Biogeochemistry of nutrients, metals and organic micropollutants to the North Sea

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Air-sea exchange of nutrients and inorganic micropollutants above the North Sea

The North Sea suffers already many years from intensified and extended algae blooming periods. The intensity and duration of these blooms can be dependent on the availability of micronutrients such as many trace elements and macronutrients such as nitrogen and phosphorus compounds.

In case of the North Sea, the water is nitrogen limited. Main input sources of these nitrogen compounds are rivers and the atmosphere. The contribution of the rivers depends in many ways on the estuarine removal processes and sea currents, with negative influences generally limited to the coastal zones. The intermittency of atmospheric inputs means that while they may not dominate the overall cycle of marine productivity, large atmospheric nutrient input (in most cases wet deposition) may result in short term blooms of algae under certain circumstances. Especially during summer, when the central part of the North Sea is somewhat isolated from the North Atlantic inflow and the Channel and when the run-off from the rivers is at a minimum, the atmospheric input gains importance and can be the exclusive source for nutrients

The different nitrate and ammonium compounds are the most important inorganic atmospheric components, due to their very high concentrations above The Netherlands and Flanders (the highest concentrations of ammonia in the world) and due to their fast uptake by the phytoplankton. The different ammonium and nitrate compounds are very stable in the air mass and can be transported over hundreds of kilometers.

Intensive sampling campaigns on the Research Vessel Belgica, at Knokke-Heist and at Adinkerke show a clear seasonal influence and wind-direction dependence. The ammonia concentration is strongly correlated with the daily maximum temperatures and it is removed very quickly by precipitation. The concentrations of the nitrate and ammonium compounds are the highest with winds coming from the northeast and southwest, while the lowest concentrations are coming from the northwest.

Different trace elements and toxic metals have also been analyzed and it was concluded that after the enormous decrease in the various heavy metal concentrations around the mid 80’s, the concentrations further decreased or stabilized.

Mathematical models are used to calculate the concentrations and wet and dry fluxes for nutrients above the North Sea, using the new input data from the two coastal sampling points (ACDEP, Atmospheric and Chemical DEPosition model, National Environmental Institute, Denmark). This model visualizes the pollution of the different compounds on a 16.7 x 16.7 km grid over the entire North Sea.

The combination of different analysis techniques (including Thin Window-Electron Probe Micro Analysis and Ion Chromatography) delivers additional information concerning the composition and quantity of the different particles. Comparable size fractions are quantified with the bulk analysis technique and interpreted with the individual particle analysis technique, resulting in a more detailed interpretation of the pollution.

Biogeochemistry of nutrients and trace metals in the North Sea

The aim of this subproject was to quantify and qualify the nitrogen cycle (nutrient concentrations and nitrogen uptake) and to study the biogeochemical behaviour of trace metals.

The study area is the Southern Bight of the North Sea, the Scheldt estuary, the Channel and the Central North Sea, as the North Sea can be considered as one of the most productive areas on earth, and since it is strongly influenced by anthropogenic supplies of nutrients as well as contaminants.

To better understand the nitrogen cycle, pools and processes were assessed and models were developed. The spatio-temporal distribution of nitrate, nitrite, ammonia, urea, phosphate, silicate, dissolved organic nitrogen, particulate organic nitrogen and particulate organic carbon was studied. Most of the time, dissolved organic nitrogen was the dominant pool, while ammonia was often almost negligible. This DON pool can account for up to 95% of the total dissolved nitrogen pool. Nutrient pools are reconstituted during winter and therefore higher concentrations in the beginning of spring compared to the other seasons are found for most of the nutrients. The Scheldt estuary is characterized by high nutrient concentrations and they decrease with increasing salinity. Concerning the North Sea, the low salinity zone of the Belgian coastal waters is strongly influenced by the Scheldt outflow and coastal inputs, leading to significantly higher nutrient pools compared to the high salinity zone. The Channel as well as the more central part of the North Sea is marked by relatively lower pools in nutrients.

The uptake rates of inorganic nitrogen compounds was measured through the addition of N^{15}-spikes (nitrate, ammonia and urea) and recently also C^{13} to the natural samples.

Although ammonium is the preferred nutrient for uptake, nitrate uptake rates are much higher than these of ammonium (especially in spring) since the ammonium pool is often negligible.

Highest ammonium uptake rates are found at the end of the summer as ammonium resulting from the mineralisation of the PN is available. Urea uptake is always very low and is in the same order as the ammonium uptake. The modellisation of the N^{15} incubation experiments allowed us to take the effect of transformation processes (e.g. nitrification, denitrification) and losses (e.g. adsorption onto the container wall) into account.

For trace elements, a subdivision can be made. First of all, the trace metals Cu, Ni, Zn, Cd and Pb were analyzed in the dissolved phase of the water column, parallel to determinations of these metals in the particulate fraction (by ULB), for calculation of distribution coefficients (K_ds). Secondly, the presence of some specifically toxic metals, mercury and arsenic, in the aquatic environment was investigated. Both elements are present in a variety of chemical species in natural aquatic systems, a significant fraction of arsenic even being of natural origin. Some of these compounds are many orders of magnitude more toxic than their homologues. Therefore, additionally to total assessments in the dissolved and particulate fraction of the water column, speciation techniques were developed and applied. Relationships with parameters such as Fe, Mn, phosphate, chlorofyll-a and dissolved oxygen were established in order to elucidate the biogeochemical cycling of these elements. Also, 25 species of sea fish and shellfish were subject to speciation for Hg and As. The fractions monomethylmercury, inorganic arsenic, methylated organoarsenicals and arsenobetaine were assessed, to investigate potential toxic effects of seafood consumption for humans. Both elements appeared to be bioaccumulated and metabolized by marine organisms, but evidence for biomagnification along the foodchain was found only for Hg.

Biogeochemistry of organic micropollutants to the North Sea

A wide range of organic micropollutants, e.g., polychlorobiphenyls, polycyclic aromatic hydrocarbons, chlorocyclohexanes and volatile organic compounds (VOCs), are ubiquitous in the marine environment. All have been shown to affect a number of biological and environmental systems. According to the Third International Conference on the Protection of the North Sea, far less information regarding inputs and/or concentration data are available for VOCs as compared to other organic pollutants. A number of VOCs have been classified by OSPARCOM (Oslo and Paris Comissions) as chemicals for priority action and some have been proposed by the Marine Chemistry Working Group as chemical parameters in the Water Framework Directive. This part of the project focused on the presence and behaviour of 27 VOCs, i.e., chlorinated alkanes and alkenes, monocyclic aromatic hydrocarbons and chlorinated monocyclic aromatic hydrocarbons, in the marine environment. The organic compounds were selected from priority lists published at the Third International Conference on the Protection of the North Sea.

Analytical methods allowing the determination of target VOCs in marine water and air at trace level concentrations were evaluated. Purge-and-trap combined with high resolution gas chromatography-mass spectrometry was evaluated for the simultaneous determination of 27 VOCs in marine water samples at ng l_{-1} concentration level. The reliability and performance of the analytical method were checked by determining limits of detection, precision and accuracy at concentrations of 26-67 ng VOC l_{-1}. Quality assurance and quality control were considered of paramount importance. 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. The long time reliability was also assessed by participation to inter-laboratory exercises proposed by QUASIMEME.

Concentration levels of 27 VOCs were determined in samples taken at the Southern North Sea, the Belgian Continental Platform, the Channel and the Scheldt estuary over a three-year study period (1998-2001). Chlorinated C_1-C_3 alkanes and alkenes were mostly found at very low concentration levels in marine water samples, rarely exceeding 5 ng l_{-1}. Dichloromethane, chloroform, trichloroethene and tetrachloroethene however were often found at concentrations from 100-1000 ng l_{-1}. Concentrations of 10 µg l_{-1} were even observed for dichloromethane. BTEX-compounds and chlorobenzene were present in most samples at concentrations $<$ 50 ng l_1. Toluene often exhibited higher concentration levels (100-300 ng l_{-1}). Dichlorobenzenes, trichlorobenzenes and hexachloro-1,3-butadiene were hardly detected. All target VOCs were found in samples taken along the Scheldt estuary. Chlorinated alkanes and alkenes showed increasing concentrations levels towards Antwerp, up to 1 µg 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, trichlorobenzenes and hexachloro-1,3-

butadiene were detected in ±50% of the samples. Concentration levels rarely exceeded a few ng l^{-1}, except for 1,4-dichlorobenzene with concentrations up to 100 ng l^{-1}.

Besides water sampling and analysis, a recently developed method for the sampling and analysis of volatile organic compounds in air has been evaluated. The system is based on the enrichment of analytes in tetraethylene glycol dimethylether or tetraglyme, a water-soluble organic liquid. The subsequent analysis consists of dispersion of a sample aliquot in water followed by purge-and-trap/gas chromatography. Physical-chemical data were investigated for ten target VOCs providing information on the possibilities and limitations of the tetraglyme method. From these data it was clear that the tetraglyme method could hardly cope with existing sampling tools, e.g., adsorbent trapping, for VOC measurements in remote or ambient air masses.

Biogeochemical behaviour of particulate trace elements in the North Sea

The main objective of the ULB contribution to this project is to gain a better understanding of the biogeochemical behaviour of trace metals in the Southern bight of the North sea, with a special emphasis on the particulate phase. Three different but linked aspects have been investigated:

1. Evaluation of the spatial and temporal variations of the composition of the suspended matter in terms of major (Na, K, Ca, Mg, Fe, Si, Al, C org, C inorg) and minor elements (Mn, Cr, Ni, Co, Cu, Zn, Cd, Pb) in order to elucidate their origin; special attention has been devoted to the role of phytoplankton in the transfer of trace elements from the dissolved to the particulate phase during photosynthesis;
2. Investigation of the mobility and thus the potential bio-availability of the particulate trace metals by performing batch titration experiments of suspended matter by a strong acid (1N HCl);
3. Study of the rate of uptake of radionuclides by suspended matter during incubation experiments of natural samples carried out under conditions close to the natural ones.

Concerning the distribution of trace metals between the dissolved and the particulate phase, six cruises covering around 15 stations were performed during the present study. The most interesting results concern the influence of the primary production on the concentration of trace metals in the particles. It is well known that many trace elements are important oligo-elements actively involved in the primary production process and are thus removed from the aqueous solutions during photosynthesis. However, their relative uptake versus organic carbon production by phytoplankton is such that the concentration of the trace elements tends to decrease, due to the high production of organic matter. Furthermore it has been observed during our study that the concentration of particulate metals in the solid phase decrease almost linearly with the organic C content. This has allow to calculate a mean potential trace metal composition of the phytoplankton in the Southern Bight of the North Sea during the spring bloom. Concerning the spatial distribution of particulate trace metals for the same area at a given season, our results show clearly that there are several distinct sources of particulate matter which can be identified unambiguously by their trace metal content.

We have on the other hand, developed a new method in order to gain a better understanding of the speciation of the particulate trace metals. This method consists in titrating a suspension of the particles, collected by centrifugation, in pure water by 1N HCl.

After each acidic spike, the suspension is allowed to react during 16 hours, after which the pH is recorded and the aqueous phase is analysed for the dissolved major and minor elements. It becomes then possible to identify the association of the trace metals with various mineral phases. This method also allows to evaluate a scale of progressive availability of the metals during acidification of the environment.

During the titration experiment, it was possible to identify successively the dissolution of the following mineralogical components: Ca, Mg and Mn carbonates, labile silicates and Fe, Mn oxy-hydroxides. The trace metals were released in the following order: Cd, Co, Ni, Cu, Pb and Co.

Finally, the use of radionuclides (54Mn, 63Ni, 6 5Zn, 109Cd) during incubation experiments of water samples, allowed us to elucidate the mechanism and to quantify the rate of transfer of the elements considered, from the dissolved to the particulate phase. The use of specific inhibitors of the photosynthesis (DCMU) or of antibiotics during the incubation experiments gave us the ability to identify the fraction of the uptake of the trace metals due to phytoplankton or to bacteria. The use of variable light conditions during the incubation experiments were also conducted to detect the potential effect of light intensity on the process. In addition, kinetic experiments were used to evaluate the initial step of the uptake which is due to isotopic equilibration of the solid. The reversibility of the trace metal uptake has been tested by leaching the labelled solid with fresh sea-water or by using classical sequential extraction experiments.