Cd and Mn in order to evaluate the rate of transfer of these trace metals from the dissolved to the particulate phase. Natural water samples, spiked with radionuclides were incubated under various light conditions or in the dark and in the presence or absence of specific inhibitors. The influence of light intensity allows us to evaluate the importance of photosynthesis or photochemical reactions on the transfer of the elements from the dissolved to the particulate phase. Use of DCMU (herbicide) allows to inhibit the activity of phytoplankton and that of antibiotics to suppress the influence of bacteria. Sodium azide was finally used to inhibit all biological activity.

Short term experiments (a few minutes), in the dark and in the presence of biological inhibitors allows to evaluate the rapid isotopic exchange, which occurs with the most labile fraction of the element considered. This exchange is very important for zinc and cadmium and limited for manganese. Kinetic experiments under constant conditions show a rapid uptake of this element which gives a turnover rate of 85% per day, due to biological processes either bacterial or phytoplanktonic. Experiments conducted under variable light conditions indicate photo-reduction of the particulate manganese. The

behaviour of zinc and cadmium is very different. After a fast and important isotopic exchange, the two metals are transferred linearly at a slow rate from the dissolved to the particulate phase. The uptake of Zn and Cd are faster in the presence of light and the use of an herbicide confirms the contribution of phytoplankton in this transfer. The role of abiotic processes remains nevertheless dominant for Zn.

For the three metals considered, the uptake of the radiotracers was found to be partially reversible at a time scale of one month. A rapid desorption phase is followed by a very slow release of the radiotracers.

Finally, we have developed a new method intended to provide information on the speciation of trace elements in the particulate phase. The classical sequential dissolution approach, such as the well-known Tessier method, is not always specific enough to give reliable results. In the method that we propose, a sample of suspended matter is titrated by HCl and at each step the concentration of the major and minor elements released to the solution is measured. The major elements dissolved allow to identify the mineralogical phases, which are affected by the acidification, and the minor elements indicate the metals associated to the dissolving phase.

Typically, after the initial dissolution of calcite and rhodochrosite, the addition of HCl induces a drop of pH from 5 to 3. Iron, aluminium and silica start then to be released due to the dissolution of iron oxi-hydroxides and of clay minerals. Cd and Zn are the first two trace metals released during the titration, simultaneously to rhodochrosite ( $\text{MnCO}_3$ ). Co and Ni are also partially released during this first titration phase. Pb and Cr are starting to dissolve at pH less than 4 and were not totally dissolved at pH equal to 1. Some additional Ni, Co and Zn are also dissolved under these acidic conditions. This indicates that these metals are linked to the clay fraction including iron hydroxides. This method looks very promising and allows also to evaluate the possible remobilisation of the trace metals under changing pH conditions for example in the sediments after deposition or in the gut of aquatic organisms.

## 1 INTRODUCTION

### 1.1 Boundaries

#### 1.1.1 Air/sea

The role of the atmosphere as an input route for various pollutants to the North Sea surface has been investigated for trace elements, organic and inorganic nutrients and organic micropollutants.

Although trace elements and heavy metals are nowadays defined as pollutants with a secondary priority, great care has to be invested in the follow-up of these various pollutants. Since the mid-eighties, the concentrations of various metals above the North Sea decreased drastically as a result of cleaner industries and unleaded fuel (Hoornaert et al., 1999). However, as a result of the growing industrial activity and increasing traffic density, concentrations were monitored in order to make an estimation about the tendency of these concentrations.

Algae growth in coastal waters is generally limited by the supply of nitrogen (Kronvang et al., 1993). A proper determination of the nitrogen inputs is therefore crucial for impact assessment studies (Hertel et al., 2002). Despite of its clear significance for the overall nitrogen flux to most coastal waters, the atmospheric input has often been only roughly determined and given little attention. Some studies have, however, shown the high significance of this atmospheric nitrogen deposition. In 1990 it was estimated that the atmosphere contributed by 30 to 40% of the overall nitrogen load for the Danish Kattegat Strait (Asman et al., 1994). More recent estimates are pointing at the atmosphere as the most important input pathway of nitrogen to Danish waters, now that river run-off has been reduced (Svendsen et al., 2001). Furthermore, the atmospheric inorganic input is directly consumable for the algae, which is only true for parts of the river run-off.

Increasing inputs of nutrients to the European coastal zones have resulted in a higher incidence of harmful algal blooms and other eutrophication phenomena and caused deleterious impacts on fisheries and tourism (Lancelot et al., 1989). To understand the mechanisms behind the impacts of increased nutrient loads of the coastal waters, the full magnitude and seasonality of nutrient inputs must be described. This includes the effects of extreme events such as high atmospheric deposition episodes (Spokes et al., 1993; 2000) which, while small in overall annual budgets may be able to trigger algal blooms under nutrient depleted conditions in summer and early autumn. These blooms are often followed by oxygen depletion due to decay of the algae.

Volatile organic compounds (VOCs) are ubiquitous in the marine environment throughout the world (Zoccolillo and Rellori, 1994; Dewulf and Van Langenhove, 1997). Trace levels of monocyclic aromatic hydrocarbons and chlorinated hydrocarbons have even been found in Antarctic waters and surface snows (Zoccolillo and Rellori, 1994). Anthropogenic emissions are mainly held responsible for the presence of VOCs in coastal and open sea areas, although in situ formation by macro- and microalgae has been demonstrated in the case of low molecular weight halocarbons (Nightingale et al. 1995; Giese et al., 1999). Volatile organic compounds have been shown to affect a wide number of biological and environmental systems. They are known to influence various atmospheric processes, some are carcinogens and/or mutagens, while others are persistent and show bioaccumulation effects (Glegg and Rowland, 1996). Furthermore, many VOCs exhibit toxic effects on aquatic organisms. In the list of 36 priority toxic pollutants established at the Third International Conference on the Protection of the North Sea nine VOCs, all chlorinated C<sub>1</sub>- and C<sub>2</sub>-hydrocarbons, were mentioned (Ministerial Declaration of the Third International Conference on the Protection of the North Sea, 1990). Additionally to this priority list it was stated that attention has to be paid to 13 groups of chemicals, out of which four consist of VOCs. Compared to other priority pollutants, e.g. PCBs, PAHs or heavy metals, far less information concerning the presence and input of VOCs in the North Sea is available. To acquire a better understanding on the occurrence and physical chemical dynamics of priority VOCs, twenty-seven chlorinated short-chain hydrocarbons, monocyclic aromatic hydrocarbons and chlorinated monocyclic aromatic hydrocarbons were selected from priority lists mentioned above. In order to investigate the sources, masses and (air-water) fluxes of these compounds, accurate data on concentration levels in the marine environment are required.

### 1.1.2. Land/sea

Estimates of annual land-based inputs are based on load calculations using average river flows and average contaminant concentrations. It is important to note that, when the inputs are calculated from measurements taken in the upstream part of the contributing rivers, the processes taking place in the subsequent estuarine environment are not taken into account, although they can seriously affect the actual amount of contaminants reaching the open sea. For some rivers, comparisons between observed metal increases in the coastal waters and those calculated from riverine inputs are reported (e.g. Baeyens et al., 1998).

### 1.1.3. Channel inputs

Estimates of Channel inputs are calculated in a similar way as the river inputs using average Channel flow and average contaminant concentrations. Substances originating from the Channel follow a circulation pattern characterised by a mean transport oriented to the North East up to the Skagerrak. Most of the North Sea water flows through this area before leaving via the Norwegian Coastal Current.

## 1.2 Reservoir concentrations

Highest concentrations are found in the coastal zones where river discharges are the major source of contaminants, particularly in the Southern Bight. High nutrient concentrations can lead to eutrophication and oxygen depletion problems. Marine areas such as the Kattegat, the eastern Skagerrak, the central North Sea and various Norwegian fjords, all suffer from periodic low oxygen levels.

The fate of metals is closely linked to their distribution between dissolved and particulate phases. It is estimated that 70% of the substances associated with the particulate matter remain trapped in sedimentation areas such as the Wadden Sea, the deepest part of the Kattegat-Skagerrak area, the Norwegian Trench and the estuaries (Laane et al., 1998), while the water mass flow governs the transport of the dissolved fraction.

The behavior of particulate trace metals in the water column or after deposition in the sediments is strongly influenced by their speciation. A new methodology, based on the acidic titration of the suspended solid, is used to evaluate the fraction of elements bound to various phases and progressively mobilized under decreasing pH conditions.

## 1.3 Internal cycling processes

Estuarine systems often play a nutrient reduction role. As a matter of fact, nitrogen compounds can be denitrified to gaseous forms and lost to the atmosphere while phosphorus can be stored in sediments. Other processes are internal recycling of organic and inorganic compounds as dissolved inorganic nitrogen (DIN) uptake by phytoplankton, particulate and dissolved organic nitrogen (PON and DON) mineralisation, sedimentation, DON exudation and nitrification. There are also source and sink processes like biological N-fixation, sediment storage and denitrification. Phosphorus is submitted to internal recycling processes such as phosphate- uptake by

phytoplankton, organic P mineralization, adsorption-desorption to particulate matter and to sink processes like sediment storage. In the same way, Si is taken up by phytoplankton and submitted to mineralization and sedimentation processes.

Metal compounds can be produced or degraded as a consequence of physico-chemical conditions (e.g. As-III versus As-V or Hg-II versus Hg-0) but mainly by bacterial (detoxification) reactions.

It is now possible to identify and to evaluate the rate of transfer of trace metals due to biological or abiotic processes by using radiotracers (Wollast and Loijens, 1991). Incubations of natural water samples under various light conditions allow to evaluate the importance of photosynthesis on the uptake of metals. On the other hand, the use of specific inhibitors (herbicides, antibiotics) makes it possible to distinguish between the activity of phytoplankton and bacteria.

#### **1.4 Trophic levels**

The assessment of the uptake kinetics of nutrients by phytoplankton is an essential part of the transfert of those nutrients through the food-chain, but also allows to understand the eutrophication phenomenon.

Important characteristics of the metal cycles are bioconcentration (metal enrichment in suspended matter and plankton versus water column), bioaccumulation (increase of metal levels in fish with age) and biomagnification (increase of metal levels through the trophic food chain).

## 2 METHODS AND MATERIALS

### 2.1 Sampling expeditions

Sampling expeditions on the North Sea involving the participation of all research groups in the project were organised twice a year between 1998 and 2000 on board of the research vessel 'Belgica'. The Scheldt estuary was sampled by the various research groups by means of the 'Belgica', the 'Luctor' from the 'Nederlands Instituut voor Oecologisch Onderzoek' (NIOO) and the 'Zeeleeuw' from the 'Vlaams Instituut voor de Zee'. An overview of the sampling expeditions is given in Table 1. Sampling locations on the North Sea and Scheldt estuary are provided in Figures 1 and 2, respectively.

Samples for nutrients in air and rain were taken for a period of ten months at Knokke-Heist, Het Zwin, at a distance of 500 meter from the sea (51° 21' 30"N, 3°21'E) near the Dutch border. Sampling took place from July 26, 1999 until June 9, 2000. Samples were also taken at Adinkerke, De Panne (51° 04'45"N, 2° 35' 45" E) near the French border. The first sampling was started at June 9, 2000 and was terminated at July 25, 2000. The seasonality of the pollution was investigated by organizing a second expedition in the winter period, from December 4, 2000 till January 3, 2001 and from February 5, 2001 till March 2, 2001. Finally, the last campaign was executed from May 28, 2001 until June 18, 2001.

### 2.2 Sampling methods and sample handling

#### 2.2.1 Atmospheric sampling and sample preparation

##### 2.2.1.1 Atmospheric sampling

###### 2.2.1.1.1 Aerosol sampling

###### High-volume pump

In order to collect sufficient amounts of aerosols, a high volume sampling system was constructed with an adjustable flow between 1 and 40 m<sup>3</sup> per hour. Glass fibre filters (Whatman GF/F, 135 mm) were used and an appropriate filter holder was constructed. A digital flow meter was connected to the pump outlet, with reproduction of flow and sampled air volume.

###### Low-volume pumps

Becker VT/4.4 and Edwards Speedivac II vacuum pumps were used for the sampling with standard filter holders (Millex® 47mm) or impactors. The pumps have a maximum flow of 4 m<sup>3</sup> per hour. The aerodynamic resistance of the filters or the impactors however reduced the flow to less than 2 m<sup>3</sup> per hour. The sampled air mass was measured by standard gas meters.

## Impactors

Two types of cascade impactors were used. The first was a Berner impactor, with 9 different stages with cut-offs of 16, 8, 4, 2, 1, 0.5, 0.25, 0.12 and 0.06  $\mu\text{m}$ . For an optimal size fractionation, the flow is adjusted to 26 l/min.

The second type of impactor is a May, with cut-offs of 20, 8, 4, 2, 1, 0.5 and 0.25  $\mu\text{m}$ . The flow of the May impactor is adjusted to 22 l/min.

### 2.2.1.1.2 Rain sampling

An automatic sequential rainwater sampler, Eigenbrodt, type ARS 721/S, was used for the collection of precipitation. The sampler is programmable for a period of 8 days, using a timer and a multi-valve to collect the precipitation in 8 different storage vessels. It is a "wet-only" collector, avoiding contamination by dry deposition, with a lockable funnel commanded by a rainwater sensor. An internal heating protects the sampler from frost damage.

### 2.2.1.1.3 Gas sampling

A dual sequential fine particle and gas sampler, URG 2000-01-K, from United Research Glassware, N.C., U.S.A., was used for the sampling of basic and acidic gases. The system is built out of a double sampling circuit, with separate pumps, mass flow controllers and sampling channels, offering the advantage of an internal control and an increased reliability because of the use of a dual (spare) channel.

In our device, we used two denuders in a serial set-up. The first denuder was coated with a sodium carbonate solution, in order to adsorb the most aggressive acidic gases and the second denuder was coated with a citric acid solution, to adsorb the basic gases. The particulate fraction was restrained by a PM10 inlet and a PM2.5 cyclone unit.

### 2.2.1.2. Sample preparation

A sample treatment procedure for the analysis of the particulate fraction was developed. Sample treatment requires a leaching system with a quantitative recovery of the species of interest in the leaching solution within a reasonable short period of time. For this reason, a re-circulation and an ultrasound leaching method were developed, tested and optimised (Eyckmans et al., 2001).

For the analysis of the dissolved organic nitrogen fraction in the samples, a standardised microwave destruction technique was applied (Dafner et al., 1999).

## 2.2.2 Water sampling and handling

### 2.2.2.1 Trace metals

Samples of surface water were collected by hand from a rubber boat by submerging Teflon (FEP) bottles (for Hg) and PE bottles (for the other trace elements) approximately 20 cm beneath the water surface. The rubber boat moved gently against the current during sampling and was positioned approximately 100 m up current of the research vessel. When sampling from a rubber boat was not possible due to weather conditions, subsurface samples (10 m depth) are collected from the research vessel using Go-Flo type sampling bottles and plastic coated messengers. A Kevlar cable is mounted on the oceanographic winch.

Filtration was performed in the clean lab container (Class 100) on board of the research vessel directly after collection of the sample. The filtration apparatus consists of a FEP separating funnel onto which a Teflon filter holder is connected. Nuclepore polycarbonate filters (0.40 $\mu$ m) were used and filtration is performed by pressure filtration using N<sub>2</sub> gas. The samples are collected in acid cleaned FEP-bottles for Hg and PE bottles for other trace elements. After filtration, samples for Hg were acidified with 0.5% HCl (Merck, suprapur) and samples for other trace elements were acidified with 0.2% HNO<sub>3</sub>. The sampling bottles were tightly capped and double bagged in zip-loc bags. The filters are stored in Millipore filter holders, sealed in PE bags and stored deep-frozen. The filters (except for Hg and As) were transferred to the lab of the ULB for analysis whereas the dissolved metals were analysed in the VUB lab.

### 2.2.2.2. Nutrients

Samples for nutrients were collected in the same way as for trace metals. The samples were filtered on Whatman GF/F filters. NH<sub>3</sub> and urea measurements were made on board of the ship. Samples for phosphate, nitrate, dissolved organic nitrogen (DON) and total dissolved nitrogen (TDN) were stabilized with 50 $\mu$ L/100 ml of a 35g/L HgCl<sub>2</sub> solution. Filters for POC and PN were dried in an oven at 50°C.

### 2.2.2.3 Volatile organic compounds (VOCs)

Sampling was performed with a 10L Niskin bottle equipped with a CTD probe (Conductivity, temperature, depth). Water was immediately transferred to dark green bottles (volume 780 ml) by means of a silicone tube. Two flasks were filled at each station. Each bottle was filled to capacity to avoid any headspace. Thirty-seven drops of 1/1 HCl had been added prior to sampling to obtain a final pH lower than two, avoiding microbial degradation (Dewulf and Van Langenhove, 1995). Before sealing the recipients with PTFE tape, 5  $\mu$ l of a surrogate solution in methanol containing 50  $\mu$ l of [<sup>2</sup>H]chloroform, [<sup>2</sup>H<sub>8</sub>]toluene and [<sup>2</sup>H<sub>5</sub>]chlorobenzene was injected. All samples were stored at 4°C.

### 2.2.3. Suspended matter sampling and handling

The samples of suspended matter were collected by either filtration on 0.4  $\mu\text{m}$  Nuclepore filters or continuous centrifugation of surface seawater.

The sampling procedure by filtration is described in paragraph 2.2.2.1. The filters for the analysis of trace metals were preserved in the deep freezer prior to their further treatment.

In addition, surface water collected from the rubber boat (or with a Go-Flow bottle in case of bad weather) were filtered on pre-weighed Nuclepore polycarbonate filters for the determination of the suspended particulate matter content (SPM), on ashed GF/F glass fibre membranes to analyze the carbon and nitrogen species (PTC/POC, PN) and on GF/F membranes to estimate the chlorophyll content.

In order to collect large amount of suspended matter, water pumped at three meters depth was continuously centrifugated at 4500 rounds per minute. The particulate matter collected was preserved in the deep freezer prior to its further treatment. In the laboratory, the samples were defrozen, rinsed three times with ultrapure water, dried overnight at 70°C, ground in an agate mortar and preserved in decontaminated flasks.

### 2.2.4 Incubation experiments

#### 2.2.4.1 Nutrient uptake experiments

For the uptake of different nitrogenous nutrients by phytoplankton, the  $^{15}\text{N}$  technique as described by Dugdale and Goering (1967) is used. Polycarbonate incubation bottles of 2.7L are filled with sea water and to each bottle a specific labelled nitrogen with known concentration is added ( $^{15}\text{NO}_3^-$  (99.5%),  $^{15}\text{NH}_4^+$  (99.8%),  $\text{CO}(^{15}\text{NH}_2)_2$  (99%)). The concentration of the added spike is maintained at a level of less than 10% of the ambient nutrient concentration. All bottles are incubated for a period of 6h under natural light and temperature conditions. Also an incubation bottle without tracer is incubated as a blank.

Samples for the determination of final nutrient concentrations are taken from each incubation bottle at the end of the incubation and a POC/PN sample is taken from the blank incubation bottle. The sample is then filtered through decontaminated GF/F filters to collect the particulate matter and dried for  $^{15}\text{N}$  abundance measurements.

The nitrogen uptake rates are calculated according to the model developed by Dugdale and Goering (1967).

### 2.2.4.2. Radiotracers uptake experiments

Water samples collected using a Niskin type sampling bottle are filtered through a 63  $\mu\text{m}$  nylon sieve (elimination of coarse material and zooplankton) and then stored in the dark in PE containers. If necessary, biological inhibitors (azide, herbicide, antibiotics) are added to different aliquots of the sample which are then spiked with  $\text{H}^{14}\text{CO}_3^-$  or with a mixture of carrier-free radio-isotopes:  $^{54}\text{Mn}$ ,  $^{109}\text{Cd}$  and  $^{65}\text{Zn}$ .

The bottles are then placed in different incubators following the type of experiment conducted (constant or variable artificial light, dark). The incubators are constantly supplied with fresh seawater to ensure a constant temperature during the incubation time. After a fixed time, the sample is filtered on a 0.45  $\mu\text{m}$  membrane filter. The radioactivity present on the filter and in the filtrate is then measured to estimate the transfer (uptake) of radionuclides from the dissolved to the particulate phase.

Sub-samples of 500 ml surface water were spiked with 2.6 kBq  $^{65}\text{ZnCl}_2$ , 5.8 kBq  $^{109}\text{CdCl}_2$  and 1.5 kBq  $^{54}\text{MnCl}_2$  which corresponds respectively to an addition of < 0.1 %, < 3 % and < 0.1 % of the dissolved concentration of Zn, Cd and Mn present in the sample.

## 2.3 Analytical methods

### 2.3.1 Trace elements in aerosols

X-Ray Fluorescence (XRF): A Spectrace 5000 was used for the analysis of the particulate trace elements, sampled on a Nuclepore® 47 mm filter with a 0.4  $\mu\text{m}$  pore size. The analyses were performed using an accelerating voltage of 15 kV, a current of 0.35 mA and an irradiation time of 3000 s.

Thin- Window Electron Probe Micro Analysis (TW-EPMA): Electron Probe Micro Analysis offers the possibility to analyse samples on a single particulate level. Using automated analysis, many hundreds of aerosol particles can be analysed within a short time. Afterwards, all these analysis data are statistically processed and this offers a qualitative and quantitative interpretation of the results.

TW-EPMA uses an ultra-thin polymer window, instead of the conventional beryllium detector window. This technique offers the advantage of detecting also elements with atomic number between 6 and 11 (such as carbon, oxygen and nitrogen). Aerosols were sampled using a Berner impactor with Al, Si and Ag impaction substrates.

### 2.3.2 Nutrients in aerosol and rain

Ion Chromatography (IC): A Dionex DX-120, equipped with a Dionex AS-50 auto sampler was used for the analysis of the various aqueous solutions for major ions. The analytical columns were an AS 14 for the anionic and a CS 12 for the cationic fraction. The flow was adjusted at 1 ml/min.

### 2.3.3 Trace metals in seawater

#### 2.3.3.1 Dissolved Cu, Zn, Cd, Pb and Ni

Trace metals are extracted from seawater using a solvent extraction method, slightly modified from Danielson (1978, 1982). The trace metals are complexed with ADPC and DDDC and extracted in freon. The trace metals are then back-extracted in water after acidification of the freon phase. Analysis is performed by ICPMS (VG PlasmaQuad II).

#### 2.3.3.2. Particulate trace metals

The composition of the sediments was determined after complete dissolution of the solid by acid digestion with a mixture of HF, HCl, and HNO<sub>3</sub>. This step is conducted in closed PARR Teflon vessels (high temperature and high pressure system) heated by a micro-wave furnace and submitted to an experimentally established thermal program.

The concentration of the metals in the resulting solution were determined either by electrothermal atomic absorption spectrometry using a VARIAN SpectrAA-300 Zeeman device (Cd, Pb, Cu, Co, Cr and Ni) or by inductively coupled plasma atomic emission spectrometry using a PERKIN ELMER 6000 (Ca, Mg, Fe, Mn, Al, Si and Zn).

#### 2.3.3.3. Trace metals speciation - acidimetric titration

A new method consisting of measuring the concentration of trace elements released after titration by HCl of the solid initially suspended in pure water has been tested in order to obtain information about the speciation of the trace metals in the particulate phase.

About 0.16 g of sediment dried at 50°C to constant weight are transferred in polypropylene flasks containing 20 ml of ultrapure water (MILLIPORE Milli-Q Plus). Increasing volumes of a 1N HCl solution are then added to the suspensions: from 0 (blank) to 2000 µl. The suspension is kept under agitation during 16 hours. This period is sufficient to reach steady conditions and to dissolve almost completely the different elements under each pH condition. The suspensions are then filtered on 0.45 µm decontaminated SARTORIUS cellulose nitrate membranes and the filtrate stored in PP flasks. To avoid adsorption of analytes on the walls of the flasks, the dissolved phases are acidified with 40 µl of HNO<sub>3</sub> 65% Suprapur (MERCK). These filtrates are finally used for the determination of the content of major elements and trace metals released in solution during the titration. The solid phase collected by filtration are rinsed with ultrapure water, dried, ground in an agate mortar and may be further eventually analyzed for the evaluation of the residual content of selected components.

In order to evaluate the trace metal content of the organic carbon fraction without dissolving the other mineralogical phases, about precisely 1 gram of dried sediment was attacked with  $\text{H}_2\text{O}_2$  30% at  $85^\circ\text{C}$ . Two types of experiments were conducted: one testing the reproducibility of a 4 hours attack on 5 replicates and the other consisting in a kinetic experiment during 2, 4, 8 and 12 hours of contact.

#### 2.3.3.4 Hg speciation

Total dissolved Hg ( $\text{Hg}_{\text{TD}}$ ), was determined by cold vapour atomic fluorescence spectrometry (CVAFS, Brooks Rand) using a  $\text{BrCl}$  oxidation step and reduction with  $\text{NH}_2\text{OH.HCl}$  prior to reduction with  $\text{SnCl}_2$  and Au- amalgamation preconcentration step (Gill & Fitzgerald, 1987).

Total dissolved MMHg ( $\text{MMHg}_{\text{D}}$ ) was analyzed by aqueous phase ethylation - gas chromatography - AFS detection (Bloom, 1989, Liang et al, 1994). MMHg was separated from the interfering chloride matrix by an extraction with methylene chloride (Bloom, 1989).

The successive steps to determine total particulate Hg were: (1) digesting the filters in 5 ml  $\text{HNO}_3/\text{HCl}$  (4:1) at  $60^\circ\text{C}$  for 12 hours in Teflon digestion vessels; (2) diluting the sample to 50 ml; (3) analysis of a fraction of the sample by CVAFS as described above.

Particulate MMHg ( $\text{MMHg}_{\text{P}}$ ) was using a room temperature KOH extraction (Bloom, 1989). After extraction the Hg compounds are analyzed in the same way as  $\text{MMHg}_{\text{D}}$ . For the 1999 samples, MMHg was extracted using 4M  $\text{HNO}_3$  and analyzed by ethylation-GC-AFS using a headspace injection method (Leermakers et al., in preparation).

#### 2.3.3.5 As speciation

Analysis for total As in the dissolved phase was done by Hydride Generation - Atomic Fluorescence Spectrometry (Excalibur 10.003, P.S. Analytical, England). As compounds were reduced to As(III) upon manual addition of a mixture of 1% (w/v) potassium iodine / 0.2% (w/v) ascorbic acid / 30% (v/v) hydrochloric acid. After 30 minutes reaction time, 1.2% (w/v) sodiumborohydride, stabilised in 0.4% (w/v) sodiumhydroxide was added automatically by the HG apparatus. Arsine was produced and spectrometrically measured.

The filters and retained SPM were acid-digested. The filters were placed in Teflon bombs, and 3ml of  $\text{H}_2\text{O}_2$  p.a. was added. The bombs were closed and heated for one hour up to  $60^\circ\text{C}$ . After cooling down, 5ml of sub-boiled  $\text{HNO}_3$  were added and the digestion bombs were left for 22 hours in an oven at  $105^\circ\text{C}$ . 20ml of milli-Q water were added and the mixture was transferred to clean HDPE bottles. Analysis for particulate As was performed by ICP-MS (VG PlasmaQuad II).

### 2.3.4 Analysis of nutrients and organic matter and related parameters

An improved method for the analysis of dissolved organic nitrogen (DON) was developed. Dissolved organic nitrogen (DON) measurements are based on the combination of a total dissolved nitrogen (TDN) and an independent dissolved inorganic nitrogen (DIN) measurement. The method is based on the peroxodisulphate oxidation method, originally described by Valderrama (1981), but the digestion is performed in a microwave oven instead of an autoclave under strict control of the digestion conditions (Dafner, 1999). Nitrate concentration measurements of the digested sample are performed with a Technicon Autoanalyser II system (Elskens and Elskens, 1989).

Particulate organic carbon and particulate nitrogen are analyzed by a Carlo Erba NA 1500 elemental analyzer (Niewenhuize et al., 1994). The glass fibre filters are exposed to HCl fumes for 2 hours to remove inorganic carbonates and afterwards wrapped in tin cups prior to elemental analysis.

Ammonium is measured spectrophotometrically and is based on the indophenol blue complex method according to Koroleff (1969).

Urea concentrations are determined with the diacetylmonoxime method as described by Goeyens et al., 1998).

Nitrate, nitrite, phosphate and silicate are automatically analysed with a Technicon™ AutoAnalyser according to Elskens and Elskens (1989) and Koroleff (1983a and 1983b).

### 2.3.5 N-15 analysis

The modified Dumas method is used to convert the assimilated nitrogen to nitrogen gas and the determination of the  $^{15}\text{N}$  abundance is performed by emission spectrometry with a Jasco NIA 151  $^{15}\text{N}$  analyser according to Fiedler and Proksch (1975).

### 2.3.6. Mn-54, Cd-109 and Zn-65 analysis

The activities of the gamma emitters ( $^{54}\text{Mn}$ ,  $^{109}\text{Cd}$ ,  $^{65}\text{Zn}$ ) are measured with a HPGe Canberra detector with a relative efficiency of 20% and a multi-channel spectrometer series 20, model 2802. The beta activities ( $^{14}\text{C}$ ) are measured by a Packard Tri-Carb 3255 liquid scintillation counter. A minimum of 1000 counts was measured for all the elements in order to have an uncertainty on the counting less than 1%. For each sample, the filter as well as the filtrate are counted in order to detect the eventual losses of radioactive elements during the experiment.

## 2.3.7 VOC analysis

### 2.3.7.1. Selection of target compounds

Twenty seven volatile organic compounds (VOCs) were selected from priority and additional priority lists published at the 3<sup>rd</sup> International Conference of the Protection of the North Sea (Ministerial Declaration of the Third International Conference on the Protection of the North Sea, 1990). Target VOCs are listed in Table All.

### 2.3.7.2. Analysis of 27 VOCs in marine water samples

VOCs were analysed by purge-and-trap/gas chromatography-mass spectrometry (GC-MS).

#### Equipment

The purge-and-trap stage was conducted in a separate off-line device, while desorption and subsequent analysis and detection were done in an on-line apparatus. The off-line construction was made of a purge vessel (3.4 cm I.D., height 20 cm) equipped with a glass frit at the bottom and an injection septum. Helium was passed through a liquid nitrogen trap before it was introduced into the vessel. To avoid water vapour from entering the on-line system, a second condenser was placed between the purge vessel and the sorbent trap. The end of the condenser was directly connected to a sorbent trap containing 17 cm Tenax TA, 6 cm Carboxen 1000 and 1 cm Carboxen 1001 (Supelco).

The on-line apparatus consisted of a microprocessor controlled purge-and-trap system, CDS Peakmaster (CDS Analytical Instruments, USA), coupled to a gas chromatograph-mass spectrometer Carlo Erba QMD 1000 (Carlo Erba Instruments, Italy) by means of a transferline maintained at 275°C. The transfer line was a 0.53 mm I.D. Hydroguard FS (Restek, USA) deactivated fused silica capillary. A cryogenic focuser was positioned onto the injection port of the gas chromatograph and provided a focusing zone to recollect the trapped organic analytes. Separation was done on a 60 m × 0.32 mm I.D. Rtx-502.2 (Restek) fused silica capillary column with a 1.8 µm film thickness. *m*- and *p*-xylene were not separated and were determined together. The quadrupole mass spectrometer was operating in the selected ion monitoring mode (SIM). Analytes were identified and quantified by means of two or three selected ions for each compound (see Table All). The ion source temperature of the mass spectrometer was held at 200°C. The emission electron energy was set to 70eV and the trap current to 150 µA. Data acquisition was controlled by Masslab v1.3 data system (Fisons Instruments, UK).

#### Preparation of blanks and reference materials

Blank water was prepared by purging 60 ml of natural seawater for at least 1 hour at 45°C and a He flow rate of 50 ml min<sup>-1</sup>. System blanks, laboratory reference materials (LRM) and calibration materials (CM) were prepared by injecting 5 µl of the appropriate analytical stock solution in water, purged to blank. Concentration levels

of 25.97 to 66.68 ng l<sup>-1</sup> for LRM and 64.92 to 166.70 ng l<sup>-1</sup> for CM were obtained this way. With the exception of LRM, system blanks and CM were analysed daily.

#### Analysis of samples, system blanks and reference materials

A sample aliquot of 60 ml was brought into the purge vessel off-line, kept in a water bath set at 45°C. Five µl of an internal standard (IS) solution in methanol, containing  $\alpha, \alpha, \alpha$ -Trifluorotoluene (Aldrich) (IS<sub>1</sub>) and *p*-bromofluorobenzene (Fluka) (IS<sub>2</sub>), was added and the sample was allowed to thermally equilibrate for 7 min before purging for 20 min at a rate of 50 ml He min<sup>-1</sup>. The target compounds were trapped at room temperature onto the sorbent. The trap was thermally desorbed in the on-line apparatus at 275°C during 15 min. In the meantime the cryofocussing temperature was held at -150°C. After desorption, the cryofocussing device was heated at a rate of 800°C min<sup>-1</sup> to 260°C and kept at that temperature for 6 min. Temperature programming of the GC and data acquisition were started simultaneously. The temperature of the GC oven was held at 40°C for 10 min, then increased to 150°C at a rate of 10°C min<sup>-1</sup> and finally heated to 220°C at 8°C min<sup>-1</sup>. Temperature was kept at 220°C for 10 min. System blanks, CM and LRM were analysed as described above.

## 2.4 Analytical Quality Assurance

A lot of attention was focussed on the analytical reliability of the data. This included the analysis of blanks, reference materials, the plotting of QC charts, the participation in interlaboratory comparison exercises (QUASIMEME) for dissolved and particulate trace metals, nutrients and volatile organic pollutants as well as the participation in intercomparison exercises for the certification of new reference materials (BCR 710: Arsenic and Hg species in oyster tissue, IAEA 405: methylmercury in sediments).

## 2.5 Modelling

### 2.5.1. Atmospheric modelling

For the interpretation of the concentrations, a model, the Atmospheric Chemistry and Deposition model (ACDEP) (Hertel et al., 1995) was applied. Over the years, the model's performance have been increased considerably, since the geographical resolution in emission data and the temporal and geographical resolution in meteorological input data have been increased (Ambelas Skjoth et al., 2002).

### 2.5.2. Hydrodynamic modelling

Estimates of riverine inputs from the Scheldt were made based on average contaminant concentrations found in the downstream part of the estuary and an average annual river discharge of 120 m<sup>3</sup>sec<sup>-1</sup>. A box model was applied to evaluate the mass balance of the transport of pollutants through the estuary (Baeyens et al., 1998a). Trace metal fluxes in the coastal waters were calculated based on residual

flow patterns and salinity gradients (Baeyens et al., 1998b). Estimates of inputs from the English Channel were calculated using average contaminant concentrations and a net annual inflow of  $1800 \text{ km}^3\text{y}^{-1}$  (Wollast, 2000).

### 3. RESULTS

#### 3.1 Nutrients

##### 3.1.1. Boundaries

###### 3.1.1.1 Air/sea

Samples for nutrients have been taken for a period of ten months at Knokke-Heist, Het Zwin, at a distance of 500 meter from the sea (51°21' 30"NW, 3°21'EL) near the Dutch border. Sampling took place over a period of more than 10 months, from July 26, 1999 until June 9, 2000.

Various sampling campaigns were also organized at Adinkerke, De Panne (51°04'45"NW, 2°35'45"EL), near the French border. The first sampling was started at June 9, 2000 and was terminated on July 25, 2000. The seasonality of the pollution was investigated by organizing the second campaign in the winter period. The first part of this campaign was from December 4, 2000 until January 3, 2001, the second part from February 5, 2001 until March 2, 2001. Finally, the last campaign was executed from May 28, 2001 until June 18, 2001. Samples for nutrients were also taken on the R.V. Belgica, but the interpretation of the output of this limited data set is rather speculative because the data are more a function of the trajectory of the air mass and the subsequent removal processes than of the position of the sampling. In order to achieve a better understanding concerning the geographical distribution of the pollution, it would be better to make an interpretation using the large data set of coast samples using a model (see paragraph 3.3).

For the Knokke campaign, the particulate nitrate and sulfate concentrations were generally the highest, with peaking concentrations during the dry period in August-September. For the Adinkerke campaigns, it is very obvious that the highest concentrations were measured during the winter period. The sea salt concentrations as well as the concentrations of anthropogenic compounds have more than doubled during the winter campaign. The results of the two measuring campaigns in spring showed comparable concentrations for the anthropogenic compounds. The nitrite concentrations were as usual very low, and most of the time under the detection limit. The phosphate concentrations seemed to be under the detection limit for all the samples.

Table I: Comparison of the average concentrations for the different sampling campaigns (concentrations in  $\mu\text{g}/\text{m}^3$ )

		# meas	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Knokke	July 1999- June 2000	48	2.23	1.84	0.74	0.35	0.53	1.10	2.17	0.04	8.27	6.13
Adinkerke	June-July 2000	8	1.90	0.66	0.28	0.10	0.71	0.02	1.90	0.00	2.31	3.58
	December 2000	6	5.90	1.48	1.10	0.25	2.52	0.10	8.74	0.00	4.39	8.44
	February 2001	9	2.35	0.73	0.42	0.14	1.67	0.06	3.17	0.00	2.31	4.24
	May-June 2001	6	3.45	0.11	0.38	0.12	1.14	0.12	2.37	0.00	1.81	3.41

There are some clearly visible trends between the pollutants. The correlation between the sodium and chloride is significant at the 99% reliability interval, a result of the sampling in the direct neighbourhood of the sea. Generally, we can see that around one third of the sea salt has aged, meaning that the chloride in the sea salt is already replaced by other components. However, the correlations between the nitrate, sulfate and ammonium components are very low and not significant. This is a result of the numerous mixing ratios between the individual components and particles in the air masses, indicating the complexity of the pollution problem. Therefore, it is not possible to subdivide the pollution problem in a certain amount of scenarios.

Only in some cases, a clear wind direction dependency of the concentrations can be demonstrated. The sulfate and nitrate concentrations seemed to be lower with western to northern winds, where the sodium and chloride concentrations reached a maximum.

The dissolved organic nitrogen (DON) part was also investigated. The filter samples were digested (Dafner et al., 1999) and the regression was calculated in order to obtain a broader insight concerning the soluble organic nitrogen fraction. In figure 1, it is clearly demonstrated that the DON fraction is responsible for about the same amount of input of nitrogen compounds to the North Sea as the inorganic nitrogen. These data however have to be interpreted with great care. It is better to say that this DON fraction represents the maximum organic soluble fraction, because it was possible that during the microwave destruction of the samples, also the very small organic particles (particles not restrained by the 0.22  $\mu\text{m}$  Millex® filter), insoluble under normal conditions, were destructed and caused an overestimation of the DON concentration. These data are however very important because they give a clear indication about the massive importance of the organic nitrogen fraction.

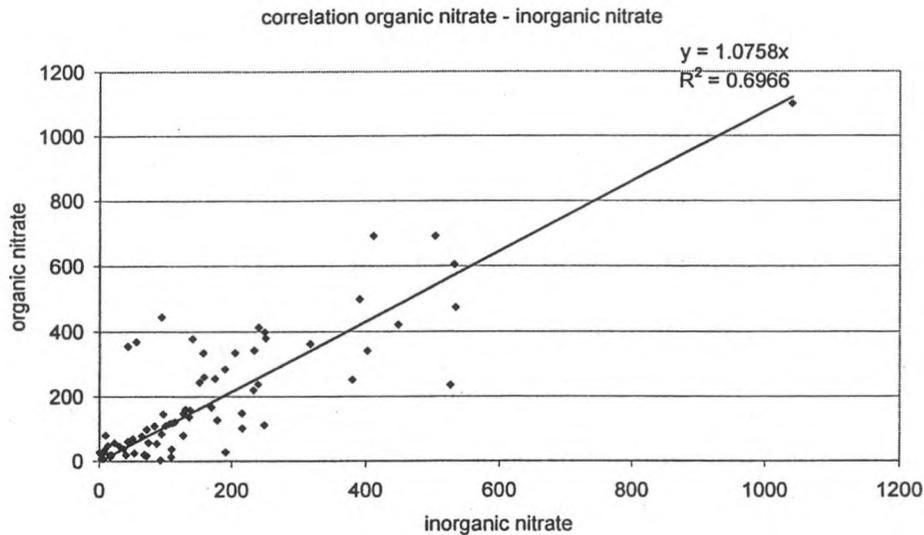


Figure 1: Fraction of the DON concentration

A total of 54 24-hours gas samples were taken during the Knokke campaign. As with the daily average temperatures, a sinusoidal tendency can be noticed for the ammonia concentrations. The ammonia reaches a maximum in the warm and dry period at the end of August. The concentrations remain very high until the end of September. At that time, there is a last increased agricultural fertilization activity, before the fertilization prohibition during wintertime from September 21 until January 21. After wintertime, the ammonia concentrations increase again very fast, with peaking concentrations in May as a result of the fertilization for corn. During wintertime, a background concentration of  $5 \mu\text{g}/\text{m}^3$  was measured. The yearly average concentration of ammonia measures  $10 \mu\text{g}/\text{m}^3$ , the yearly average concentration of the sum of nitric and nitrous acid is  $2 \mu\text{g}/\text{m}^3$ .

The correlation between the daily maximum temperature and the ammonia concentration was calculated and seemed to be significant for a 99% reliability interval. More than half of the concentrations under the regression line could be explained by precipitation, resulting in a strong decrease of the ammonia concentrations. Concentrations above the regression could be explained by dry periods, periods of fertilization activities or local contamination. Other parameters, such as wind direction, wind speed, and relative humidity only play a secondary role. However, it has to be noted that air coming over sea enhances the temperature effect, since less polluted and cooling marine air will decrease the concentrations during peaking concentrations in summertime.

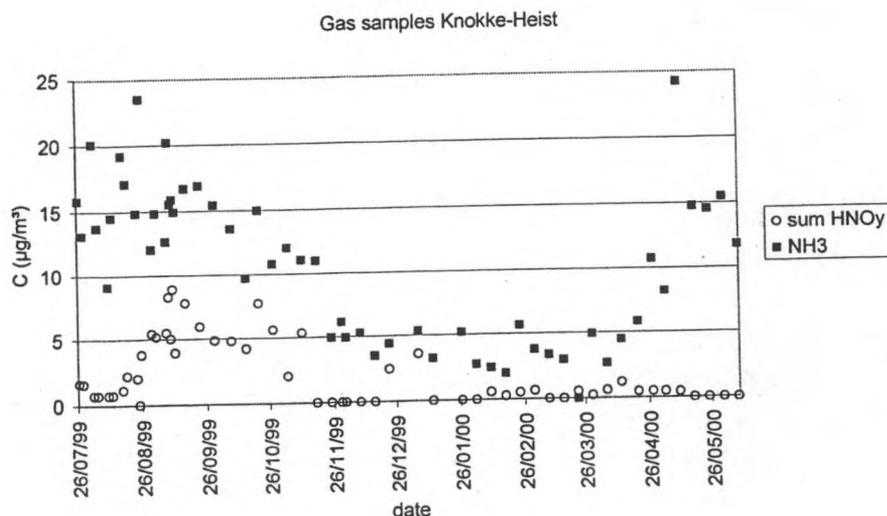


Figure 2: Weekly gas concentrations at Knokke-Heist

Compass roses were constructed for all the individual pollutants, and there is only a strong wind direction dependency for ammonia and ammonium compounds.

For the Adinkerke samples, the average concentrations of nitric and nitrous acid (based on 15 measurements) seemed to be somewhat lower during wintertime ( $1.57 \mu\text{g}/\text{m}^3$ ) is compared to  $2.34 \mu\text{g}/\text{m}^3$  for the June campaign, while the average ammonia concentration was surprisingly higher for this winter period, with almost  $10 \mu\text{g}/\text{m}^3$  while there was much precipitation and while the average temperature was more than  $10 \text{ }^\circ\text{C}$  colder. Possible explanations for these higher concentrations are exceptionally low concentrations during the June period (average of  $6.46 \mu\text{g}/\text{m}^3$ , based on 17 measurements), and a period of high pollution, combined with periods of inversion for the month of December. Here again, the highest ammonia concentrations were measured during dry and warm periods, with winds coming from the southwest to the southeast. The evaporation of volatile ammonium compounds from soils of adjacent agricultural areas seemed to be the most important source

Precipitation was collected at Adinkerke during the June-July 2000 and December 2000-January 2001 sampling campaigns and wet deposition fluxes were calculated for these periods.

Table II: Wet deposition fluxes for the Adinkerke measuring campaigns

Flux (mg/m <sup>2</sup> )	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
June 9 –July 25 2000	10.0	463	113	490	360	123	18.9	37.2	54.3
December 4 2000 – January 3 2001	4.5	174	38.5	177	143	47.3	11.3	16.0	64.0

*The massive importance of the amount of wet deposition will be further discussed in more detail in the paragraph 3.3.*

General conclusions for the Knokke-Heist and Adinkerke campaigns can be drawn. The particulate phase shows only a slight wind direction dependency for the ammonium concentrations. This indicates the stability of the small nitrate and sulfate particles in the atmosphere, in such a way that they are transported over very long distances and that the concentrations of these compounds are more a question of the various deposition mechanisms at that moment than of local emission or contamination sources. For the ammonium particles, the higher concentrations from continental winds indicate the very fast conversion reaction from ammonia to ammonium aerosol from the various sources. The strong correlation between the ammonia concentration and the maximum daily temperature suggests that the soil is the major contributor for the high ammonia values. It is very clear that the highest concentrations were measured on dry warm days, more than during the fertilization periods. Agricultural activities have however an indirect major role in saturating the soil with volatile ammonium components during fertilization activities. The measured ammonia concentrations are very high. These concentrations are together with data from the Netherlands the highest in the world.

Future research should also focus on the importance of DON, since our measurements proved the massive importance of these compounds in the total nitrogen budget.

In order to achieve a broader insight concerning the consequences of these gas and particle concentrations, a model was used for the calculations of the deposition fluxes for these compounds. The model used was the Atmospheric Chemistry and Deposition model (ACDEP) (Hertel et al., 1995). The ACDEP model is a Lagrangian transport chemistry model, a trajectory model, which calculates concentrations and depositions for various chemical compounds. Air packets are transported to the receptor points in the model domain, where the depositions and concentrations of the chemical species are needed. The way the air packets are transported - the trajectories - are calculated backwards for 96 hours on an hourly basis and on a 0.25° x 0.25° grid resolution, provided from the ETA model run (Nickovic et al., 1998) at NERI within the forecasting system THOR (Brandt et al., 2000). At the starting point of the trajectory, the air packets

are given initial concentrations and are thereafter transported along the trajectory to the receptor points. In the transport along the trajectory, the air packets receive emissions from the sources which are passed, an emission inventory based on a 16.67 km x 16.67 km from the GENEMIS project and the 50 km x 50 km EMEP data base. The resulting emission inventory has a geographical resolution of 16.67 km x 16.67 km for the entire European network and is separated into surface emissions and high emissions (above 80 m). The concentrations of the different chemical species in the air packets are changed through chemical reactions and through diffusion and deposition. The model is separated into 10 layers from the ground and up to 2 kilometers above ground. The model's performance has recently been increased considerably, since the geographical resolution in emission data and the temporal and geographical resolution in meteorological input data have been increased (Ambelas Skjoth et al., 2002).

In a first step, the model's output and the measured concentrations were compared and adaptations to the model were executed in order to improve the resemblance. An adaptation was made for the seasonal variation of the concentration profiles of the pollutants, improving the correlation of the daily averages as a consequence (from 0.39 to 0.52, see figure 3). The models' performance was optimized for the ammonia concentrations, because, as a result of the very high concentrations above Flanders, it was assumed that this would be the most important contributor for the nitrogen input to the North Sea. As can be noticed, the models' calculations still slightly underestimate the ammonia concentrations, probably a direct consequence of the many local ammonia emission sources in the direct neighborhood of the sampling point. The adaptation to the model was found to be sufficient, because further interpretations of the depositions will be executed on the level of monthly averages, and thus averaging outlying daily values.

Using this adaptation for the seasonality of the pollution, wet and dry depositions (over land and over sea) were calculated for the nutrient compounds (ammonium compounds and the variety all the nitrogen oxide compounds) and these data were interpreted for the direct environment of the sampling points (see figure 4). There clearly can be concluded that the ammonium compounds are responsible for the most important atmospheric nitrogen input over land (yearly average of 2.3 t N /km<sup>2</sup>.yr) and over sea (yearly average of 1.1 t N /km<sup>2</sup>.yr). After that, the wet deposition of the ammonium compounds becomes the most important input source (1.0 t N /km<sup>2</sup>.yr), followed by the wet deposition of the nitrogen oxides (0.8 t N /km<sup>2</sup>.yr), the dry deposition of the nitrogen oxides over land (0.6 t N /km<sup>2</sup>.yr) and over sea (0.1 t N/km<sup>2</sup>.yr). This makes that, generally, the wet deposition of

nitrogen compounds to the North Sea is the most important deposition route with a yearly average of 1.8 t N/km<sup>2</sup>.yr (60% of the total deposition).

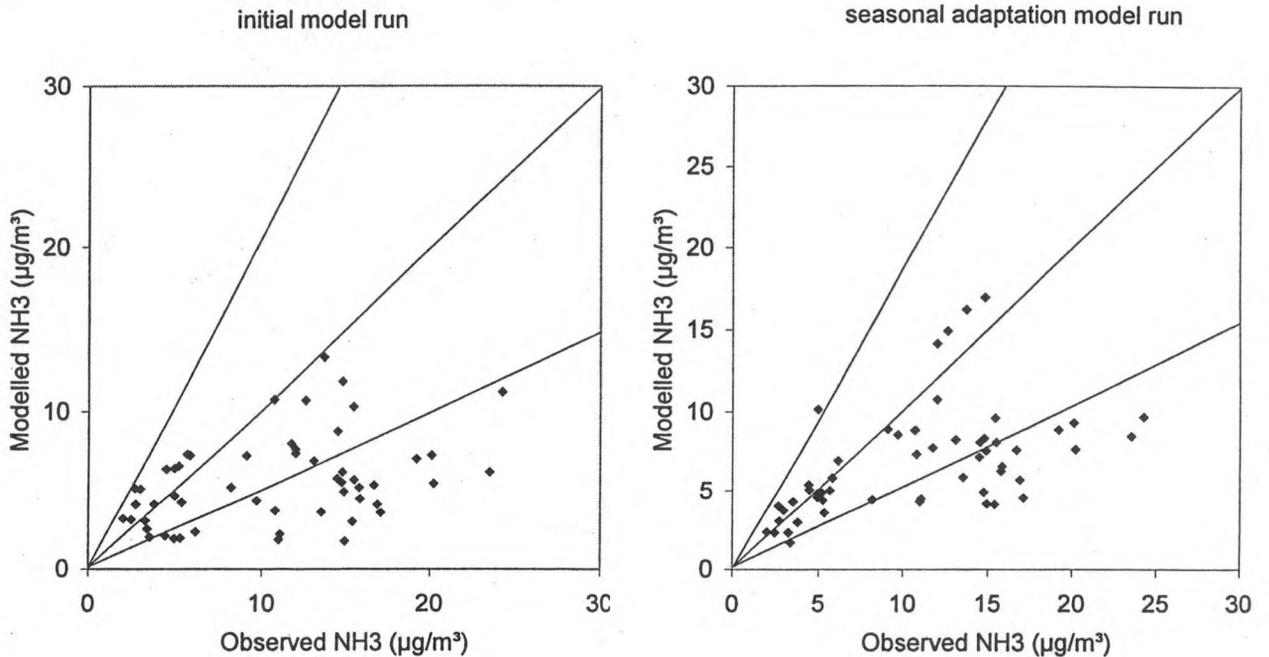


Figure 3: Correlation between the measured data and the data of the two model runs. The three lines in the figures show the one to one line, the two to one line (50% underestimation) and the one to two line (50% overestimation).

The model was also run in 1999 for the entire North Sea, concluding that wet deposition also was the most important input source (81% of the total deposition) (Hertel et al., 2002). Main difference between our findings and the results for the entire North Sea was the major importance of the deposition of ammonium compounds for the Belgian coastal zone. The ammonium components were responsible for only 38% of the total deposition for the entire North Sea surface, while this is around 70% for the Belgian coastal zone. The calculated total deposition of nitrogen compounds amounts 3.0 t N /km<sup>2</sup>.yr, which doubles the modeled values for 1999, a direct consequence of the adaptations made to the model.

These depositions were already the highest for the entire North Sea (see figure 5), definitely the result of the very high ammonia concentrations above Belgium (De Fré et al., 1999) and the Netherlands (Bouwman et al., 1998), a result of agricultural activities and the cattle and pig farms density.

The total average deposition of nitrogen compounds for the entire North Sea amounted 709 kT N/yr (Hertel et al. 2002), which is 100-50% of the total riverine

input (minimum – maximum estimation) (OSPAR, 2000). Taking these new adaptations to the model into account, with higher deposition fluxes, the atmospheric depositions gain even more importance. There can be concluded that both rivers as the atmosphere deserve equal attention, as their contribution to the total nitrogen input can be stated as of equal importance.

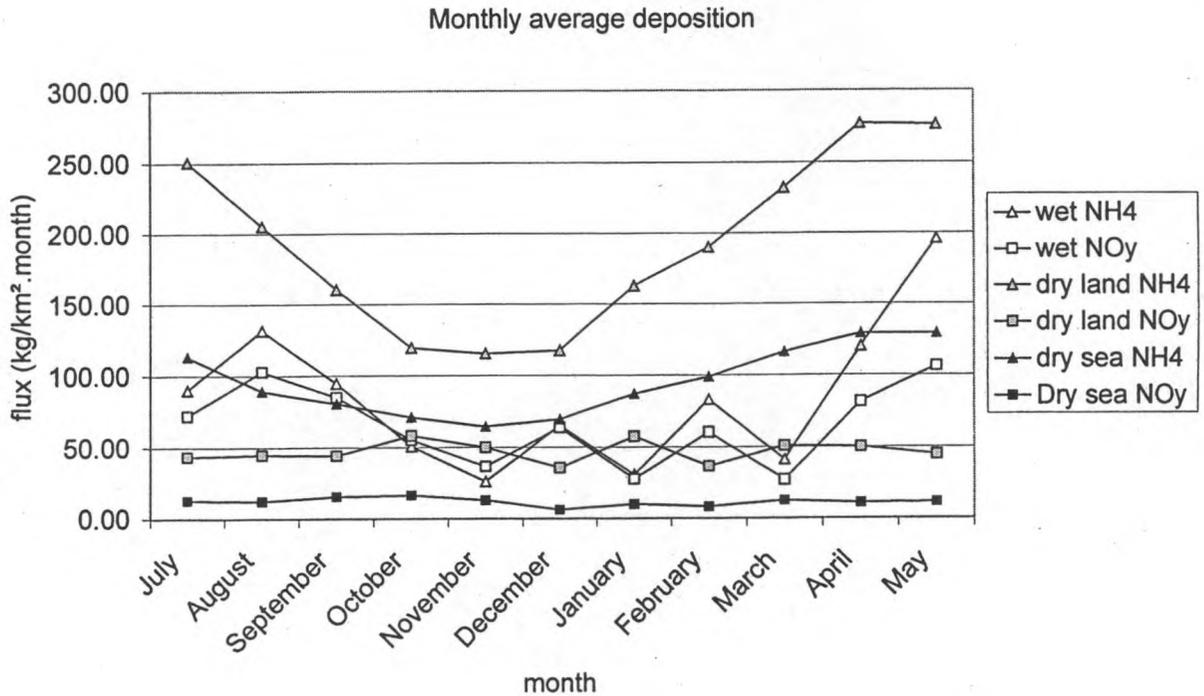


Figure 4: Monthly average depositions for the various nutrient compounds

A more detailed description about the modeling and the interpretation of the data for the entire North Sea will be published soon after this final report (Eyckmans et al., 2002 b). The mapping of the depositions presented in figure 5 will be recalculated for this publication. The mapping executed for 1999 (figure 5, Hertel et al., 2002), is presented because it gives a very accurate and realistic idea about the spreading of the intensity of the deposition for the entire North Sea.

For the mapping of the 1999-2000 data, more pronounced depositions can be expected in the neighborhood of the Belgian and Dutch coastal zones, because the results of the sampling campaigns at Knokke-Heist pointed the massive importance of the very high ammonia concentrations above Flemish and Dutch territories. The subsequent models' adaptations take greater care for these very high ammonia concentrations and will provide useful information concerning the geographic spreading of these increased depositions.

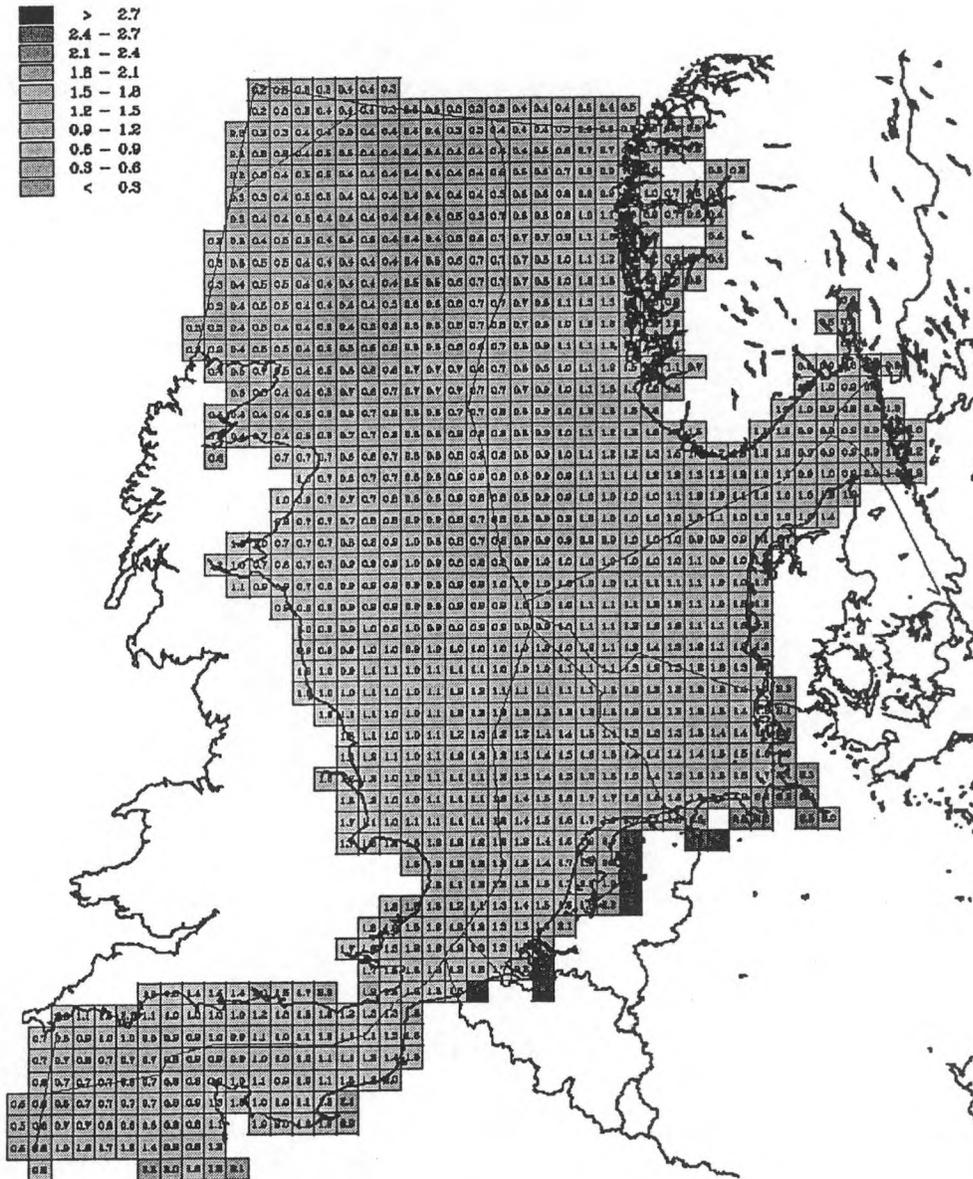


Figure 5: The total atmospheric nitrogen deposition to the North Sea in 1999. Depositions are given in Tonnes N per km<sup>2</sup>. The results reflect to a large degree the distribution of the source areas around the North Sea, but also the distribution of precipitation is important. For example, the large depositions at the Norwegian coast reflect the high precipitation amounts due to the mountains in this region. For the 1999-2000 data, there can be expected more pronounced depositions in the neighbourhood of the Belgian and Dutch coastal zones.

Much effort has also been put in the development of the thin-window electron probe micro-analysis technique (TW-EPMA) (Szaloki et al., 2001, Osan et al., 2000, Ro et al., 2000, Szaloki et al., 2000, Posfai et al., 1995).

This technique offers the determination of the concentration of light elements, such as carbon, nitrogen and oxygen in atmospheric aerosol particles and is therefore very important for the study of atmospheric pollution. North Sea aerosol samples were analysed using the TW-EPMA technique (de Hoog et al., 2002) providing additional useful information to marine aerosol studies, compared to the conventional EPMA studies. The complementarities between conventional IC analysis and the relatively new and promising TW-EPMA were also investigated. The output data of the chromatographic bulk analysis technique were compared with the results from the individual particle analysis technique after statistical processing. Both techniques show the same trends for the particle compositions and their output is very complementary. They show different types of analytical results and, therefore, the interpretation of these results is done on a different level for both methods. This might seem a limitation for both techniques separately, but it could be turned into an advantage when both methods are combined. Due to their different approaches, we have been able to make a more detailed interpretation of the aerosols in the air mass (Eyckmans et al., 2002 a). Combining the IC results with the TW-EPMA output, we were able to determine which inorganic compounds were present in the most important size fractions, for which IC only provided quantitative ion concentrations. Before the interpretation of TW-EPMA with the IC output, some irresolvable, undefined clusters could only be seen as a mixture of different compounds. The TW-EPMA technique was very limited in offering adequate information, but the combination with the IC data made it possible to quantify these mixed clusters. Using IC and TW-EPMA, one gains clearer insights in the contribution of the different aerosol fractions. In the near future, it will be possible to give more precise information about the air mass history (marine and continental), a better definition of the pollution sources (speciation) and a better insight in the different atmospheric interactions of the pollutants (primary, secondary or coagulated particles). The combination of both methods could be most helpful in the study of processes like e.g. sea salt aging.

### 3.1.1.2 Fluxes at the Scheldt estuary

The coastal sea environment of the North Sea is strongly influenced by the input of nutrients from land (Sanders et al., 1997) through rivers and estuaries, and high nutrient loads can lead to eutrophication problems in the coastal region.

The nutrient flux through the estuary depends on river flow, residence time, sewage discharge, local agricultural and industrial practices but also on a variety of processes occurring in the water column, sediments and intertidal areas (Balls, 1992). Estuaries are highly dynamic regions with significant salinity gradients (Morris et al., 1995) and nutrient behavior in estuaries and coastal areas is usually considered as a process dominated by biological factors.

One of the main estuaries entering the Southern Bight of the North Sea is the highly polluted Scheldt estuary.

Several cruises performed at different seasons of the year determined concentration-salinity profiles allowing the estimations of yearly nutrient fluxes from the Scheldt to the Southern Bight of the North Sea. Typical summer and winter results are presented in figures 6 and 7.

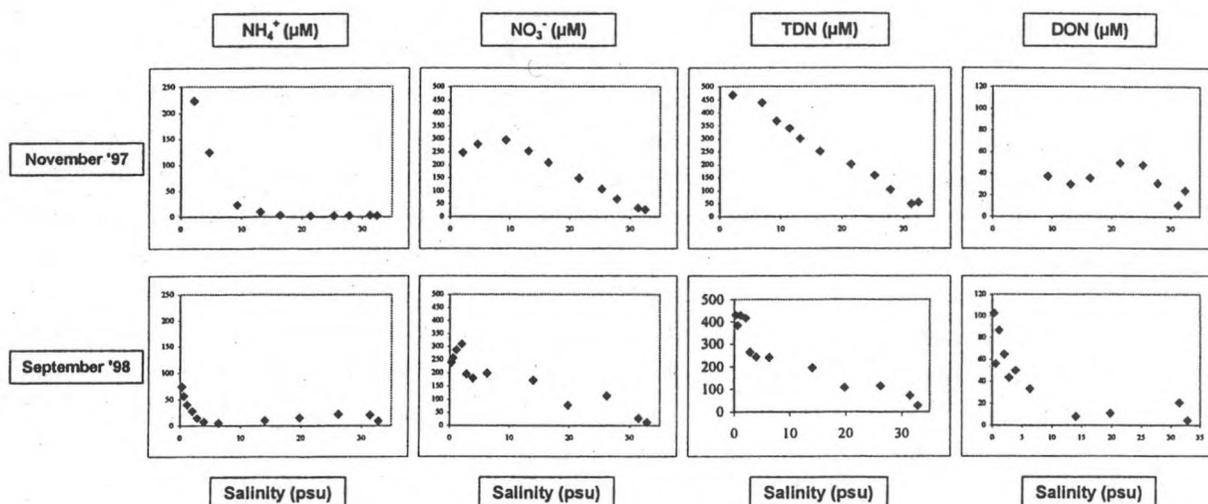


Figure 6: Ammonium, nitrate, dissolved organic N and total dissolved N versus salinity during different surveys in the Scheldt estuary.

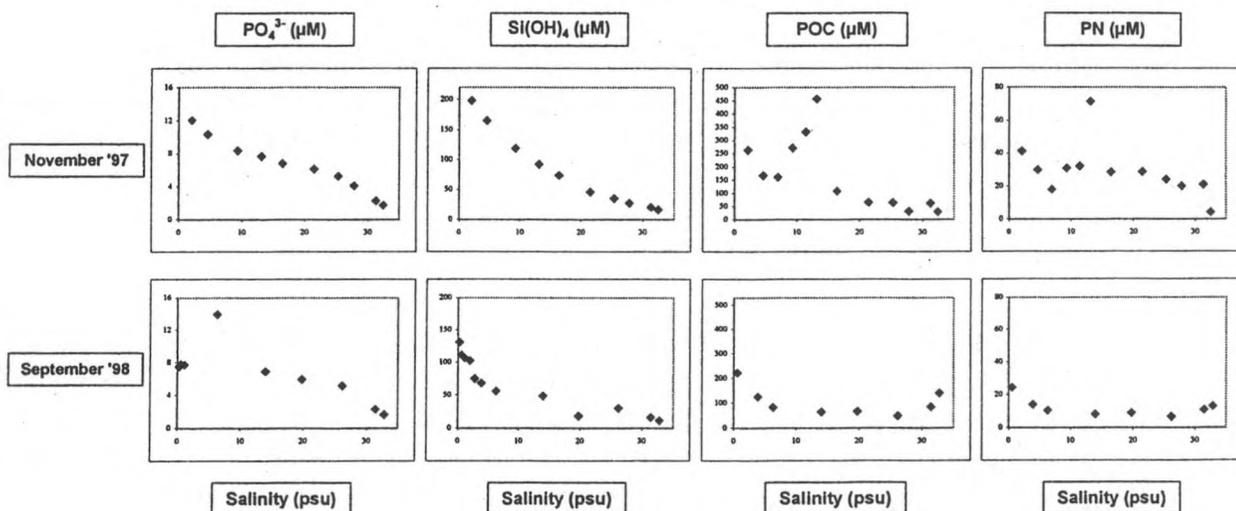


Figure 7: Orthophosphate, silicate, particulate organic C and N concentrations versus salinity during different surveys in the Scheldt estuary.

Estimations of annual nutrient fluxes from the Scheldt to the North Sea were extrapolated from the collected profiles. For each nutrient-salinity profile, the

nutrient concentrations of Scheldt water entering the North Sea (table III) was determined according to the effective zero salinity end member concentration method. These concentration data were then averaged over a year and then multiplied by the yearly average freshwater flow of the Scheldt ( $120 \text{ m}^3 \cdot \text{sec}^{-1}$ ). Results are presented in table III.

Table III: Calculated nutrient concentrations at the mouth of the Scheldt estuary ( $\mu\text{M}$ ), annual average of nutrient concentration and yearly fluxes ( $\times 10^3 \text{ T/y}$ ) through the Scheldt estuary into the North.

	TDN	$\text{NO}_2 + \text{NO}_3$	$\text{PO}_4$	$\text{Si(OH)}_4$
July '97	495.0	440.50	11.44	108.1
November '97	504.48	418.15	11.94	136.2
April '98	605.33	586.87	8.018	175.1
September '98	427.5	267.05	19.31	102.4
April '99	561.58	532.11	5.95	
Yearly average	518.78	448.94	11.33	130.45
Average Annual flux	27.5	23.8	1.33	13.8

### 3.1.1.3. The Channel

The Southern Bight of the North Sea receives high amount of nutrients from the rivers, but another important source for nutrients is the Atlantic Ocean. Water from the Atlantic Ocean enters the North Sea mainly through the Strait of Dover in the South and leaves the system in the North along the coast of The Netherlands. Although the nutrient concentrations in the Atlantic water are relatively low, the amount of water is enormous compared to the river output (Laane et al. 1993). Nutrient input estimations by several scientists have been made and they resulted in enormous ranges. Brion et al. (submitted) for example estimated that the nutrient exchange flux through the Channel varies from an output of 80 kT N/y and 14 kT P/y to an input of 230 kT N/y and 39 kT P/y.

Offshore water samples for nutrient determinations have been taken in the English Channel in April '98, September '98 and July '99 and analyzed for nutrient concentrations. These results together with average yearly water flux values given in literature were used to make an estimate of the nutrient flux entering the Southern Bight of the North Sea through the Channel.

Table IV presents average nutrient concentrations determined in the Channel. The most abundant dissolved inorganic nitrogen compound at any moment is nitrate. The total dissolved nitrogen pool in the Channel consists mainly of dissolved organic nitrogen. (range of 61-97% with an average of 81.9%). So, the DON pool is even more important than the nitrate pool. The particulate nitrogen

pool is only 9.7  $\mu\text{M}$  which is much lower than the dissolved pool. Phosphates average 0.2  $\mu\text{M}$  and silicates 1.5  $\mu\text{M}$ .

Yearly fluxes are calculated by multiplying the average concentrations with the net inflow of ocean water to the North Sea shelf via the Channel ( $1.8 \times 10^{12} \text{ m}^3/\text{y}$ ; Ersem, Wollast, 2002). An annual flow of 320 kT N, 11.6 kT P and 74.4 kT Si has been calculated for the Channel and these fluxes are of the same order as these calculated by Laane et al. (1993) who also stated that these values are all very high and therefore indicate that the Channel is one of the nutrient sources of the North Sea. In general, it can be stated that although the nutrient concentrations measured in the Channel are very low compared with the concentrations of the rivers, the fluxes are much more important due to the enormous water mass that is transported.

Table IV: nutrient exchange fluxes through the English Channel ( $\times 10^3 \text{ T/y}$ ).

Dissolved N-compounds:	$\text{NH}_4\text{-N}$	$\text{NO}_x\text{-N}$	DON-N	TDN
average concentration ( $\mu\text{M}$ )	0.2	2.9	9.7	12.7
Flux ( $\times 10^3 \text{ T/y}$ )	5.76	72.6	244	320
Other nutrient compounds	$\text{PO}_4\text{-P}$	$\text{Si(OH)}_4$	PN	
average concentration ( $\mu\text{M}$ )	0.2	1.5	0.95	
Flux ( $\times 10^3 \text{ T/y}$ )	11.6	74.4	24	

#### Comparison with atmospheric fluxes

In Section 3.1.1.1., important fluxes of inorganic N atmospheric deposition were determined in the area of concern (Results summarized in table V). Also it was concluded that DON fluxes could be as important than the  $\text{NO}_y$  fluxes.

Table V: Yearly averages of wet and dry deposition flux of inorganic nitrogen over the sea as determined in section 3.1.1.1..

	Wet deposition ( $\text{t/km}^2.\text{yr}$ )	Dry deposition ( $\text{t/km}^2.\text{yr}$ )
$\text{NH}_x$	1.0	0.1
$\text{NO}_y$	0.8	0.1

### 3.1.2. Reservoirs

Continental coastal regions are very dynamic and are subject to varying influences of riverine and atmospheric input, coastal and seafloor erosion and biological activities.

High nutrient contents in the water in combination with high primary production or large biomasses are biochemical properties characteristic of the continental zone.

A distinction between the coastal area and the offshore area is necessary because the concentrations of the different nutrients are higher in the coastal zone due to human activities and because of the existing of strong salinity gradients perpendicular to the coast due to the freshwater discharge of rivers.

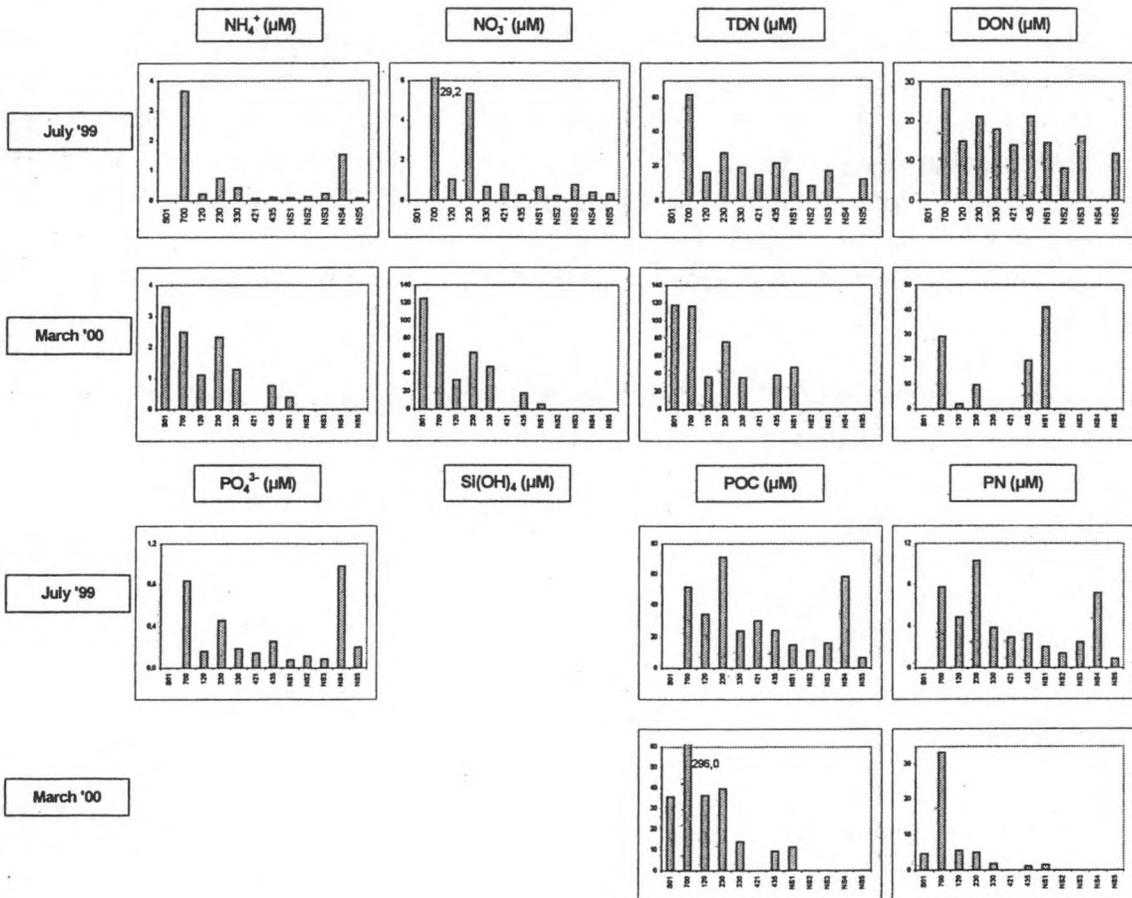


Figure 8: Coastal and offshore distribution of nutrients in summer and winter for the southern bight of the North Sea.

Distribution of the most important nutrients in the Belgian coastal and offshore waters as well as in the Southern Bight during a winter (march '00) and a summer (July '99) campaign are given in figure 8.

In general, highest dissolved nutrient concentrations are found in winter, corresponding with a minimum in biological activity, while lowest values are found in summer.

Highest nutrient concentrations occur in the coastal zones and smaller ones in the offshore zones. This general trend is also observed by Prandle et al. (1997). Average ammonium concentrations in the coastal area are respectively 2.3  $\mu\text{M}$  and 1.5  $\mu\text{M}$  in winter and summer, while for the offshore area the concentrations are 0.3  $\mu\text{M}$  in summer and 0.8  $\mu\text{M}$  in winter. For nitrate, very high concentrations are found during winter while in summer, almost the entire area is depleted in summer. Only some coastal stations show high nitrate concentrations in summer. Summer nitrate concentrations are 11.9  $\mu\text{M}$  in the coastal area and only 0.6  $\mu\text{M}$  in the offshore stations.

The nitrate winter stock amounts to 76.5  $\mu\text{M}$  at the coast and 23.9  $\mu\text{M}$  offshore. The total dissolved nitrogen pool is twice as high in winter as in summer. This is 35  $\mu\text{M}$  versus 86.7  $\mu\text{M}$  for the coastal stations and 15.5  $\mu\text{M}$  versus 40.5  $\mu\text{M}$  for the offshore ones. For the DON stock, differences with the other nutrients are observed. Summer DON concentrations only differ slightly for all the stations (average value 18.05  $\mu\text{M}$ ). Moreover, in winter higher DON values (average 30.3  $\mu\text{M}$ ) are found in the offshore stations than in the coastal stations (average 13.6  $\mu\text{M}$ ).

The particulate organic C and N pool is halved from coast to the offshore area in summer. Concentrations are 52.4  $\mu\text{M}$  and 7.6  $\mu\text{M}$  respectively and 23.2  $\mu\text{M}$  and 3.0  $\mu\text{M}$ . The most striking feature is the very high POC and PN pool in the coastal area during winter compared with the one found at the same moment in the offshore area. This is 102  $\mu\text{M}$  POC and 12.1  $\mu\text{M}$  PN in the coastal area and 11.5  $\mu\text{M}$  and 1.5  $\mu\text{M}$  in the offshore area.

### 3.1.3. Internal cycling

The ecological situation of the North Sea, especially its spatio-temporal variability, depends on a profound knowledge of the nutrient status in terms of concentrations and ratios and its relation with primary production, phytoplankton species abundances and phytoplankton-zooplankton interrelationships.

Nutrient concentrations in the Southern Bight of the North Sea show clear temporal as well as spatial differences. In general, highest dissolved nutrient concentrations are found in winter, corresponding with a minimum in phytoplankton growth. Nitrate and ammonia are used during the bloom period and the dissolved nutrient stocks are reconstituted in autumn. This is in agreement with the findings of Van Bennekom and Wetsteijn (1990) and Gentilhomme and Lizon (1998).

Most of the time, ammonium is lower than  $1 \mu\text{M}$  for the majority of the area. Highest values are found in winter (average  $2.8 \mu\text{M}$ ) when biological activity is at a minimum. In April, the Southern Bight is depleted in ammonium (range DL –  $0.55 \mu\text{M}$ ) due to the development of the phytoplankton bloom. At the end of summer the ammonium concentrations are increased as a result of the remineralization of dead organic material by bacteria.

Nitrate has the same seasonal trend as ammonium although the concentrations are much higher. Average nitrate concentrations are  $13.4 \mu\text{M}$  in spring (range  $0.1 \mu\text{M}$  -  $93.3 \mu\text{M}$ ),  $3.7 \mu\text{M}$  in summer ( $0.2 \mu\text{M}$ – $30 \mu\text{M}$ ) and  $54.5 \mu\text{M}$  at the end of winter ( $5.9 \mu\text{M}$  –  $127 \mu\text{M}$ ).

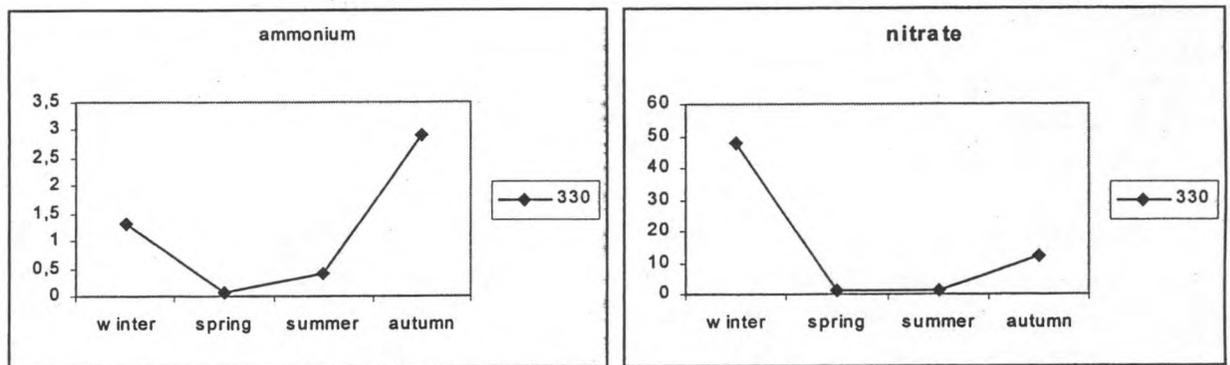


Figure 9: Seasonal variation of ammonium and nitrate for one selected station (station 330)

Phosphate concentrations are low throughout the year and are on average  $0.70 \mu\text{M}$ . For silicate an average value of  $8.6 \mu\text{M}$  is found. Coastal stations have higher values than the offshore ones for P and Si, and again highest values are observed in winter (average  $1.3 \mu\text{M}$  for P and  $19.3 \mu\text{M}$  for Si) and lowest in summer (average  $0.44 \mu\text{M}$  P and  $4.75 \mu\text{M}$  Si) with intermediate values between these seasons (average  $0.70 \mu\text{M}$  P and  $8.1 \mu\text{M}$  Si).

Particulate organic C and N show high spatial variations and they are in the range  $4.54 \mu\text{M}$  -  $173.9 \mu\text{M}$  and  $0.47 \mu\text{M}$  –  $24.4 \mu\text{M}$  respectively. Highest POC and PN values are found in spring and begin of summer, and they decrease at the end of summer. These highest values coincide with the development of the phytoplankton bloom in spring while at the end of summer the decrease is due to the remineralization of the particulate matter pool.

One of the most striking features is the importance of the DON pool in the total dissolved nitrogen pool. Most of the time a high percentage of the TDN pool is DON, going from 2.5% to even 98% with an average value of 65%. Especially the offshore stations have very high DON percentage values. Although, a deviation is visible in winter; All coastal stations have low DON fractions (2%-24%) and only in 2 offshore stations the DON pool is >50%. A seasonal trend in

DON is not easy to distinguish and the DON concentration is on average  $17.8 \mu\text{M}$  but varies between a minimum of  $3 \mu\text{M}$  and  $41 \mu\text{M}$ .

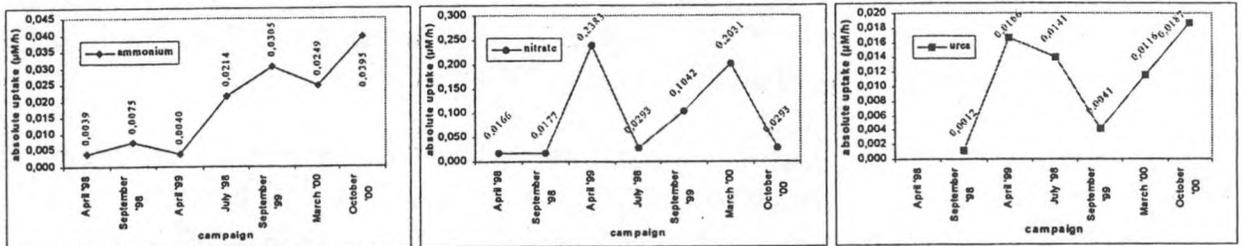


Figure 10: Absolute uptake rates (for ammonium, nitrate and urea) as a function of time for sampling station 330.

N-compound uptake rate measurements at several stations and in different seasons prevail seasonal trends as well as differences in the uptake of the studied nutrient.

Although it is general accepted that ammonium is the preferred nutrient by phytoplankton, N uptake during this study was mainly in the form of nitrate. Nitrate uptake rates are often one order of magnitude higher than these for ammonium. Only in a few cases, at the end of summer, higher ammonium than nitrate uptakes have been measured.

Urea uptake is generally very low and varies between  $0.0006 \mu\text{Mh}^{-1}$  and  $0.0222 \mu\text{Mh}^{-1}$ . Ammonium is, on average, taken up twice as fast as urea and uptake rates for ammonium vary between  $0.0019 \mu\text{Mh}^{-1}$  and  $0.130 \mu\text{Mh}^{-1}$ . For nitrate, uptake is in the range  $0.0034 \mu\text{Mh}^{-1} - 0.238 \mu\text{Mh}^{-1}$ .

Highest nitrate uptake rates occur in spring while highest ammonium uptake rates are encountered at the end of summer. This is clearly demonstrated in Fig 3.10, which shows the seasonal N-uptake rates for station 330.

This clearly demonstrates that new production dominates during spring. In spring f-ratio (ratio of new production over total production) vary between 78% and 93%, while in summer an average f-ratio of only 39% is measured. Riegman et al. (1998) also observed new production values up to 80% in the central North Sea and this is most likely related to the nitrate availability.

To conclude it can be stated that speciation of nitrogen uptake indicated the importance of nitrate as main nitrogen source for phytoplankton.

## 3.2. Trace elements

### 3.2.1 Boundaries

#### 3.2.1.1. Air-sea

As stated in the Quality Status Report, (OSPAR, 2000) trace metals and heavy metals fortunately became less important human stress factors and are now defined as pressures with second priority.

Trace elements were sampled on the R.V. Belgica (campaigns 2198, 1099, and 1699) and during the sampling campaigns in Adinkerke (from June 17 until July 25, 2000 and from December 14, 2000 until March 2, 2001). Averages were calculated for these periods and compared for a certain amount of metals, such as lead, copper, zinc, nickel and chrome with data found in literature (Hoornaert et al., 1999).

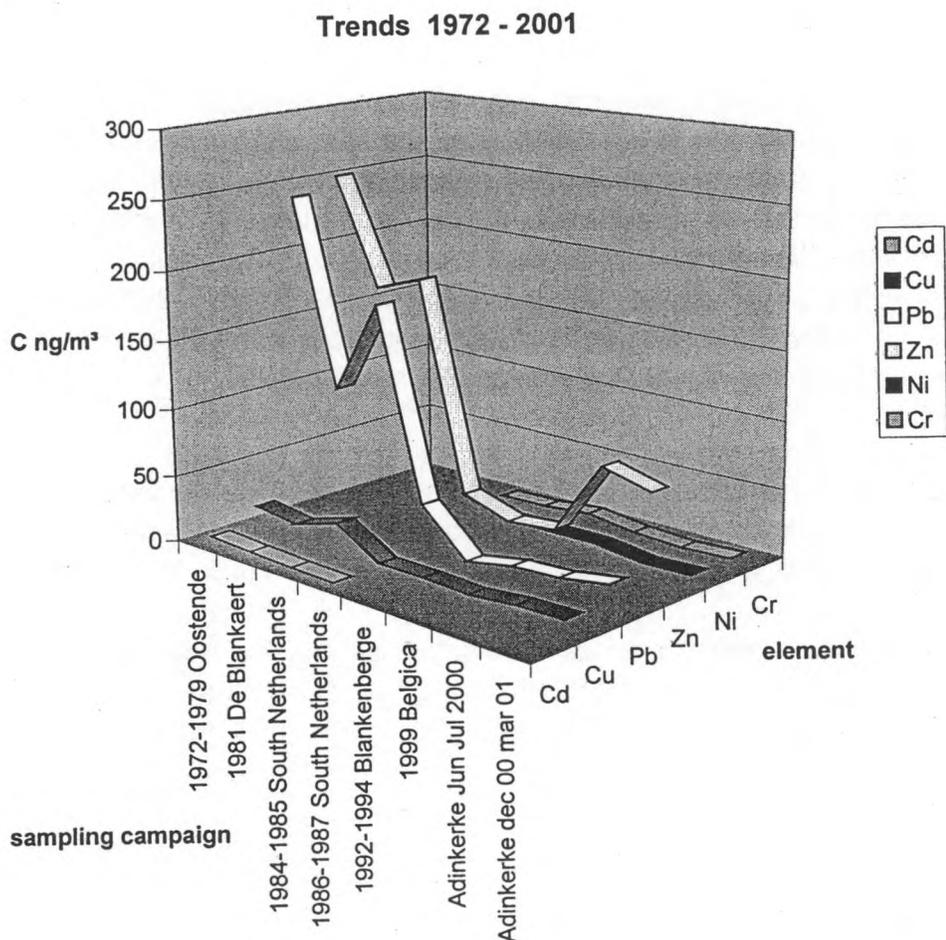


Figure 11: Trend analysis of the various metals above the North Sea

It is clearly demonstrated that the concentrations from the middle of the eighties have drastically decreased, as a result of the development of a cleaner industry and the use of unleaded fuel. Since the beginning of the nineties, the concentrations nearly stabilized. The concentrations measured on the Belgica are the same for copper and lead and have nearly doubled for lead, compared with the measuring campaign at Blankenberge from 1992 until 1994. A possible explanation for this growth is the exclusive sampling of on shore winds at Blankenberge, where direct contamination from land was avoided. This is also demonstrated with the Adinkerke samples, with generally higher concentrations compared with the Blankenberge campaign. The Zn concentrations for the Adinkerke campaigns are elevated probably a result of direct contamination from the neighbourhood such as the influence of the Dunkerque industrial harbour area.

### **3.2.1.2 Scheldt-Sea fluxes**

#### **3.2.1.2.1 Mercury**

Both riverine inputs and atmospheric deposition of Hg to the North Sea has significantly decreased in the last decade as stated in the Quality Status Report (OSPAR, 2000). Estimations of riverine inputs based on freshwater concentrations overestimate the net input to the coastal waters as they do not take estuarine retention into account. A box model was used to establish the relationship between the Hg inputs and its fate in the Scheldt estuary (Baeyens et al., 1998b). Annual budgets were calculated for particulate and dissolved Hg species based on concentrations measured after 1996.

The most important carrier of Hg is the particulate phase (about 50 times larger than the dissolved phase in the upper part, and 10 times in the lower part of the estuary). In the area of high turbidity and sedimentation, about 2/3 of the particulate Hg burden disappears from the water column.

The net flux of the Hg species from the Scheldt estuary to the North Sea are: particulate total Hg (HgP) 28.9 kg/y; total dissolved Hg (HgTD): 3.9 kg/y; dissolved methylmercury (MMHgD) 0.29 kg/y and particulate methylmercury (MMHgP) 0.094 kg/y.

#### **3.2.1.2.2 Arsenic**

According to literature, concentrations of dissolved arsenic in seawater do not appear to be very variable, especially below the photic zone (ICES, 1993). They are usually between 1 and 2  $\mu\text{g}\cdot\text{L}^{-1}$ . In estuaries, the values are however more variable, partly because of natural elements supplied by rivers themselves, but mostly due to local human waste discharges. For the Tagus estuary, concentrations may reach 58  $\mu\text{g}/\text{L}$ , due to complex chemical and iron-steel works

there. In the Humber estuary, discharges of 1000 kg As/day from a copper smelter have been measured (Kitts et al., 1994). In the Scheldt estuary, no such dramatic sources of As are known, but still, due to the intense industry along part of the estuary, As is likely to be discharged into the water. In the Loire estuary, the influence of urban wastes, electric power stations or petrochemical industries has been demonstrated (Seyler, 1985). Thus, rivers are the main sources of As input into the marine environment. According to Chilvers and Peterson (1987) their estimated contribution world-wide is 242.000 T.yr<sup>-1</sup>, one-quarter in dissolved form, three-quarters in particulate form.

Daily total dissolved As fluxes from the Scheldt are estimated at 30 to 100 kg As.day<sup>-1</sup>. These fluxes are markedly influenced by river flow and maximum values coincide with the typically high river discharges in winter. This can be explained by the mobilization of highly contaminated sediments and transfer to the dissolved phase in the river and the upper estuary, during flood conditions, as was seen in the Seine (Michel, 1993). On a yearly basis, the daily fluxes can be translated into an overall contribution of 57.4 T.yr<sup>-1</sup> of the Scheldt to the North Sea. One third of this As input (17.5 T.yr<sup>-1</sup>) consists of dissolved forms of the element, while two thirds (39.9 T.yr<sup>-1</sup>) is associated with suspended particulate matter.

### 3.2.1.3. Offshore fluxes and Channel-North Sea

#### 3.2.1.3.1 Mercury

An estimation of the Hg flows through the Belgian coastal zone (parallel to the coast) can be made based on the residual steady state currents, the diffusion coefficients related to these residual currents and the steady state Hg distribution (Baeyens et al., 1998a). The calculated flows are 485 kg/y for HgTD and 2222 kg/y for HgP for a water flow of 1260 km<sup>3</sup>/y. The fluxes through the English Channel can be estimated using an annual net water flow of 1800 km<sup>3</sup>/y (Wollast, 2002) and average Hg concentrations measured in the English Channel sampling stations in 1998 and are 468 kg/y for HgTD and 128 kg/y for HgP. The particulate Hg flux in coastal waters is significantly higher.

#### 3.2.1.3.2 Arsenic

Also the English Channel should be taken into account when considering the input of contaminants into the North Sea, as pollutants contained in Atlantic Ocean water are carried into the Belgian Coastal zone, through a net inflow of ocean water into the North Sea of  $1.8 \times 10^{12} \text{ m}^3 \cdot \text{y}^{-1}$  (Ersem, Wollast, 2002). Using this water mass balance, the inflow of dissolved As through the Channel is calculated as 2080 T.y<sup>-1</sup> and particulate As 200 T.y<sup>-1</sup>. For the latter, the suspended matter flux through the Dover Strait towards the North Sea of 20 106 T.y<sup>-1</sup> was used (Lafite et al., 2000).

### 3.2.2. Reservoirs

#### 3.2.2.1 Scheldt estuary

##### 3.2.2.1.1. Mercury

Hg species do not behave conservatively in the Scheldt estuary and show seasonal variations. Nevertheless, a decreasing trend can be observed in the average dissolved and particulate Hg concentrations from 1991 until now (Leermakers et al., 2001). An important decrease in methylmercury concentrations was also observed between the period 1993-1994 and the measurements made after 1996.

In the Scheldt estuary in winter, dissolved Hg concentrations are elevated in the upper estuary, decrease exponentially in the low salinity range followed by a very slow decrease towards the mouth. In summer, they are low in the fluvial part, increase in the low salinity range or in the mid-estuary and sometimes show an increase in the lower estuary. Particulate Hg concentrations do not show any seasonal trend.

Dissolved MMHg concentrations are much lower in winter ( $0.050\text{-}0.075\text{ pmol.L}^{-1}$ ) than in summer ( $0.075\text{-}0.6\text{ pmol.L}^{-1}$ ). In winter, maximum concentrations are found in the upper estuary while they remain relatively constant in the lower estuary. In summer, the MMHg concentrations are low at low salinity; they show a first increase in the salinity range from 3 to 12, a decrease in the mid-estuary and a second increase in the lower estuary. The higher dissolved MMHg values at the mouth extend further in the coastal-estuarine zone.

Highest particulate MMHg concentrations are found in the upper estuary, while in the lower estuary generally lower and more constant values are observed. Cruise averages range from  $7\text{ to }35\text{ pmol.g}^{-1}$ . Compared to the fraction of dissolved MMHg to dissolved Hg (cruise averages between 1.3 and 20 %), the fraction of particulate MMHg is much lower. Particulate MMHg accounts for 0.27 to 0.90 % (cruise averages) of particulate Hg.

In the North Sea: dissolved and particulate mercury concentrations range respectively from  $0.5\text{ to }9.5\text{ pmol.L}^{-1}$  and from  $0.1\text{ to }2.2\text{ nmol.g}^{-1}$ . In the offshore stations dissolved Hg concentrations are generally higher in winter than in summer while the reverse is true for particulate Hg. Dissolved methylmercury concentrations vary from  $0.05\text{ to }0.25\text{ pmol.L}^{-1}$  in summer and from the detection limit to  $0.23\text{ pmol.L}^{-1}$  in winter and particulate methylmercury concentrations from  $1.8\text{ to }36\text{ pmol.g}^{-1}$  in summer and from  $0.9\text{ to }21\text{ pmol.g}^{-1}$  in winter.

### 3.2.2.1.2 Arsenic

In the Belgian coastal zone and the Southern Bight, the dissolved As levels are very comparable to those found in literature, average concentrations range from 0.80 to 1.55  $\mu\text{g.L}^{-1}$ . The As levels in the area of the Belgian coast that is under direct influence of the Scheldt, are only slightly elevated (1.60 to 2.20  $\mu\text{g.L}^{-1}$ ).

In general, highest dissolved As concentrations are found in winter. This seasonal decline from winter maxima to spring minima can almost entirely be attributed to phytoplankton productivity, as arsenic is easily assimilated and reactivated by phytoplankton. Particulate As concentrations in the Southern Bight range from 9.7 to 22.0  $\mu\text{g/L}$  and show the inverse seasonal variation pattern of dissolved As, but only to a limited extent, as the seasonal variability is much less pronounced. However, phytoplankton has the ability to enhance sedimentation (transfer from particulate phase to sediment), next to partitioning (transfer from dissolved to particulate phase). Thus during the productive period, phytoplankton can be a major source of settling particles and increase the particle flux to the sediment (Millward et al., 1996).

### 3.2.2.2. Channel – North Sea

#### 3.2.2.2.1. Distribution of particulate trace metals in the Southern bight of the North Sea

There are usually only few data about the distribution and behavior of particulate metals compared to dissolved metals in aquatic environments. This is partly due to the heterogeneity of the suspended matter and the difficulty in marine systems to collect enough material to perform the analysis. The knowledge of the distribution, origin and properties of the particulate trace elements is however fundamental for the understanding of their biogeochemical cycle in the marine system. The objective of our study was to obtain preliminary results about the distribution of the composition of the particulate matter in the Southern bight of the North Sea under various seasonal conditions. It is well known that many trace elements play an essential role in the metabolic processes. Dissolved trace elements may therefore be transferred to the solid phase in relation to the biological activity. The influence of these processes is well demonstrated in the open ocean by the vertical distribution of dissolved trace metals such as Zn, Cd, Cu, Ni which exhibit depletion in euphotic zone. This is in contrast with other elements, which are enriched in the surface waters due to their atmospheric origin, such as Pb, and the existence of photochemical reactions, such as Mn. In the coastal area, the occurrence of these phenomena is much more difficult to establish due to the vertical mixing of the water column. It is nevertheless possible to identify the role of the marine organism on the behavior of trace metals by considering the seasonal variations of the composition of particulate material. In order to obtain useful additional information, the concentration of the dissolved trace metals was performed by the VUB on water samples obtained by the filtration (porosity 0.4  $\mu\text{m}$ ) carried out to collect the suspended matter. The

results of the analysis for all the cruises are presented in the appendix (A3, A4 and A5).

The map indicating the location of the sampling stations on the Belgian Continental Plateau, covered during this study, is shown in figure 12a. On two occasions, two additional stations were sampled in the Channel and four in the Northern part of the Southern bight (see map of figure A1 in the appendix). Figure 12b shows the mean concentration of chlorophyll in the four zones of the Belgian Continental Plateau. This figure indicates that the maximum of the phytoplankton activity in zone I and II occurs in July. These two zones are strongly influenced by the input of the Scheldt estuary where the maximum primary production is observed during the summer period (Muylaert *et al*, 2000). In zone III, under the influence of the input of Channel waters, the highest concentrations of chlorophyll are occurring in the spring, but remain high in the summer, possibly because of the Scheldt influence. In zone IV, the biomass of phytoplankton remains always low and is rather constant.

Besides primary production as a major source of particulate matter in the coastal zone, estuarine input of terrigenous components is another important source of solids for this environment. Atmospheric input may also contribute to the suspended load but is difficult to distinguish from riverine material.

In order to characterize the continental input, the Al (or Fe) content of the suspended matter is generally considered. Aluminum is a conservative major element present in clay minerals, which dominates both the riverine suspended matter and the atmospheric dust. As shown in figure 13a, the Al content is strongly diminishing when the organic carbon produced by the phytoplankton is developing in April and July. A separate plot of Al versus  $C_{org}$  for April and September, allows to better distinguish the seasonal variation of the composition of the suspended matter.

In April (figure 13b) the particles are essentially composed of phytoplankton at stations far enough from the estuary (stations 435, NS1, 330, 421) and where the phytoplankton bloom has already occurred. At the more Northern stations (NS2, NS3, NS4), or in the Channel (CH1, CH2), or at the mouth of the Scheldt (700), the amount of organic carbon remains low and the suspended matter is still dominated by continental input.

At the end of September (figure 13c), the solid phase is strongly depleted in organic matter but contains variable concentrations of Al. This is due to the fact that the inorganic phase contains also variable amounts of other mineral phases such as calcite and quartz. Nevertheless, the highest Al content are observed near the mouth of the Scheldt (S01, 700) and in the Northern part of the area investigated (NS2, NS3, NS4) which may be due to atmospheric input.

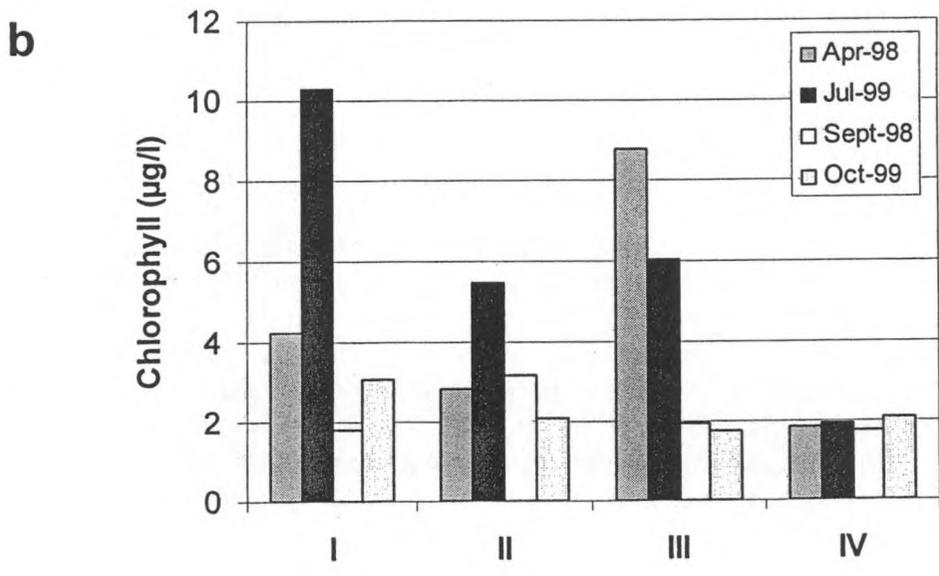
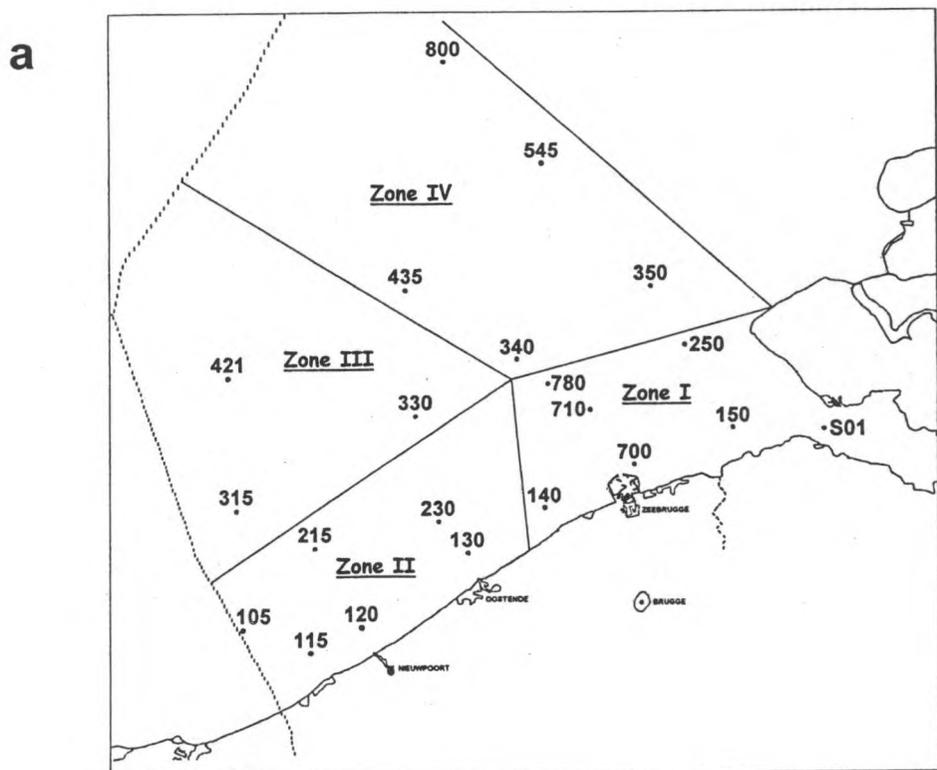


Figure 12: (a) Map of the sampling points on the Belgian Continental Plateau, (b) concentration of chlorophyll for the four zones during various seasons.

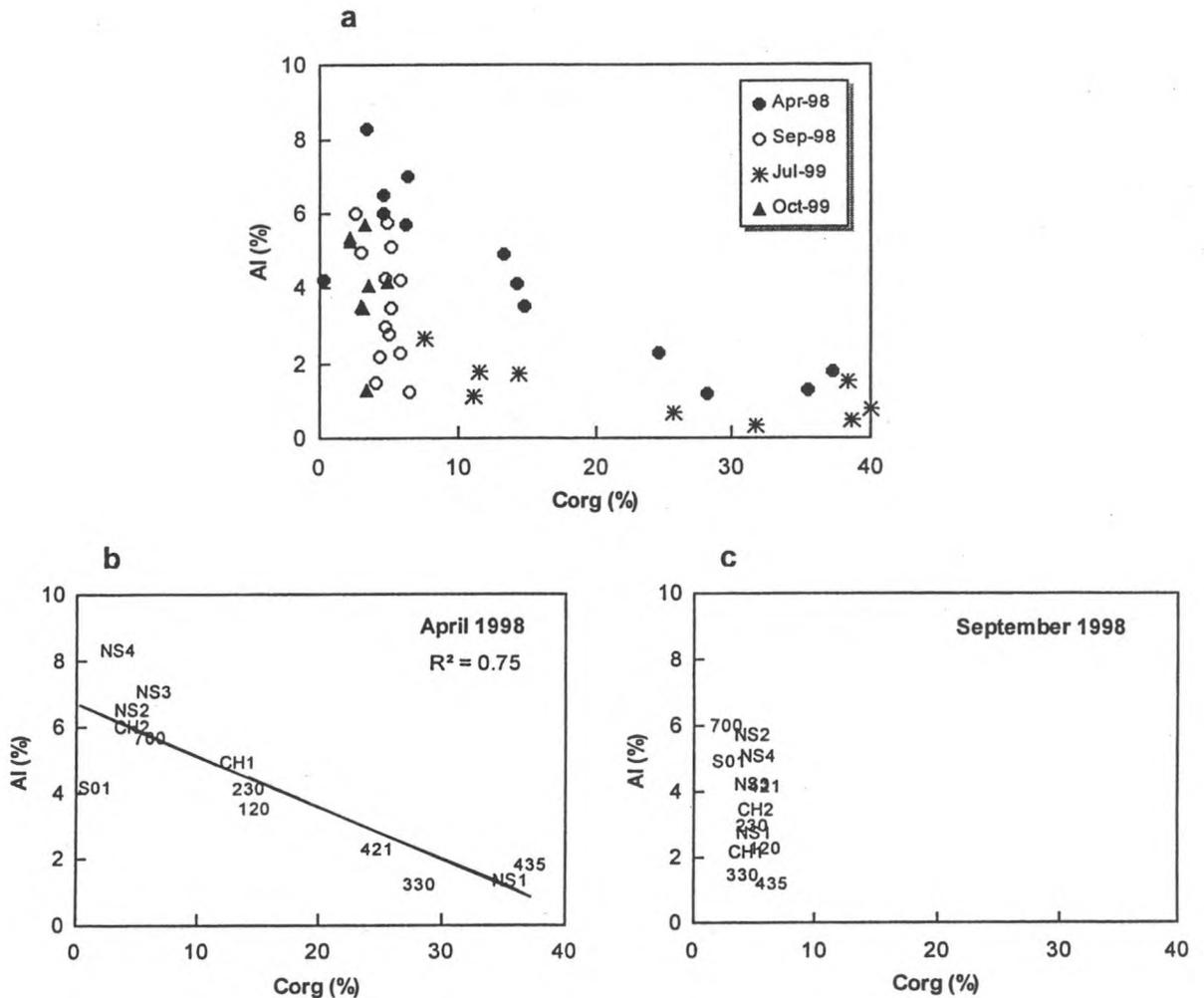


Figure 13: Relation between concentrations of organic carbon and aluminum in the suspended matter of the North Sea: a) for all seasons; b) for April 1998; c) for September 1998.

The aluminum content in riverine particles is generally well correlated with other major elements such as Fe, Si, Mg and K. The figure 14 presents the relation of the aluminum concentration with other major elements for the data collected during various seasons. In our case, the correlation coefficient between Fe and Al is very high ( $R^2 = 0.87$ ) with a Fe/Al ratio equal to 0.58 close to the global mean value (0.51) for riverine particles given by Martin and Meybeck (1979). We have also observed a significant positive correlation between Al and Si ( $R^2 = 0.66$ ), but high value of the intercept at Al = 0 indicates the presence of  $\text{SiO}_2$  as quartz or opal. The correlation between Al and Ca is relatively high ( $R^2 = 0.56$ ), which may be attributed to the presence of fine particles of Ca carbonates, possibly of phytoplanktonic origin (coccolithophorides).

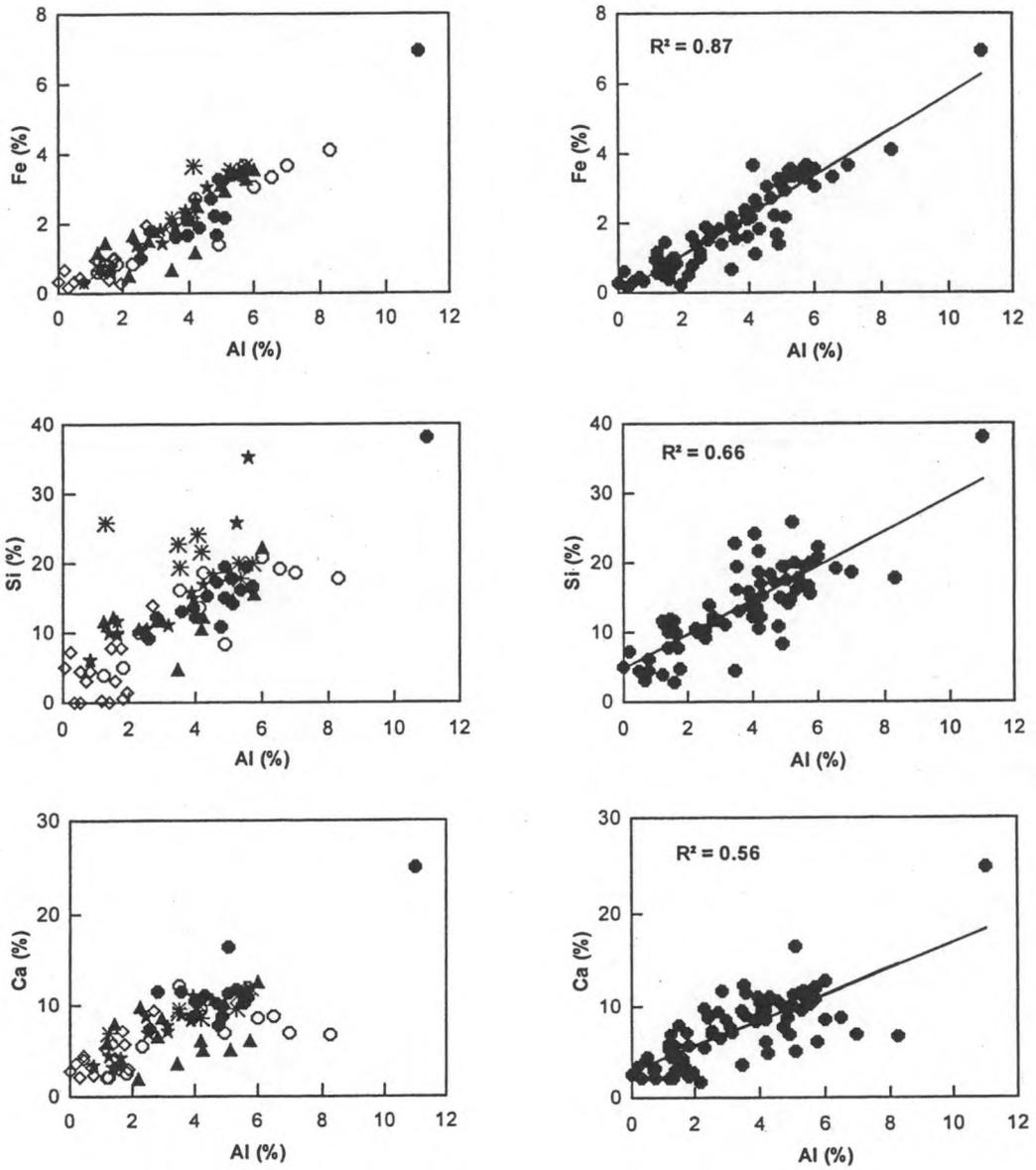


Figure 14: Abundance of major elements of the suspended matter as a function of concentration of Al for various periods (left) \* jul-97 ● nov-97 ○ apr-98 ▲ sept-98 ◇ jul-99 \* oct-99. The column to the right shows the regression coefficient for all the data collected over the various seasons.

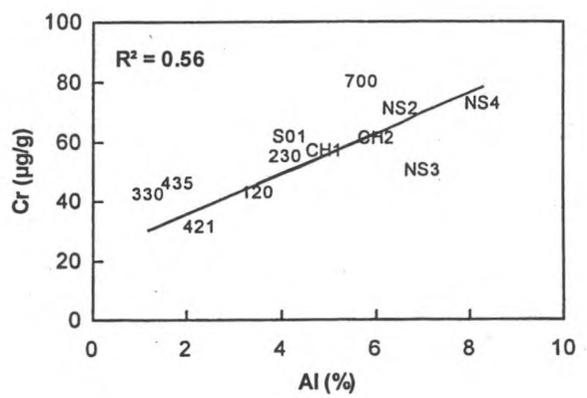
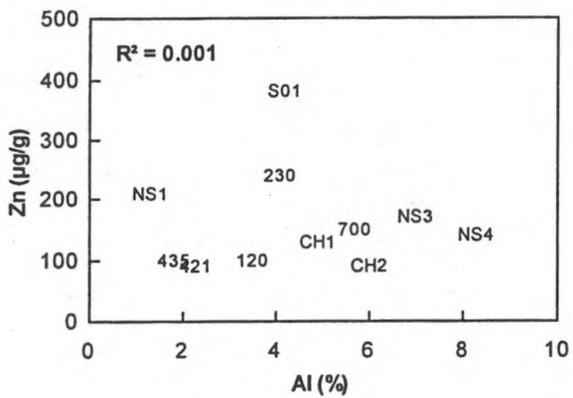
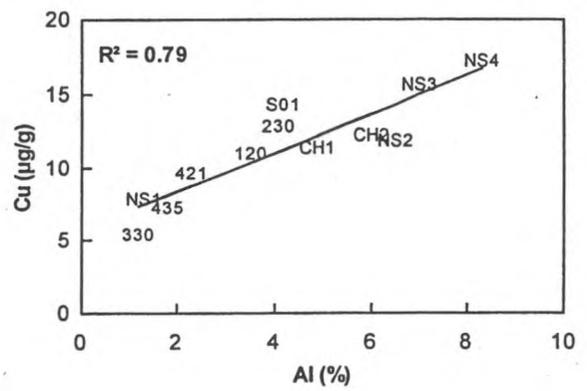
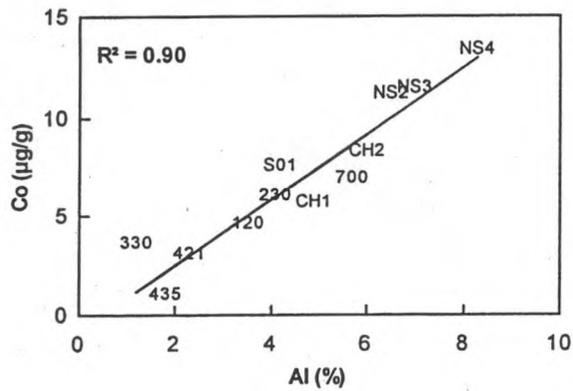
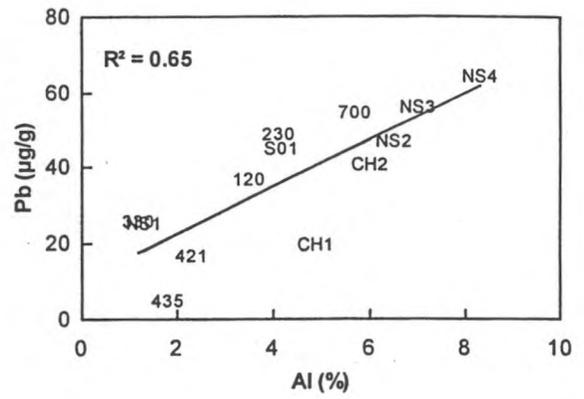
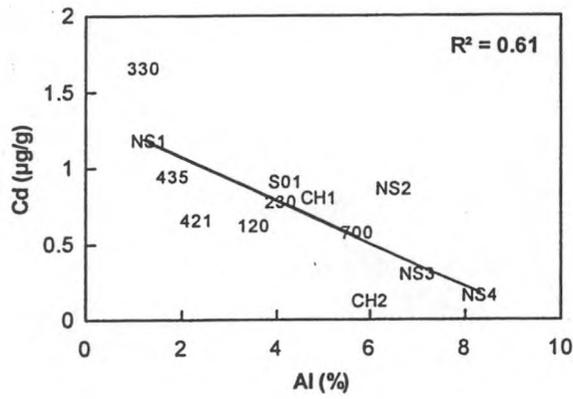


Figure 15: Relation between the concentration of trace metals and aluminum in April 1998

The aluminum content is also used to normalize the concentration of trace elements in the particles, because of their preferential occurrence in fine particles. Figure 15 shows the correlation between the concentration of trace metals and that of aluminum for the cruise of April 1998. The correlation is positive for Co, Cu, Cr and Pb, indicating the association of these elements with the clay fraction. Cd is negatively correlated with Al and may be explained by the strong uptake of this element by the phytoplankton. There is no correlation between Zn and Al ( $R^2 = 0.01$ ).

Most elements (except Cd, Zn and Ni) are negatively correlated with the organic matter (figure 16), even if the samples have been collected during a period of high phytoplanktonic activity. In fact, the trace elements are strongly diluted by the organic matter produced by photosynthesis, even if some trace metals are incorporated in the organic matter. The only exception is the cadmium whose concentration increases slightly with the organic carbon content. Ni and Zn are not significantly correlated with organic matter.

It is possible to estimate roughly, from the data shown in figure 16, the trace element content of the inorganic fraction of the suspended matter by extrapolating the regression line to  $C_{org} = 0$ . On the other hand, it is also possible to estimate the trace metal content in the organic fraction by considering its concentration at 40 % organic carbon, which corresponds roughly to 100 % of organic matter. The calculated values of the concentration of trace metals for the inorganic and organic fractions are given in the table below (table VI).

Table VI: Calculated values of the concentration of trace metals in the inorganic and the organic fraction.

<b>fraction</b>	<b>Cd</b> ( $\mu\text{g/g}$ )	<b>Pb</b> ( $\mu\text{g/g}$ )	<b>Co</b> ( $\mu\text{g/g}$ )	<b>Cu</b> ( $\mu\text{g/g}$ )	<b>Cr</b> ( $\mu\text{g/g}$ )	<b>Mn</b> ( $\mu\text{g/g}$ )
<b>inorganic</b>	0.3	54	10.6	16.6	71	572
<b>organic</b>	1.3	9	0.0	5.3	19	21

We have in addition performed a statistical analysis of the composition of the suspended matter. Correlations between samples for each cruise have been calculated by using normalized concentrations. They are obtained by calculating the difference between the concentration of one element in a given sample and the mean value of the concentration for all samples divided by the standard deviation. The results of the correlations obtained for the November 1997 cruise are shown as an example in figure 17.

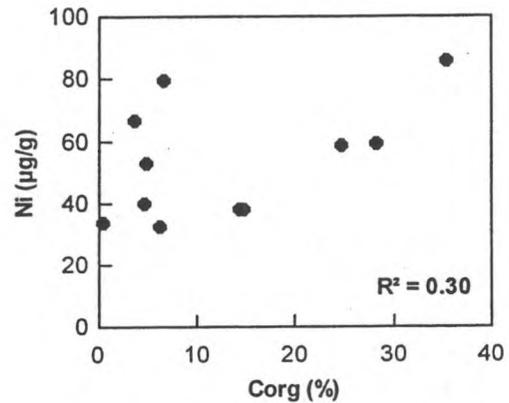
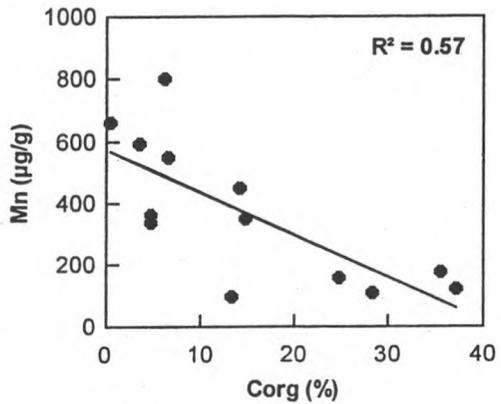
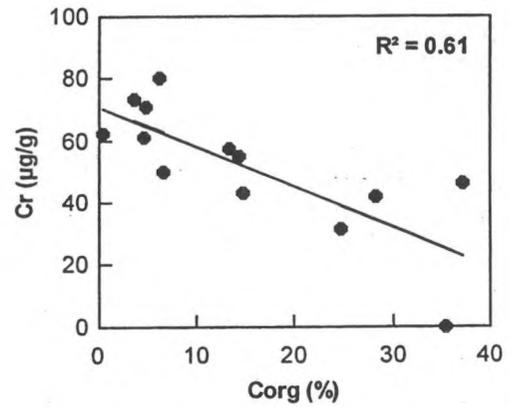
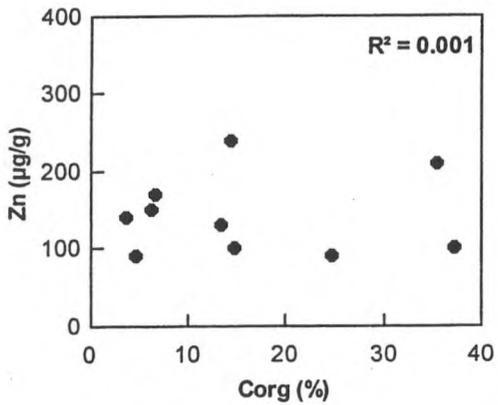
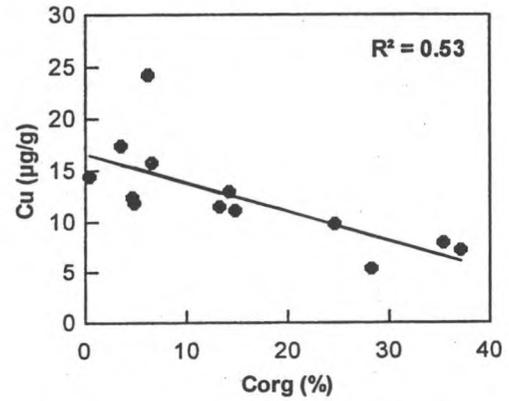
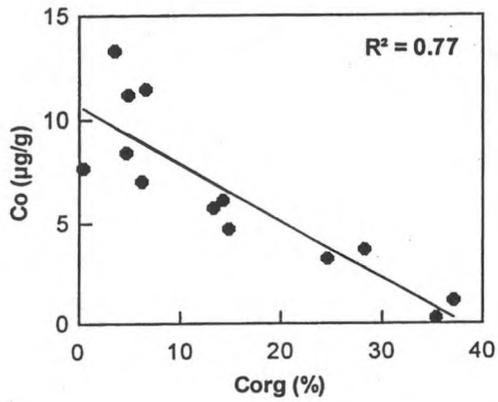
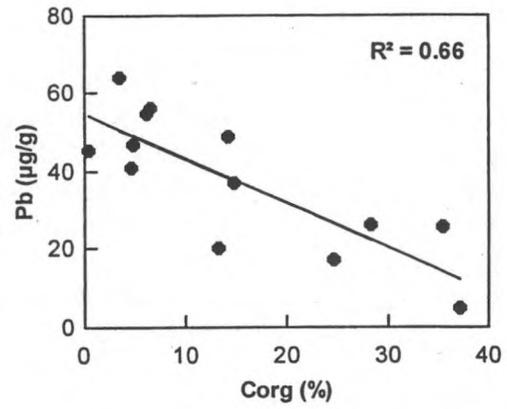
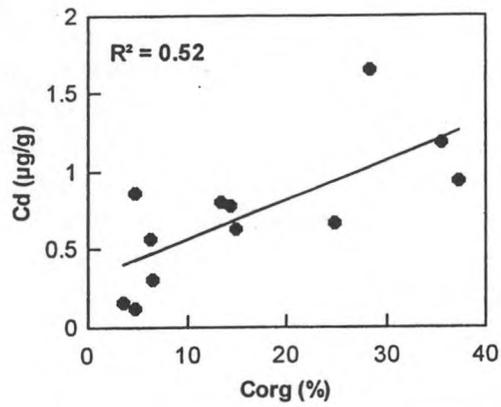


Figure 16: Relation between the concentration of trace metals and the content of organic carbon in particulate matter in April 1998.

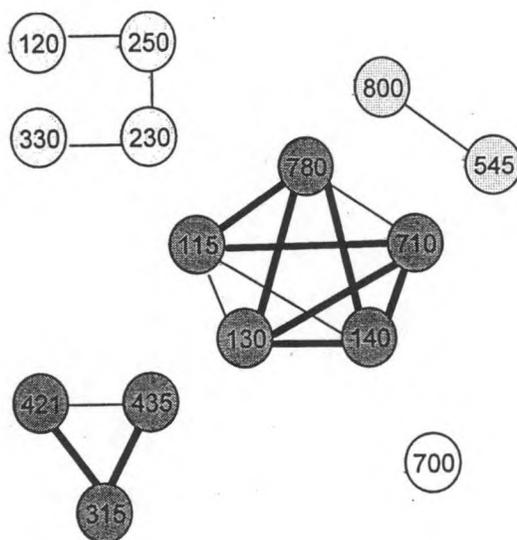


Figure 17: Example of cluster analysis obtained for the cruise of November 1997. The thick lines represent a correlation coefficient  $R^2 > 0.8$  and the fine line a  $0.6 < R^2 < 0.8$  between samples. The number indicate the station considered.

The method allows to identify distinct groups of stations with a similar composition of the suspended matter. This approach allowed us to distinguish between four classes of particles, based on their composition, within the area of investigation. The composition of each class is given in table AVII of the appendix. The occurrence of the various classes in the area are shown in figure 18.

In April 98, the composition of the suspended matter is rather uniform and dominated by the influence of the spring bloom. Two stations in the North and one in the Channel correspond to points where the phytoplanktonic activity is still limited. In July and September, four classes of particles are clearly identified. The first one (◆) is essentially located along the coast and corresponds to the influence of the Scheldt estuary. The second class (●), mainly present in September, may be related to water masses transferred from the Channel to the North Sea. Off-shore water (△) exhibits often a different composition of the suspended matter especially in November and July. Finally the Northern stations (■) are characterized by suspended matter dominated by the inorganic fraction with a low organic matter content. They may correspond to aeolian input.

Finally, we have calculated the distribution coefficients  $K_d$  defined as the concentration of the elements in solid phase ( $\mu\text{g}/\text{kg}$ ) divided by their concentration in the aqueous phase ( $\mu\text{g}/\text{kg}$ ) provided by the VUB. This factor indicates the affinity of the element for the solid phase and is generally expressed on a logarithmic scale.

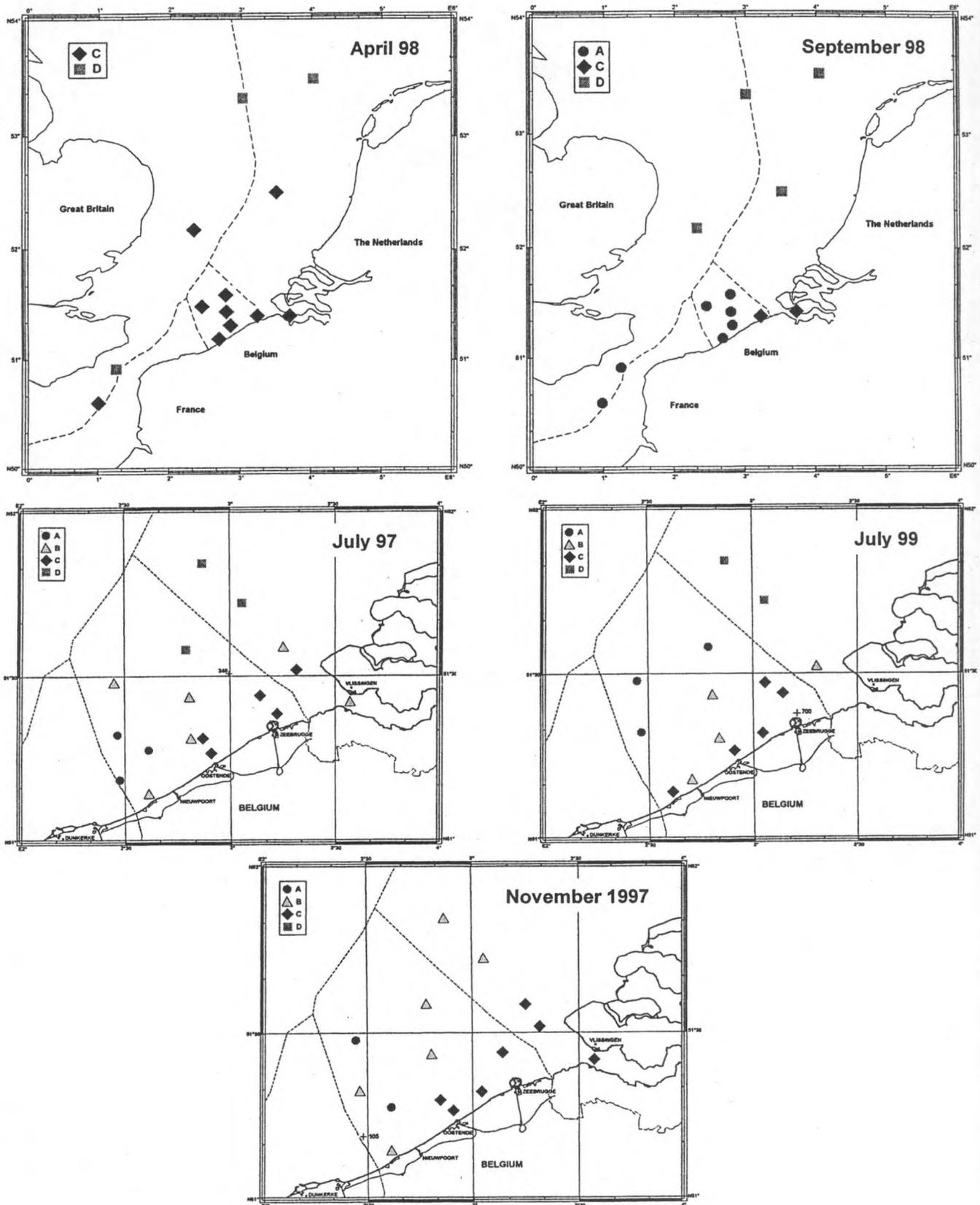


Figure 18: Distribution of the various classes of suspended matter composition according to the cluster analysis.

The results are shown in VII, where they are also compared to the values obtained by Paucot and Wollast (1997) in the Scheldt estuary and by Baeyens *et al* (1987) in the North Sea. The agreement between the three sets of data is very good. The mean affinity of the trace metals for the solid phase is  $Pb > Zn > Ni > Cu > Cd$ .

Table VII: Calculated  $\log K_d$  obtained for each element.

Element	Scheldt Paucot 1997	North Sea Our results		North Sea Baeyens 1987
	Range	Range	Mean	Mean
Cd	3.9 – 5.3	3.3 – 5.5	$4.4 \pm 0.4$	4.5
Cu	4.2 – 5.6	4.1 – 5.2	$4.6 \pm 0.2$	4.6
Ni	3.8 – 4.2	3.4 – 6.2	$4.9 \pm 0.5$	-
Zn	4.3 – 4.6	4.7 – 6.5	$5.3 \pm 0.4$	4.8
Pb	-	4.6 – 6.4	$5.6 \pm 0.4$	-

We have also compared the evolution of the  $K_d$  in the various areas (figure 19). For all the elements, except Pb, there is a significant decrease of the  $K_d$  in the vicinity of the mouth of the Scheldt, especially for Ni. This is essentially due to the higher values of the dissolved species in the area I under the influence of the Scheldt estuary.

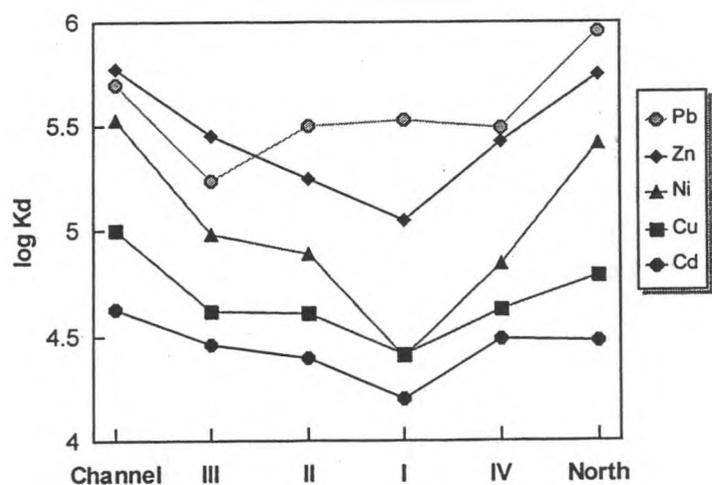


Figure 19: Calculated  $\log K_d$  from the various areas investigated.

This suggests that these metals are rapidly transferred from the dissolved to the particulate phase. The  $K_d$  for Pb is more constant as is its concentration in the dissolved phase.

We have also performed a Principal Component Analysis (PCA) on the 82 samples collected during this study. Multivariate analysis is a valuable tool to correlate elements with similar behaviour in geochemical studies. Our analysis revealed that the five principal components account for about 80 % of the variance (table VIII).

Table VIII: Weight of the five principal component according to the PCA analysis

Factor	Weight	% weight	Cumulated %
1	4.7053	36.2	36.2
2	1.8552	14.3	50.5
3	1.5301	11.8	62.2
4	1.2387	9.5	71.8
5	0.9709	7.5	79.2

Table IX: Scores of the various elements for the three first principal components.

Element	1	2	3
Fe	<b>0.94</b>	-0.01	-0.01
Al	<b>0.90</b>	0.03	-0.13
Pb	<b>0.81</b>	0.05	0.06
Ca	<b>0.80</b>	-0.16	0.01
Co	<b>0.78</b>	0.05	<b>0.24</b>
Si	<b>0.68</b>	-0.13	-0.38
Mn	<b>0.56</b>	-0.09	<b>0.50</b>
Cu	<b>0.34</b>	-0.25	<b>0.21</b>
Cr	<b>0.25</b>	-0.38	-0.66
Zn	0.19	<b>0.40</b>	-0.51
Ni	0.14	<b>0.63</b>	-0.37
Cd	0.02	<b>0.72</b>	-0.10

The very high scores of Fe, Al, Pb, Ca for the first component are characteristic of the fine fraction of detrital origin (table IX). This first principal component has highest values in the vicinity of the mouth of the Scheldt. The second principal component exhibits high scores of Cd, Ni and Zn. As shown previously the metals are strongly bound to organic matter (figure 16). The values of the second principal component are highest and positive for all samples for the April cruise and minimum or negative for November.

The third principal component is characterized by a high score for Mn and medium scores for Co and Cu. These metals are often highly correlated. This principal component is probably related to the chemical precipitation of Mn with co-precipitation of Co and Cu. The eigen-values for the principal component of individual stations during various cruises are given in the appendix (from A7 to A12).

#### 3.2.2.2. Trace metal speciation - acid titration experiments of the solid phase

The behavior of particulate trace elements in the environment is strongly dependent on the chemical and physical properties of the species containing the element of interest. Their mobility during diagenetic processes as well as their potential bio-availability for living organisms are determined to a large extent by the mineralogical phases with which they are associated.

Attempts have been made by various authors to characterize the properties of the solid phase and the speciation of particulate elements by using "selective" dissolution procedures (i.e. Tessier *et al.*, 1979). In a previous work (Ladner, 1996), results obtained, with the method suggested by Tessier and often adopted in the literature, for particles collected in the Scheldt estuary by our laboratory have indicated that the selectivity of the speciation was rather poor. This was also demonstrated by a number of investigators who have highlighted pitfalls in the use of sequential extraction, the most serious of which appear to be related to the lack of selectivity of certain reagents used and the redistribution of released metals between various phases (Davidson *et al.*, 1998).

The method proposed here is original and based on acidimetric titration experiments of the solids initially suspended in pure water. The analysis of the dissolved element major and minor after each titration step allows one to identify the different mineralogical phases with which the elements are associated (carbonates, oxyhydroxides of Fe and Mn, alumino-silicates). The evolution of pH during a titration experiment of the suspended matter collected at station 330 during April and September 1998 is shown in figure 20.

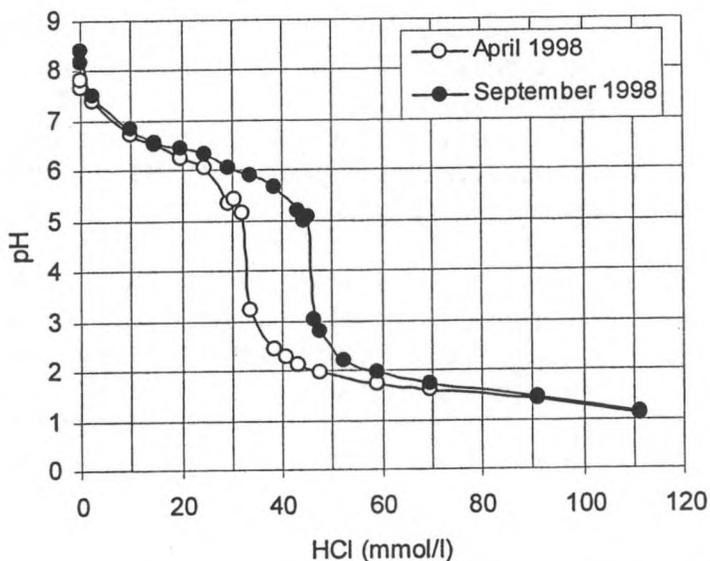
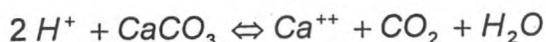


Figure 20: Evolution of pH during the acid titration of suspended matter in April (o) and in September (●) 1998.

When the particulate matter is resuspended in MQ water, the initial pH of the suspension reaches instantaneously a value above 7 due to the dissolution of calcium carbonate. The protons added during the initial titration period are consumed by the reaction:



as shown by the release of the major elements during the experiment (figure 21). Almost 100% of the calcium present in the solid is released when the solution reaches pH 5.5. During this initial stage, about 50 % of the magnesium present in the sample is released and may be attributed to the presence of magnesium calcite ( $Mg_x Ca_{(1-x)} CO_3$ ). The major difference between the titration curves of the two samples collected in April and September respectively, are due to the different calcium carbonate content. The ratio of Mg:Ca released at pH 5.5 corresponds to an hypothetical composition of the Mg-calcite of  $Mg_{0.06}Ca_{0.94}CO_3$  for the April sample and  $Mg_{0.10}Ca_{0.90}CO_3$  for the September sample.

To reach pH 5, 30 mmoles of HCl was added per liter of suspension and 14.9 moles of  $Ca^{++}$  was released in good agreement with the value predicted by the stoichiometry for a total dissolution of  $CaCO_3$ . During this initial step, we have also observed the dissolution of almost 70 % of the manganese present in both samples. Under aerobic conditions, Mn is usually occurring as oxy-hydroxides but it can also be easily reduced and present as  $MnCO_3$  (rhodocrosite). Furthermore, it has been suggested that rhodocrosite may be precipitated at the surface of calcite when small variations of pH or redox conditions occurs. If the percentage

of Mn dissolved is plotted as a function of the dissolved Ca (figure 23a), one obtains a very satisfactory linear regression. This suggests that the manganese can well be related to the carbonate phase, more likely as a solid solution of rhodocrosite in calcite. This has been confirmed by a Mössbauer investigation of sediments of the Scheldt estuary performed at the University of Lille (Prof. Wartel).

It is also interesting to note that cadmium is not released during the initial step of the titration (see figure 22) and that almost 20 % of  $\text{CaCO}_3$  has been dissolved before Cd starts to be released (figure 23b). Zinc exhibits a similar behavior and starts to dissolve at pH 7. The release of labile Zn representing 40 % of the total zinc content and that of cadmium are very well correlated (figure 23c). The experiment indicates that both elements are relatively mobile and a small acidification of their environment (pH 5) is sufficient to mobilize 80 % of the cadmium and 40 % of the Zn. Both Cd and Zn may be related to a carbonate phase slightly more stable than calcite and rhodocrosite. Another possibility would be the accumulation of these two elements in the organic matter. A few preliminary tests carried out with  $\text{H}_2\text{O}_2$  or low temperature calcination on suspended matter, have shown that only trace amounts of metals are released during the mineralization of the organic matter.

A significant fraction of Co (50 %), as well as a small amount of Ni (10-15 %), are also dissolved under mild acidic conditions (pH 7 to 5),

After the initial dissolution of calcite and rhodocrosite, the addition of HCl drops rapidly the pH from 5 to 3, without significant dissolution of major minerals (figure 21). Below pH 3, a continuous release of Fe and Al is observed. At pH 1, almost 20 % of the iron and 3 % of the aluminum present in the sample have been dissolved. There is a good correlation between the amounts of the two elements released (figure 23d). These pH conditions are favorable to the dissolution of Fe oxy-hydroxides. The Al may come from the dissolution of hydroxides or from clay minerals. The concentration of dissolved silicium increases also markedly at pH below 3. This element exhibits furthermore a very good correlation with iron and aluminum (see figure 23e). The simultaneous release of Al and Si strongly suggest that the main dissolution reaction is that of clay minerals. In the case of Si, there is also a small release, even before the addition of HCl, which may be due to the presence of amorphous silica.

Under very acidic conditions, the most stable trace metals are starting to dissolve. It is the case for Cr and the refractory part of Ni and Co, which are very likely associated with the iron oxy-hydroxides. Some manganese is also dissolved under acid conditions and is known to be a good scavenging phase for other trace elements. Lead is very stable and starts to dissolve only at pH below 3. It is also the case for the refractory part of Zn and Cd. Lead can be present as carbonate which is a poorly soluble mineral.

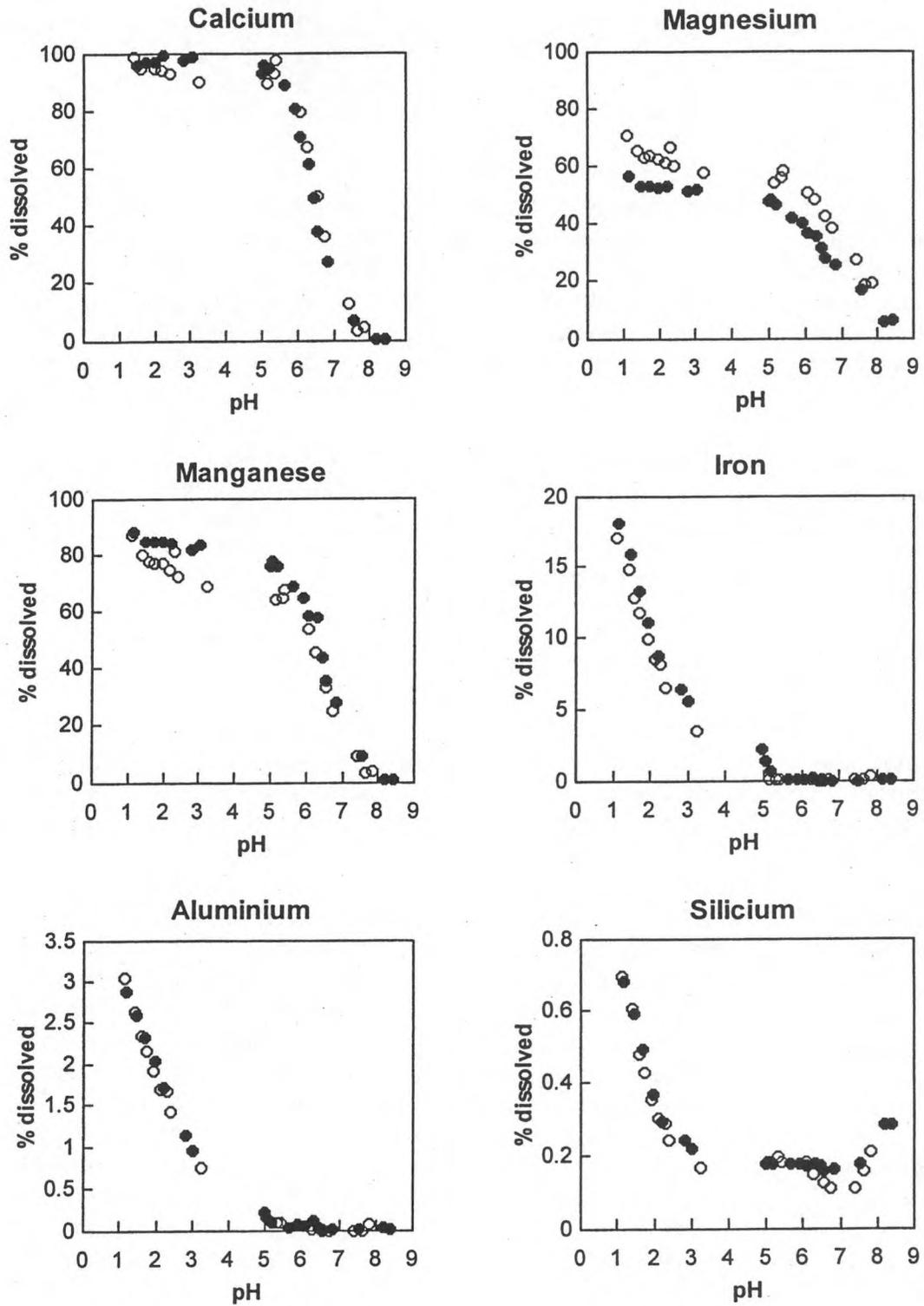


Figure 21: Percentage of major elements released during the titration experiment in April (○) and September (●) 1998.

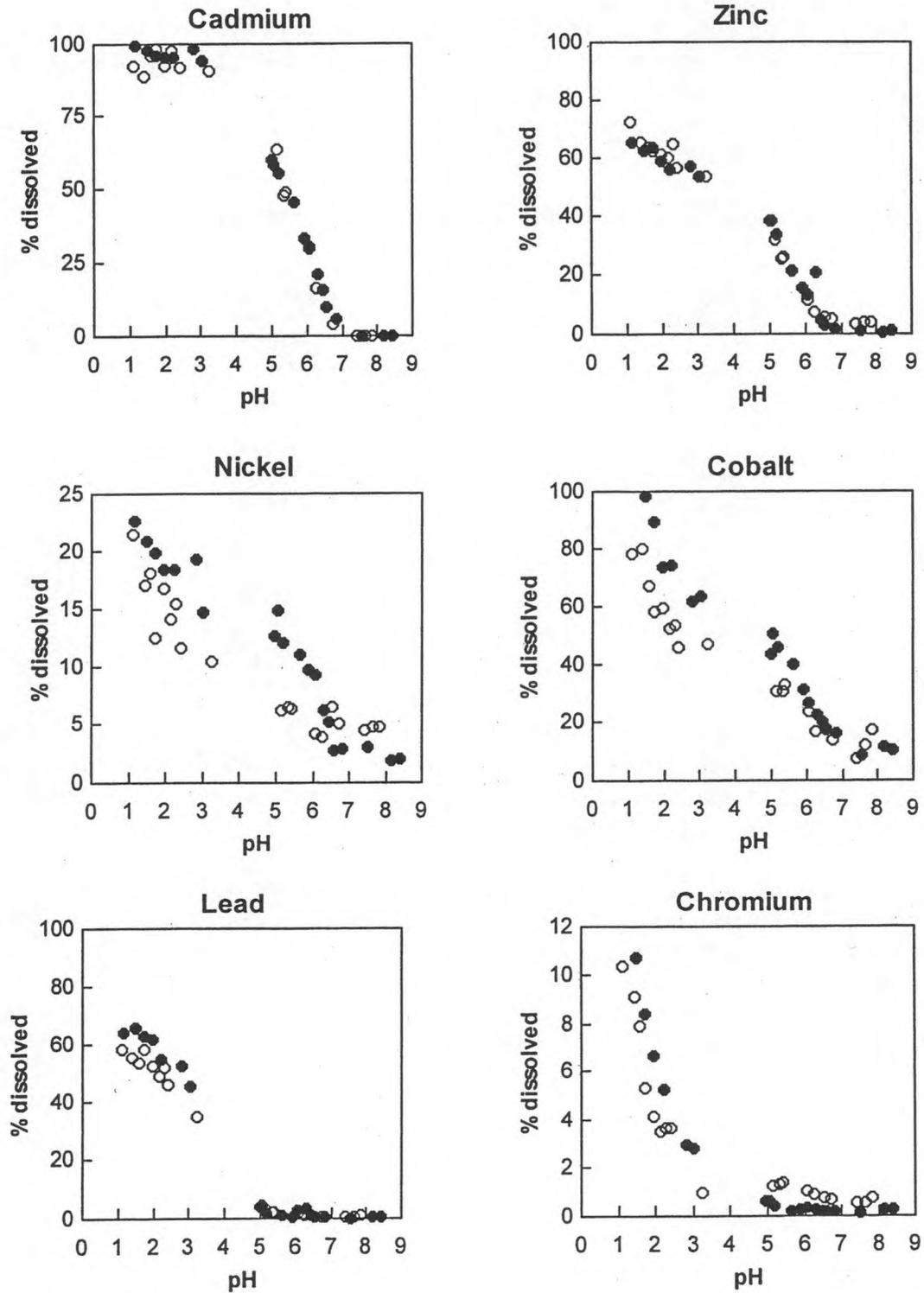


Figure 22: Percentage of minor elements released during the titration experiment in April (○) and in September (●) 1998.

The titration experiment appears to be a very interesting approach in the evaluation of the speciation of trace metals. It also allows to establish a scale of availability of the metals when the pH conditions are changed, for example after deposition in the sediments or in the gut of the biological organisms. We have for example calculated, from our results, the fraction of the trace metals which were released at pH 5 and pH 1 (table X).

Table X: Fraction of minor elements released at pH 5 and pH 1.

Trace metal	Fraction released (%)	
	pH 5	pH 1
<b>Cd</b>	79-92	100
<b>Co</b>	16-43	63-90
<b>Ni</b>	1-14	17-21
<b>Zn</b>	32-38	65-72
<b>Pb</b>	3-5	58-64
<b>Cr</b>	0.4-0.6	10-12

Cadmium, cobalt and zinc are already redissolved at moderate pH and are thus very labile. Lead starts to dissolve at lower pH but is significantly released at pH1. Nickel and chromium are only slightly affected by the acidic conditions reached at the end of the titration experiment.

One of the weaknesses of the method at its present state, is the fact that it gives no indication on the metals possibly released by the organic matter during the titration. As indicated above, preliminary experiment of oxidation of the organic matter or calcination of the sample seems to indicate that the trace metal content of the organic fraction is very small, which may be surprising but has been confirmed by the application of the Tessier speciation method.

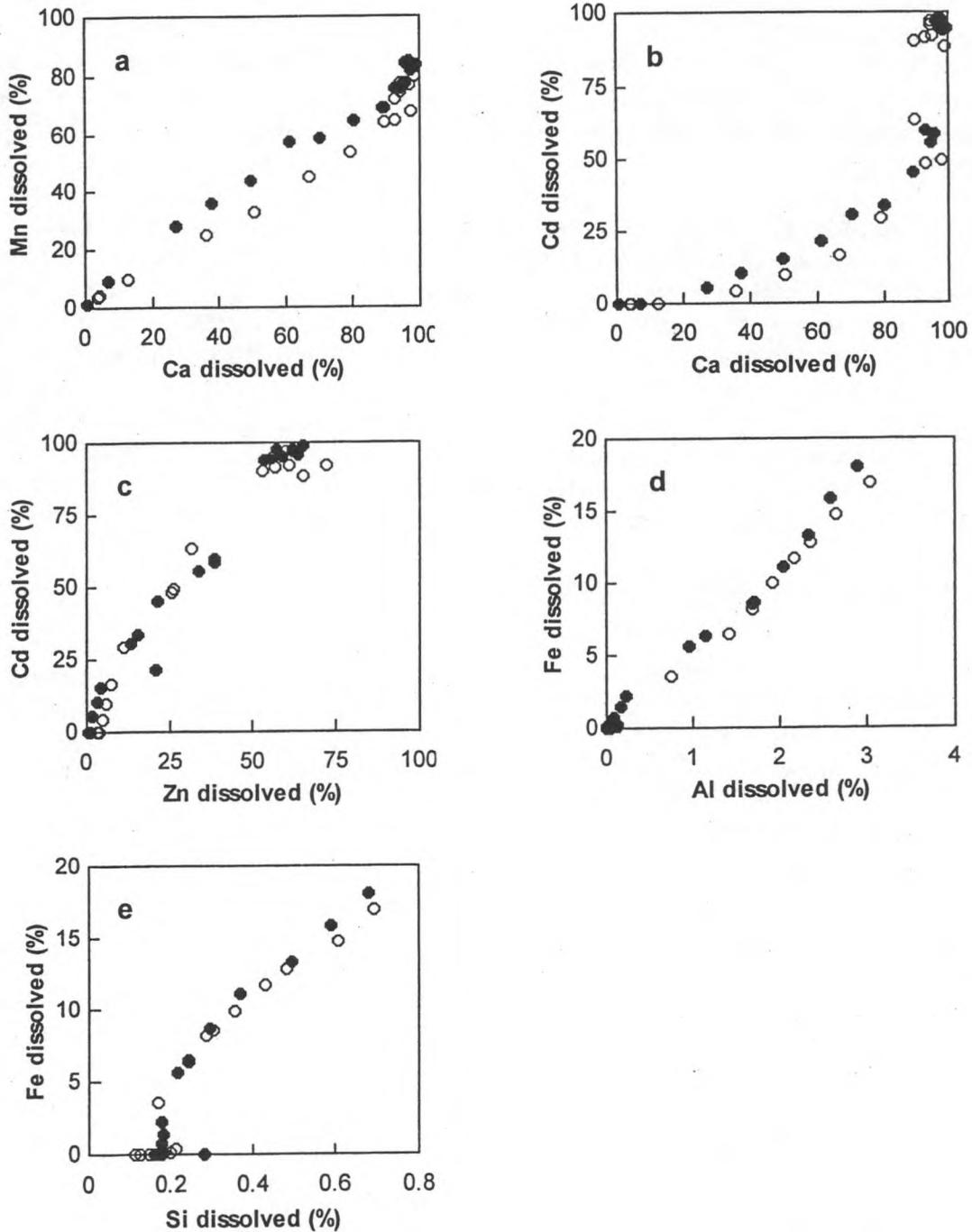


Figure 23: Relation between the percentage of various elements released during acid titration experiments of two samples of suspended matter in April (○) and September (●).

### 3.2.3. Internal cycling

#### 3.2.3.1. Transfer mechanism of trace metals

It is well known that several trace metals act as essential metabolic oligo-elements for phytoplankton species. Their dissolved fraction is thus consumed in the euphotic zone and transferred to the organic particulate phase. The trace metals are further released and re-dissolved in the water column during the biodegradation of the dead organic matter. These metals are therefore called "nutrient-like" elements and exhibit a minimum in their concentration in the euphotic zone

There are however only very scarce data concerning the mechanism and rate of these processes. We have therefore developed an original method similar to the incubation experiments of  $^{14}\text{C}$  spiked water samples used to evaluate primary production in aquatic systems. In this case, surface water samples are spiked with unsupported radionuclides of the studied metals and incubated under various light conditions (Herzl *et al*, 1997). The use of unsupported radionuclides avoids the contamination of the samples by dissolved metals. Furthermore the use of specific inhibitors of the biological activity allows to identify the origin of the transfer of radionuclides from the dissolved to the particulate phase (Herzl, 1999 and Rosson *et al*, 1984). The results presented and discussed here, were obtained on two samples collected in the Southern Bight of the North Sea during the month of July 1999 (see table XI).

Table XI: Characteristics of the sampling points

Parameter	Station 700	Station 330
Date + time (UT)	07/07/1999 12h00	08/07/1999 05h40
Longitude Latitude	N 51° 22' 35" E 03° 12' 52"	N 51° 25' 58" E 02° 48' 41"
Suspended matter (mg/l)	11.0	2.8
Particulate organic carbon ( $\mu\text{g/l}$ )	500	300
Particulate organic carbon (% in SPM)	4.5	10.7
Chlorophyll ( $\mu\text{g/l}$ )	10.3	6.0
Phaeopigment ( $\mu\text{g/l}$ )	3.7	2.1

The first sample was taken near the mouth of the Scheldt estuary (station 700) where high productivities are observed from spring to fall. The estuarine plume is also characterized by a high content of suspended matter of continental origin. The second station (330) is situated in an area outside the estuarine plume and more under the influence of the Channel water masses. The productivity at this time period of the year is at a minimum and the concentration of particulate matter small. The two stations correspond thus to contrasting summer conditions in the Southern Bight of the North Sea.

In order to understand the influence of the biological processes on the transfer of metals from the dissolved to the particulate phase, we have first investigated the rate of labeled  $H^{14}CO_3$  uptake under various light conditions. This allowed us to quantify primary production at the stations 330 and 700. The next step is devoted to the description of the influence of biological inhibitors on the uptake of trace metals during incubation experiments of spiked water samples collected at the two stations, under variable light or in the dark. The reverse reaction of release of the trace metals to the dissolved phase was also investigated by prior labeling the suspended matter with radiotracers and following their re-dissolution in fresh seawater.

### 3.2.3.1.1. Primary production and $^{14}C$ experiment

In order to evaluate the phytoplanktonic activity, incubation experiments of  $^{14}C$  spiked water samples were carried out under various light conditions. The spiked samples were incubated on board under variable artificial light conditions and in the dark for 8 hours. The carbon uptake as a function of light intensity (figure 24 a) was interpreted according to the Platt et al (1980) equation to evaluate the photosynthetic parameters (table XII).

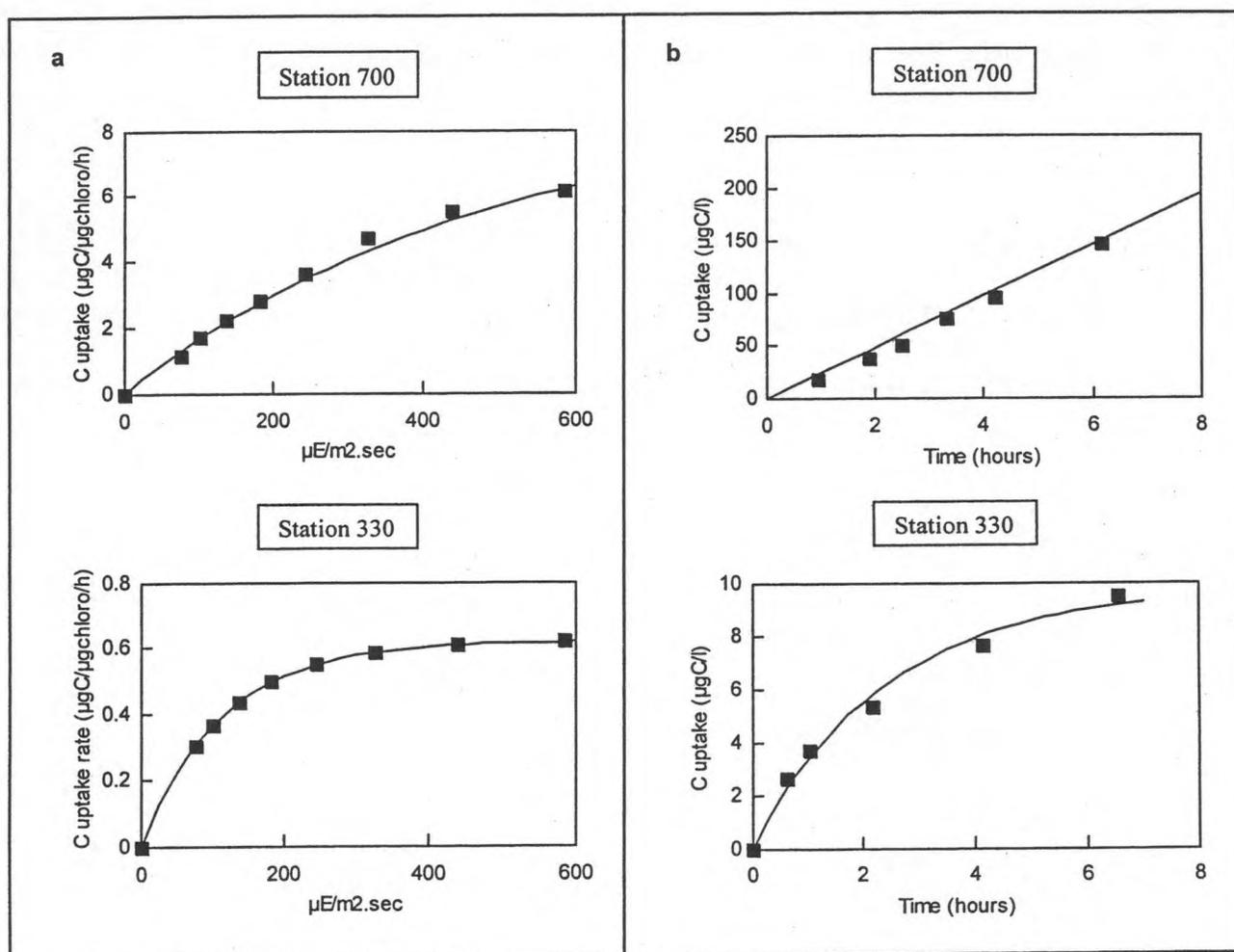


Figure 24: Carbon uptake under variable light conditions (a) and kinetic experiment under constant light (b)

$$GPP = \mu_{\max} \left(1 - e^{-\frac{I}{I_k}}\right) C_{\text{chloro}} \quad \text{where} \quad I_k = \frac{\mu_{\max}}{\alpha}$$

The same equation is utilized to calculate the depth integrated primary production by taking into account the light penetration (PAR) and the daily incident light intensity measured on board of the ship. Finally potential primary production was compared between the two water samples, by measuring the  $^{14}\text{C}$  uptake under constant light ( $180 \mu\text{E m}^{-2} \text{sec}^{-1}$ ) over a short time period (6 hours), figure 24b.

The results (table II) indicate that the photosynthetic parameter  $\mu_{\max}$ , the potential and gross primary production are about one order of magnitude larger at station 700 than at station 330. This can be easily explained by the influence of the nutrient input from the Scheldt at station 700. It is also important to notice that for the kinetic experiments (figure 24b) the uptake rate of  $^{14}\text{C}$  during incubation under constant light conditions remains constant during 8 hours at station 700. On the contrary, at station 330 there is a rapid decrease of the net uptake rate of  $^{14}\text{C}$  which can be attributed to a rapid recycling of the labeled organic matter. The curve in figure 24b for station 330 has been calculated by assuming that the rate of recycling of the labeled organic matter is a first order reaction with respect to its concentration, according to the following equation:

$$\frac{d^{14}\text{C}_{\text{org}}}{dt} = k^+ - k^- C_{\text{org}}$$

The curve shown in figure 24b is the best fit obtained by using values of  $6.0 \mu\text{g C l}^{-1} \text{h}^{-1}$  and  $0.41 \text{h}^{-1}$  for  $k^+$  and  $k^-$  respectively. This allows to estimate that the labeled organic matter in this experiment is recycled on the average every 6 hours.

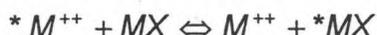
Table XII: Phytoplanktonic activity and primary production

ID	Station 700	Station 330
<b>Light attenuation coefficient</b> ( $\text{m}^{-1}$ )	0.78	0.40
<b>Specific maximum productivity</b> ( $\mu\text{g C } \mu\text{g chloro}^{-1} \text{h}^{-1}$ )	9.00	0.48
<b>Specific photoefficiency</b> $\mu\text{g C } \mu\text{g chloro}^{-1} (\mu\text{E m}^{-2} \text{s}^{-1})^{-1} \text{h}^{-1}$	0.018	0.004
$I_k$ ( $\mu\text{E m}^{-2} \text{sec}^{-1}$ )	500	113
<b>Potential primary production</b> <b>at <math>180 \mu\text{E m}^{-2} \text{sec}^{-1}</math></b> ( $\mu\text{g C l}^{-1} \text{h}^{-1}$ )	24	2.3
<b>Gross primary production</b> ( $\mu\text{g C m}^{-2} \text{day}^{-1}$ )	3.82	0.46

### 3.2.3.1.2. Study of the uptake of trace metals using radionuclides

In order to identify the origin of the transfer of trace metals from the dissolved to the particulate phase, we have carried on a series of incubation experiments of water samples spiked with radionuclides in the presence or absence of various inhibitors of the biological activity, under constant and variable light conditions.

A first run was devoted to the estimation of the importance of rapid isotopic exchange between dissolved and particulate metals, according to the equation:



where  $MX$  represents the exchangeable metal in the solid phase and  $*M$  the radioactive metal.

This relation allows to calculate the amount of exchangeable metal in the solid phase by assuming that the isotopic exchange constant of the above reaction is equal to 1.

$$MX = M^{++} \frac{*MX}{*M^{++}}$$

This reaction is achieved within a few minutes after the addition of the radiotracer (Sunda and Huntsman, 1994). The exchange was estimated here by measuring the amount of radiotracer transferred after 10 minutes. The results of the experiments are presented in table XIII.

Table XIII: Evaluation of the exchangeable fraction of the metals in the solid phase

	Relative uptake (%)		Metal uptake (nmol/l)		Exchangeable metal (ng/l)		Fast isotopic exchange (%)	
	700	330	700	330	700	330	700	330
<b>Mn</b>	1.9	2.3	0.19	0.13	10.6	6.9	0.083	0.30
<b>Zn</b>	5.4	2.0	0.68	0.13	46.8	8.9	5.4	3.9
<b>Cd</b>	2.0	0.4	$1.6 \cdot 10^{-3}$	$0.3 \cdot 10^{-3}$	0.18	0.04	5.3	13.6

The exchangeable fraction of Mn is very small but significantly higher at station 330 than in the vicinity of the mouth of the Scheldt (station 700). This may be explained by the affinity of phaeocystis species for Mn, which is adsorbed by the mucus produced by the colonies. The fast isotopic exchange is much more important in the case of zinc and cadmium, and affects around 5% of the total metal present in the solid phase. In the case of Cd, it can reach 13.6% at station 330, where organic matter is abundant.

We have first performed kinetic measurements of the uptake of the metals under constant light conditions and in the dark (figure 25). We also have investigated the influence of light intensity on the transfer of the metals in the presence or absence of azide, which inhibits

totally the biological activity (figure 26). In order to identify the biological processes which are potentially responsible for the metal transfer, we have compared the uptake of radionuclides after short time incubations (8h30) of the water samples spiked with biological inhibitors (Na azide, antibiotics, herbicide) in the presence or absence of light. The results are presented in figure 27.

The efficiency of the inhibition was successfully tested by measuring the absence of uptake of  $^3\text{H}$ -leucine and  $^3\text{H}$ -thymidine for antibiotics and of  $\text{H}^{14}\text{CO}_3$  for samples inhibited by DCMU.

The effect of the inhibitors and light conditions on the activity of organisms is shown in table XIV.

Table XIV: Processes occurring (X) under the different incubation conditions. (Az: sodium azide; Ab, antibiotics: mixture of streptomycin sulfate and polymyxin B sulfate; DCMU, herbicide: dichlorophenyl dimethyl urea)

Condition	Isotopic Exchange	Biotic transfer			Abiotic transfer
		Bacteria	Phyto.	Precip./adsorp	Photored./ox.
Light	X	X	X	X	X
Dark	X	X	(X)*	X	
Light + Az	X			X	X
Dark + Az	X			X	
Light + Ab	X		X	X	X
Light +DCMU	X	X		X	X

\* in the dark, the active uptake by the phytoplankton linked to photosynthesis is inhibited but there may be inactive uptake of certain metals.

In the case of manganese, the kinetic experiment (figure 25) shows that there is no influence of light on the rate of uptake of this element. The initial transfer due to isotopic exchange is small and followed by a rapid uptake which represents 33 % and 78 % after 16 and 17.6 hours of incubation at station 330 and 700 respectively. In the case of station 330, the uptake rate is constant over the time interval considered whereas for station 700 there is a decrease due to the consumption of a significant fraction of the dissolved manganese. The curve of figure 2 for station 700 corresponds to the integrated kinetic equation:

$$[MX] = 9.6 (1 - e^{-0.080t})$$

where  $t$  is the reaction time expressed in hours and the concentration of  $MX$  in  $\text{nmol/l}$ .

The total concentration of dissolved  $\text{Mn}^{++}$  at the beginning of the experiment was  $9.8 \text{ nmol/l}$ , which indicates that 85 % of the dissolved manganese has been exchanged between the aqueous and the solid phase within one day. This corresponds also to a renewal of Mn in the solid phase every 28 days.

The use of  $\text{NaN}_3$  (figures 26 and 27) demonstrates that this process is intensively related to the biological activity, either bacterial or planktonic. It is also important to note that there is a slight but consistent decrease of the Mn uptake with increasing light intensity (figure 26). It is well known that particulate manganese is affected by photoreduction (Sunda and Huntsman, 1994) and accelerates the turnover of this element also very sensitive to redox fluctuations.

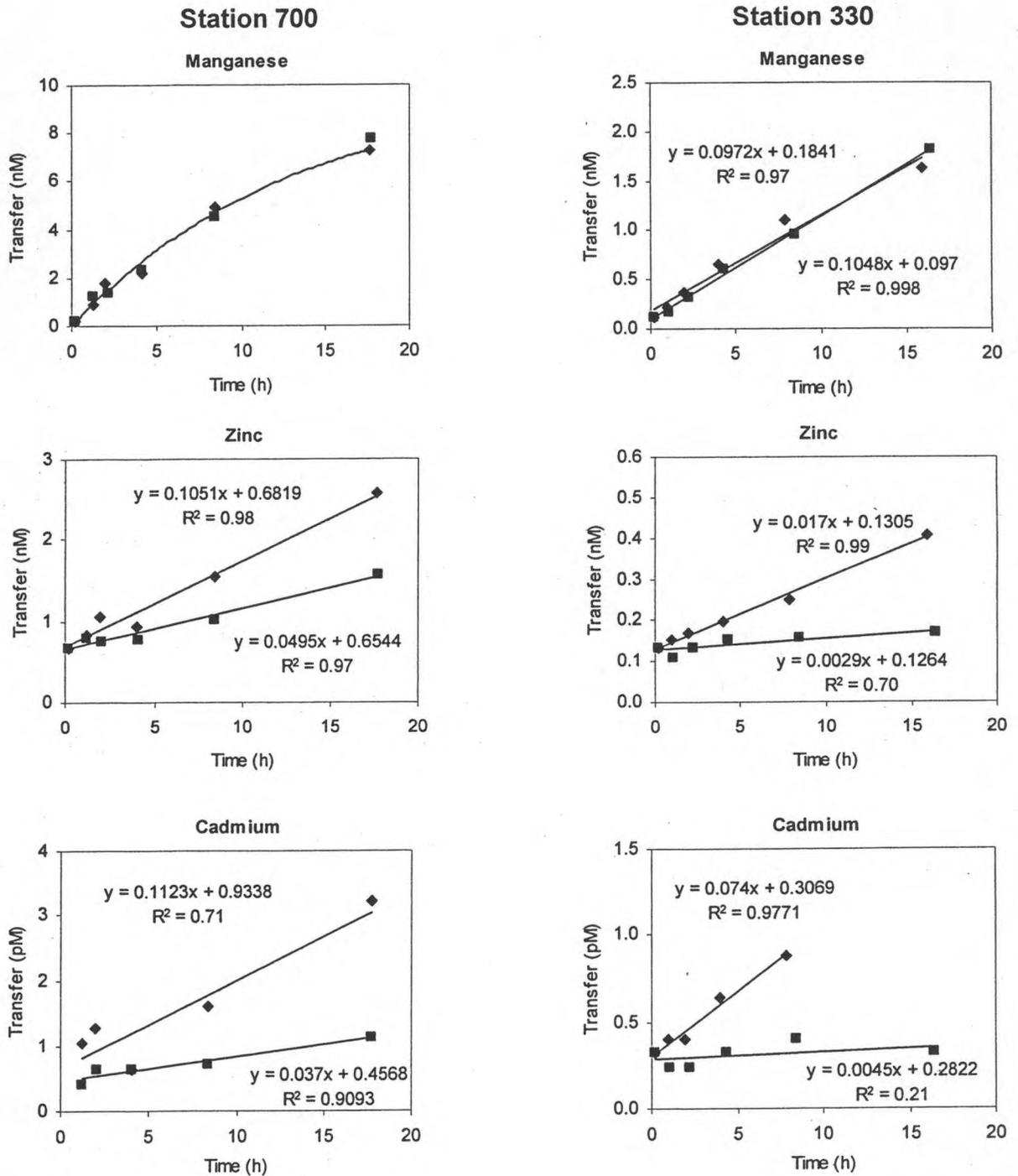


Figure 25: Amount of dissolved elements transferred from the dissolved to the particulate phase as a function of time under constant light conditions (◆) or in the dark (■).

Station 700

Station 330

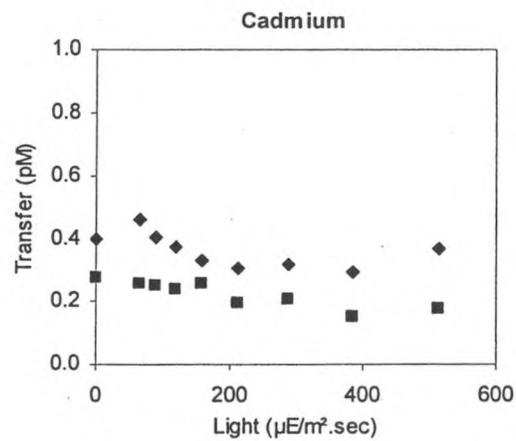
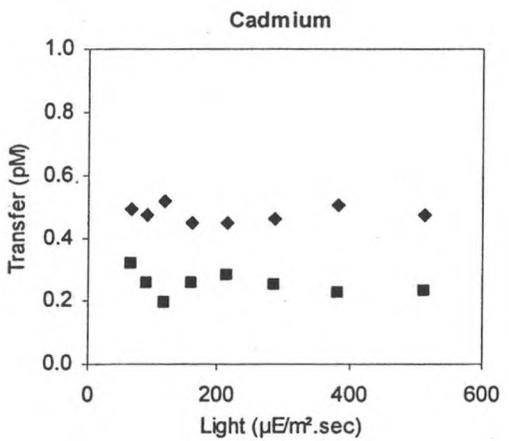
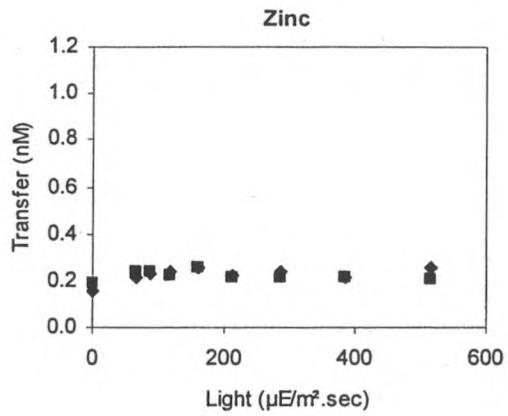
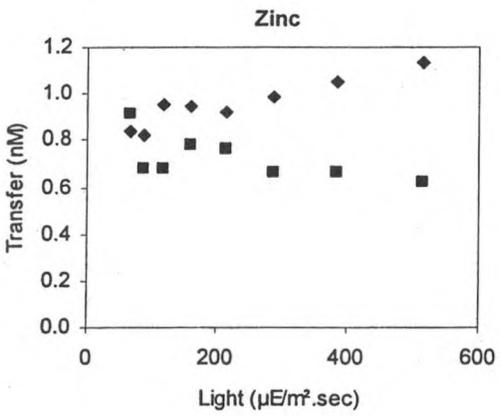
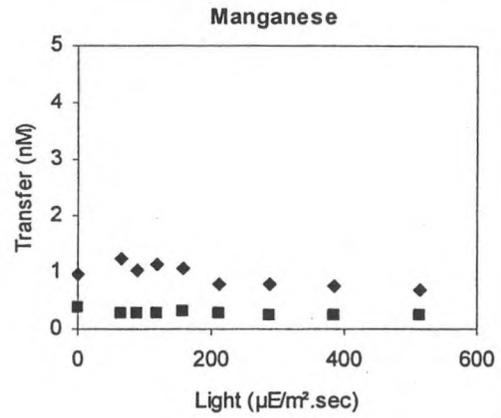
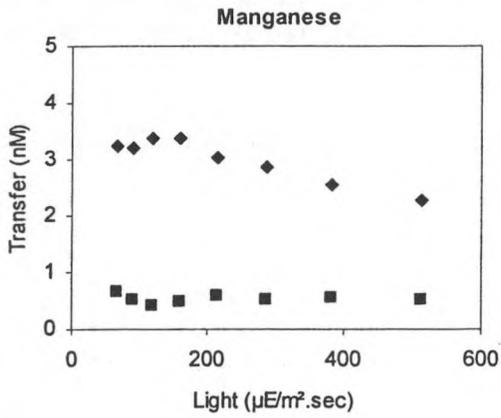
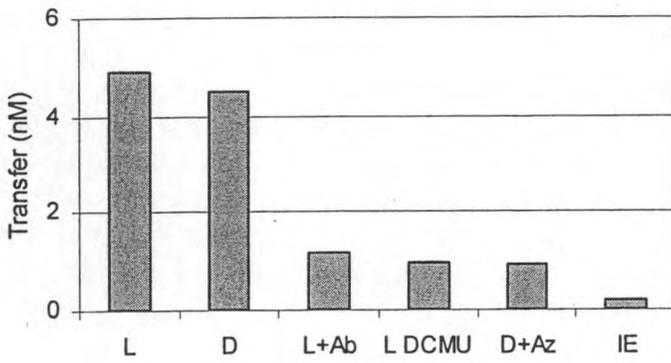


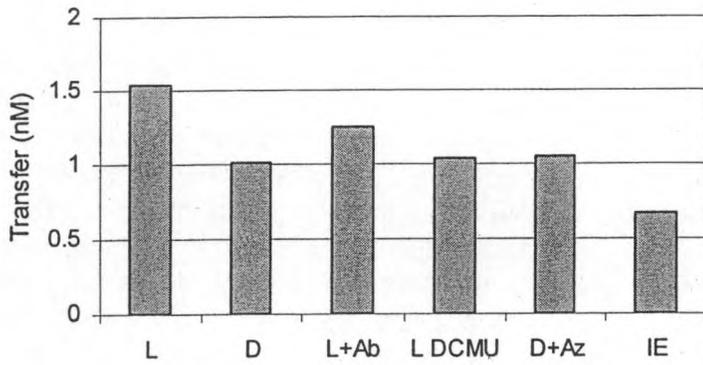
Figure 26: Amount of dissolved elements transferred from the dissolved to the particulate phase as a function of light intensity in the absence ( $\blacklozenge$ ) or presence ( $\blacksquare$ ) of sodium azide, which inhibits all biological activity

## Station 700

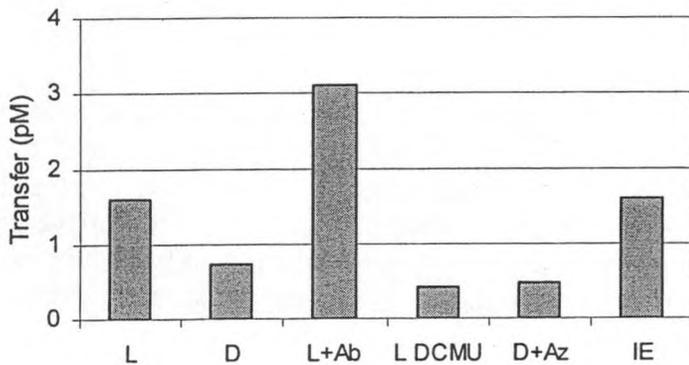
## Manganese



## Zinc

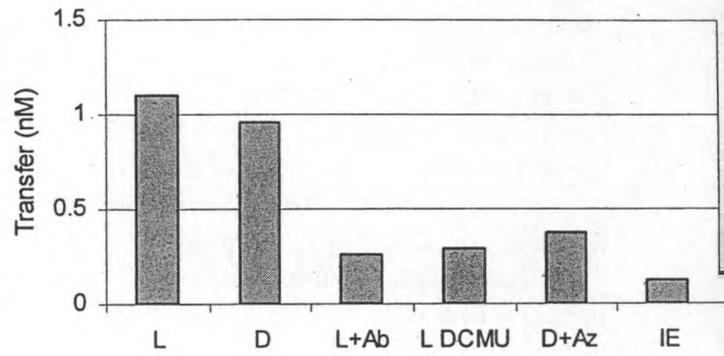


## Cadmium

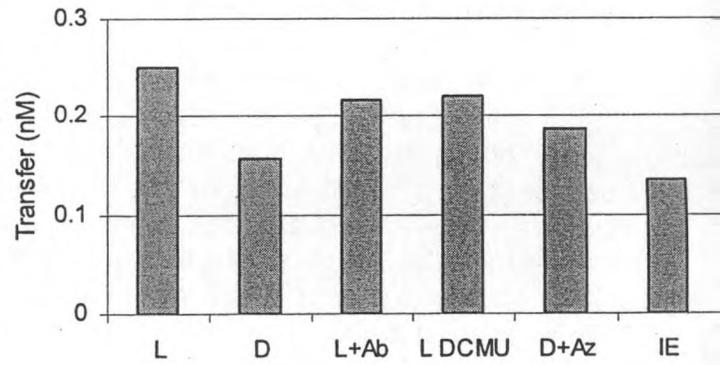


## Station 330

## Manganese



## Zinc



## Cadmium

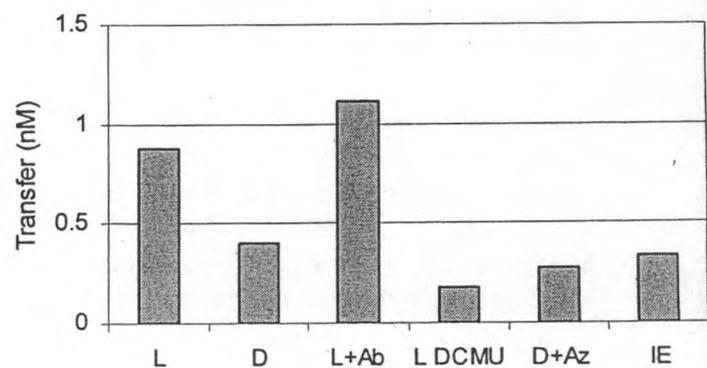


Figure 27: Amount of dissolved elements transferred from the dissolved to the particulate phase under different light conditions and in presence of different biological inhibitors.

The behaviour of zinc during the incorporation experiments is very different. First, the initial adsorption due to the isotopic exchange represents a large fraction of the total uptake (figures 25 and 27). Furthermore, there is a marked influence of light on the uptake of this metal, well demonstrated by the kinetic experiment (figure 25) and confirmed by figure 27. Zinc is known as an important oligo-element for plankton and is often depleted in the euphotic zone of the oceanic water column. Nevertheless, the role abiotic transfer remains dominant as shown by the effect of addition of  $\text{NaN}_3$  (figure 26 and 27) and the reduced influence of the addition of inhibitors of photosynthesis (DCMU) and of bacterial activity (antibiotics). The influence of the addition of inhibitors is better demonstrated for station 700 where photosynthesis is more important. The uptake of Zn which can be attributed to photosynthesis from figure 25, is 57 pmol/l.h and only 15 pmol/l.h at station 330.

A similar behaviour to that of zinc is observed for cadmium with an important contribution of isotopic exchange during the initial step (figure 25). The influence of light is more pronounced than for zinc (figure 25 and 26), which is confirmed by the very marked inhibition of Cd uptake in the presence of DCMU (figure 27).

The reversibility of the metal uptake by the solid phase in the North-Sea water samples was also investigated. Spiked water samples from station 330 with radiotracers ( $^{54}\text{Mn}$ ,  $^{109}\text{Cd}$ ,  $^{65}\text{Zn}$ ) were incubated under constant saturation light conditions ( $185 \mu\text{E}/\text{m}^2.\text{sec}$ ) during 72 hours. The solid was recovered from several 500 ml aliquots of water on  $0.45 \mu\text{m}$  filters which were further used in different desorption experiments. One filter was first washed continuously at a rate of 1ml/min during 5 hours. The amount desorbed was estimated independently from the activity of both the solid and aqueous phases. The results are shown in figure 28a. All three elements show a rapid initial release of more than 40 % of the radionuclide present initially in the solid phase after 10 minutes. This fast reaction can be attributed to the isotopic exchange at least for Zn and Cd. In the case of these metals, there is a second step of release at a much lower rate, which may be attributed either to the fraction of radiotracers which have diffused in the bulk of the solid or to organically bounded metals remineralized. In the case of Mn, around 55 % of the radioisotope is released within half an hour and no significant amounts are transferred to the aqueous phase during the next 5 hours.

A long-term experiment was also carried on by washing the filters with pure seawater collected at the same station. The filter was maintained in contact with 100 ml of seawater, in a batch reactor, renewed after a given time varying from 1 hour to several days. The results (figure 28b) confirm those obtained by continuous washing (figure 28a). After one month, all the labeled Cd and Zn were restored to the aqueous phase. On the contrary, except for the release of around 55 % of labeled manganese during the initial step, no transfer to the aqueous phase is observed during the next 25 days.

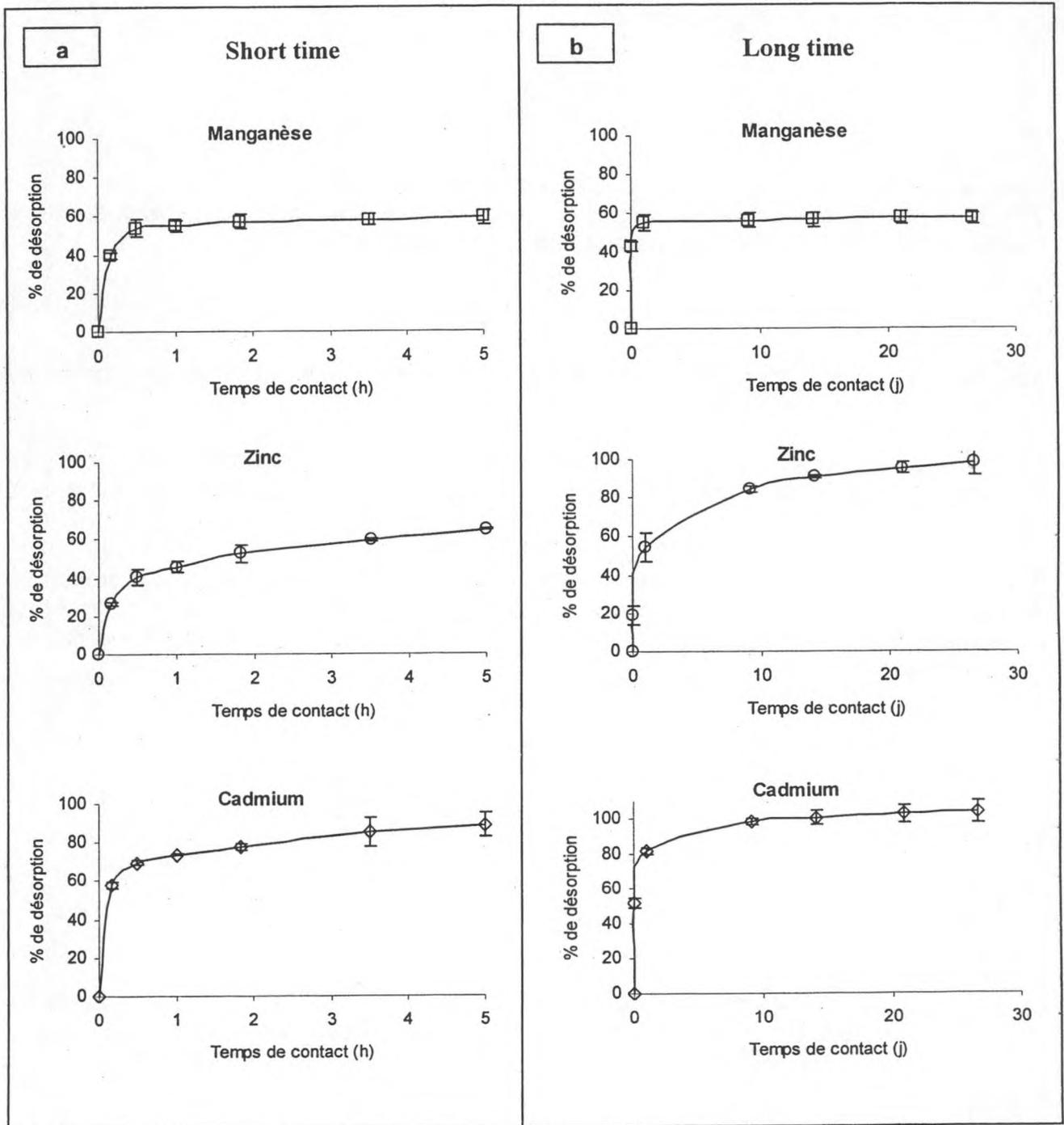


Figure 28: Percentage of the elements released after a fixed contact time with prefiltered seawater for short time continuously washing (a) and long time batch reactors (b).

During a last experiment, we have investigated the influence of the concentration of the dissolved metal on the rate of its uptake. The water samples of station 330 were spiked with various amounts of trace metals as well as their radioactive isotopes and incubated under constant saturated light ( $80 \mu\text{E}/\text{m}^2.\text{sec}$ ) during 2 hours. A typical result is shown in figure 29 in a case when the three metals were added simultaneously. For short periods of reaction time, the

transfer of the trace metals from the dissolved to the particulate phase generally obeys to a Langmuir isotherm, which can be written:

$$M_{solid} = \frac{k_1 M^{++}}{k_2 + M^{++}}$$

where  $k_1$  represents the maximum transfer at saturation when  $M^{++} \gg k_2$ . The three metals represent each extreme cases. For cadmium (figure 29c), the concentration of the dissolved metal is far from saturation and much lower than  $k_2$ . Thus

$$M_{solid} \approx \frac{k_1}{k_2} M^{++}$$

and there is a linear increase of the concentration of Cd in the solid phase with increasing concentration in the liquid phase.

On the contrary, the system is rapidly saturated in the case of manganese and zinc (figure 29a and 29b). The low transfer of cadmium in seawater may be attributed to the formation of chloride complexes.

In another series of experiment, the concentration of the trace metals in the water sample was increased individually for each element before spiking with the three radiotracers. This experiment demonstrates that there is a significant competition for the adsorption sites between zinc and manganese.

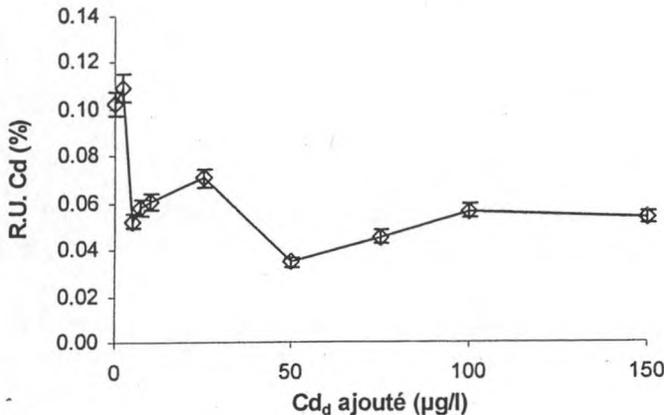
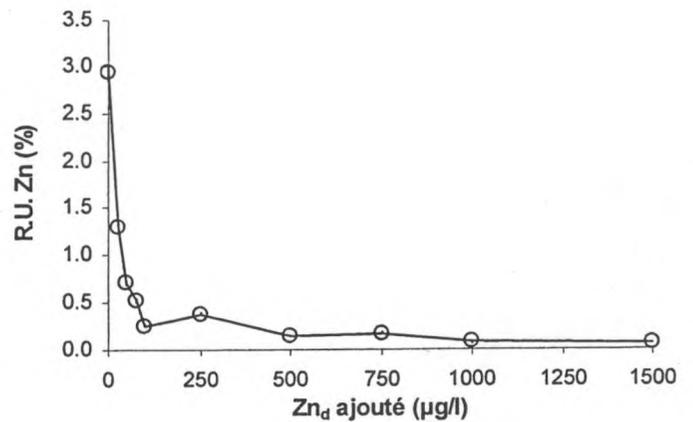
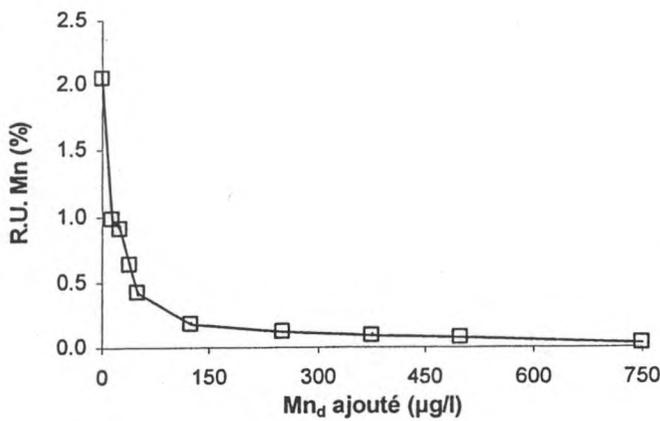


Figure 29: Influence of the concentration of dissolved metals on the rate of uptake

### 3.2.3.2. Mercury

Several processes such as adsorption/desorption, biological uptake, methylation/demethylation, sedimentation/remobilization and gaseous Hg evasion govern the spatial and temporal variability of the concentrations of mercury species in the North Sea. Estuaries and coastal areas are very reactive areas and important sources of methylated Hg species to the North Sea.

In summer, the upper Scheldt estuary can be subdivided into two parts: the most upstream part with low dissolved MMHg concentrations and the downstream part with higher dissolved MMHg concentrations. The increase of the MMHg concentration in the salinity range 3-12, corresponds to the reappearance of dissolved oxygen in the water column. The presence of dissolved sulphide (0.2-0.9  $\mu\text{M}$  of total dissolved sulphide) in the anoxic, most upstream part of the estuary (Zwolsman and van Eck, 1993) results in a scavenging of dissolved  $\text{Hg}^{2+}$  species from the water column. These sulfide concentrations are insufficient for the formation of polysulfides (Davies-Colley et al., 1985) but sufficient for the removal of all  $\text{Hg}^{2+}$  from solution by sulfide precipitation. Possible reasons for the fact that we find in summer still about one third of the winter concentration are: (1) the strong complexation of Hg with organic ligands such as humic acids (Mantoura et al., 1978) and (2) colloidal precipitates that pass the 0.45  $\mu\text{m}$  Millipore filter (Guentzel et al., 1996). The amount of substrate available for methylation in the water column as well as in the sediments is, however, significantly reduced. In addition, MMHg produced in the summer period will also interact with the high concentration of sulfides and suspended matter and enrich the particulate rather than the dissolved phase. For those reasons no high dissolved MMHg concentrations will be found in the anoxic most upstream estuarine area. However, once the oxygen level slowly restores in the water column the conditions for a high sulfate reduction rate (SRR) are still good, especially in the sediments, while the sulfide concentrations in the water column drop; this is the zone where the  $\text{MMHg}_D$  concentrations reach their maximum.

Outside the upper estuary ( $S > 10$ ) the dissolved MMHg levels in winter are low and comparable to the values in the Southern Bight. This shows that the production of MMHg in winter is limited to the upper estuary. While in summer the decrease of total dissolved Hg is very quick, MMHg concentrations drop much more slowly. The faster removal of  $\text{Hg}^{2+}$  compared to MMHg can be attributed to (1) a differential association with Fe and Mn oxides, precipitating in the middle estuary (Paucot and Wollast, 1997) and (2) the difference between  $\text{Hg}^{2+}$  and MMHg species in complexation with organic ligands.

The sediments are an important production site of MMHg and a potential source for this compound in the water column after resuspension of the upper sediment layer and mobilization from interstitial waters. MMHg concentrations in suspended matter in the upper estuary are comparable to the concentrations of MMHg in the organic rich sediments of the mud flats (Muhaya et al., 1997).

Seasonal variations are observed in the distribution coefficient (KD) of MMHg with lower values in summer (30,000-65,000) than in winter (77,000-114,000). This supports the observation that reducing conditions in the sediments promote the liberation of MMHg from sediments. In Lavaca Bay sediments similar variations in the KD values in sediments were found (Bloom et al., 1999).

In summer dissolved and particulate MMHg concentrations observed at the mouth and in the coastal-estuarine zone ( $S < 32$ ) are increased. The higher MMHg concentrations found in those oxygenated waters may be related to at least 2 factors:

1. Mobilisation of MMHg from sediments:

Reducing conditions in the muddy sediments of the estuarine coastal area may favor, especially in summer, the production and mobilisation of MMHg. After the spring phytoplankton bloom, large amounts of fresh organic matter produced in the euphotic zone are deposited resulting in reducing conditions in the sediments. In combination with the higher temperature in summer the activity of the sulphate reducing bacteria and hence the production of MMHg, is stimulated. Like in the upper Scheldt estuary, the resuspension of fine sediment grains enriched in MMHg and the subsequent adjustment to the water column KD is an input route for the coastal- estuarine zone. Under less reducing (suboxic) conditions, bacterial degradation of organic matter in the sediments is accompanied by the reduction and dissolution of Fe and Mn. Important seasonal mobilisation of Fe and Mn from sediments has been observed in the North Sea (Dehairs et al., 1988; Schoemann et al., 1998). Fe and Mn remobilisation from sediments may be accompanied by the mobilisation of MMHg from sediments (Bloom et al., 1999).

2. Direct influence of phytoplankton blooms and associated pelagic heterotrophs:

Pongratz and Heumann (1998) found maximal methylated species (DMHg and MMHg) in the remote ocean regions (Southern Atlantic, Arctic, Southern Pacific) in areas with highest biological activity and showed the production of MMHg and DMHg by polar macroalgae in model experiments.

Cleckner et al. (1999) showed that Hg could be methylated by periphyton communities of the Everglades and that SRB were methylating Hg. Methylation was found to be coupled to photosynthesis. Photosynthetic microbial sulfide

oxidation may stimulate methylation through the removal of sulfide and/or providing substrate for SRB.

The coastal estuarine waters are characterised by increased Chla, POC, PN, DOC concentrations in summer due to the development of phaeocystis sp. phytoplankton blooms and also of increased MMHg concentrations. Colonial phaeocystis sp. forms can be considered as reducing microenvironments playing an important role in the speciation of elements such as Fe and Mn (Davidson and Marchant, 1987, Hutchins and Bruland, 1994). During summer significantly higher amounts of dissolved gaseous Hg, and lower amounts of reactive Hg were also found in that zone (Baeyens and Leermakers, 1998).

The relative importance of both sources (sediments and phytoplankton) has still to be determined.

#### 3.2.4. Trophic levels

##### 3.2.4.1. Mercury

Total Hg and MMHg concentrations were assessed in more than 350 samples of various fish and shellfish species of the Greater North Sea, (including the English Channel, the Belgian Coastal area and the Scheldt estuary. The Hg concentrations in Greater North Sea fish range for Category A (fishes of prey) from 0.039 mg kg<sup>-1</sup> w.w. for ray to 0.61 mg kg<sup>-1</sup> w.w. for dogfish and for Category B (all other fish species) from 0.045 mg kg<sup>-1</sup> w.w. for plaice to 0.33 mg kg<sup>-1</sup> w.w. for sand sole, with 95 ± 2 % of the Hg content in the MMHg form. In the Belgian Coastal zone four Category B fish species were studied, showing concentrations from 0.063 mg kg<sup>-1</sup> w.w. for plaice to 0.13 mg kg<sup>-1</sup> w.w. for flounder, with 82 to 87% of the Hg content in the MMHg form. Hg levels, as well as the % MMHg of the total Hg, in fish of the Scheldt, which is a very polluted estuary, were lower than in the 2 previous zones.

The intra-species variability is of the order of 50% in each of the 3 zones. In liver tissue, a much larger variability than in muscle tissue was observed, except for fish species of the Scheldt. In most cases, the MMHg fraction in a particular fish species is inversely related to the intra-species variability. The Bioconcentration Factor (BCF) for total Hg slightly increased from the open sea to the Scheldt estuary. This is not the case for MMHg where the BCF is higher in the marine area than in the estuary. Biomagnification for both total Hg as MMHg is always highest in the Greater North Sea and lowest in the Scheldt, for the same species. For each of the 4 studied species from the Belgian Coastal Zone, a positive

correlation exists between Hg content and fish length, however, the larger the size-range the better the correlation.

It is widely assumed that the principal pathway for mercury exposure in humans is through food consumption, in particular of fish, although exceptions exist: for example contaminated sites such as the Carson River Drainage Basin (CRDB) of Nevada (Gustin et al., 1994), and the Katun River Drainage Basin (KRDB) in Altai, Siberia (Baeyens et al., 2002). In both cases, the pathways through which humans are exposed to mercury are likely to be complex, including inhalation, dermal contact and ingestion of contaminated water. Gustin et al. (1994) reported that fish species from several sites in the CRDB exceeded the federal action level of  $1.0 \mu\text{g g}^{-1}$  w.w. In our study, only 2 dogfish samples showed Hg-total concentrations around  $1.0 \mu\text{g g}^{-1}$  w.w. Thus, consumption of North Sea fish does not seem to be a major health risk, concerning mercury.

#### 3.2.4.2. Arsenic

Total and Toxic Arsenic Levels in North Sea Fish Levels of arsenic contamination in muscle and liver tissue of 25 sea fish and 4 shellfish species from the North Sea were determined. Analyses were done by both ICP-MS and HG-AFS in order to distinguish between non-toxic and toxic fraction of As. Highest total As concentrations were found in lemon sole, dogfish, ray and witch. Average total As concentrations in these fish species were higher than  $20 \text{ mg.kg}^{-1}$  ww. The same species as well as the other flatfish contained the highest amounts of toxic As ( $>0.1 \text{ mg.kg}^{-1}$  ww). Toxic fractions (AsTox/AsT %) above 2% were found in the following six species: seabass, ling, john dory, pouting, dab and brill). No preferential concentration of AsT nor AsTox in the liver compared to the muscle was observed.

In a worst case scenario (when fish has been dried or smoked and the toxic As level is high; for example  $0.5 \text{ mg.kg}^{-1}$  w.w.), the As content of North Sea marine food may reach harmful levels. A classification reflecting the toxic potential of sea fish, based on normalization, was made. The class of sharks and rays and most flatfish species have positive (high) normalized AsT and AsTox values.

By ANOVA testing we compared the individual AsT concentrations of samples of the same species (intra species variability). Significant differences for some fish species were observed; significantly higher AsT concentrations were found in dogfish from the French coast versus the western North Sea and in common sole from the Bay of the Seine, in the North of France, versus the western North Sea. A summary of total arsenic concentrations in fish reported in literature as well as our data is presented in Table A1. In general, our data compare well with those

found in literature, but some small peculiarities can be noticed: dogfish, saithe, and sole show relatively higher As levels in our samples, while the opposite is true for scallops. The turbot and conger results are also deviating, but these findings are based on a very limited amount of samples.

Literature data on AsTox concentrations in sea fish are rather scarce and are only reported in the framework of developing and optimizing analytical techniques. Toxic arsenic fractions of less than 10 % are mentioned (Alberti et al. 1995; Le et al. 1994) coinciding with the values observed in this study.

### 3.3 Organics

#### 3.3.1. Evaluation of an analytical method for the determination of 27 volatile organic compounds in marine water at $\text{ng l}^{-1}$ concentration level

An analytical method based on purge-and-trap combined with high resolution gas chromatography and detection by mass spectrometry (P&T/HRGC/MS) was evaluated for the analysis of 27 volatile organic compounds (VOCs) in marine water samples down to  $\text{ng l}^{-1}$  concentration levels. The reliability and performance of the analytical method were checked by determining limits of detection, precision and accuracy. Besides method validation, emphasis was put on quality control and assessment during routine determination of VOCs in marine water samples. Analytical quality control charts were plotted for all VOCs and a standard addition test was performed, as proposed by the QUASIMEME (Quality Assurance of Information in Marine Environmental Monitoring Programmes in Europe) working group. The analytical charts were incorporated in a working scheme containing guidelines to be applied during routine determinations, ensuring the long time reliability of the analytical method. Last but not least, regular participation to QUASIMEME interlaboratory exercises on organohalogen measurements in sea water was ensured.

##### 3.3.1.1. Method validation

###### Limits of detection

Limits of detection were calculated according to recommendations formulated by IUPAC (Currie, 1995). IUPAC defined three limiting levels to describe the detection capability of an analytical method: the limit of decision, the limit of detection and the limit of quantification. Only the first two were considered in this study. Assuming homoscedasticity of variance, limits of detection (LODs) were

calculated as twice the limits of decision. LODs ranged from 0.6 ng l<sup>-1</sup> (1,1,2-trichloroethane) to 6.6 ng l<sup>-1</sup> (toluene), except for dichloromethane (90.8 ng l<sup>-1</sup>), chloroform (28.0 ng l<sup>-1</sup>) and benzene (92.0 ng l<sup>-1</sup>). An overview of all LODs is given in Table III in Appendix. High blank levels were sporadically observed for these analytes, enhancing the LODs. The presence of benzene in method blanks was attributed to artefact formation, due to thermal degradation of the sorbent Tenax TA. High blank values of dichloromethane and chloroform were due to contamination from laboratory air.

### Precision and accuracy

Precision and accuracy were assessed by analysing a laboratory reference material (LRM) ten times in a 20-day period. At a concentration level of 25.9 to 66.7 ng VOC l<sup>-1</sup>, precision, measured as the relative standard deviation, was better than 12.9% for all analytes and surrogates except for dichloromethane (103.1%) and benzene (26.0%). The accuracy ranged from 82.9% to 103.9% for 28 VOCs and surrogates, except for dichloromethane (54.4%) and benzene (66.9%). The poor results observed for dichloromethane and benzene can be caused by the relatively high background levels found in method blanks, compared to the concentrations present in LRM, and the daily variability of blank levels. Precision and accuracy for all VOCs and surrogates are reported in Table IV in Appendix.

#### 3.3.1.2. Analytical quality assessment

The growing need for quality control (QC) and assurance (QA) in environmental monitoring has been underlined by many authors in recent years (Law and Biscaya, 1994; Megginson et al., 1994; Batley, 1999; Dewulf and Van Langenhove, 1999; Asmund and Cleemann, 2000). Both QA/QC are essential for the proper functioning of an analytical laboratory and the integrity of the data it produces. Therefore, a system of quality control and assessment proposed by the QUASIMEME working group (Topping et al., 1993) was applied to all stages of field and laboratory work.

#### Analytical quality control charts

According to QUASIMEME guidelines the analytical data for reference material were plotted on an analytical quality control chart (AQCC) or Shewart chart (Topping et al., 1993). Control charts are an inherent part of the method validation protocol. Furthermore, the charts form the basis for continuous evaluation of the analytical method, ensuring the long term accuracy and precision. Laboratory reference material (LRM) was analysed ten times ad

random in a period of time corresponding to 20 days. Results were used to construct an AQCC, with  $\bar{X}$  the mean value of measured concentrations, SD the standard deviation,  $\bar{X} \pm 2 \cdot SD$  the upper and lower warning limits (WL) and  $\bar{X} \pm 3 \cdot SD$  the upper and lower control limits (CL). The bias was evaluated using QUASIMEME guidelines. Ninety-five percent of the analytical data should fall within the upper and lower warning limits (WL). Similarly 99.7% of the results should fall between the upper and lower control limit (CL). The analytical quality control charts were considered satisfactory according to QUASIMEME guidelines, except for benzene and dichloromethane. The analytical quality control chart of 1,1-dichloroethane is shown in Figure 30.

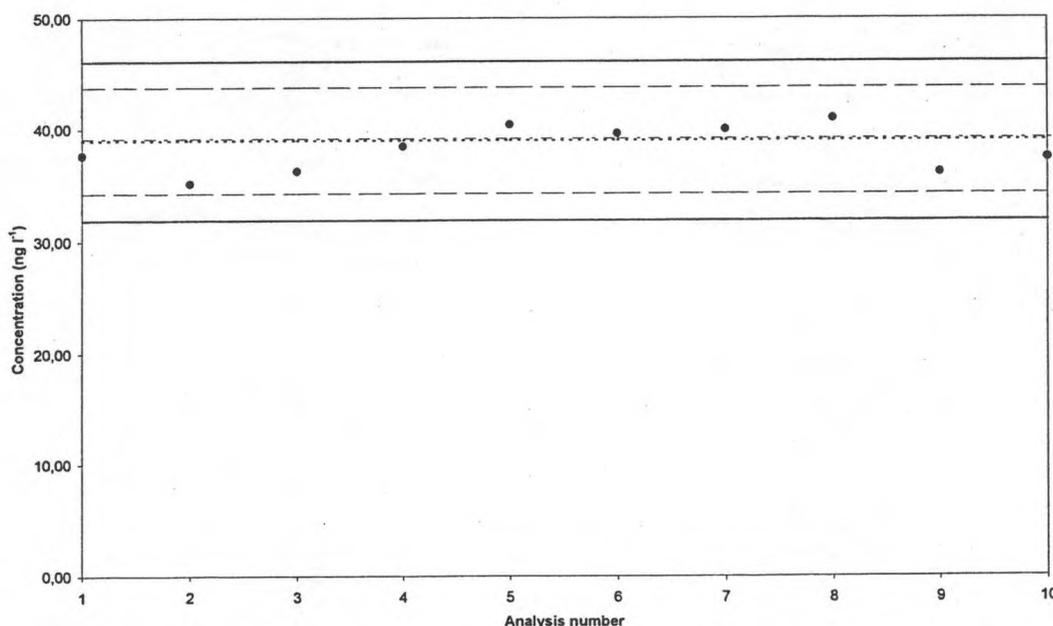


Figure 30. Analytical quality control chart (AQCC) of 1,1-dichloroethane: - - - true concentration; • = measured concentration; - - - = mean measured concentration ( $\bar{X}$ ); - - - = warning limits (WL); — — — = control limits (CL)

#### Standard addition test

Besides analytical quality control charts, bias was also evaluated by means of a standard addition test (Topping et al., 1993). The test consisted of adding a known amount of LRM to a sample with known concentrations. The sample was fortified with concentrations of target VOCs and surrogates ranging from 11.7 ng l<sup>-1</sup> to 30.0 ng l<sup>-1</sup>. The experimental results were then compared with the expected concentrations. Recoveries were within 80 and 120% for all VOCs and surrogates except for chloroform (72.2%), benzene (185.0%), toluene (53.8%), [<sup>2</sup>H<sub>8</sub>]toluene (133.8%), 1,4-dichlorobenzene (64.1%), 1,3,5-trichlorobenzene

(69.9%) and 1,2,3-trichlorobenzene (68.4%). In the case of dichloromethane, the amount recovered was lower than the amount found in the non-fortified sample. Results of the standard addition test are listed in Table V in Appendix.

### Analytical quality control for routine analysis of marine water samples

All results obtained during method validation, as well as a detailed description of all steps involved in sample collection, pretreatment and analysis were written down in a standard operating procedure (SOP). The manual includes a working scheme for routine analysis of samples, to further guarantee the analytical quality of generated sets of data. The working scheme is presented in Figure 31.

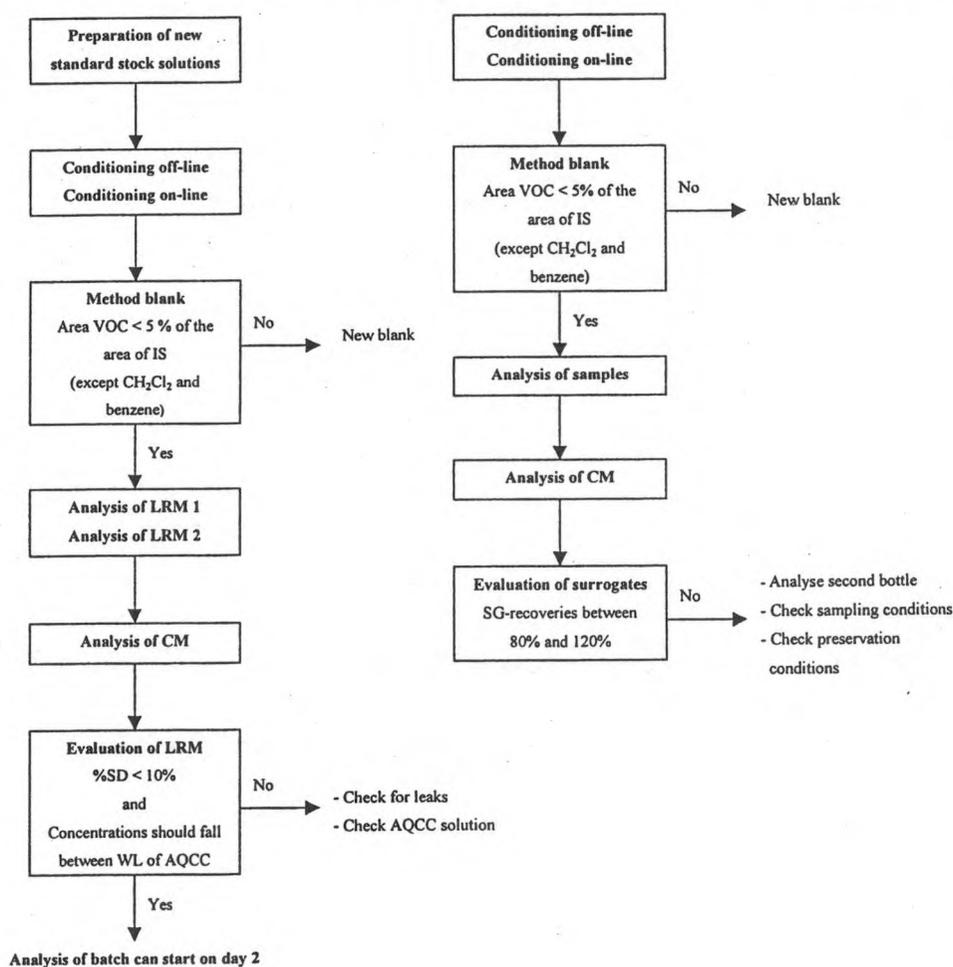


Figure 31. Guidelines for routine analysis of 27 VOCs in marine water samples

In order to maintain an accurate estimate of the long term bias and precision, replicate analyses of LRM are performed at the beginning of each batch of samples. If the results fall within the acceptable limits, defined from the

previously constructed control charts, the routine analysis of samples can start. If not, the process is not under control. The source of systematic error is investigated and the findings recorded in a log book. Furthermore, less than 10% RSD should be observed between both replicates. A method blank is analysed daily. Blanks are considered acceptable with respect to the analytical goals defined in this study as long as the peak area of each analyte does not exceed 5% of the peak area corresponding to the internal calibration standard. This way, blank levels up to 1.9 - 7.9 ng l<sup>-1</sup> can be encountered depending on the analyte, except for 1,2-dichloroethane (11.1 ng l<sup>-1</sup>) and hexachloro-1,3-butadiene (15.6 ng l<sup>-1</sup>). This measure was not applicable for dichloromethane and benzene as higher background levels were always found. Therefore these compounds were not considered when evaluating the blank. Limits of detection were re-evaluated batchwise. A calibration material was analysed at the end of each day to provide response factors for the calculation of concentration levels. Response factors are compared at regular time intervals to check the stability of the analytical instrument. Blanks, laboratory reference materials and calibration materials are prepared using natural sea water in order to avoid interferences caused by the use of different matrices. Possible losses of target compounds during storage and sample treatment are detected by calculating the amount of surrogate recovered after analysis. Recoveries between 80 and 120% are considered acceptable. If not, a sample aliquot from the other bottle is analysed.

#### Interlaboratory comparison exercises

Interlaboratory comparison exercises provide laboratories with opportunities to obtain independent assessments of the quality of their analytical capability. Interlaboratory tests for VOCs in water are rather scarce compared to other pollutants such as trace metals, nutrients or PCBs. To our knowledge, only QUASIMEME provides round robin tests for VOC measurements in marine waters. The VOCs included in the test consist of the halocarbons chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene. The performance is assessed by calculating Z-scores (Wells and Cofino, 1997).

$$Z = (\text{deviation from assigned value})/(\text{maximum allowable deviation})$$

Measurements are considered satisfactory if Z-values < 2 are obtained. Results yielded by the participation to the QUASIMEME intercomparison exercise 383 (QVC009SW and QVC010SW) are summarized in Table XV. The exercise was attended by 7 out of 8 laboratories who agreed to participate (QUASIMEME Laboratory Performance Studies, 1998). The results of QVC010SW met the QUASIMEME quality demands. In the case of QVC009SW the requirements

were almost fulfilled: 83% of the Z-scores were below 2, while 17% fell between 2 and 3. Strictly speaking, the data produced was not under control as the target value of 95% was not achieved. However as the Z-score of -2.04 obtained for trichloroethene is a rather marginal value, the results obtained for QVC009SW were considered satisfactory. The number of VOCs proposed by QUASIMEME is rather limited and should be extended towards other VOCs of environmental importance, e.g. VOCs listed as additional priority substances at the 3<sup>rd</sup> International Conference on the Protection of the North Sea (Ministerial Declaration of the Third International Conference on the Protection of the North Sea, 1990).

Table XV. Results, expressed as Z-values [-], obtained in QUASIMEME laboratory performance study AQ-6 Volatile organochlorines in seawater, Round 15 - Exercise 383 (October 1998 to January 1999)

Determinand	QVC009SW				QVC010SW			
	C <sub>Ass</sub>	C <sub>Lab</sub>	E <sub>T</sub> %	Z	C <sub>Ass</sub>	C <sub>Lab</sub>	E <sub>T</sub> %	Z
Chloroform	0.78	0.69	18.9	-0.60	1.54	1.33	15.7	-0.88
1,1,1-Trichloroethane	1.17	0.93	16.8	-1.23	2.32	2.48	14.7	0.48
Tetrachloromethane	0.79	0.56	18.8	-1.55	1.55	1.58	15.7	0.12
1,2-Dichloroethane	2.74	2.02	30.7	-0.85	5.41	3.52	21.7	-1.61
Trichloroethene	1.18	0.78	16.7	-2.04	2.33	1.78	14.6	-1.60
Tetrachloroethene	0.93	0.68	17.9	-1.47	1.83	1.50	15.2	-1.17
% Z-scores								
< 2				83				100
2 - 3				17				0
> 3				0				0

C<sub>Ass</sub> = Assigned Value [ $\mu\text{g l}^{-1}$ ]; C<sub>Lab</sub> = Laboratory value [ $\mu\text{g l}^{-1}$ ]; E<sub>T</sub>% = Maximum allowable error

### 3.3.2. Concentration levels of 27 VOCs in the North Sea and Scheldt estuary

#### 3.3.2.1. Long-term analytical quality assessment

Concentrations of 27 VOCs were measured twice a year in water samples of the North Sea and Scheldt estuary during a 3-year monitoring study (April 1998 to October 2000). A total number of 47 marine and 84 estuarine water samples were analysed, resulting in a 'North Sea' and 'Scheldt estuary' data set. All data were produced by analyses deemed "in control" by the rigorous quality control/quality assurance (QA/QC) program described above, except for benzene and dichloromethane. Concentrations of trichlorobenzenes (1,2,3-, 1,3,5- and 1,2,4-) and hexachloro-1,3-butadiene, measured in water samples from the 'Luctor 9802' campaign were also discarded from the data set for reasons of quality assessment. The benefit from using analytical quality control charts is illustrated for 1,1-dichloroethane in Figure 32. Results from replicate measurements of LRM, analysed prior to the analysis of a sample batch, are plotted against the analytical quality assurance chart. The analytical method is clearly under control for the analysis period considered as shown in Figure 32.

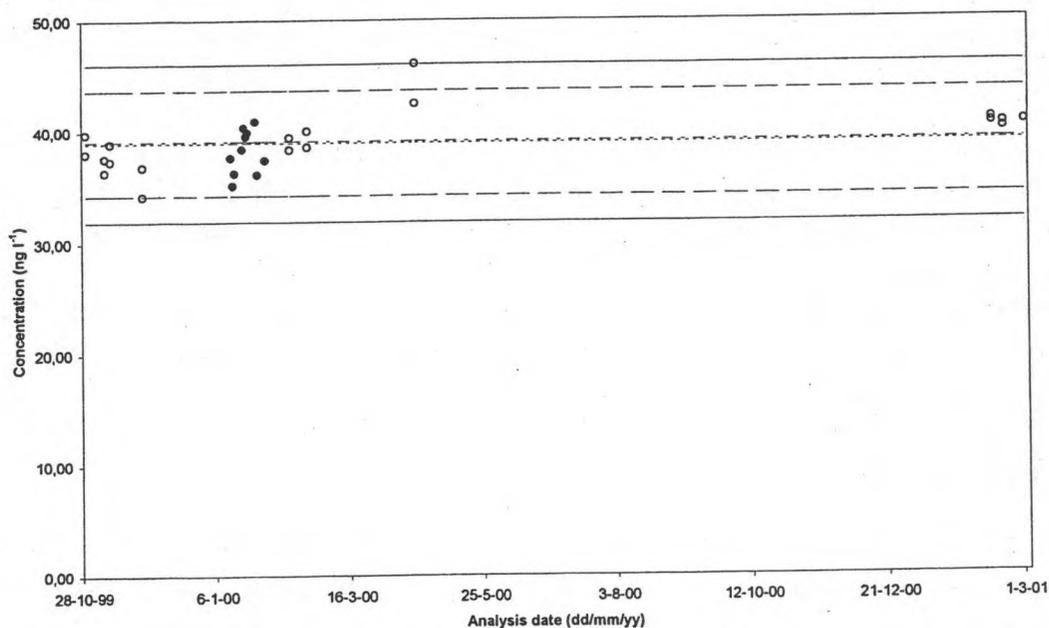


Figure 32. Long-term analytical quality assessment of 1,1-dichloroethane: - - - true concentration; • = measured concentration; - - - = mean measured concentration (X); - - - = warning limits (WL); — — — = control limits (CL); ○ = replicate LRM measurements prior to analysis of sample batch

### 3.3.2.2. Concentration levels of 27 VOCs in the marine environment

#### *Estimation of summary statistics from censored data-sets*

Target VOCs were commonly found at trace level concentrations in marine waters, typically  $\text{ng l}^{-1}$ . Despite the use of state-of-the-art analytical methods and laboratory instrumentation, several measurement results were censored. That is, some concentrations were below the decision limit or critical level defined by IUPAC (Currie, 1995). Censored observations were reported as " $< x_{\text{det}}$ ", with  $x_{\text{det}}$  the numerical value of the detection limit, rather than as numerical values. While the occurrence of censored measurements is common in the analysis of trace contaminants, they greatly complicate statistical analysis of environmental data. Standard calculation methods fail as only part of the data points are numerically known, while the other fraction is only known to occur within a restricted range of values.

To adequately describe environmental data sets, the mean, standard deviation, median and interquartile range are usually calculated. Several statistical methods have been described and reviewed in the literature to estimate these statistics in the presence of censored measurements (Helsel and Hirsch, 1992).

In order to identify the most appropriate procedure for this specific study, several approaches based on the maximum likelihood principle and probability-plot regression method were evaluated using three uncensored analytes from the monitoring survey (1,1,2-trichloroethane and tetrachloroethene from the 'Scheldt estuary' data set and o-xylene from the 'North Sea' data set). Method performance was assessed by artificially censoring the observed concentrations and estimating moments and quantiles at each censoring level. Results showed that summary statistics could be estimated with little bias (5-10%) up to 80% of censoring using a statistically sound methodology.

Figure 33 illustrates the comparative performance of several statistical methods, each implemented with a robust imputation technique, for estimating the standard deviation (SD) of artificially censored tetrachloroethene data.

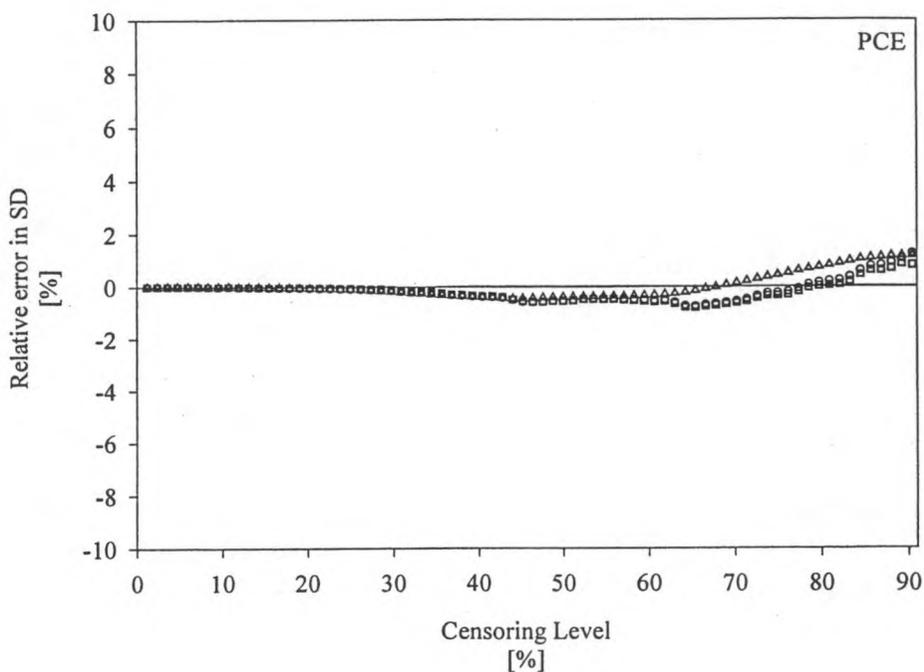


Figure 33. Comparative performance of statistical methods implemented with a robust imputation method for estimating the standard deviation (SD) of artificially censored tetrachloroethene (PCE) data sets:  $\circ$  robust Cohen's ML;  $\square$  robust bias-corrected restricted ML;  $\Delta$  robust probability plot regression

The robust bias-corrected restricted maximum likelihood method was preferred over the other methods (Huybrechts, 2002).

#### Concentration levels in the North Sea

Chlorinated  $C_1$ - $C_3$  alkanes and alkenes were mostly found at very low concentration levels in marine water samples, rarely exceeding  $5 \text{ ng l}^{-1}$ .

Chloroform, trichloroethene and tetrachloroethene however were often found at concentrations from  $100$ - $1000 \text{ ng l}^{-1}$ . Toluene, xylenes and chlorobenzene were present in most samples at concentrations  $< 50 \text{ ng l}^{-1}$ . Toluene often exhibited higher concentration levels ( $100$ - $300 \text{ ng l}^{-1}$ ).

Table XVI. Overview of summary statistics [ $\text{ng l}^{-1}$ ], estimated by the robust bias-corrected restricted maximum likelihood estimation method, and censoring levels [ $\text{ng l}^{-1}$ ] for 23 VOCs in the North Sea;  $n = 47$

Compound	Censoring level	% <sub>censored</sub>	Mean	SD	Median	IQR
1,1-Dichloroethene	0.8	55.3	1.2	1.8	0.7	1.8
trans-1,2-Dichloroethene	0.5	55.3	1.6	2.1	0.3	5.1
Chloroform	14.0	27.7	134.6	315.5	60.3	190.1
1,1,1-Trichloroethane	0.4	10.6	5.9	9.7	1.6	9.1
Cyclohexane	2.1	29.8	7.7	9.4	6.7	12.1
Tetrachloromethane	1.1	14.9	4.7	11.8	2.1	1.7
1,2-Dichloroethane	8.2	76.6	7.8	16.6	3.2	6.6
Trichloroethene	6.2	23.4	49.5	76.3	19.5	67.9
1,2-Dichloropropane	0.6	61.7	0.9	1.0	0.5	1.8
Toluene	9.3	19.1	59.6	112.3	29.7	53.9
1,1,2-Trichloroethane	0.3	14.9	2.0	2.9	1.0	2.1
Tetrachloroethene	1.4	48.9	23.0	66.3	3.9	12.9
Chlorobenzene	3.7	63.8	4.1	4.4	2.6	12.3
Ethylbenzene	2.1	10.6	9.1	9.6	7.0	8.4
m/p-Xylene	5.4	14.9	20.8	26.9	15.3	20.5
o-Xylene	1.6	0.0	12.9	17.8	6.9	11.1
1,3-Dichlorobenzene	1.4	83.0	1.0	1.3	0.6	0.9
1,4-Dichlorobenzene	7.5	57.4	21.8	39.0	6.3	51.8
1,2-Dichlorobenzene	1.8	80.9	3.6	17.5	0.3	1.2
1,3,5-Trichlorobenzene	0.9	70.2	1.3	2	0.4	4.7
1,2,4-Trichlorobenzene	2.9	78.7	2.2	2.5	1.3	1.9
1,2,3-Trichlorobenzene	3.3	85.1	2.2	4.4	0.7	1.7

SD = standard deviation; IQR = interquartile range

Dichlorobenzenes, trichlorobenzenes and hexachloro-1,3-butadiene were hardly detected. Estimates of summary statistics are reported in Table XVI. No results are given for 1,1-dichloroethane and hexachloro-1,3-butadiene since censoring levels for both compounds exceeded 90% (100% and 95.7% respectively).

### Concentration levels in the Scheldt estuary

Most VOCs were found in samples taken along the Scheldt estuary. Chlorinated alkanes and alkenes showed increasing concentrations levels towards Antwerp, up to  $1 \mu\text{g l}^{-1}$  for tetrachloroethene in the vicinity of Antwerp. Monocyclic aromatic hydrocarbons displayed a more complex profile with alternating maxima along the trajectory Vlissingen-Antwerp.

Dichlorobenzenes and trichlorobenzenes were detected in  $\pm 35\%$  and 60-80% of the samples respectively. Concentration levels rarely exceeded a few  $\text{ng l}^{-1}$ , except for 1,4-dichlorobenzene with concentrations up to  $100 \text{ ng l}^{-1}$ . Estimates of the mean, standard deviation, median and interquartile range for the 'Scheldt estuary' data set are given in Table XVII. Summary statistics were not calculated for hexachloro-1,3-butadiene since the censoring level exceeded 95%. Only two measurements yielded results above the censoring limit of  $2.4 \text{ ng l}^{-1}$ .

Table XVII. Overview of summary statistics [ $\text{ng l}^{-1}$ ], estimated by the robust bias-corrected restricted maximum likelihood estimation method, and censoring levels [ $\text{ng l}^{-1}$ ] for 24 VOCs in the Scheldt estuary;  $n = 84$  (except for 1,2-dichlorobenzene  $n = 83$ ; trichlorobenzenes and hexachloro-1,3-butadiene  $n = 70$ ).

Compound	Censoring level	% <sub>censored</sub>	Mean	SD	Median	IQR
1,1-Dichloroethene	0.8	40.5	1.9	1.9	1.3	1.9
trans-1,2-Dichloroethene	0.5	32.1	2.0	2.3	2.1	3.8
1,1-Dichloroethane	1.6	39.3	5.2	5.5	2.7	7.2
Chloroform	14.0	3.6	80.7	106.3	46.5	67.7
1,1,1-Trichloroethane	0.4	2.4	14.4	13.7	9.5	17.5
Cyclohexane	2.1	4.8	46.2	99.7	11.7	26.4
Tetrachloromethane	1.1	6.0	3.3	3.8	2.6	1.5
1,2-Dichloroethane	8.2	9.5	40.1	30.1	31.7	41.3
Trichloroethene	6.2	9.5	90.6	126.7	39.3	118.7
1,2-Dichloropropane	0.6	6.0	6.8	25.45	2.7	2.6
Toluene	9.3	4.8	70.9	150.4	36.3	49.2
1,1,2-Trichloroethane	0.3	0.0	26.7	35.0	16.1	27.2
Tetrachloroethene	1.4	0.0	199.2	472.9	84.5	181.2
Chlorobenzene	3.7	7.1	16.8	11.9	14.3	13.5
Ethylbenzene	2.1	3.6	9.0	7.5	7.3	6.9
m/p-Xylene	5.4	4.8	21.4	17.6	15.7	16.4
o-Xylene	1.6	2.4	11.2	9.6	8.2	8.8
1,3-Dichlorobenzene	1.4	35.7	3.1	3.8	2.9	4.2
1,4-Dichlorobenzene	7.5	38.1	26.8	28.5	31.9	47.2
1,2-Dichlorobenzene	1.8	34.9	7.4	7.9	8.9	12.1
1,3,5-Trichlorobenzene	0.9	68.6	22.0	106.7	0.2	4.4
1,2,4-Trichlorobenzene	2.9	57.1	5.19	12.1	2.2	5.2
1,2,3-Trichlorobenzene	3.3	81.4	16.7	81.6	0.2	1.64

SD = standard deviation; IQR = interquartile range

## 4. DISCUSSION

### 4.1 Air/sea boundary

#### 4.1.1. Trace elements

The distribution and behaviour of particulate trace elements in marine systems has received until now much less attention than the dissolved fraction. The aim of our study was to examine the composition of suspended matter in the Southern Bight of the North Sea and adjacent area, under various climatic conditions. Both major elements (Si, Al, Fe, Ca, Mn, Corg) and minor elements (Zn, Cu, Co, Ni, Cd, Pb) were analysed. As one may expect the major factor controlling the distribution of particulate elements is the origin of the solid material, either continental and transported to the sea by rivers and by the atmosphere, or biologically produced in-situ essentially by primary production.

It was possible to identify in our case four classes of particles on the basis of a statistical analysis. In the area investigated, the input of suspended material from the Scheldt estuary is dominant along the Belgian coast. Particles of continental origin probably transported by the atmosphere are also the most abundant in the Northern part of the area. In the central part, the detrital continental particles are less abundant and more diluted by authigenic organic carbon.

It is well known that many trace elements are used as oligo-elements by organisms and that phytoplankton consumes efficiently the dissolved trace elements. However, we have shown that the concentration of trace metals in the the particulate organic phase is lower in the organic fraction than is the inorganic detrital fraction, except for Cd. The primary production has thus a diluting effect on the amount of trace elements in the solid phase, except for Cd for which the particulate concentration is almost doubled during the spring bloom.

Trace element and heavy metal concentrations should be further monitored for a detailed follow-up of the concentrations. As noticed in the trend analysis, further insights should be developed in order to define possible causes for the elevating concentrations of some metals. Special attention should also be paid to investigate the role of some local contaminant sources, in order to achieve an optimized risk assessment.

#### 4.1.2. Nutrients

##### inorganic nutrients

The role of the atmosphere as a very important input route for nutrients has been proved. The importance of phosphate compounds can be stated as very limited, as a result of the general nitrogen limitation of the North Sea and the very low phosphate concentrations in the air. Nitrogen compounds are, however, very important. Traffic and industry are responsible for the highest contribution with high nitrogen oxide concentrations over the entire North Sea. As a result of the very high ammonia concentrations above Flanders and The Netherlands, however, the contribution of ammonium compounds becomes much more important for the deposition of nutrients to the Belgian, Dutch and neighboring coastal waters. These high ammonia concentrations are a result of a dense spreading of cattle - and pig farms and intense agricultural activities. In order to decrease ammonia concentrations in the air, ammonia emissions from these sources should be minimized.

Total budgets have been estimated and there was stated that the atmosphere contributes to a comparable amount to nitrogen components as the riverine inputs do.

##### organic nutrients

The huge potential of the organic nutrients has been demonstrated and further research should be focused on the identification, concentration, solubility and bio availability of these compounds, in order to make a better nutrient budget estimation possible.

##### precipitation

The massive importance of wet deposition in the total budget was stated. High uncertainties concerning the amount of precipitation over sea should also be further investigated in order to improve wet deposition estimates over sea.

#### 4.1.3. Organics

A major part of this study focused on the elaboration of an adequate analytical method to determine VOCs in marine water samples down to the  $\text{ng l}^{-1}$  concentration level. The reliability and performance of an analytical method, based on purge-and-trap/GC-MS, were checked by determining limits of detection, precision and accuracy. At a concentration level of 26.0 to 66.7  $\text{ng VOC L}^{-1}$ , the method proved its applicability towards the analysis of all target VOCs, except for benzene and dichloromethane. High detection limits, and lack of precision and accuracy for these compounds were attributed to the relatively high

concentrations found in method blanks as compared to the concentration levels investigated. In the case of dichloromethane the laboratory environment acted as a source of contamination. The presence of benzene in method blanks was attributed to artefact formation from the sorbent material Tenax TA. The use of different trapping materials, compared to the monitoring of 13 VOCs in marine water, allowed the measurement of a broader range of volatile organic compounds, but was accompanied with a considerable increase of LOD for benzene, hence affecting its precision and accuracy. Lowering the desorption temperature would certainly diminish artefact formation. However care must be taken not to alter the desorption efficiency of the target compounds, especially for the high boiling chlorinated aromatics. Adequate quality assurance and quality control measures were implemented. The analytical control charts of dichloromethane and benzene were not considered satisfactory at the concentration levels considered in this study. New charts should be constructed for both compounds at higher concentration levels, while re-evaluating precision and accuracy to find out at which concentration levels reliable measurements can be obtained. The charts were incorporated in a working scheme containing guidelines to ensure the quality of measurements during routine analysis of water samples. Independent quality assessment of the analytical method was obtained by participating to interlaboratory tests proposed by QUASIMEME. Long-term quality assessment was satisfactory for all target analytes, except dichloromethane and benzene.

Water samples from the North Sea and Scheldt estuary were analysed along a three-year monitoring campaign. Concentration levels varied from a few  $\text{ng l}^{-1}$  to  $\mu\text{g l}^{-1}$  depending on the analyte, while a number of VOCs such as trichlorobenzenes and hexachloro-1,3-butadiene remained mostly undetected. Each data set contained a number of censored values, *i.e.* values below the analytical detection limit. The presence of censored data greatly complicates any statistical analysis of the data sets. Further research is necessary to find adequate statistical procedures to solve the problem of censoring.

#### **4.2. Land/sea and Channel boundaries, reservoir, internal cycling and trophic level**

Concerning the nutrient dynamics, the results obtained allowed us to make estimates of major nutrient inputs to the Southern Bight of the North Sea via the Scheldt, the Channel and the atmosphere. Spatial and seasonal distributions of nutrients were also determined in the area of concern. However, uncertainties on the fluxes through the

Channel and data distribution are important because data on nutrient concentrations and water flows were not collected systematically (on a regular base). Despite this, one of the major findings concerns the dissolved organic nitrogen pool. This pool, rarely measured in the past, is one of the most important nitrogen pool (more than 50 % of the total dissolved nitrogen) in seawater, freshwater and in the atmosphere. This means that ancient data, taking no account of the DON pool, greatly underestimated the true N pool. Studies on the internal N cycling allowed us to determine major fluxes of dissolved to particulate nitrogen mediated mainly by phytoplanktonic species. Major findings stated that nitrate is the main nitrogen source for phytoplankton.

However to be able of determining a complete nitrogen budget in the area, much information is still missing concerning the major N sinks as denitrification in sediments and sediment burial. Therefore, for future research in this area we recommend (1) systematic (every 2 months for example) data collection in the Channel, (2) Determination of denitrification processes in the sediments as the major N sink.

Similar remarks can be made for the trace elements mercury and arsenic. Analytical methods were developed which allowed us to determine the different forms of mercury and arsenic in water, sediments and in the trophic chain. Temporal and spatial patterns of the different forms of these elements could be identified and estimates were made of inputs from the Scheldt estuary and through the Channel. As for the nutrients, a large uncertainty exists on the fluxes through the Channel as these are based on a limited amount of data.

Important factors influencing the speciation of mercury in estuarine and coastal waters could be identified. Both mobilization of methylmercury from contaminated sediments where it is formed by sulfate reducing bacteria as methylation of mercury in the water column under influence of phytoplankton blooms are potential sources of methylmercury to the North Sea. Dissolved methylmercury concentrations were correlated to DON, though the nature of this source needs to be identified. The relative importance of both sources (sediments and phytoplankton) has still to be determined.

Assimilation of arsenic by phytoplankton was clearly demonstrated, with minimum dissolved arsenic levels in spring and winter maxima. However, the formation of methylated arsenic species could not be investigated due to important interference of the sea salt matrix in the HPLC analysis. This problem has not yet been solved and

further analytical developments are required in order to fully understand the biogeochemical cycle of arsenic in the North Sea.

We have furthermore used radionuclides of Zn, Cd and Mn in order to evaluate the rate of transfer of these trace metals from the dissolved to the particulate phase. Short term experiments, in the dark and in the presence of biological inhibitors allows us to evaluate the rapid isotopic exchange, which occurs with the most labile fraction of the element considered. This exchange is very important for zinc and cadmium and limited for manganese. Kinetic experiments under constant conditions show a rapid uptake of this element which gives a turnover rate of 85% per day, due to biological processes either bacterial or phytoplanktonic. Experiments conducted under variable light conditions indicate photo-reduction of the particulate manganese. The behaviour of zinc and cadmium is very different. After a fast and important isotopic exchange, the two metals are transferred linearly at a slow rate from the dissolved to the particulate phase. The uptake of Zn and Cd are faster in the presence of light and the use of an herbicide confirms the contribution of phytoplankton in this transfer. The role of abiotic processes remains nevertheless dominant for Zn.

A new approach intended to provide information on the speciation of trace elements in the particulate phase. In the proposed method, a sample of suspended matter is titrated by HCl and at each step the concentration of the major and minor elements released to the solution is measured. The major elements dissolved allow to identify the mineralogical phases, which are affected by the acidification, and the minor elements indicate the metals associated to the dissolving phase.

Typically, after the initial dissolution of calcium and manganese carbonate, iron oxihydroxides and clays minerals are successively mobilized. It was found that calcium and partially zinc and nickel are released together with the manganese carbonate and not by the calcium carbonate as often suggested. Dissolution of chromium and lead starts only at pH below 4 in relation to oxihydroxides of iron and the clay fraction.

This method looks very promising and allows furthermore to evaluate the possible remobilisation of the trace metals under changing pH conditions.

**Acknowledgements**

We thank Prof. Michel WARTEL of the «Université des Sciences et Technologies de Lille (France)», laboratory of Analytical Chemistry and Marine Ecosystems for the analysis of manganese by Mossbauer.

## Appendix

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## List of extra tables and figures

Table A1: AsT concentrations versus literature data

Species	Location	AsT mg As.kg <sup>-1</sup> ww	Reference
Seafish			
Dogfish	French Atlantic Coast	7.96-25.34	Cossa, 1990
	Ostkante	5.62-10.78	Ballin et al., 1994
	North Sea and Channel	21.3-64.0	This study
Ray	Southern North Sea	31	Luten et al., 1982
	North Sea and Channel	6.2-35.9	This study
Conger	French Atlantic Coast	11.7-42	Cossa, 1990
	Northern North Sea	12-30	Luten et al., 1982
	North Sea and Channel	2.4	This study
Cod	Greenland	1.97-4.33	Ballin et al., 1994
	Dogger bank	3.65-7.08	Ballin et al., 1994
	Baltic Sea	0.50-0.64	Ballin et al., 1994
	Belgian Coast	2.5-5.4	De Clerck et al., 1990
	Northern North Sea	15.3	Luten et al., 1982
	NO Atlantic	0.4-2.3	Stange et al., 1996
	Norway	4.1	Staveland et al., 1993
	North Sea and Channel	3.1-7.0	This study
Saithe	Northern North Sea	1.4	Luten et al., 1982
	North Sea and Channel	1.8-5.7	This study
Whiting	French Atlantic Coast	2.24-11.34	Cossa et al., 1990
	English Channel	2.1	Luten et al., 1982
	North Sea	1.7	Luten et al., 1982
	North Sea and Channel	4.0-6.5	This study
Ling	Northern North Sea	6.0	Luten et al., 1982
	North Sea and Channel	2.1-8.5	This study
Angler	French Atlantic Coast	3.7-14.52	Cossa, 1990
	North Sea and Channel	4.1-13.7	This study
Seabass	French Atlantic Coast	0.72-1.64	Cossa, 1990
	North Sea and Channel	1.1	This study
Dab	North Sea	2.4-12.5	Cardinaals et al., 1985
	Southern North Sea	6.8	Luten et al., 1982

	Denmark	11.6	Luten et al., 1982
	Eastcoast England	12.6	Luten et al., 1982
	NE Atlantic	1.0-1.2	Stange et al., 1996
	North Sea and Channel	3.7-21.4	This study
Plaice	Fladenground	16.58-55.72	Ballin et al., 1994
	German Bight	7.39-12.72	Ballin et al., 1994
	French Atlantic Coast	2.08-12.04	Cossa, 1990
	North Sea	3-166	Luten et al., 1982
	Central North Sea	31.3	Luten et al., 1982
	Westcoast Denmark	17.5	Luten et al., 1982
	Southern North Sea	9.4	Luten et al., 1982
	North Sea and Channel	5.9-26.0	This study
Lemon sole	Wadden Islands	25	Luten et al., 1982
	Dogger bank	46	Luten et al., 1982
	North Sea and Channel	14.9-76.1	This study
Common sole	North Sea	6.2-10.2	Cardinaals et al., 1985
	French Atlantic Coast	2.74-15.98	Cossa, 1990
	Westcoast Denmark	10.4	Luten et al., 1982
	Southern North Sea	4.6	Luten et al., 1982
	Central North Sea	6.6	Luten et al., 1982
	North Sea and Channel	4.1-48.8	This study
Brill	Southern North Sea	0.8	Luten et al., 1982
	Westcoast Denmark	2.2	Luten et al., 1982
	Eastcoast England	1.9	Luten et al., 1982
	North Sea and Channel	1.4-2.9	This study
Turbot	Southern North Sea	6.4	Luten et al., 1982
	Westcoast Denmark	14.8	Luten et al., 1982
	Eastcoast England	4.4	Luten et al., 1982
	North Sea and Channel	17.9	This study
Shellfish and crustaceans			
Common shrimp	French Atlantic Coast	1.4-2.88	Cossa, 1990
	Belgian Coast	4-10	De Clerck et al., 1990
	North Sea and Channel	5.2	This study
Great scallop	French Atlantic Coast	2.3-5.28	Cossa, 1990
	North Sea and Channel	0.99-3.6	This study

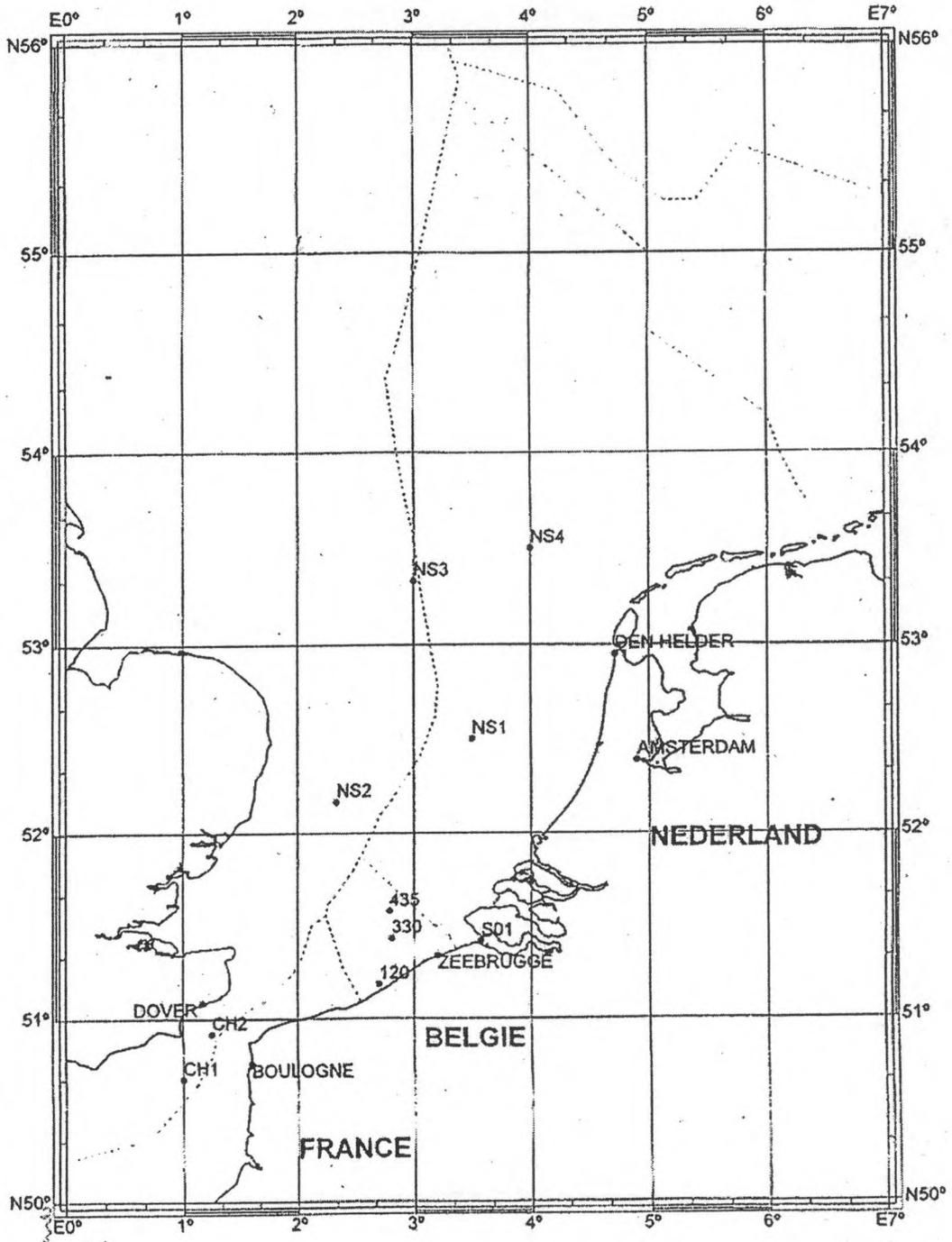


Figure A1. Sampling locations in the southern North Sea, Belgian Continental Platform and Channel

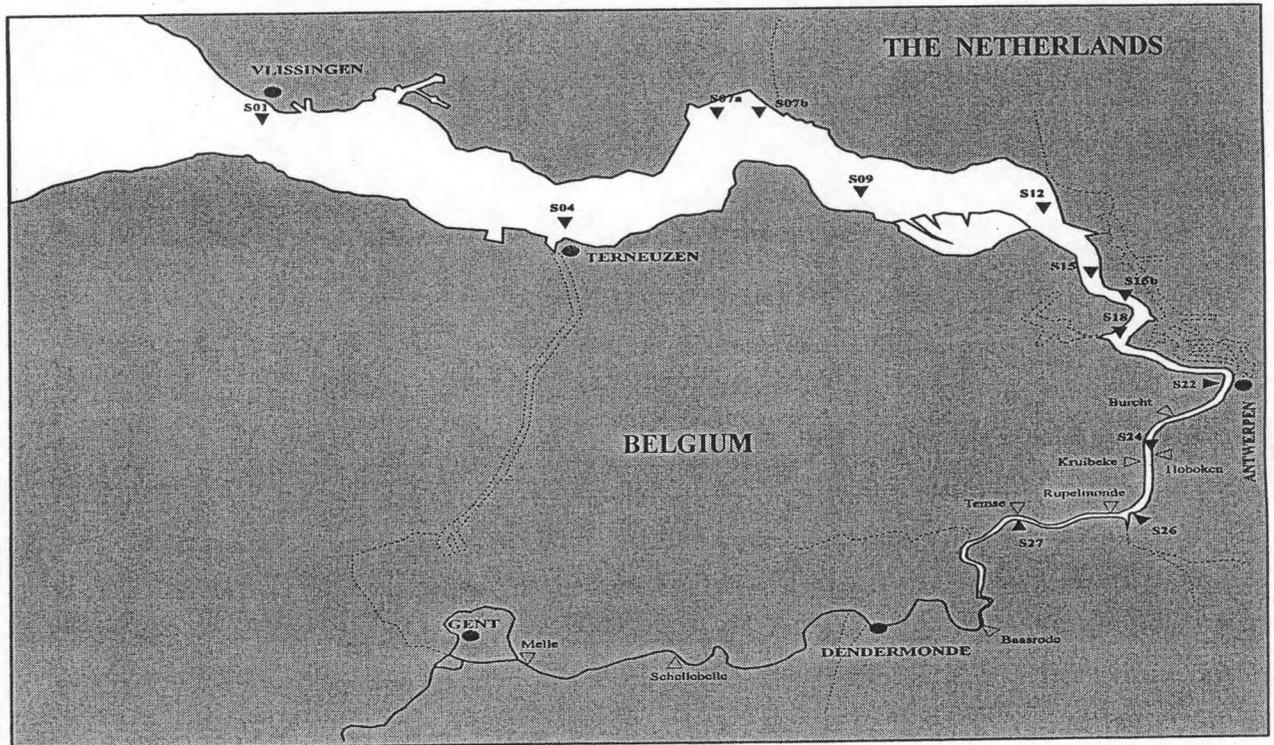


Figure A2. Sampling sites along the Scheldt esuary, from Breskens to Temse (Antwerp)

Table All. Selected ion masses [m/z] and time windows [min] for the mass spectrometer operating in the SIM-mode, and internal standard (IS) used for quantification (na = not applicable)

Compound	Selected ion masses	Time window	IS
1,1-Dichloroethene	61, 96, 98	8.55 – 12.35	IS <sub>1</sub>
Dichloromethane	49, 84, 86	8.55 – 12.35	IS <sub>1</sub>
<i>trans</i> -1,2-Dichloroethene	61, 96, 98	8.55 – 12.35	IS <sub>1</sub>
1,1-Dichloroethane	63, 65, 83	12.35 – 13.50	IS <sub>1</sub>
[ <sup>2</sup> H]Chloroform	84, 86	14.00 – 15.45	IS <sub>1</sub>
Chloroform	83, 85	14.00 – 15.45	IS <sub>1</sub>
1,1,1-Trichloroethane	61, 97, 99	15.45 – 16.15	IS <sub>1</sub>
Cyclohexane	41, 56, 84	15.45 – 16.15	IS <sub>1</sub>
Tetrachloromethane	117, 119, 121	16.15 – 17.50	IS <sub>1</sub>
1,2-Dichloroethane	62, 64	16.15 – 17.50	IS <sub>1</sub>
Benzene	77, 78	16.15 – 17.50	IS <sub>1</sub>
Trichloroethene	95, 130, 132	17.50 – 19.20	IS <sub>1</sub>
$\alpha,\alpha,\alpha$ -Trifluorotoluene	127, 145, 146	17.50 – 19.20	na
1,2-Dichloropropane	62, 63, 76	17.50 – 19.20	IS <sub>1</sub>
[ <sup>2</sup> H <sub>8</sub> ]Toluene	70, 98, 100	19.70 – 21.20	IS <sub>1</sub>
Toluene	65, 91, 92	19.70 - 21.20	IS <sub>1</sub>
Tetrachloroethene	129, 164, 166	21.20 - 23.00	IS <sub>1</sub>
1,1,2-Trichloroethane	83, 97, 99	21.20 - 23.00	IS <sub>1</sub>
[ <sup>2</sup> H <sub>5</sub> ]Chlorobenzene	82, 117, 119	23.00 - 25.50	IS <sub>2</sub>
Chlorobenzene	77, 112, 114	23.00 - 25.50	IS <sub>2</sub>
Ethylbenzene	91, 105, 106	23.00 - 25.50	IS <sub>2</sub>
<i>m/p</i> -Xylene	91, 105, 106	23.00 - 25.50	IS <sub>2</sub>
<i>o</i> -Xylene	91, 105, 106	23.00 - 25.50	IS <sub>2</sub>
<i>p</i> -Bromofluorobenzene	95, 174, 176	25.50 - 27.00	na
1,3-Dichlorobenzene	111, 146, 148	27.00 - 30.00	IS <sub>2</sub>
1,4-Dichlorobenzene	111, 146, 148	27.00 - 30.00	IS <sub>2</sub>
1,2-Dichlorobenzene	111, 146, 148	27.00 - 30.00	IS <sub>2</sub>
1,3,5-Trichlorobenzene	180, 182, 184	30.50 - 37.00	IS <sub>2</sub>
1,2,4-Trichlorobenzene	180, 182, 184	30.50 - 37.00	IS <sub>2</sub>
Hexachloro-1,3-butadiene	223, 225, 227	30.50 - 37.00	IS <sub>2</sub>
1,2,3-Trichlorobenzene	180, 182, 184	30.50 - 37.00	IS <sub>2</sub>

Table AIII. Sampling campaigns

Campaign	Period	Location	Sampling points
Belgica 9809	20-25/4/1998	North Sea	NS1, NS2, NS3, NS4, CH1, CH2, 120, 330, 435, S01
Luctor 9801	19-20/5/1998	Scheldt estuary	S01 to S27
Belgica 9821	28/9-2/10/1998	North Sea	NS1, NS2, NS3, NS4, CH1, CH2, 120, 330, 435, S01
Luctor 9802	14-15/10/1998	Scheldt estuary	S01 to S27
Luctor 9901	11-12/5/1999	Scheldt estuary	S01 to S27
Belgica 9916	29/6-9/7/1999	North Sea	NS1, NS2, NS3, NS4, CH1, CH2, 120, 330, 435
Belgica 9922	18-22/10/1999	North Sea	NS1, 120, 330, 435, S01
Luctor 9902	2-3/11/1999	Scheldt estuary	S01 to S27
Belgica 0009	27-31/3/2000	North Sea	NS1, 120, 330, 435, S01
Luctor 0001	3-4/4/2000	Scheldt estuary	S01 to S27
Belgica 0024	2-6/10/2000	North Sea	NS1, NS2, NS3, NS4, 120, 330, 435
Luctor 0002	13-14/11/2000	Scheldt estuary	S01 to S27

Table AIV. Decision limits  $x_{\text{dec}}$  [ $\text{ng l}^{-1}$ ] and detection limits  $x_{\text{det}}$  [ $\text{ng l}^{-1}$ ] for VOCs and deuterated surrogates

Compound	$x_{\text{dec}}$	$x_{\text{det}}$
1,1-Dichloroethene	0.6	1.2
Dichloromethane	32.1	64.2
<i>trans</i> -1,2-Dichloroethene	0.3	0.7
1,1-Dichloroethane	1.1	2.2
[ $^2\text{H}$ ]Chloroform	1.7	3.4
Chloroform	9.9	19.8
1,1,1-Trichloroethane	0.3	0.6
Cyclohexane	1.5	3.0
Tetrachloromethane	0.8	1.6
1,2-Dichloroethane	5.8	11.6
Benzene	32.5	65.1
Trichloroethene	4.4	8.8
1,2-Dichloropropane	0.4	0.8
[ $^2\text{H}_8$ ]Toluene	0.3	0.6
Toluene	6.6	13.1
1,1,2-Trichloroethane	0.2	0.4
Tetrachloroethene	0.9	1.9
[ $^2\text{H}_5$ ]Chlorobenzene	0.4	0.7
Chlorobenzene	2.6	5.2
Ethylbenzene	1.5	3.0
<i>m/p</i> -Xylene	3.8	7.7
<i>o</i> -Xylene	1.1	2.3
1,3-Dichlorobenzene	0.9	1.9
1,4-Dichlorobenzene	5.3	10.6
1,2-Dichlorobenzene	1.3	2.6
1,3,5-Trichlorobenzene	0.6	1.3
1,2,4-Trichlorobenzene	2.1	4.1
Hexachloro-1,3-butadiene	1.7	3.4
1,2,3-Trichlorobenzene	2.3	4.6

Table AV. Precision [%] and accuracy [%], determined as the relative standard deviation and mean recovery of a laboratory reference material (LRM), at the given concentration level [ $\text{ng l}^{-1}$ ] ( $n = 10$ )

Compound	Concentration	Precision	Accuracy
1,1-Dichloroethene	40.4	6.8	97.9
Dichloromethane	44.2	103.1	54.4
<i>trans</i> -1,2-Dichloroethene	41.7	7.0	96.5
1,1-Dichloroethane	39.1	5.2	97.6
[ $^2\text{H}$ ]Chloroform	50.0	4.4	99.8
Chloroform	49.6	9.7	91.6
1,1,1-Trichloroethane	43.7	5.4	91.6
Cyclohexane	25.9	9.7	100.3
Tetrachloromethane	53.1	5.2	96.0
1,2-Dichloroethane	41.8	4.1	97.1
Benzene	29.3	26.0	66.9
Trichloroethene	48.8	4.7	94.8
1,2-Dichloropropane	38.6	7.5	103.9
[ $^2\text{H}_8$ ]Toluene	31.5	7.2	102.4
Toluene	28.9	9.2	89.0
1,1,2-Trichloroethane	47.8	8.2	98.6
Tetrachloroethene	54.1	4.2	96.1
[ $^2\text{H}_5$ ]Chlorobenzene	38.6	4.7	99.5
Chlorobenzene	36.9	5.5	95.9
Ethylbenzene	28.9	6.8	98.1
<i>m/p</i> -Xylene	57.5	5.9	93.5
<i>o</i> -Xylene	29.4	4.6	95.7
1,3-Dichlorobenzene	42.9	4.3	93.4
1,4-Dichlorobenzene	66.7	11.2	82.9
1,2-Dichlorobenzene	43.5	5.9	93.5
1,3,5-Trichlorobenzene	66.7	12.2	95.5
1,2,4-Trichlorobenzene	48.5	10.0	93.4
Hexachloro-1,3-butadiene	56.0	12.9	99.6
1,2,3-Trichlorobenzene	66.7	11.4	103.2

Table AVI. Standard addition test: analysis of a laboratory fortified matrix (LFM) [ng l<sup>-1</sup>] and determination of the recovery [%] of the amount added [ng l<sup>-1</sup>] to the original sample S15 [ng l<sup>-1</sup>] (n=1)

Compound	S15	Added amount	LFM	% <sub>recovery</sub>
1,1-Dichloroethene	3.2	18.2	19.3	88.8
Dichloromethane	178.3	19.9	134.5	-
<i>trans</i> -1,2-Dichloroethene	0.5	18.8	18.2	94.3
1,1-Dichloroethane	1.8	17.6	18.9	97.2
[ <sup>2</sup> H]Chloroform	115.8	22.5	137.8	97.5
Chloroform	70.3	22.3	86.4	72.2
1,1,1-Trichloroethane	4.3	19.6	25.8	109.2
Cyclohexane	38.9	11.7	51.0	104.0
Tetrachloromethane	1.6	23.9	27.0	106.3
1,2-Dichloroethane	34.2	18.8	53.6	103.0
Benzene	1.5	13.2	25.9	185.0
Trichloroethene	21.1	21.9	42.9	99.2
1,2-Dichloropropane	1.3	17.4	18.7	100.5
[ <sup>2</sup> H <sub>8</sub> ]Toluene	66.3	14.2	85.3	133.8
Toluene	36.4	13.0	43.4	53.8
1,1,2-Trichloroethane	22.9	21.5	42.3	90.0
Tetrachloroethene	42.8	24.3	64.8	91.2
[ <sup>2</sup> H <sub>5</sub> ]Chlorobenzene	82.4	17.4	96.4	80.6
Chlorobenzene	30.9	16.6	45.5	87.4
Ethylbenzene	3.7	13.0	16.9	101.2
<i>m/p</i> -Xylene	9.6	25.9	32.7	89.2
<i>o</i> -Xylene	3.8	13.2	16.0	92.4
1,3-Dichlorobenzene	3.8	19.3	20.1	84.0
1,4-Dichlorobenzene	5.5	30.0	24.7	64.1
1,2-Dichlorobenzene	4.0	19.6	20.7	85.3
1,3,5-Trichlorobenzene	0.4	30.0	21.3	69.9
1,2,4-Trichlorobenzene	2.8	21.8	21.6	86.1
Hexachloro-1,3-butadiene	0.5	25.2	24.4	94.9
1,2,3-Trichlorobenzene	1.2	30.0	21.7	68.4

### July 1997

cluster	Julian day	station	Fe (mg/g)	Si (mg/g)	Mn (mg/g)	Al (mg/g)	Ca (mg/g)	Mg (mg/g)	Zn (µg/g)	Cd (µg/g)	Cr (µg/g)	Co (µg/g)	Cu (µg/g)	Ni (µg/g)	Pb (µg/g)
Channel	35621	105	3.3	62	0.19	8	32	24.2	90	0.33	141	0.5	7.8	36.5	14
	35621	215	7.6	110	0.27	13	44	10.4	170	0.44	104	1.0	13.5	27.5	23
	35621	315	6.2	100	0.34	14	31	12.5	80	0.31	105	2.3	10.6	31.8	20
Coast	35625	S01	34.5	353	1.29	56	117	23.7	310	0.77	112	8.8	14.6	17.3	44
	35620	350	14.2	112	1.70	32	71	12.1	120	0.38	101	10.6	11.2	13.6	71
	35620	330	18.4	453	1.40	31	78	12.7	240	0.36	162	7.8	14.5	6.3	48
	35622	115	13.8	103	0.42	24	88	14.6	150	0.38	92	2.9	11.8	9.2	33
	35621	421	19.5	492	0.37	36	90	22.6	230	0.23	178	3.6	7.2	3.9	16
Scheidt	35622	230	22.8	150	0.86	39	111	13.3	130	0.32	97	6.2	13.5	14.9	52
	35620	250	24.1	159	0.81	39	83	11.2	140	0.51	75	8.9	13.2	25.0	50
	35620	700	34.8	257	0.91	52	114	12.5	180	0.54	108	7.7	25.9	25.9	49
	35620	710	26.7	171	0.79	42	105	11.2	150	0.54	80	8.0	17.6	25.6	51
	35621	130	30.4	183	0.87	45	107	11.8	150	0.46	86	6.3	16.8	25.8	41
North	35620	435	7.7	100	1.75	17	34	10.4	140	0.87	110	8.8	20.4	5.5	5
	35620	545	6.3	117	1.14	16	35	13.0	90	0.88	85	6.2	10.2	10.7	24
	35620	800	7.0	98	1.93	16	42	18.1	100	0.88	137	9.8	9.9	3.1	34
	35621	340	12.0	105	1.36	25	68	18.4	420	0.37	99	9.8	12.3	47.2	68

### November 1997

cluster	Julian day	station	Fe (mg/g)	Si (mg/g)	Mn (mg/g)	Al (mg/g)	Ca (mg/g)	Mg (mg/g)	Zn (µg/g)	Cd (µg/g)	Cr (µg/g)	Co (µg/g)	Cu (µg/g)	Ni (µg/g)	Pb (µg/g)
Channel	35748	421	16.7	151	0.31	49.0	88	21.4	119	0.13	152	3.3	14.9	61.7	14.0
	35748	215	16.4	122	0.47	40.0	105	22.6	94	0.31	125	4.4	25.0	39.5	31.0
Coast	35746	545	21.0	137	0.39	39.0	88	30.0	104	0.06	75	7.3	11.1	33.8	30.0
	35746	800	22.2	109	0.45	48.0	78	30.5	89	0.05	85	8.2	11.5	47.5	41.0
	35746	435	21.9	142	0.35	51.0	77	25.0	81	0.27	127	8.1	11.1	49.7	35.0
	35748	330	18.6	154	0.47	43.0	111	21.5	68	0.15	82	4.4	9.7	30.9	29.0
	35748	315	10.1	92	0.22	26.0	74	43.5	56	0.19	112	2.3	6.4	34.3	20.0
	35748	115	17.8	123	0.57	28.0	116	27.6	119	0.31	81	4.2	11.2	24.7	36.0
Scheidt	35746	250	34.8	164	0.90	57.0	108	15.5	170	0.21	93	8.5	16.1	30.2	30.0
	35746	350	69.6	379	1.79	110.0	250	27.2	350	0.27	90	8.8	15.1	36.8	50.0
	35747	230	33.6	161	0.85	53.0	118	13.4	172	0.26	86	7.8	15.0	33.7	60.0
	35747	130	32.0	177	0.82	50.0	113	13.5	143	0.30	83	7.2	15.7	29.3	53.0
	35747	140	32.7	195	0.95	49.0	99	9.3	155	0.31	95	8.2	16.8	30.9	66.0
	35747	710	27.4	172	0.71	47.0	102	17.3	165	0.25	79	12.7	13.2	26.0	9.0
	35747	S01	33.6	195	0.98	55.0	103	12.4	140	0.43	105	8.9	20.6	32.6	70.0
	35748	105	15.9	130	0.42	36.0	115	11.7	82	0.39	149	3.4	9.8	38.7	32.0

Figure A3: Results of the analysis of the suspended matter collected during the cruises of 1997

### April 1998

cluster	Julian day	station	Fe (mg/g)	Si (mg/g)	Mn (mg/g)	Al (mg/g)	Ca (mg/g)	Mg (mg/g)	Zn (µg/g)	Cd (µg/g)	Cr (µg/g)	Co (µg/g)	Cu (µg/g)	Ni (µg/g)	Pb (µg/g)	Corg (%)	Chloro (µg/l)
<b>Scheldt</b>	35906	NS2	33.5	191	0.36	65.0	88	11.4	820	0.86	71	11.2	11.8	53.2	47.0	4.71	0.93
	35905	NS1	9.4	145	0.18	14.0	21	6.8	210	1.18	89	0.2	7.8	85.5	26.0	35.53	6.39
	35907	330	5.8	39	0.11	13.0	21	5.2	1410	1.65	42	3.7	5.4	58.9	26.0	28.25	8.77
	35907	435	8.2	49	0.12	18.0	24	5.6	100	0.93	46	1.1	7.2	122.4	5.0	37.26	1.87
	35907	421	8.2	101	0.16	23.0	55	6.7	90	0.66	31	3.2	9.7	58.3	17.0	24.74	6.97
	35908	CH1	13.8	83	0.10	49.0	69	7.3	130	0.80	56	5.8	7.4	115.9	20.0	13.33	0.49
	35908	120	18.9	162	0.35	35.0	123	8.7	100	0.62	43	4.7	11.0	37.8	37.0	14.77	2.81
	35908	700	36.4	168	0.80	57.0	120	12.2	150	0.57	80	7.0	24.2	32.3	55.0	6.22	4.21
	35908	230	21.8	137	0.45	40.0	91	9.1	230	0.78	55	6.1	12.8	38.1	49.0	14.28	32.58
	35909	S01	27.0	186	0.66	42.0	96	9.8	380	0.91	62	7.7	14.3	33.5	45.0	0.37	13.69
<b>North</b>	35906	NS4	41.2	179	0.59	83.0	66	14.3	140	0.16	73	13.3	17.3	66.8	64.0	3.47	0.89
	35906	NS3	36.8	185	0.55	70.0	69	14.3	170	0.30	50	11.5	15.6	79.7	56.0	6.47	1.63
	35907	CH2	30.7	209	0.34	60.0	85	10.5	90	0.12	61	8.4	12.3	40.2	41.0	4.64	1.49

### September 1998

cluster	Julian day	station	Fe (mg/g)	Si (mg/g)	Mn (mg/g)	Al (mg/g)	Ca (mg/g)	Mg (mg/g)	Zn (µg/g)	Cd (µg/g)	Cr (µg/g)	Co (µg/g)	Cu (µg/g)	Ni (µg/g)	Pb (µg/g)	Corg (%)	Chloro (µg/l)
<b>Channel</b>	36068	330	14.4	121	0.35	14.8	80	43.3	230	0.23	135	5.1	16.5	15.2	21.9	4.1	2.0
	36068	435	11.8	116	0.37	12.2	59	27.7	640	0.56	124	3.3	34.0	19.1	44.4	6.5	1.8
	36068	230	17.6	116	0.52	29.7	85	21.1	320	0.36	162	4.1	16.3	22.7	41.3	4.8	2.7
	36068	120	14.8	107	0.43	22.8	98	26.1	320	0.42	140	3.3	10.6	16.3	35.3	5.9	3.2
	36068	CH2	6.7	46	0.09	34.7	35	51.1	130	0.15	193	2.8	24.8	36.9	46.5	5.2	0.8
	36069	CH1	21.9	449	0.16	38.7	66	41.6	570	0.43	232	2.7	20.6	41.8	33.8	4.4	0.9
	36069	421	11.4	106	0.19	41.9	61	27.3	170	0.42	112	4.2	22.1	22.6	25.5	5.9	2.3
<b>Scheldt</b>	36069	700	35.6	223	0.97	59.9	126	14.7	220	0.29	75	7.5	23.4	26.1	51.8	2.7	1.8
	36069	S01	31.3	195	0.94	49.5	102	18.8	230	0.50	84	7.5	18.7	24.6	53.8	3.0	1.6
<b>North</b>	36066	NS1	15.2	118	0.19	27.9	64	30.1	310	0.02	130	7.1	16.1	26.3	34.5	5.0	0.8
	36067	NS4	29.6	148	0.46	51.1	51	16.9	220	0.19	117	10.2	23.6	33.3	45.9	5.3	2.0
	36067	NS3	25.0	122	0.49	42.4	49	38.0	220	0.15	96	9.7	18.7	27.1	28.1	4.9	1.5
	36067	NS2	32.6	156	0.36	57.5	61	29.5	490	0.09	151	12.5	22.6	36.3	28.6	4.9	1.0

Figure A4: Results of the analysis of the suspended matter collected during the cruises of 1998

## July 1999

cluster	Julian day	station	Fe (mg/g)	Si (mg/g)	Mn (mg/g)	Al (mg/g)	Ca (mg/g)	Mg (mg/g)	Zn (µg/g)	Cd (µg/g)	Cr (µg/g)	Co (µg/g)	Cu (µg/g)	Ni (µg/g)	Pb (µg/g)	Corg (%)	Chloro (µg/l)
Channel	36348	315	2.5	14	0.07	19.1	28	50.7	164	0.21	87	1.4	6.0	4.9	1.8	-	2.1
	36348	421	4.0	29	0.07	15.6	30	22.4	113	0.15	42	2.6	10.7	12.0	5.2	38.4	3.1
	36348	435	3.5	45	0.17	7.8	22	22.9	102	0.19	48	2.4	7.0	10.2	4.5	40.0	-
Coast	36348	230	10.2	78	1.43	17.2	71	26.8	85	0.11	79	6.5	11.8	12.2	30.3	14.4	8.4
	36348	250	4.4	30	0.48	7.0	31	19.7	29	0.07	14	3.0	8.2	7.2	6.4	25.7	9.4
	36349	330	8.2	78	0.83	14.3	42	27.5	82	0.10	93	4.7	8.5	8.5	9.8	-	6.0
	36349	120	3.4	44	0.32	4.9	45	24.9	86	0.10	23	3.2	11.5	7.9	8.2	-	5.4
Scheldt	36349	140	9.7	4	0.59	11.6	53	15.0	75	0.19	31	4.7	24.3	13.2	19.0	11.2	7.4
	36349	130	5.4	1	1.36	13.8	56	24.8	57	0.16	19	5.0	37.0	9.6	17.2	-	6.3
	36349	115	3.4	0	0.20	4.8	40	20.1	75	0.12	13	2.4	9.8	7.0	9.2	38.6	4.6
	36349	710	10.2	5	0.42	17.8	57	20.1	72	0.14	28	3.8	14.9	11.6	17.9	11.6	7.8
	36349	780	1.9	0	0.33	3.4	21	16.7	48	0.11	14	2.0	11.9	12.6	9.9	31.7	7.3
North	36349	545	3.2	51	0.15	0.3	26	23.2	36	0.29	48	1.6	34.0	9.6	13.0	-	1.9
	36349	800	6.4	74	0.12	2.2	34	27.1	64	0.08	58	2.1	9.3	11.0	12.8	-	1.5
	36348	700	19.2	139	1.16	26.9	95	15.6	79	0.31	89	7.8	21.5	18.8	38.2	7.7	10.29

## October 1999

cluster	Julian day	station	Fe (mg/g)	Si (mg/g)	Mn (mg/g)	Al (mg/g)	Ca (mg/g)	Mg (mg/g)	Zn (µg/g)	Cd (µg/g)	Cr (µg/g)	Co (µg/g)	Cu (µg/g)	Ni (µg/g)	Pb (µg/g)	Corg (%)	Chloro (µg/l)
Coast	36452	330	21.6	194	0.44	35.0	93	22.3	66	0.20	73	6.4	6.3	20.6	31.2	3.1	1.8
	36452	435	20.1	227	0.43	34.8	96	26.6	48	0.16	60	7.1	6.4	19.6	22.4	3.2	2.1
Scheldt	36452	230	36.9	201	0.85	57.1	119	15.7	138	0.14	77	8.5	21.0	18.9	66.1	3.3	1.7
	36452	700	36.8	216	0.93	41.6	85	12.7	140	0.16	70	8.5	26.2	16.4	58.2	4.9	3.1
	36452	S01	35.5	200	1.01	52.8	96	15.0	180	0.69	79	9.0	24.8	23.0	59.6	2.3	2.1
	36452	120	34.2	178	0.78	53.6	110	14.0	132	0.20	77	8.1	24.1	19.9	46.5	2.2	2.1
	36451	NS1	6.9	259	0.03	12.8	69	39.1	51	0.35	68	1.5	4.5	14.5	25.9	3.4	1.7
	36452	421	21.8	241	0.33	40.5	95	18.7	62	1.58	71	7.3	19.3	22.6	25.6	3.6	2.5

Figure A5: Results of the analysis of the suspended matter collected during the cruises of 1999

Table AVII: Mean concentration of metals in the suspended matter for the various clusters during the cruises of July and November 1997

Element	Unit	July	Nov	July	Nov	July	Nov	July	Nov
		Channel		Coast		Scheldt		North	
Al	mg/g	12	45	36	39	44	60	16	-
Fe	mg/g	6	17	21	19	28	38	7	-
Si	mg/g	91	137	277	126	184	206	105	-
Ca	mg/g	36	97	92	91	104	128	37	-
Mg	mg/g	16	22	17	30	12	16	14	-
Mn	mg/g	0.27	0.4	1	0.4	0.9	1	1.6	-
Zn	µg/g	113	107	197	86	150	185	110	-
Cu	µg/g	11	20	12	10	17	16	14	-
Ni	µg/g	32	51	11	37	23	31	6	-
Cr	µg/g	117	139	124	94	89	90	111	-
Co	µg/g	1.3	3.9	6.7	5.8	7.4	8.9	8.3	-
Pb	µg/g	19	23	44	32	49	48	21	-
Cd	µg/g	0.36	0.22	0.41	0.17	0.47	0.29	0.88	-

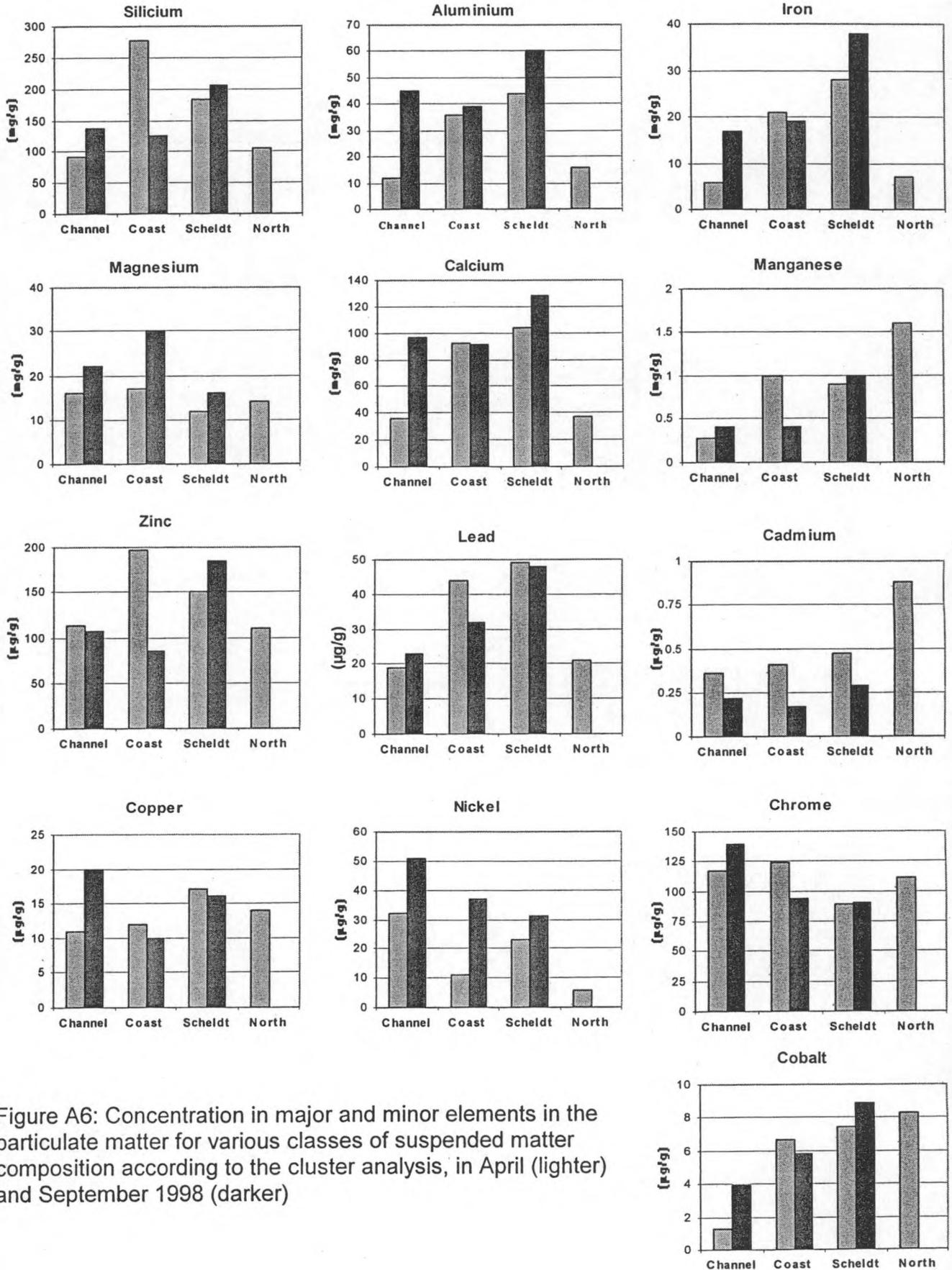


Figure A6: Concentration in major and minor elements in the particulate matter for various classes of suspended matter composition according to the cluster analysis, in April (lighter) and September 1998 (darker)

JULY 97

	1	2	3
S01	3.05	545	2.80
700	2.74	340	0.83
330	2.13	250	0.59
710	1.61	215	0.54
350	1.51	710	0.42
130	1.50	315	0.33
250	1.16	435	0.25
230	1.14	130	0.19
340	1.07	350	-0.03
421	0.50	800	-0.13
800	-0.16	700	-0.16
435	-0.74	115	-0.17
115	-0.98	230	-0.29
545	-1.30	105	-0.30
215	-2.19	S01	-0.30
315	-2.38	330	-0.97
105	-3.23	421	-1.66

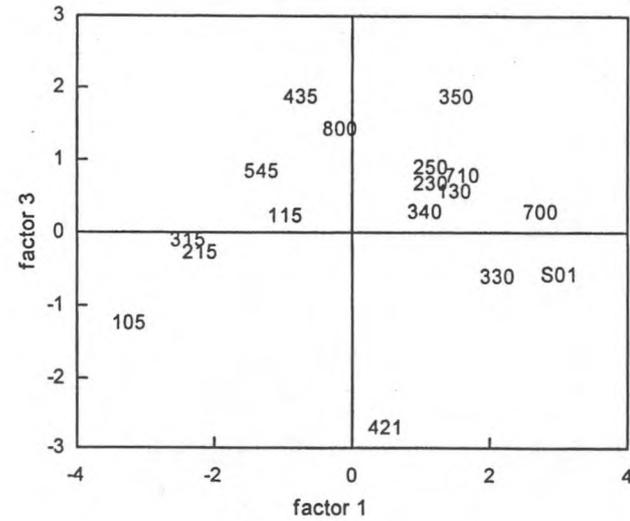
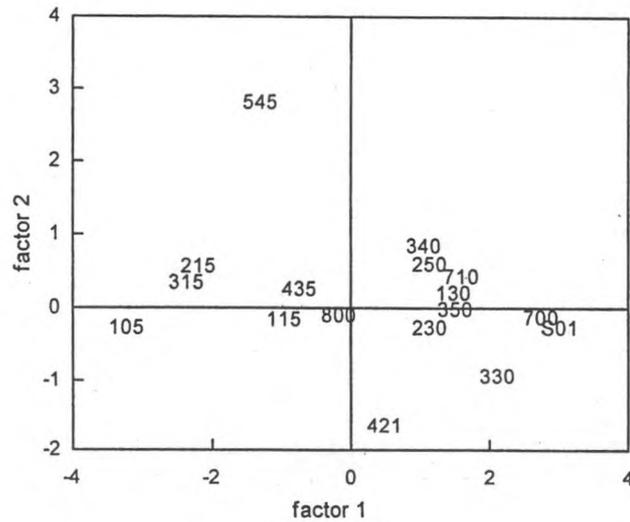


Figure A7: Results of the Principal Component Analysis for the cruise of July 1997, scores of the various stations in regard to the three first principal factors.

NOVEMBER 97

	1	2	3
350	7.22	140	0.24
S01	2.92	230	0.13
140	2.47	S01	0.09
230	2.33	105	0.08
130	1.96	130	0.02
250	1.85	710	-0.15
710	1.15	250	-0.23
435	0.50	435	-0.25
800	0.36	421	-0.34
215	0.19	330	-0.50
330	-0.05	800	-0.58
105	-0.06	115	-0.70
545	-0.10	215	-0.77
115	-0.29	545	-0.82
421	-0.34	350	-1.06
315	-2.12	315	-1.50

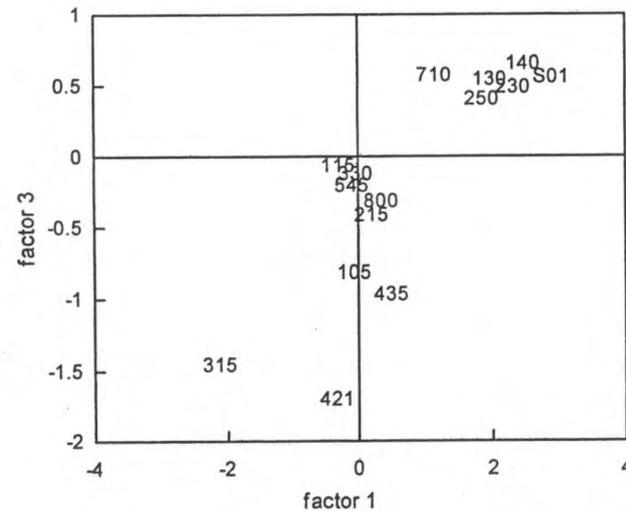
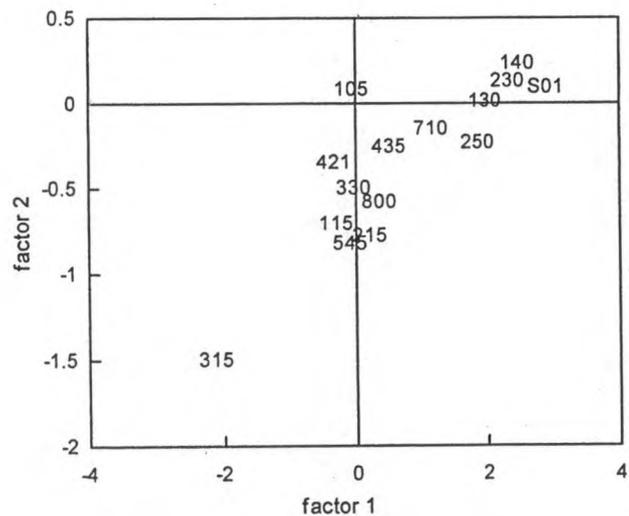


Figure A8: Results of the Principal Component Analysis for the cruise of November 1997, scores of the various stations in regard to the three first principal factors.

APRIL 98

	1	2	3
NS4	3.39	330	5.89
NS3	2.57	435	4.06
700	2.53	CH1	3.45
NS2	2.48	NS1	3.34
CH2	1.45	NS2	2.82
S01	1.37	421	2.18
230	0.60	S01	1.75
120	0.20	230	1.66
CH1	-0.57	NS3	1.56
421	-2.00	120	1.23
330	-2.05	NS4	0.90
NS1	-2.23	CH2	0.46
435	-2.92	700	0.32

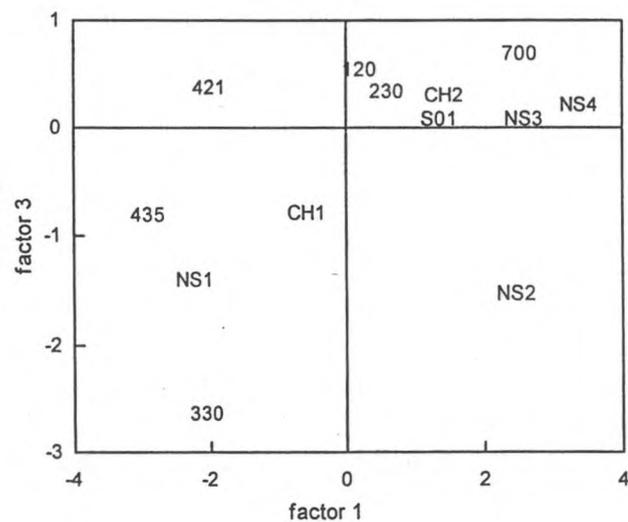
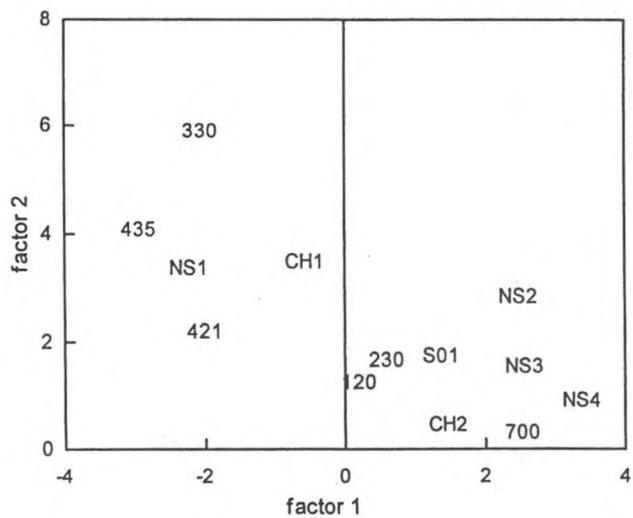


Figure A9: Results of the Principal Component Analysis for the cruise of April 1998, scores of the various stations in regard to the three first principal factors.

SEPTEMBER 98

1		2		3	
700	2.85	S01	-0.03	700	0.63
S01	2.04	NS4	-0.24	S01	0.33
NS2	1.71	700	-0.26	NS4	-0.10
NS4	1.44	435	-0.38	NS3	-0.49
CH1	0.91	230	-0.59	421	-0.68
NS3	0.12	120	-0.64	NS1	-1.19
230	-0.02	421	-0.75	230	-1.21
NS1	-0.54	NS2	-0.80	120	-1.24
435	-0.61	NS1	-1.11	435	-1.27
120	-0.71	NS3	-1.28	330	-1.36
421	-0.91	CH1	-1.63	NS2	-1.64
330	-1.27	330	-2.06	CH2	-2.41
CH2	-1.46	CH2	-2.58	CH1	-5.08

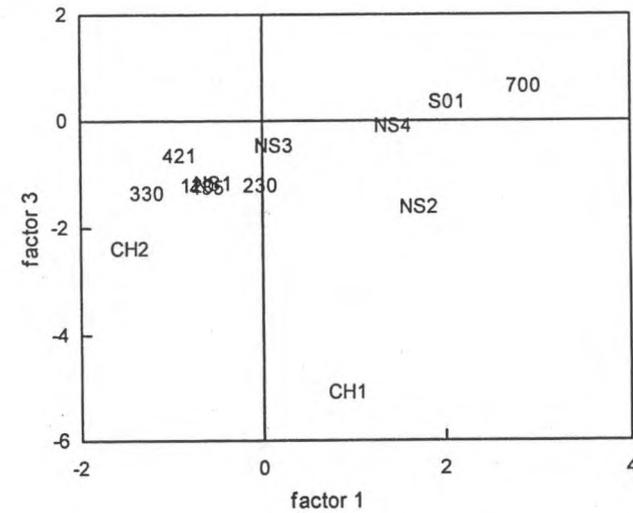
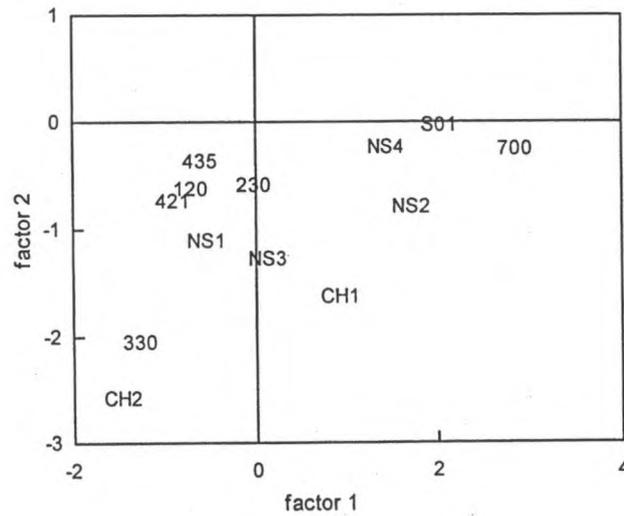


Figure A10: Results of the Principal Component Analysis for the cruise of September 1998, scores of the various stations in regard to the three first principal factors.

JULY 99

	1	2	3
700	0.75	780	0.07
230	-0.78	115	-0.14
130	-1.49	140	-0.23
140	-1.97	435	-0.25
330	-2.25	421	-0.27
710	-2.31	250	-0.27
545	-3.15	710	-0.33
120	-3.30	120	-0.58
800	-3.38	700	-0.58
250	-3.45	800	-0.85
421	-3.45	545	-0.98
115	-3.65	230	-1.18
435	-3.72	330	-1.19
780	-3.78	130	-1.28
315	-4.03	315	-1.93

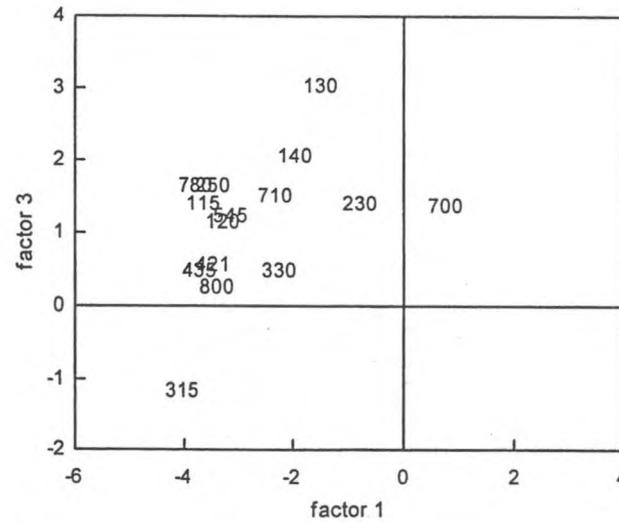
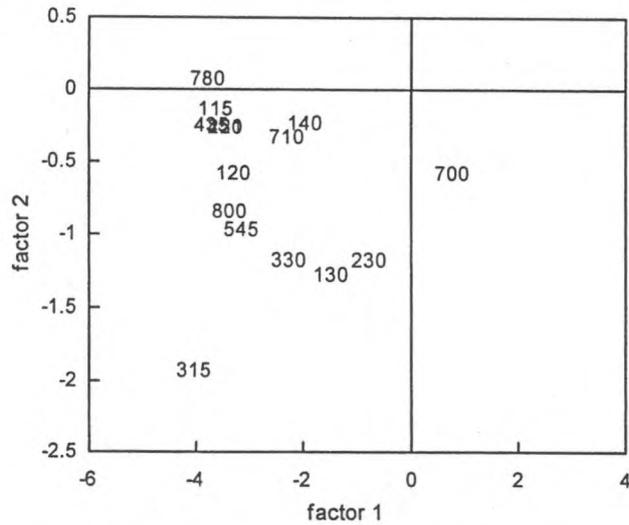


Figure A11: Results of the Principal Component Analysis for the cruise of July 1999, scores of the various stations in regard to the three first principal factors.

OCTOBER 99

	1	2	3
230	2.90	421	1.24
S01	2.70	S01	0.22
700	2.29	330	-0.50
120	2.18	120	-0.53
421	0.56	700	-0.56
330	-0.05	230	-0.65
435	-0.18	435	-0.80
NS1	-2.25	NS1	-1.26

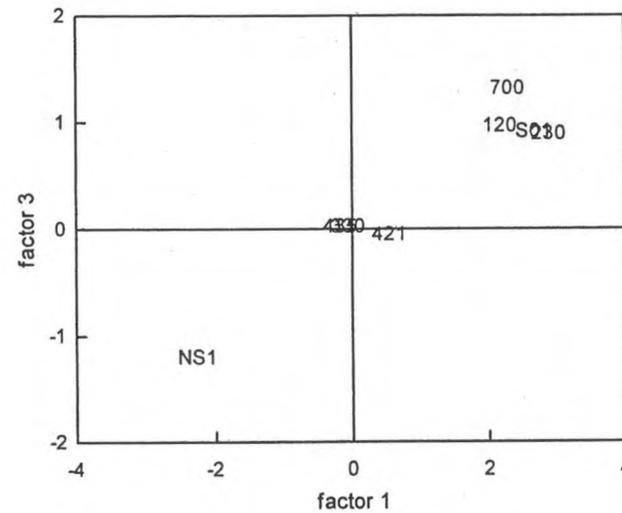
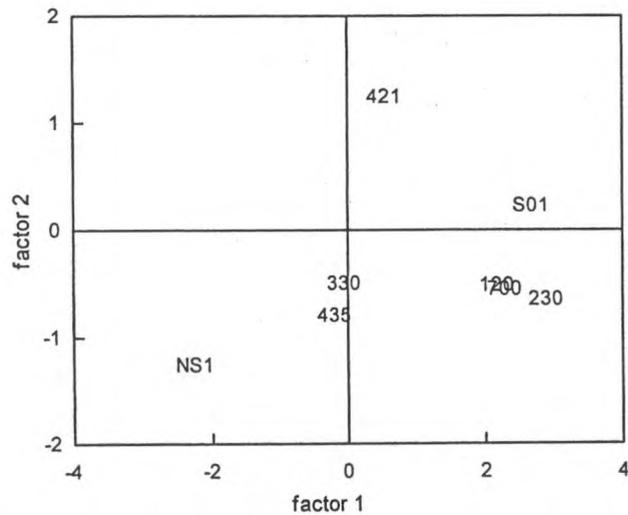


Figure A12: Results of the Principal Component Analysis for the cruise of October 1999, scores of the various stations in regard to the three first principal factors.

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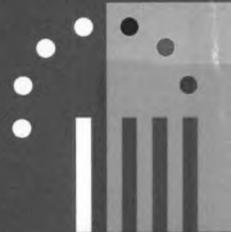
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