ATMOSPHERIC INPUTS OF NITROGEN COMPOUNDS INTO THE NORTH SEA: INITIAL RESULTS FROM THE ANICE PROJECT

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INTRODUCTION

The productivity of marine planktonic ecosystems is generally considered to be limited by the availability of nitrogen (Kronvang et al., 1993). Terrestrial inputs of nitrogen are often dominated by riverine transport, especially in the winter (Sanders et al., 1997). However, the atmospheric contribution to the total land based nitrogen input has been reported to be in the order of 30% for the total North Sea (North Sea Task Force, 1993). The atmospheric nitrogen load is directly available for algae growth, which makes this contribution more significant because a large fraction of the river run off contributes nitrogen fixed to biological material and hence is not directly available.

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 impacts of increased nutrient additions to the coastal area, the full magnitude and seasonality of nutrient inputs must be described, including the effect of extreme events such as high atmospheric deposition episodes (Spokes et al., 1993; 2000) which, while small in overall annual budget terms, may be able to trigger algal blooms under nutrient depleted conditions in summer and early autumn. These blooms will be followed by oxygen depletion due to decay of the algae when the growth season is over.

Estimates of nitrogen inputs are often based on measurements over land and sometimes on measurements at open sea. Coastal effects on the total nitrogen depositions are included in a simplistic way, if at all. However, the largest changes in both the physical and chemical properties of an air mass advected from land over sea, and therefore also in the resulting processes, are expected in coastal regions. Since continental sources of atmospheric nitrogen species dominate, sharp gradients in concentrations and associated fluxes are expected across the coastal zone. Reduction of ammonia concentrations in the German Bight by a factor of 4 after 70 km transport out to the sea has been observed (Plate et al., 1995).

The sudden change in the surface properties at the coastline leads to a non-uniform situation. As a consequence, the horizontal homogeneity condition on which current descriptions of the boundary layer physics is based, does not strictly apply. Because the physical processes involved in gas exchange are related to the same physical processes governing momentum exchange, similarity in the range dependent patterns of momentum and gas fluxes can be anticipated. However, while momentum and heat fluxes can generally be regarded as "conservative quantities," gaseous nitrogen compounds are often so reactive that source and sink terms must be taken into account to evaluate their fluxes. Source and sink terms depend on governing chemical reactions, which in turn are dependent on temperature, humidity, and the time scales compared to the horizontal and vertical mixing rates.

The ANICE project

Atmospheric Nitrogen Inputs into the Coastal Ecosystem are addressed in the ANICE project (De Leeuw, 1998). ANICE focuses on quantifying the deposition of atmospheric inputs of nitrogen compounds (HNO_3, NO_3^-, NH_3 and NH_4^+) into the sea, both near the coast and in open water, and the governing processes. The Southern North Sea is studied as a prototype. Because the physical and chemical processes are described, as opposed to empirical relations, the results can also be applied to other regional seas like the Mediterranean, the North Atlantic continental shelf area and the Baltic.

The *aim* of the ANICE project is to improve transport-chemistry models that estimate nitrogen deposition to the sea. To achieve this, experimental and modelling work is being conducted which aims to improve understanding of the processes involved in the chemical transformation, transport and deposition of atmospheric nitrogen compounds, with emphasis on the influence of coastal zone processes. Most current models use grids that are too coarse to describe the governing processes with sufficient accuracy, particularly in coastal regions.

Experimental work within ANICE consists of a long-term observational program using scientific equipment mounted on commercial ferries, complemented by two intensive field experiments . The latter focus on process studies and provide information on the concentrations in air and water and their spatial and temporal variability. The field experiments were undertaken in June 1998 and in August 1999. The ferry measurements started in May 1998 and lasted about 1.5 years.

An interesting feature of the ANICE project is the use of two atmospheric chemistry transport models, ACDEP (Hertel et al., 1995) and METRAS (Schlünzen, 1990; Schlünzen et al., 1996). An aerosol module is developed for ACDEP, based on a 1-D model for the coastal zone (Vignati, 1999), to account for emission, diffusion and deposition, as well as heterogeneous processes. ACDEP is used to estimate atmospheric inputs of nitrogen to the whole North Sea, integrated over periods varying from 6 hours to a year. ACDEP also provides the ‘large’ scale lateral boundary conditions for the calculations in the coastal model domain using METRAS. METRAS in turn, will be used for studying scenarios for specific days, to calculate the atmospheric nitrogen input to coastal waters with a high resolution in space (some 100 meters) and time (minutes). METRAS is coupled with the Chemical Transport Model (MECTM) which includes the complex RACM gas phase chemistry (Stockwell et al., 1997) and the aerosol model SEMA (Von Salzen and Schlünzen, 1999a, 1999b, 2000).

The combined modelling effort is expected to lead to a major improvement in the estimate of atmospheric inputs into the North Sea, which can subsequently be used in effect studies. The models are complementary because of the different scales, the different mixing schemes and the different initialisations.

RESULTS AND DISCUSSION

The initial results of the ANICE project (De Leeuw et al., 2000) support the primary hypothesis on the importance of coastal effects on nitrogen inputs to the regional seas. Gaseous nitrogen compounds are primarily produced over land and very high concentrations were observed close to the coast in off-shore winds. The ANICE experimental results indicate that these concentrations decrease rapidly with increasing fetch resulting in a reduction to 'background' levels when the air mass is transported across the North Sea, over a distance of only about 200 km. The gases are highly soluble and are therefore either directly deposited to the surface or taken up by aerosols where they are accommodated through chemical reactions. The reactions with aerosols obviously affect the gaseous air-sea fluxes as evidenced from the shape of the gas concentration profiles (Geernaert et al., 1998). The aerosol dry deposition flux is in part due to different physical processes and depends on particle size, and thus the dry deposition velocities for gases and particulate nitrogen compounds are different. Moreover, the direct gas fluxes are determined by the partial pressure difference of the gaseous species in the water and in the air directly above the water, both of which have been observed during the ANICE experiments to vary strongly in both space and time. In model calculations such variations, especially those in the sea, are usually not taken into account. Examples presented in De Leeuw et al. (2000) show that neglecting spatial variations may lead to a significant overestimation of dry deposition of NH_3.

Both NH_3 and HNO_3 play a role in heterogeneous chemistry, as discussed in the introduction. In particular, HNO_3 reacts directly with sea spray aerosol. Current atmospheric chemistry transport models do not include such reactions. Work is underway in several groups to implement heterogeneous chemistry involving HNO_3. In ANICE this occurs through the implementation of heterogeneous reaction schemes in both METRAS, using the SEMA model, and in ACDEP using a 1-D model. The latter is in part based on the model of Vignati (1999), which was applied to show the large influence of the reaction between nitric acid and sea spray on both the concentrations and the gradients of HNO_3, over a fetch of only 25 km. The strong variations imply that a coarse grid model will not be able to correctly predict the effect of coastal processes at very short fetches on the nitrogen input, unless these processes are included through a coastal sub-grid or a proper parameterisation.

The experimental efforts included simultaneous measurements of bubbles generated in the water by breaking waves and aerosols just above the water surface. The comparison of the respective size distributions leads to conclusions on the bubble-mediated aerosol source function and the amount of fresh sea spray available for heterogeneous reactions. These small scale measurements are supported by lidar measurements on atmospheric boundary layer properties that influence the atmospheric mixing of both gases and aerosols. The lidar measurements also reveal aerosol plumes generated by waves breaking at the sea surface or in the surf zone. In off-shore winds, plumes of surf generated sea spray aerosol were observed to be transported out over the sea and were visible over distances of at least 5 km, in good agreement with model calculations using CAT (Vignati et al., 2000). Hence, also in off-shore wind large amounts of sea spray (sea spray aerosol concentrations may be enhanced by 1-2 orders of magnitude; De Leeuw et al, 2000) are available for heterogeneous reactions, at least in the study area along the Dutch coast. Other experimental efforts included micro-meteorological studies on fluxes of NH_3, HNO_3, CO_2, as well as momentum, heat and water vapour, which are used in studies on air-sea exchange processes. The modelling effort includes the construction of a model that accounts for effects of non-homogeneity across the coast line (Geernaert and Astrup, 1999).

Effects on regional scales were addressed through co-ordinated measurements at the WAO site on the UK coast and at MPN near the Dutch coast, as well as through ferry measurements. The large concentration differences measured on the ferry during different periods shows the necessity of long term measurements to establish a representative data set on nitrogen inputs into the southern North Sea. The analysis of cases with connecting air flow between the WAO site and MPN shows the change in aerosol particle size distributions and chemical properties, see Figure 1. The 16 June case was modelled using the SEMA box model in a Lagrangian sense. The encouraging results give confidence on the use of SEMA in METRAS for fine gritted estimates of the nitrogen inputs into the southern part of the North Sea. METRAS prognostically calculates the three-dimensional fields of wind, temperature, humidity, cloud and rain water content and derives exchange coefficients from first order closure theory. This scheme has been thoroughly tested with favourable results. Finally, the ACDEP model extended with a detailed aerosol module will be used to calculate the nitrogen inputs for the whole North Sea. Computed annual mean ammonia concentrations, reflecting mainly the emission areas over the Netherlands and Great Britain, are qualitatively in reasonable agreement with the 1999 ferry measurements. Generally the concentrations range between 0.1 and 1 μg m^{-3}, with highest concentrations in the coastal regions of England and the Netherlands/ Germany. The annual nitrogen deposition calculated from the loads ranges between 0.3 and 1.3 tonnes N km^{-2}.

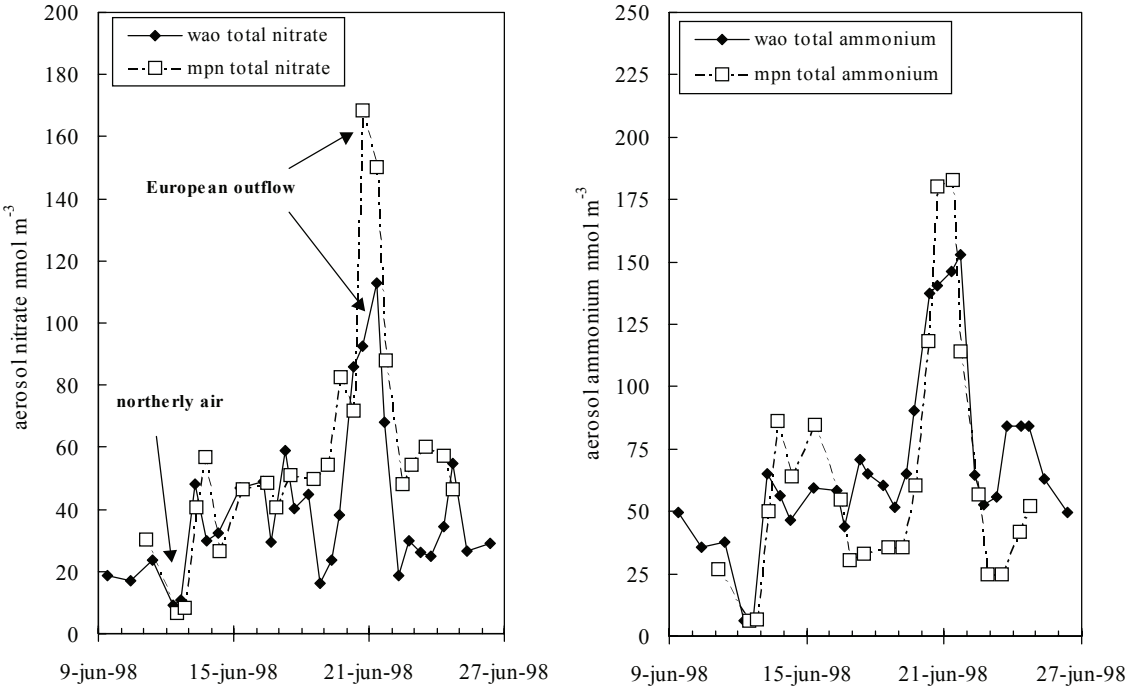

Figure 1. Comparison of aerosol nitrate and ammonium concentrations at WAO and MPN during the 1998 ANICE field campaign. Connecting air flow was observed on 16 June (WAO to MPN) and on 20-21 June (MPN to WAO). Effects on aerosol composition are evident, e.g. from the significant reduction of both nitrate and ammonium between MPN and WAO.

The updated atmospheric chemistry transport models will be used for the assessment of the impact of atmospheric nitrogen on coastal ecosystems. Both episodic and chronic nitrogen inputs will be considered and the assessment will be based on comparisons of phytoplankton nitrogen requirements, other external nitrogen inputs to the area of interest to ANICE and the direct nitrogen fluxes provided by ANICE.

In the study presented above, only inorganic nitrogen has been considered. A limited effort is made in the ANICE project to characterise DON in rain and in aerosols. Dissolved organic nitrogen species are ubiquitous in rain and aerosols and comprise between ~20 and 80% of total dissolvable nitrogen. Further analysis is currently underway to quantify these species. This data will both increase our knowledge of the size distribution of this, largely chemically uncharacterised, material and improve our estimates of the total flux of combined nitrogen species to the surface waters of the North Sea.

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