



Vlaams Instituut voor de Zee
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MATHEMATICAL MODELLING OF GLOBAL EXCHANGES
BETWEEN CONTINENTS AND OCEANS AND BETWEEN
OCEAN BASINS

36262

by

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Abstract

Global scale studies resolve very badly the exchanges occurring at the oceans' boundaries where the dynamics is considerably influenced by intricated non-linear shelf processes.

The determination of the fluxes at the oceans' margins requires the "local" application of sophisticated shelf sea models.

This paper describes briefly the GHER 3D mathematical model and its application to the Northern Bering Sea and shows how the results can be used to assess the fluxes and transports from the North Pacific Ocean to the Arctic Mediterranean Sea and, ultimately, the Atlantic Ocean.

Introduction

Global ocean fluxes are governed by large scale processes and continental shelves are little more, in their context, than boundary separations between oceans and continents or between ocean basins.

Global scale studies resolve very badly the exchanges occurring at these boundaries where the dynamics is considerably influenced by intricate non-linear shelf processes.

The determination of the fluxes at the continent-ocean and ocean-ocean interfaces is however vital for the understanding of the global changes of the geophysical system.

The only solution to this problem is the application, locally, of highly sophisticated shelf sea models which can resolve the delicate "boundary processes" and deduce from them appropriate "transfer functions" to be used in larger scale models.

An instructive example of this procedure is the application of the GHER 3D mathematical model to the general circulation of the Northern Bering Sea and subsequent water transports through the Bering Strait. It is shown in the following how the results of the Northern Bering Sea Model can be used to assess the fluxes and transports from the North Pacific Ocean to the Arctic Mediterranean Sea and, ultimately, the Atlantic Ocean and how these fluxes may affect the earth's global environment.

The GHER 3D Mathematical Model

The GHER 3D mathematical model has been described in previous reports and publications (e.g. NIHOUL et al 1986, NIHOUL and DJENIDI 1987). The model is fully non-linear with turbulent energy closure. The products of each simulation with the model are the values of all state variables and auxiliary variables and parameters at all grid points of the domain as functions of depth. These are :

1. the two components u_1, u_2 , the amplitude u_h and the direction of the horizontal velocity vector
2. the vertical velocity w and the "transformed vertical velocity" \tilde{u}_3
3. the temperature T

4. the salinity s
 5. the buoyancy b
 6. the turbulent kinetic energy e
 7. the mixing length l
 8. the turbulent dissipation rate ϵ
 9. the eddy viscosity $\tilde{\nu}$
 10. the eddy diffusivity $\tilde{\lambda}$
- and,
11. the depth-averaged horizontal velocity vector \bar{u} (or the transport $\underline{U} = H\bar{u}$)
 12. the bottom friction u_* .

In the GHER 3D Model, the calculations are carried in σ -coordinates and the results are later interpreted in the physical coordinate system. The transformed vertical velocity \tilde{u}_3 is the vertical velocity in the σ -coordinate system. It can be interpreted as the difference between the actual vertical velocity and the vertical velocity which is induced by the slope of the bottom and the surface. \tilde{u}_3 may thus be regarded as indicative of truly upwelling or downwelling motions.

The bottom friction velocity u_* is a measure of the bottom stress (u_*^2) and of its erosive power ($\sim u_*^3$) and it can be useful in interpreting the distributions of bottom sediments and benthic populations.

The Northern Bering Sea

The Northern Bering Sea is a relatively shallow basin limited by the Bering Strait to the north and St Lawrence Island to the south (Fig. 1). The flow passing through the Bering Strait, from the Pacific Ocean to the Arctic Ocean, penetrates the Northern Bering Sea through the Strait of Anadyr, to the west of St Lawrence Island, and by the Strait of Shpanberg, to the east. More than 60 % of the mean northward transport of water through the Bering Strait is derived from the "Anadyr Stream", a subsidiary of the Bering Slope Current which flows around the coasts of the Gulf of Anadyr, following the 60-70 isobaths, to the Anadyr Strait and the western part of the Shpanberg Strait (COACHMAN et al, 1975). The proportion of

that stream which goes through the Strait of Anadyr or skirts St Lawrence Island, as well as the orientation, with respect to the Strait's axis, and seasonal variations of the entering flow, is likely to have a strong influence on the subsequent deployment of that flow in the Northern Bering Sea and in the Chukchi Sea.

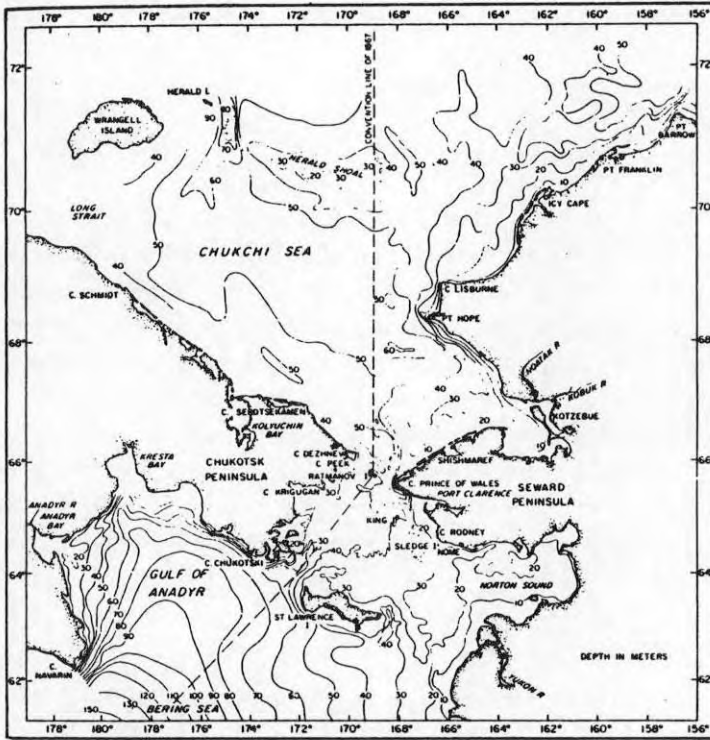


Fig. 1.: The Northern Bering and Chukchi Seas including Bering Strait

The Anadyr Water is the main provider of nutrients, fueling the enormously productive region to the north of St Lawrence Island, where a carbon fixation of more than $10 \text{ g C m}^{-2} \text{ day}^{-1}$ was found by the ISHTAR project.

Mathematical simulations of the Northern Bering Sea's general summer circulation with the GHER 3D model confirm the general trend of the Anadyr Stream to spread to the east after passing the Anadyr Strait : the nutrient rich Anadyr waters deploying eastwards and progressively fostering biological productivity in the whole basin (Fig. 2).

The three-dimensional model also provides valuable informations on vertical stratification, mixing and advection as well as on horizontal gradients of buoyancy, fronts and large scale horizontal structures associated with the main flow.

The model shows a permanent upwelling along the Siberian coast of the Anadyr Strait. The upwelling brings cold nutrient-rich waters to the surface. The cold plume deploys eastwards in the Northern Bering Sea following the current field (Figs. 3, 4).

Global fluxes from the North Pacific to the Arctic

Recent chemical studies of the distributions of nutrients (JONES and ANDERSON 1986), radionuclides (MOORE and SMITH 1986), and freons (WALLACE et al 1987) in the Arctic Ocean under the CESAR ice camp have been used to constrain estimates of vertical and lateral exchange processes within the deep (> 2000 m) Canadian and Eurasian basins. Advection-diffusion models of these processes and the observed vertical distributions of oxygen have been used to estimate apparent oxygen utilization (AOU) rates, in terms of carbon oxidation, of $5.8 - 20.6 \text{ g C m}^{-2} \text{ yr}^{-1}$.

Such AOUs imply "new" production rates of the same amount within the euphotic zone of the overlying water, yet total primary production measured under the ice pack of the Arctic basins is $< 5 \text{ g C m}^{-2} \text{ yr}^{-1}$, with high chlorophyll values of $\sim 1 \mu\text{g chl l}^{-1}$ encountered only during absences of snow cover (ENGLISH 1961). Over the area of the slopes and basins of the Arctic Ocean ($5.6 \times 10^{12} \text{ m}^2$), this AOU suggests a total carbon input of the order of $10^{14} \text{ g C yr}^{-1}$, an estimate confirmed by a separate analysis of the ice camp data on calcium carbonate dissolution (WALLACE et al 1987, ANDERSON et al 1987).

Import from the seasonally, ice-free Arctic shelves can only account for approximately one half of the AOU demand (WALSH et al 1988).

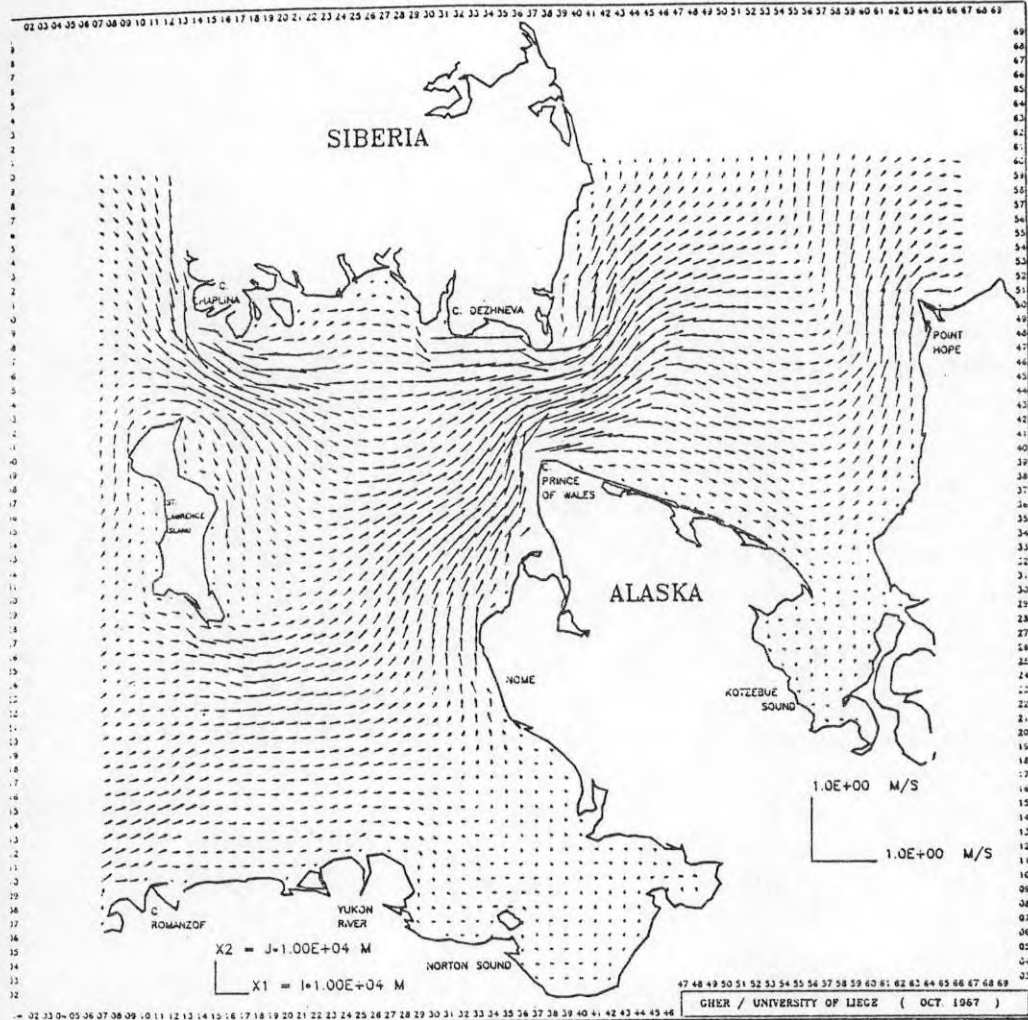


Fig. 2. : Northern Bering Sea General Summer Circulation (1.8 Sv through Bering Strait). Mean current field.

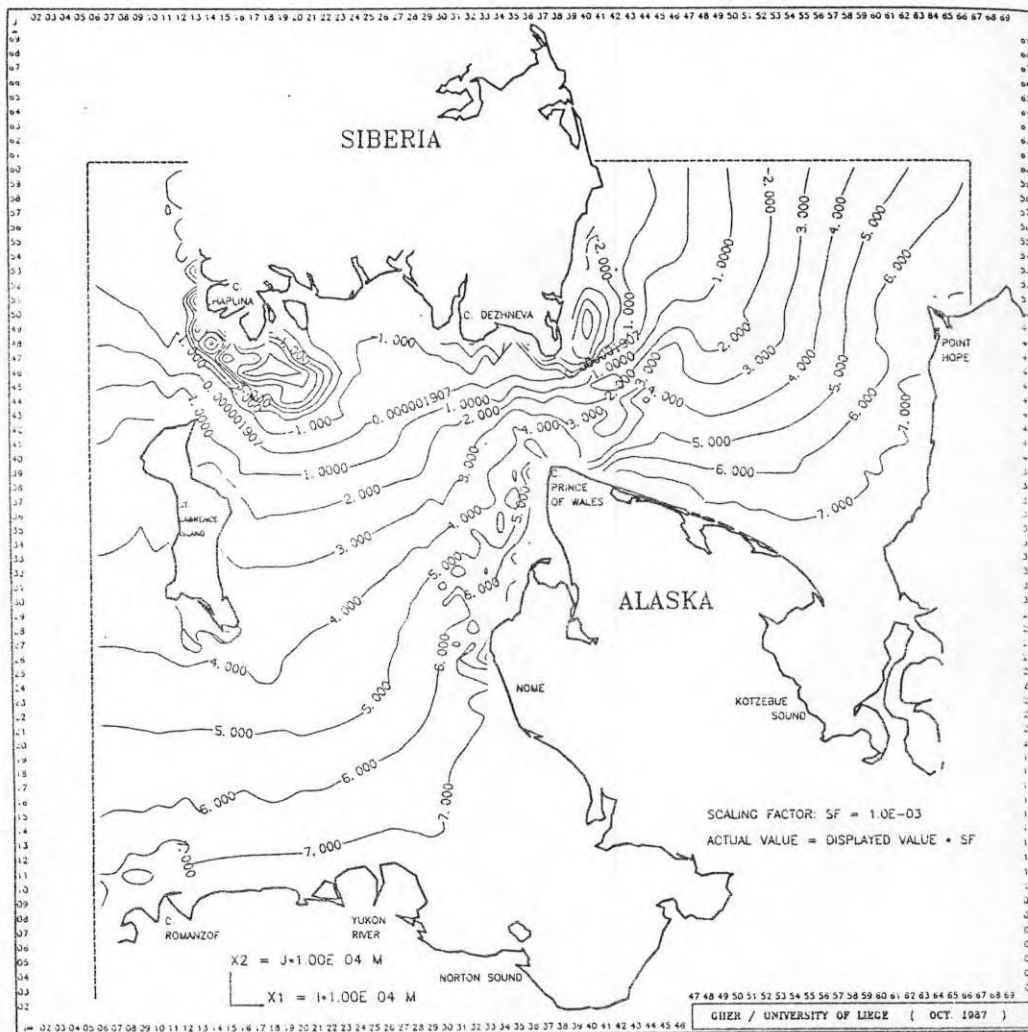


Fig. 3. : Northern Bering Sea General Summer Circulation
(1.8 Sv through Bering Strait).
Buoyancy field at 5 m depth.

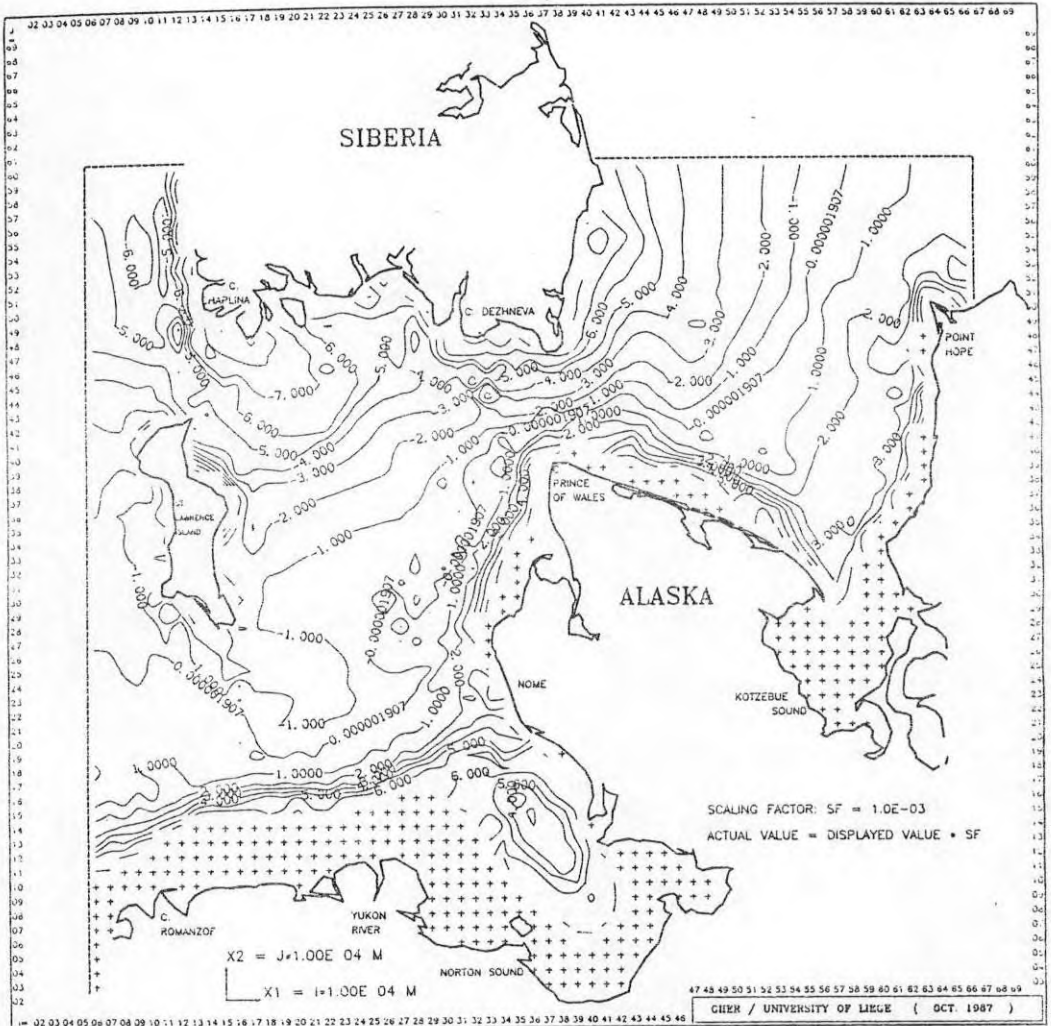


Fig. 4. : Northern Bering Sea General Summer Circulation
(1.8 Sv through Bering Strait).
Buoyancy field at 15 m depth.

The model of the Northern Bering Sea shows that organic matter fixed south of the Arctic Ocean and entrained north through Bering Strait, together with a concomitant import of "new" dissolved nitrogen to the Chuckchi and East Siberian shelves, can balance the carbon budgets of the polar basins.

Combining for instance the results of the hydrodynamic model with a simple model of primary production in the Northern Bering Sea, one estimates that the accumulated spring stock of nitrate in the Chuckchi/East Siberian Seas is of the order of $\sim 1.2 \text{ g at NO}_3 \text{ m}^{-2}$ (WALSH et al 1988). ϵ

This accumulated stock must be removed by protein synthesis, during a carbon production (with a C/N ratio of 6/1) of $\sim 10^2 \text{ g C m}^{-2} \text{ yr}^{-1}$ over the next year, to avoid buildup of nitrate stocks from one year to the next. The amount of local primary production, which is buried in the Chuckchi sediments, is unknown, and may constitute a significant sink (WALSH 1988). As an upper bound, however, this estimated new production, over the 10^{12} m^2 area of the Chuckchi/East Siberian shelves, amounts to $\sim 10^{14} \text{ g C yr}^{-1}$.

Export of this new production, minus a small shelf burial loss, could today satisfy most of the AOU demands of the Arctic basins.

The role of the Arctic Ocean and adjacent shelves in global carbon budgets has thus far been neglected. Changes in deep-water formation and/or a decline of marine primary production at high latitudes, perhaps as a results of increased light limitation on geological time scales, is suspected to have been an important component of atmospheric CO_2 rise, and thus global control of warming trends, begun 15,000 yr ago (KNOX and McELROY 1984). This and other simple 4-5 box models of a high latitude ecosystem, embedded within the global oceans (SARMIENTO and TOGGWEILER 1984, SIEGENTHALER and WENK 1984), ignore the Arctic Ocean, however, assuming that ice cover curtails gaseous exchange between atmosphere and ocean.

Circumvention of this ice cover constraint on CO_2 exchange occurs by primary production within open waters of the Bering/Chuckchi/East Siberian Seas, at the margins of the permanent ice pack in the Arctic Ocean. Satisfaction of present AOU demands lead to a brine-mediated, shelf input of $\sim 10^{14} \text{ g C yr}^{-1}$ to the halocline of the Eurasian and Canadian Basins, for eventual southward export via Fram Strait. In terms of anthropogenic

release of CO_2 of $\sim 5 \cdot 10^{15}$ g C yr^{-1} to the atmosphere, such a present Arctic sink is small. If projected greenhouse warmings of $> 2^\circ\text{C}$ were to melt most of the Arctic ice pack, however, a future organic carbon sink of at least $5 \cdot 10^{14}$ g C yr^{-1} might ensue here, for eventual sequestration within deep water formation in either the Atlantic or Arctic Oceans.

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BIOGEOCHEMICAL CYCLES IN ESTUARIES AND COASTAL ZONES
AND THEIR DISTURBANCES BY MAN

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ABSTRACT

Estuaries and coastal zones constitute main pathways from continents to oceans. Various biogeochemical processes may affect the behaviour and the fluxes of components between the two systems. These processes may also influence interactions between the ocean and the atmosphere by emission or uptake of gaseous products.

A particular effort has been devoted in Belgium to studies concerning the cycle of carbon, nutrients and trace elements, mainly in the Scheldt estuary, the Southern Bight of the North Sea, and in the Mediterranean sea along the Corsican coast. These cycles have been drastically affected by man's activities. A few examples are given to illustrate these studies.

INTRODUCTION

The scientific activities of the Belgian oceanographic teams have been mainly oriented towards the study of processes occurring in estuaries and coastal zones. These areas play a dominant role in the global biogeochemical cycles, because they are obligatory pathways between the continents and oceans for numerous dissolved and particulate components.

These areas are also the center where very active processes take place, affecting the fluxes between the terrestrial and oceanic ecosystems. They are generally areas of high population density and man's activities have usually drastically disturbed the fluxes or induced modifications of the processes occurring in these zones.

Many of the research activities of the Belgian Oceanographic community thus may be closely linked to global change which is the subject of the

present meeting. I shall show below with a few examples the diversity of the problems that may be encountered.

THE CARBON DIOXIDE PROBLEM

According to a set of data that I have selected, the present day fluxes of carbon dioxide to the atmosphere generated by combustion and deforestation is estimated to be approximately 6×10^9 T.C/y. The accumulation in the atmosphere as recorded by the increase in concentration of CO_2 represents only 2.6×10^9 T.C/y. This increase of concentration of CO_2 however, induces, a flux of CO_2 from the atmosphere to the ocean which represents an important sink for this gas. The flux to the ocean can be calculated by considering the basic properties of the inorganic carbonate system and the depth of the mixed layer of surface water which is able to equilibrate with the atmosphere (Broecker and Peng, 1982). The thickness of this layer has been estimated to be only 350 to 550 meters which gives roughly a flux of 1.9×10^9 T.C/y to the ocean. An example of this calculation is summarized in Table 1. This evaluation indicates that of the 6×10^9 T.C/y emitted to the atmosphere approximately one third is missing and cannot be accounted for. Some authors estimate that some of this CO_2 may be stored in land biomass, but another possibility is that the flux to the ocean has been underestimated. With respect to this problem, it must be recognized that coastal areas seldom have been taken explicitly into consideration in the global biogeochemical cycles used in the previous models. This is rather surprising because these areas are zones of intensive productivity and sedimentation, affecting to a large extent the organic and inorganic carbon cycle (Garrels and Mackenzie, 1981).

An extended study of the carbon cycle has been performed by Belgian teams in the Bay of Calvi (see also Frankignoul, (1988) this volume). Our laboratory was mainly involved in the study of the behaviour of calcium carbonates deposited in the bay of Calvi. If calcium carbonate present in sea water is allowed to react with CO_2 then the uptake capacity of the oceanic system can be significantly increased (see Table 1, column 3). However, this dissolution is only possible if the system becomes undersaturated with respect to the solid phase considered. This mechanism has never

been introduced in the climatic models for CO₂ because surface seawater is largely oversaturated with respect to pure calcite and aragonite. However, surface seawater is almost in equilibrium with respect to the dissolution-precipitation reaction affecting high Mg-calcites, which are abundant biogenic phases in coastal carbonate deposits. Thus increase of pCO₂ may induce dissolution of these carbonates in coastal environments.

Table 1 : Potential uptake of CO₂ by the ocean

| | 1 | 2 | 3 |
|-------------------|------------------|------------------|------------------|
| | pCO ₂ | pCO ₂ | pCO ₂ |
| Atmosphere | 300 ppm | 600 ppm | 600 ppm |
| <hr/> | | | |
| Total dissolved C | 2.00 mM/l | 2.11 mM/l | 2.76 mM/l |
| Total alkalinity | 2.26 meq/l | 2.26 meq/l | 2.81 meq/l |
| pH | 8.25 | 7.99 | 8.10 |
| max uptake | - | 30 % | 63 % |

Column 1 represents the composition of sea-water equilibrated with the atmosphere under the initial condition. Column 2 : the change induced in surface water owing to dissolution of CO₂ when the atmospheric CO₂ is doubled and column 3 : the same change if solid calcium carbonate is taken into account. The maximum uptake is evaluated considering a mixing depth of 550 m and the total surface area of the ocean. It is expressed as the percentage of total CO₂ emitted to the atmosphere.

The early diagenesis of Mg-calcites has been studied in detail in our laboratory (Moulin *et al.*, 1985). The composition of the pore waters of the bay of Calvi indicates that the total alkalinity is increasing with increasing total dissolved inorganic carbon (figure 1). The increase of inorganic carbon is partly due to the respiration of organic carbon, and it can be shown from a chemical equilibrium model that the resulting production of carbon dioxide must lead to undersaturation of the pore water environment with respect successively to magnesian calcite, aragonite and finally pure

calcite. Because sulfate reduction could not be detected in these sediments, the slope of 1 obtained in figure 1 suggests that each carbon released by respiration of organic C as carbonic acid is used to dissolve one carbonate according to the following reaction :

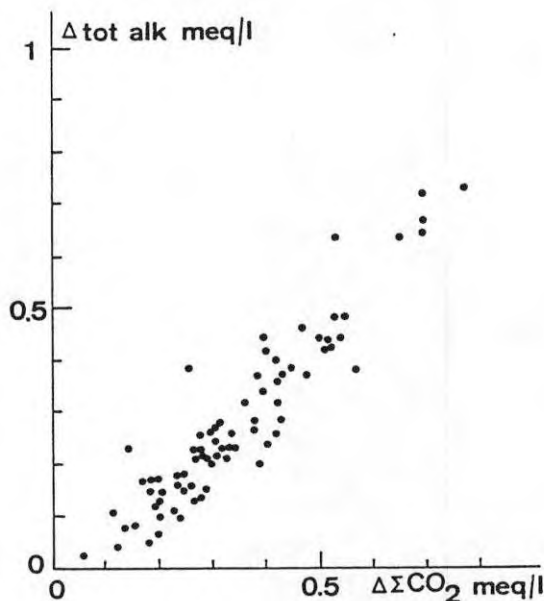
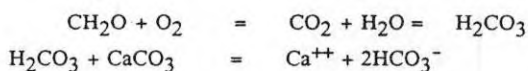


Figure 1. Increase of alkalinity as a function of increase of total inorganic carbon in the pore waters of the sediments of the Gulf of Calvi. The equation of the regression line is $\text{Alk} = 1.04 \times \Sigma\text{C} - 0.0074$

The dissolution reaction was also investigated using laboratory experiments in which sediments of the Bay of Calvi were enriched in easily degradable organic matter, in the presence of pure oxygen to maintain aerobic respiration and to avoid sulfate reduction. The results of these experiments (figure 2) indicate an increase of alkalinity corresponding to the increase of total dissolved C. One would expect this correspondance if each carbonic acid released by respiration is used to dissolve calcium carbonate. The increase of Ca^{++} in the pore water confirms this dissolution

reaction of calcium carbonate. The time scale of the experiments indicates that this reaction is very fast.

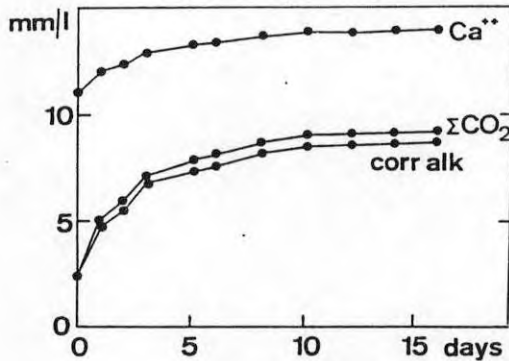


Figure 2. Evolution with time of the concentration of total C, alkalinity (corrected for NH_4^+) and Ca^{++} during the respiration of organic matter in a reactor containing sediments of the Bay of Calvi.

Another possible sink for carbon is the accumulation of organic matter in coastal marine sediments. The eutrophication of the coastal zone may induce an increased amount of organic carbon preserved in the sediments. A tentative global estimation of the carbon stored in coastal areas (Wollast and Billen 1981) indicates that although it is a small fraction of the organic carbon produced in the coastal zone, it may represent a significant fraction of the missing CO_2 .

THE NITROGEN AND PHOSPHORUS CYCLE

Among the strong interferences of man's activities with natural global biogeochemical cycles, the fluxes of dissolved N and P species in the aquatic environment are of special concern. On a global basis, the river fluxes of both dissolved N and P have been approximately doubled owing to anthropogenic input (Wollast, 1983).

However, there are large differences of the human impact in regions of

different development, and the problem is particularly critical in most European rivers, especially those discharging into the North Sea.

A tentative budget of nitrogen and phosphorus has been established for the Scheldt estuary (Wollast, 1982) and of organic carbon and nitrogen for the Southern Bight of the North Sea (Joiris *et al.*, 1982).

Among the consequences of the perturbations of the carbon and nutrient cycles, one should underline the intensive denitrification observed both in the estuary and in the coastal zone. Due to anaerobic conditions prevailing in a large part of the Scheldt estuary, approximately 1/3 of the total dissolved N input is lost to the atmosphere by denitrification.

Nitrification and denitrification are also responsible for the production of N_2O and its release to the atmosphere (figure 3).

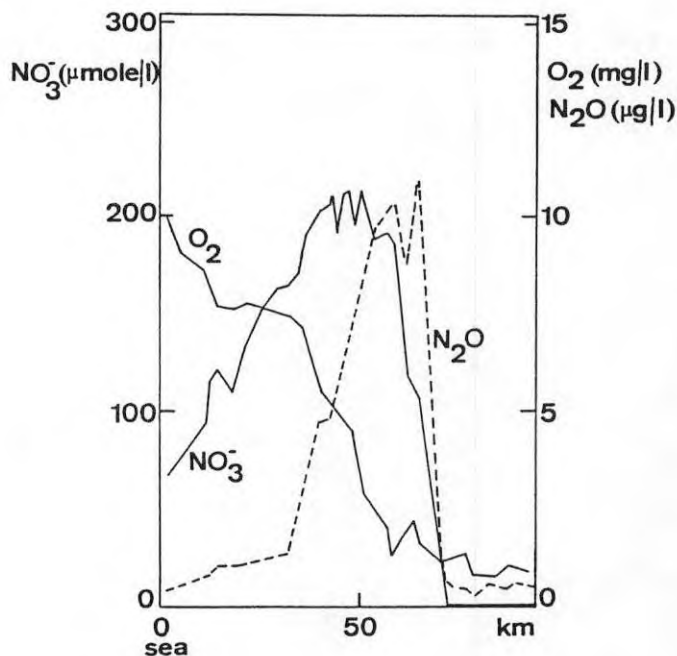


Figure 3. Longitudinal profile of concentration of O_2 , NO_3^- and N_2O in the Scheldt estuary. Distance to the sea mouth.

A similar process occurs in the sediments of the North Sea. Approximately 1/5 of the nitrogen initially deposited as organic N is lost by denitrifica-

tion and partially converted into N_2O . There is no doubt that the large supply of detrital organic matter to rivers or the production of new organic matter related to the eutrophication of aquatic systems has increased the denitrification process in those systems, and thus the fluxes of N_2O to the atmosphere.

Another important possible consequence of the large input of nutrient in the North Sea has been raised recently (Lancelot *et al.*, 1987) and concerns the occurrence of spectacular blooms of the planktonic alga *Phaeocystis*.

It is not only a major nuisance leading to the development of massive foam banks on shore, but also the peculiar physiology of this flagellate has strongly disturbed the structure and function of the North Sea biological population. *Phaeocystis* blooms may also have an impact on the atmosphere, because these organisms actively produce dimethyl sulfide which has in turn an important role in photochemical reactions occurring in the atmosphere.

TRACE METALS

Abnormally high concentrations of dissolved and particulate trace metals are also carried by river systems like the Rhine and the Scheldt (Wollast *et al.*, 1985). The atmospheric transport of these elements to the North Sea is significant (Dedeurwaerder *et al.*, 1985, Bruynseels *et al.*, 1985). Several laboratories in Belgium have joined their efforts to gain a better understanding of the transport and behaviour of trace metals in the estuarine and marine systems (Bayens *et al.*, 1985).

Many toxic trace elements have contaminated significantly the marine system and in particular semi-enclosed seas like the North Sea. The effects of these contaminations on the marine ecosystem are not well understood. These aspects are fundamental to a better understanding of global changes of our environment, and it must be hoped that similar studies will be expanded or started in other areas of the world.

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TRACE METAL FLUXES AT THE AIR-SEA INTERFACE

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Mercury: According to several global-scale mercury models, deposition rates of mercury to the sea (particulates and rain water) are balanced by the gaseous mercury flux to the atmosphere. However, Hg^0 is thermodynamically unstable in sea water. Recently, Kim and Fitzgerald (1986) found in upwelling water masses Hg^0 concentrations (although on the femtomolar level) supporting a positive flux to the atmosphere. In addition, the existence of Hg^0 was related to the biological activity. Therefore, Hg^0 determinations in the atmosphere and the watercolumn of open and coastal sea areas, the relation with the biological productivity and the development of adequate air-sea gas transfer models including also wave breaking (e.g. Kitaigorodskii and Donelan, 1984) will contribute strongly to the understanding of the biogeochemical cycle of mercury.

Lead, copper, zinc, cadmium, iron, manganese,...: Recently, dry and wet deposition models of trace and major metals have been developed and tested above the North Sea. With these models, annual deposition fluxes could be derived. Quite different fluxes were observed between the sea station and a nearby coastal station, mainly due to the lower precipitation above sea. It would be interesting to apply these models to other sea areas.

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IGBP: Panel on marine biosphere-atmosphere interactions

BARIUM BIOGEOCHEMISTRY IN THE OCEANIC WATERCOLUMN

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It is known that particulate barium (i.e. barite) occurrence in oceanic suspended matter is highly correlated with primary production (DehaIRS et al., 1980; Collier and Edmond, 1984; Dymond, 1986; Bishop, 1988). As a consequence of the much more conservative character of barite relative to particulate organic matter, barite in both sediments and sub-surface suspended matter has been recognized as a reliable tracer of past- and paleo- primary production.

Our group is presently involved in research concerning a better understanding of the mechanisms involved in the biologically mediated translocation of Ba from the dissolved to the particulate phase. This research includes the study of:

- (1) High resolution profiles in the upper part of the Western Mediterranean watercolumn for investigation of the short-term (days, weeks) variability of dissolved Ba contents resulting from intense atmospheric input events and the biologically controlled transfer to the deep sea.
- (2) The impact of advecting dissolved and particulate Ba, of Mediterranean origin, on the Ba cycling in the local N.E. Atlantic watercolumn.
- (3) Barite occurrence and organic matter mineralisation rates in the upper part of the Southern Ocean watercolumn, including the oxygen minimum layer, for understanding the pathways of Ba transfer and assessing relative importance of active biological barite production (precipitation in living cells) and passive production (precipitation in biogenic detritus).

Future Southern Ocean research by our group will focus on mineralisation rates of organic matter and the sub-surface barite flux, in order to document more thoroughly relative importance of recycled and new production.

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In situ monitoring of CO₂ seawater system including exchanges with the atmosphere and a seagrass bed.

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Abstract

The CO₂ chemistry in a water column above a seagrass bed has been monitored while were measured air-sea CO₂ exchanges and the diel carbon budget of the seagrasses. Measurements cover all seasons and show that even at their maxima, the two sinks of carbon constituted by the atmosphere and the seagrasses are negligible for the daily carbon budget of the water column. Moreover, the seasonal evolution of CO₂ parameters seems to especially depend on physical and hydrodynamic factors such as temperature and mixing of water masses.

Introduction

It is known that the understanding of the carbon cycle - and it's response to human induced perturbation in term of climatic change - needs as complete as possible in situ observations of the physical, chemical and biological processes involved. Such observations are aleatory and uneasy to interpret since the primary production in the euphotic zone is most often heterogeneously distributed in open ocean.

Results and discussion

The bay of Calvi (Corsica, France) is the site of a large POSIDONIA OCEANICA (L) DELILE seagrass bed which induces in the water column a regular daily variation of CO_2 - according to photosynthesis and respiration processes - the amplitude of which is function of the seasonal activity and reaches 50 moles l^{-1} of CO_2 (FRANKIGNOULLE and DISTECHE, 1984, FRANKIGNOULLE and BOUQUEGNEAU, 1987). During 24 campaigns, from 1980 to 1985 and covering the 4 seasons (FRANKIGNOULLE, submitted), those daily changes have been monitored together with, when possible, air-sea CO_2 exchanges measurements (using a direct method, see FRANKIGNOULLE, in press) and with the determination of the diel CO_2 budget of the seagrass bed (using a plexi-glas incubator, see FRANKIGNOULLE and BOUQUEGNEAU 1987). As a consequence of the partial CO_2 pressure of it's surface water, the Bay of Calvi is a source of CO_2 for the atmosphere with a maximum in June (about $2 \cdot 10^{-7}$ moles of $\text{CO}_2 \text{ m}^{-2} \text{ s}^{-1}$). The seagrass bed ecosystem serves as a sink of carbon from December to July and, due to the temperature and the senescence of the seagrasses, as a source of carbon from August to November. A maximum of activity is simultaneously observed in June, with a diel budget of about $30 \text{ mmoles of C m}^{-2} \text{ d}^{-1}$. By integrating on the ten meters water column, one can calculate that the diel loss of carbon in June is equal to 6 moles of $\text{CO}_2 \text{ l}^{-1} \text{ d}^{-1}$ (2 to the atmosphere and 4 to the seagrass bed). So, even at their maximum, these two net sinks have a negligible daily effect on the carbon budget of the water column.

The numerous obtained data also allow to discuss the seasonal evolution of the CO_2 seawater system in the Bay. As shown by figure 1, the pH values of the water have a very good seasonal reproducibility and regularly evolve between 7.9 in August to 8.25 in Winter. FRANKIGNOULLE and

DISTECHE (1984) have calculated that half of this variation results from a temperature effect (25 to 12°C.).

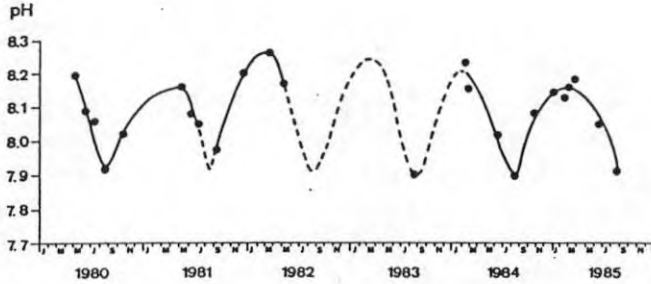


Figure 1. Evolution of pH in the Bay of Calvi (Corsica, France).

In order to correlate the second half of the pH changes to air-sea CO₂ exchanges and the seagrass bed activity, it would be necessary to know the residence time of the water in the Bay. Nevertheless, it is worth noticing while those processes are both net annual sinks of carbon in regard to the water column and in spite of their seasonal variations, those pH changes could be induced by a cyclic mixing of water masses, such as the one occurring in Autumn with the breakdown of the liguro-provencal front (HECQ et al., 1986). So, from figure 1, one can conclude :

- The water of the Bay is the site of large and regular pH seasonal variations which do not mainly depend on the sinks constituted by the atmosphere and the seagrass bed. Other parameters, such as currents, local upwellings, should be examined in this regard.

- The most acidic summer condition is interesting in term of solid carbonate phase dissolution. Indeed, KOCH (1985) has calculated that such a seawater is in equilibrium with 12% Mg magnesian calcite and since 30% Mg magnesian calcites are often found in coastal waters (WOLLAST and REINHARD-DERIE, 1977), the Bay appears to be an ideal site

to study the in situ carbonate precipitation and dissolution as a function of both physico-chemical and biological (type of skeleton, organic matrix,...see Poulicek et al., in press) conditions.

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Summary

During the last century, a general rise (1,5 mm/year) level is observed. This phenomenon explains the erosion of some beaches.

Our research in Calvi (Corsica) shows that the erosion (1,4 m/year) is mainly accelerated by the housing development on the fringing dunes and on the beach since 1980.

According to a recent survey carried out by the Commission for the Coastal Environment of the IGU (International Geographical Union) most of the world's beaches are undergoing retreat. To give an example, retreats at a rate of 4 m/year can be observed in the Gulf of Taranto (Italy) and the coasts of Languedoc (France). This phenomenon, which occurs even on desert coasts, can be explained mainly by a general rise in sea level which has amounted to 1,5 mm/year during the last century. We are dealing with the consequence of the increase in CO₂ content of the atmosphere caused by the use at an ever increasing rate of fossil fuels. This layer of CO₂ serves as a greenhouse for the globe, leading to a temperature rise which is responsible for the retreat of most glaciers but above all for the melting of the western part of the Antarctic ice sheet. According to BRUUN's law (SCHWARTZ & FISHER, 1980), any rise in sea level triggers the erosion of a beach which is in equilibrium and leads to its landward retreat.

Our research in the Bay of Calvi (Corsica) shows that its beach as a whole is undergoing erosion. Air photo analysis (5 flights between 1960 and 1985) makes it possible to establish that the beach is retreating at rates which locally attain 1,4m/yr.

As no recording tide gauges are available for this area we have to depend on data from the nearest stations, namely Marseille (1885-1978) and Genoa (1884-1981) where the rise in sea level is of the order of 1,3 mm/year (PIRAZZOLI, 1986).

But careful inspection of the site shows that the rise in the level of the Mediterranean cannot alone explain the observed coastal retreat. In fact the rates of retreat are greatest where human agency has accelerated the process.

Thus at Calvi the halt in the longshore movement of sediment (following the construction of a jetty), the extraction of pebbles from the beach itself, but above all housing development on the fringing dunes and even on the beach, have destroyed the fragile equilibrium between beach and dunes and accelerated erosion;

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Possible contribution to the International Geosphere-Biosphere
Programme by the University of Antwerp (UIA)
Research Group : Prof. R. Van Grieken

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The Micro- and Trace Analysis Center of the University of Antwerp (UIA) has specialized in the multi-element trace analysis and micro-characterization of environmental samples. In the context of marine research, much emphasis has been put on the study of particulate matter in estuaries and oceans, in the ocean surface microlayer and in polluted and remote marine air.

With respect to ocean-atmosphere interaction, we have first carried out radioactive tracer experiments to evaluate the enrichment of heavy metals in the process of marine aerosol formation resulting from air bubble breaking. Recently we have focussed on trace metal analysis, using X-ray spectrometry, and on single particle analyses of particulate matter in the sea surface microlayer and in rain water collected at sea, and of marine aerosols, using electron-probe X-ray microanalysis and laser microprobe mass analysis. It appeared e.g. that, during periods of calm sea and with the air masses coming from urban areas like Southern England, the aerosols over the North Sea consisted mostly of fly-ash particles, and, to a smaller extent, of seasalt particles enriched in nitrate and sulfate due to atmospheric reactions of airborne seasalt with pollution gases. Under clean air conditions, and in remote marine air, as in Antarctica, particles of sodium chloride, gypsum and soil dust, and mixed marine/terrestrial particles, were encountered.

Future research will focus on the atmospheric input of heavy metals into the North Sea. This will be studied using trace metal analyses and samplings of aerosols from an airplane, and of aerosols and rain water from research ships and land-based stations. The intention is to develop quantitative budgets for heavy metal deposition in the Southern Bight of the North Sea. It will be possible to exclude from the budget the airborne particles that are not of the first generation (i.e. terrestrial and anthropogenic particles that have been resuspended from the sea surface after an earlier deposition step); indeed, automatic single particle analysis will allow to identify these particles on the basis of their high concomitant seasalt content. Size analysis and vertical profiles will allow to calculate and confirm deposition velocities, as a function of the meteorological conditions.

In general, we are involved in the exchange of particulate matter between the ocean and the atmosphere, and also in the atmospheric reactions of marine aerosols with pollutant gases.

Some relevant publications that deal directly with marine aerosols and ocean/atmosphere transfer

- Trace metal fractionation effects between sea water and aerosols from bursting bubbles

R.E. Van Grieken, T.B. Johansson, J.W. Winchester,
J. Recherches Atmosphériques VIII (1974) 611-621

- PIXE analysis of aerosol samples collected over the Atlantic ocean

W. Maenhaut, A. Selen, P. Van Espen, R. Van Grieken, J.W. Winchester,
Nucl. Instr. Methods, 181 (1981) 399-405

- Characterization of the atmospheric aerosol over the Eastern Equatorial Pacific

W. Maenhaut, H. Raemdonck, A. Selen, R. Van Grieken, J.W. Winchester,
J. Geophys. Res. 88 (1983) 5353-5364

- Characterization of individual particle types in coastal air by laser microprobe mass analysis

F. Bruynseels, H. Storms, T. Tavares, R. Van Grieken,
Intern. J. Envir. Anal. Chem., 23 (1985) 1-14

- Direct detection of sulfate and nitrate layers on sampled marine aerosols by laser microprobe mass analysis

Atmos. Environ. 19 (1985) 1969-1970

- Internal mixture of sea salt, silicates and excess sulfate in marine aerosols

M.O. Andreae, R.J. Charlson, F. Bruynseels, H. Storms, R. Van Grieken,
Science, 232 (1986) 1620-1623

- Nitric acid interaction with marine aerosols sampled by impaction

Ph. Otten, F. Bruynseels, R. Van Grieken,
Bull. Soc. Chim. Belges 95 (1986) 447-453

- Study of inorganic ammonium compounds in individual marine aerosol particles by laser microprobe mass spectrometry

Ph. Otten, F. Bruynseels, R. Van Grieken,
Anal. Chim. Acta 195 (1987) 117-124

- Characterization of North Sea aerosols based on individual particle analyses

F. Bruynseels, H. Storms, R. Van Grieken, L. Van der Auwera,
Atmos. Environ., in press

- Methane sulfonic acid and seasalt sulfate determination in single marine aerosol particles

L. Kolaitis, F. Bruynseels, R. Van Grieken, M.O. Andreae,
Environ. Sci. and Technol., submitted

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Since the foundation of the Universitaire Instelling Antwerpen, the Department of Chemistry has put much emphasis on analytical chemistry and its applications in environmental research. As far as budgets and manpower are concerned, the Center for Micro- and Trace Analysis represents approximately half of the Chemistry Department. In the research groups of Prof. Adams and Prof. Gijbels, most work is oriented towards the use of micro- and trace analysis in technology (micro-electronics, pure metals) and geology (thermal waters, volcanic rocks) and towards organometallic compounds in the environment. The research group of Prof. Van Grieken includes approximately 25 full-time researchers, who work exclusively on the applications of micro- and trace analysis to problems of acid rain, air pollution effects on historical buildings, and, especially, chemical oceanography.

The Center for Micro- and Trace Analysis disposes of a diverse, sophisticated and modern equipment infrastructure. Available for inorganic analysis are :

- X-ray fluorescence (XRF) with energy-dispersive detection and tube-excitation : particularly suitable for simultaneous detection of a dozen elements at the ppm-level; especially in solid samples like sediments and filters loaded with aerosols and aqueous suspensions,
- neutron activation analysis (NAA), for very sensitive determinations of various specific elements in diverse samples,
- spark source mass spectrometry (SSMS) for panoramic determination of, in principle, all elements in solid conductive materials,
- atomic absorption spectrometry (AAS), in versions with electrothermal and flame-atomization, for simple determination of individual elements. One apparatus is directly coupled to a gas chromatography, as a detector, for the study of volatile organometallic compounds,
- ion chromatography (IC) for easy determinations of inorganic anions and cations, and organic acids in solution,
- anodic stripping voltammetry (ASV) for sensitive measurements of e.g. lead, cadmium, zinc and copper in water samples.
- spectrophotometry, electrochemical and conventional analytical methods

During recent years, the laboratory has specialized in the analysis of surfaces and of samples with microscopic dimensions, like individual aerosol and suspension-particles. For this purpose, the following techniques are invoked :

- electron microprobe analysis (EMPA), in a very automated version, which yields not only morphological but also composition information, e.g. for individual particles in the micrometer size range,

- laser microprobe mass analysis (LAMMA), which allows, with a spatial resolution of one micrometer, semi-quantitative determinations at the ppm-level in addition to inorganic speciation, organic fingerprinting and characterization of particle surfaces.
- secondary ion mass spectrometry (SIMS), especially for the measurement of depth-profiles of element concentrations with nanometer-resolution,
- electron energy loss spectroscopy (EELS), a new technique which offers good perspectives for light elements in submicrometer objects.

Additionally, apparatus is available for experiments with radioactive tracers.

Especially XRF, IC, EPMA and LAMMA have hitherto been used for chemical oceanography. Because of the available apparatus and the experience of other Belgian universities with respect to the dissolved phase, special attention is paid to the study of particulate material, both in the water column and the surface micro layer of the sea and in marine air, both in polluted and remote areas.

The research projects concerning chemical oceanography, and financed by the U.S. National Geographic Society, NASA, EEC, Rijkswaterstaat of The Netherlands and the Belgian Ministries of Science Policy and Public Health can be summarized as follows :

- Influence on the chemistry of seawater of the dumping of titanium dioxide and alkaline aluminium waste
- Kinetics and equilibria of the adsorption of cadmium on particulate material, as a function of salinity and temperature
- Characterization of individual particles in the estuaries of the Scheldt, Ems, Tamar, Gironde and Rhone (in collaboration with the Netherlands Institute for Sea Research, Texel, The Netherlands, and the Environmental Research Institute, Plymouth, England)
- Characterization of individual particles as a function of location and depth in the North Sea, Baltic Sea and the Angola basin (in collaboration with e.g. the Institute for Marine Research, Rostock, DDR)
- Study of the interaction of seasalt aerosols with acid and basic atmospheric gases
- Advanced characterization of individual aerosol particles in air above the North Sea, remoted areas in the Atlantic Ocean and the Pacific Ocean, and Antarctic region (in collaboration with the Royal Meteorological Institute, Ukkel, Belgium, Florida State University, Tallahassee, USA and the University of Sao Paulo, Brasil)
- Study of atmospheric deposition of heavy metals to the North Sea, via sampling of aerosols from research vessels and airplanes, and of rainwater
- Study of heavy metal load of sediments from the North Sea and the Scheldt-estuary as a function of place and time.

Since the foundation of the UIA, the researchgroup has published approximately 200 articles in international scientific journals, all on the methodology of micro- and trace analysis and their application to environmental problems. Approximately 40 of these are directly related to chemical oceanography and marine pollution.