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Atmospheric Nitrogen Input into the North Sea: Inorganic and Organic Nutrient Fluxes

Summary report for the OSTC

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Summary

Dry and wet atmospheric fluxes of a large variety of nitrogen-containing inorganic and organic compounds have been studied by means of complementary sampling and analysis techniques applied for gaseous and aerosol phase samples of the ambient air, as well as for the daily precipitation. For this purpose, four sampling campaigns were organized between 2004 and 2006 over various seasons at a coastal site of the Southern Bight of the North Sea at De Haan, Belgium.

On the base of the concentrations of the N-containing nutrients in air, the seasonal/weekly/daily variations in the N-fluxes were evaluated with the assistance of air-mass backward trajectories (BWTs) calculated with the HYSPLIT model and of the meteorological data collected at the sampling site. For this purpose, daily and weekly concentrations and fluxes were classified into different groups of the main air-masses arriving to the sampling site, i.e., (1) continental, (2) North Sea, and (3) Atlantic/Channel/UK.

Inorganic N-containing compounds were detected from the gas phase (i.e., gaseous NO_2, HNO_2, HNO_3, and NH_3), from size-segregated aerosols (NO_2^-, NO_3^-, and NH_4^+), and from rainwater samples (NO_2^-, NO_3^-, and NH_4^+). Organic N-compounds were detected from the gaseous phase (mostly as alkyl nitrates), and also from rainwater samples as dissolved organic nitrogen (DON). Three different size-ranges of aerosols were sampled and analyzed, i.e., with an aerodynamic diameter of >10 µm (coarse), 2.0-10 µm (medium), and 0.4-2.0 µm (fine).

Ammonia has been observed as the highest contributor to the gaseous inorganic nitrogen deposition, comprising around 90 % of the gaseous N-flux, whereas the lowest, negligibly small contribution was found for NO_2. The daily average N-fluxes of HNO_2 and HNO_3 were also relatively low, around 10 % of the gaseous inorganic N-flux.

Outstandingly high N-fluxes of aerosols for the late summer campaign has been observed, with especially high deposition rates of 3.6 and 2.9 mg N/m^2 day for the Atlantic/Channel/UK and North Sea air-masses, respectively. This high level of nutrients at this late summer period, similar to that found for gaseous nitrogen in the same campaign can be associated with a typical eutrophication event of the coastal region. On the contrary, the other seasons/campaigns experienced average aerosol fluxes of 0.9-1.8 mg N/m^2 day.

For the late summer campaign, the contribution of NH_4^+ to the N-flux from all the three particulate fractions was found to be higher than that of NO_3^-, apart from the North Sea/continental air-mass influenced coarse aerosols, showing about a 5-fold higher flux of NO_3^-.

Over the late winter/spring campaign, the contribution of NH_4^+ to the N-flux was found to be similar to that of NO_3^- in the coarse and medium fractions apart from the continental influenced aerosols, showing about 2-fold higher contribution.

During the dry mid-summer campaign, the contribution of NH_4^+ to the N-flux was found to be more intensive in the medium and the fine fractions, whereas NO_3^- was contributing more in the coarse fraction.

Comparing the relative contribution of aerosols observed over various seasons/campaigns, one can see a larger contribution during the late summer campaign from the Atlantic/Channel/UK (48 %) and mixed continental/North Sea (37 %) air-masses, whereas the contribution from North Sea air was found to be low (15 %). For the late winter/spring campaign, continental air contributed more (41 %), while the Atlantic/Channel/UK and North Sea air-masses were contributing equally (~30 %). During the mid-summer campaign, all the three air-masses contributed similarly, each around 33 %.

Thin-window electronprobe microanalysis (TW-EPMA) methods was applied to individual size-segregated aerosol samples of marine and oceanic air-mass origin (assigned with the BWTs) to characterize their morphology and chemical constitution. Since TW-EPMA is able to detect light-Z elements (e.g., nitrogen and oxigen), it could be fruitfully utilized for the identification of the exact composition of sea salt and continental aerosol particles, as well as to draw conclusion on the related atmospheric processes (e.g., sea salt aging, chloride loss/replacement over continent).

Size-segregated aerosols of continental and marine origin have also been characterized with a sensitive X-ray fluorescence method to assess the concentrations of light, non-metallic elements (e.g., S, Cl), as well as several toxic heavy metals in various air-masses. Relative abundance data suggest that Cl from sea salt and soil dust elements are more abundant in the coarse aerosol fraction. For most samples, sulphur was found to be the most abundant element, followed by Cl. On the other hand, low Cl levels were found in the coarse fraction of aerosols passing over the continent, especially, the industrialized zones. The concentrations of heavy metals (e.g., Pb, Zn, Ti, and V) were found to be increased from aerosol samples that passed over industial and continental regions compared to marine aerosol, but their levels were found to be lower than 10 ng/m^3.

The average dry and wet fluxes for the autumn/early spring, the late winter/spring, and the mid-summer campaigns were found to be 2.8 and 3.4 mg N/m^2 day, respectively. However, both the dry and wet fluxes were considerably higher during a typical eutrophication event (e.g., during the late summer (August 2005) campaign), i.e., 5.4 and 5.6 mg N/m^2 day, respectively.

Dry fluxes of N-compounds have been proved to be important contributors to the total N-budget of the coastal sampling site. This rather unexpected result can be explained on the base of the large number of days without any precipitation during the sampling campaigns, which made possible the extent of dry flux approach that of the wet one.

For organic nutrient detection in atmospheric samples, a high volume air sampling method combined with liquid extraction and pre-concentration of the samples, followed by gas-chromatography mass-spectrometry based analytical methods has been elaborated and applied to the separation and quantification of a large set of alkyl nitrate compounds, generally present at the ultra-trace (pg/m^3) level in the ambient air. The applicability and robustness of the developed analytical methodology has been demonstrated on a large set of air samples, collected at the sampling site, De Haan over various seasons/campaigns.

Over the summer campaigns, eleven ANs have been identified and quantified, but only eight ANs were detected to be present in the late winter/spring samples. From these concentration data of alkyl nitrates, the extent of their deposition for the Southern North Sea could be estimated.

Comparing the results of the summer and late winter/spring campaigns, a much higher percentage of AN contribution to the N-flux by the Atlantic/Channel/UK air-masses can be experienced (i.e. ~60 % of the total average AN-flux), whereas in the late winter/spring campaign, the fluxes from the North Sea and the continental air-masses were prevailing, i.e., 38 % and 43 %, respectively.

Fluxes of alkyl nitrates have been found to be more pronounced for the summer periods than for the winter/spring months. Although their contribution to the total (inorganic and organic) N-flux has been found to be low, i.e., ranging between 10-40 ng N/m^2 day, it was high enough to be commensurable with the fairly low fluxes of NO_2 experienced for sea-surfaces.

Over the fairly dry mid-summer period, under continentally influenced air-masses, the dissolved organic nitrogen (DON) content of rainwater samples were found to be a significant contributor (around 45 %) to the total N-budget.

In comparison with the relevant literature data, the overall fluxes of the present study are comparably higher than the waterborne N-inputs from rivers in the catchment area of the North Sea. This fact raises more concern about the atmospheric N-emission originating mostly from traffic and industrialized zones along the coastal regions of the Southern North Sea. As well as the intensified ship traffic through the North Sea contributes to the atmospheric N-deposition. This addresses more questions on the impact of atmospheric nitrogen at coastal regions.

Moreover, it demands more studies on the atmospheric deposition of nitrogen, including the refinement of both model and experimental approaches, as well as the refinement of the reported emission/depostion data on nitrogen.

The nitrogen flux data offered in this study can be successfully utilized as an input to mathematical models concerning the calculation of dry and wet depositions over the North Sea. These approaches make the estimation of the extent of eutrophication of the North Sea possible, the process, which is proved to be comprised both economic and cultural impact on the surrounding countries exploiting this area.

Content

1. Introduction

The Greater North Sea, a regional sea of North Europe, has a water surface of around 775 800 km^2, including the British Channel with an area of 89 620 km^2. It has a long history of multiple uses by people from many nations surrounding this maritime region. The growing anthropogenic activities have significantly increased the input of nutrients to the North Sea during the past decades. Particularly, the biologically available inorganic and organic nitrogen-containing compounds cause proliferation of harmful algal blooms and other eutrophication phenomena, affecting the marine ecosystem, thus the fishery and the tourism. Therefore, the atmospheric nitrogen-input, especially at coastal regions, triggers increasing interest in the scientific community. Specifically, the description of atmospheric nitrogen fluxes, in terms of inorganic and organic nitrogen, is important to assess by both experimental and model approaches, particularly, to get an insight into the extent of eutrophication in coastal regions.

Connecting to this central environmental topic, the OSPAR Convention has been formulated, which is a regional convention for the protection of the marine environment of the Northeast Atlantic to which the European Community and several other countries are contracting parties (Bartnicki and Fagerli, 2006). One of the objectives of this convention, organized as “Eutrophication Strategy”, is to achieve and maintain a healthy marine environment by 2010, where eutrophication does not occur. This strategy is implemented through measures in reducing anthropogenic emission, discharges, and losses of nutrients in all areas from which nutrient input is possible, directly, or indirectly, to contribute to inputs to areas with regard to eutrophication.

The implementation of this work under the OSPAR Joint Assessment and Monitoring Program (JAMP) of waterborne inputs through the OSPAR Comprehensive Study on Riverine Inputs and Direct Discharges (RID) and of atmospheric inputs though the OSPAR Comprehensive Atmospheric Monitoring Programme (CAMP). This work is also supplemented by gathering information from international bodies out of the OSPAR.

In support of this work a first report on “Atmospheric nitrogen in the OSPAR Convention Area 1990-2001” (Bartnicki and Fagerli, 2003; 2004) had been prepared. These studies as well as the OSPAR assessment of the CAMP data (OSPAR Commission, 2005a; 2005b) suggest that atmospheric nitrogen inputs appear to play a major role for certain OSPAR Convention waters, including the North Sea.

Emission sources of nitrogen influencing the North Sea are mostly of anthropogenic origin, i.e., national emissions for NO_2 and ammonia. An additional and very important emission source of NO_x is the international ship traffic (Bartnicki and Fagerli, 2006).

The role of atmospheric nitrogen in the total fluxes to the North Sea as well as the related chemical and biological processes has been a subject of several experimental and model studies, documented in the relevant literature of the marine research (e.g., Rendell et al., 1993; Beddig et al., 1997; Hertel et al., 1995, 2002; Peierls and Paerl, 1997; de Leeuw et al., 2003). Most of these studies are related to atmospheric supply of inorganic and organic nitrogen mainly on the base of model studies. These studies, however, do not cover some important species, such as alkyl nitrates, which groups of compounds may play a significant role in atmospheric processes (Roberts, 1990), particularly, by contributing to the nitrogen-flux of coastal regions, as well as to eutrophication. Also they have not give an account on the sampling and analysis of size-segregated aerosols, the results acquired could also give an insight into chemical processes, taking part at marine and coastal regions of the North Sea. Moreover, the transport of nitrogen compounds from diverse regions surrounding the North Sea has not yet been discussed on the base of using air-mass backward trajectories (BWTs) to assign the various polluted air-masses contributing to coastal eutrophication events.

Considering the above facts, the main objectives of this atmospheric monitoring study were as follows:

- to quantify the fluxes of nitrogen compounds at a coastal site of De Haan in terms of wet and dry deposition from atmospheric samples (gaseous, aerosol, and precipitation);
- to compare and contrast temporal differences in concentrations of nitrogen compounds deposited at De Haan;
- to elaborate analytical chemical methods of high sensitivity and selectivity for the detection and quantification of the most abundant organic compounds (e.g., alkyl nitrates) in coastal/marine regions;
- to quantify the concentration and the contribution of the major nitrogen compounds, such as nitrite, nitrate, ammonium, as well as organic nitrogen, to atmospheric deposition.

2. Monitoring of atmospheric nitrogen: sampling, analysis and evaluation methods

For sampling purposes, four campaigns were organized over the years 2004-2006, to cover the yearly/seasonal variations in the deposition of nitrogen compounds. The schedule of the sampling campaigns was as follows:

- Autumn/early winter campaign (August 21st, 2004 - January 31th, 2005)
- Late summer campaign (August 8th -21st, 2005)
- Late winter/spring campaign (February 14th - April 30th, 2006)
- Mid-summer campaign (June 12th - August 8th, 2006)

The sampling site selected for this study, De Haan, in Belgium, is a small village (sea-side resort) at the coast of the North Sea located at coordinates 51.172 N and 3.037 E. The area at which the sampling equipment was deployed is a small research station of Flanders Marine Institute (VLIZ), located some 300 m of the coast among the sand-dunes, which are characteristic along the coast line of the region.

Meteorological parameters were recorded during each sampling campaign by the meteorological station of VLIZ and also a small meteorological weather-station deployed at the sampling site. Generally, a lower extent of precipitation (0.8-1.5 mm/day) was observed during all the four campaigns than in former studies over Flanders (i.e., 2.05-2.25 mm/day) (Van Grieken et al., 2003).

Gaseous nitric acid, nitrous acid, and ammonia were sampled actively with an annular denuder on a daily basis, whereas NO_2 was sampled with passive diffusive samplers on a weekly base. Three different size-ranges of aerosols were sampled with a 3-stage stacked filter unit, i.e., with an aerodynamic diameter of >10 µm (coarse fraction), 2.0-10 µm (medium fraction), and 0.4-2.0 µm (fine fraction). The daily precipitation was collected with an automatic, sequential rainwater sampler.

The inorganic N-content of these samples (nitrite, nitrate, and ammonium) was determined with ion chromatography (IC) analysis. To determine the dissolved organic nitrogen (DON) content of rainwater samples, each of them was oxidized with a strong oxidizing agent in a microwave oven, and then the total (inorganic+organic) N-content was measured with IC, from which the DON-content was calculated.

Ozone was sampled on a weekly base with the application of passive diffusive samplers, and the ozone-content of samples was determined with an UV-VIS spectrophotometric method.

Single particle analyses were performed on aerosol samples taken on a weekly basis with a time resolution of a day, using two stages of a May cascade impactor with aerodynamic diameter cut-offs of 2.0-8.0, and 0.5-2.0 µm, respectively. The single-particle analyses were carried out on an electronprobe X-ray microanalyser (EPMA) equipped with an energy-dispersive X-ray detector with a thin window (TW) in order to detect low-Z elements. The size and shape of each individual particle was measured and estimated from a high-magnification secondary electron image. For obtaining information on the possible sources of the aerosol and the possible chemical interactions between gaseous and particulate pollutants, the particles were classified into representative groups using the chemical and morphological data obtained by EPMA.

For the combined, simultaneous sampling of organic compounds (mostly alkyl nitrates – ANs) from the gas and aerosol phases of the ambient air, a common high-volume sampler has been redesigned using either a low, or a high-capacity gas adsorption trap. After a combined Soxhlet-extraction and pre-concentration step, the analyses of the samples were performed either with a gas-chromatography mass spectrometry (GC-MS) featuring an ion-trap MS and electron ionisation, or on a GC system with electron capture detector (ECD). Most of the alkyl nitrates used as reference compounds for calibration of the elaborated GC-MS and GC-ECD methods were synthesized from their corresponding halide compounds. The applicability and robustness of the developed analytical methodology has been demonstrated on a large set of diurnal samples, each collected at the sampling site, De Haan.

For the sampling of total elemental content in different size-fractions of aerosol as above, a similar 3-stage filter unit has been applied as for IC. The quantification of these samples was done with an application of an up-to-date, high-energy polarized beam X-ray fluorescence spectrometer. With this sensitive method, up to 20 elements could be determined in the aerosol samples, including anthropogenic toxic heavy metals, such as Cd, Pb, and Sb.

In order to evaluate the movement of air-masses during sampling and/or to assign the origins of gaseous and aerosol phase pollutants, 240 hour long air-mass backward trajectories (BWTs) were calculated for each day of the sampling campaign (as an end-point of the BWT) using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model (Draxler and Rolph, 2003; Rolph, 2003).

From the approach with the application of BWTs, it was also expected that the selection of a proper sampling period (day) allows to find air-masses with no, or at least negligibly low anthropogenic impact from various industrialized zones, e.g., Dunkerque in France close to the Belgian border, and/or those from the United Kingdom (UK), whose emission may considerably influence the composition of aerosols and gases sampled at the selected coastal site.

It is expected that from these clean air-masses from the Atlantic Ocean, one can receive some “baseline” pollution data for the North Sea, which could be a good basis for further studies on coastal eutrophication.

The extent of nitrogen deposition (flux) originating from various gaseous and aerosol phase compounds was calculated with the application of experimentally determined deposition rates of each compound and/or aerosol fraction for marine areas, i.e., implying an air-water interface (Hertel et al., 1995; Cohen, 1998). Concerning the deposition rates for alkyl nitrates, the relevant literature has not yet reported any data till now. Therefore, to make an estimate of the AN-fluxes, the deposition rate of peroxyacetyl nitrate (PAN), as a model was selected from the literature (Hertel et al., 1995).

On the base of BWT, the daily N-flux data were assorted into three main categories, according to the origin of major air-masses, i.e., Atlantic/Channel, North Sea, and continental (Figure 1). From these data, the average N-fluxes and their fluctuations, expressed as the standard deviation (SD), and the total N-contributions has been calculated. As well as the elemental concentration data of size-segregated aerosol were clustered in a similar way, in order to evaluate their contribution in the pollutant content of diverse air-masses.

3. Atmospheric fluxes of gaseous inorganic nitrogen

During each campaign, ammonia has been observed as the highest contributor to the gaseous inorganic nitrogen deposition, comprising around 90 % of the gaseous N-flux, whereas the lowest, negligibly small contributor was found to be NO_2 (Tables 1-4). The daily average N-fluxes of HNO_2 and HNO_3 were also relatively low, amounting around 10 % of the gaseous inorganic N-flux.

In the autumn/early winter campaign in 2004, some representative days were selected on the base of daily BWTs, which were meant to represent the contribution of different air-masses (e.g., Atlantic, North Sea, and continental), arriving to the coast of Southern North Sea at the sampling point. On the base of the daily concentration data, the "baseline" flux of the "clean", oceanic air-masses has been attempted to be calculated.

When comparing the gaseous N-fluxes during Atlantic air-mass movements with continental, a relatively large increase in the N-loading can be seen for the latter (Table 1). This is manifested in both the gaseous and aerosol phase compounds as well. The fluxes of both HNO_2 and HNO_3 are significantly (2.0-2.7-times) increased, which is the direct consequence of their increased formation from anthropogenic NO_x. The flux of NH_3 showed only a slighter, 1.8-fold increase, since its homogeneous release and distribution over Flanders, due to animal farming, even in the coastal region, could be expected. The values for the average fluxes of gaseous compounds over the season are a bit higher than that observed for the late winter/spring campaign (see Tables 1 and 3).

In the late summer campaign in 2005, a lower NH_3 flux was observed from mixed continental-North Sea air-masses compared to the North Sea and Atlantic/Channel/UK air-masses. This is possibly due to dilution of continental air with marine air, as well as the fast conversion rate of NH_3, as observed by Asman and Van Jaarsveld (1991). Comparing the average fluxes of various gaseous N-compounds for this campaign from UK/Atlantic/Channel air-mass movements to those originating from the North Sea and mixed North Sea/continental air-masses, ratios ranging between 0.7-1.9 and 1.1-5.8, respectively, have been observed (Table 2).

For the late winter/spring campaign, when comparing the average fluxes of various gaseous N-compound from continental air-mass movements with those originating from the Atlantic/Channel and North Sea air-masses, generally ratios ranging between 1.2-2 and 0.9-2.0, respectively, have been observed (Table 3). For the mid-summer campaign, a similar comparison of N-fluxes for continental air-mass movements to those originating from the Atlantic/Channel/UK and North Sea air-masses resulted in ratios ranging between 0.8-1.2 and 1.0-2.0, respectively (Table 4). This means that the contribution of the Atlantic/Channel/UK air-masses were higher during this campaign compared to the late winter/spring campaign.

Comparing the average gaseous N-fluxes over various seasons/campaigns, outstandingly high deposition rates were observed for the late summer campaign, with values of 4.8 and 2.7 mg N/m^2 day for the Atlantic/Channel/UK and North Sea air-masses, respectively. On the contrary, the other campaigns experienced average gaseous fluxes ranging between 1.2-2.1 mg N/m^2 day.

When comparing the relative contribution of gaseous flux data observed over various seasons/campaigns, one can see a larger contribution from the Atlantic/Channel/UK (56 %), and the North Sea (31 %), and a lower value (12 %) from the continental/North Sea air-masses during the late summer (August) campaign (Table 6). On the other hand, for the late winter/spring and the mid-summer (June-July) campaigns, the relative contribution of N to fluxes of gaseous N-compounds was of similar degree, being the highest for continental air-masses (each 37 %), followed by North Sea (36 %), whereas a bit decreased fluxes (28 %) were observed from Atlantic/Channel/UK air-masses (Figure 2).

4. Inorganic nitrogen in size-segregated atmospheric aerosols

In the autumn/early winter campaign, on the selected representative day under oceanic influence, NO_3^- was present mostly in the medium and coarse fractions of aerosols (Table 1), which is due to the less active secondary aerosol formation and the coagulation of fine particles in coarse mode. The NH_4^+ contributed equally to the N-flux in each fraction of Atlantic air, whereas its significantly increased flux was observed in continental air-masses. During continental air-mass movements, secondary aerosol formation becomes significant, which is manifested in the enrichment of N-species in the fine and medium particulate fractions. The total aerosol flux for Atlantic air was found to be 4-times lower than that of continental. The average flux of aerosols over the autumn/early winter season was an average of 2.75 mg N/m^2 day, which is a rather comparable value to that observed for the late winter/spring campaign (see Tables 1 and 3). Also, similar aerosol contribution to the total dry flux (40 %) has been found.

For the late summer campaign, the highest average daily deposition for the total aerosol N was found for UK/Atlantic/Channel air-masses (3.6 mg/m^2 day), followed by lower values for North Sea/continental (2.9 mg/m^2 day), and North Sea air-masses (1.0 mg/m^2 day). During mixed North Sea/continental influence, the contribution of coarse and fine fractions to the average aerosol N-flux has been found to be less significant, 25 % and 15 %, respectively, than that of the medium fraction (60 %). On the other hand, for the North Sea influenced air, the coarse fraction was enriched up to 73 % contribution to the total aerosol-N levels. For Atlantic/Channel/UK influenced air, the contribution of medium and coarse fractions was similar (45-50 %), whereas very low N-contribution was observed from the fine fraction (6 %) (Figure 3, Table 2). The percent of aerosols in the dry fraction was found to be between 30-43 %, apart from that of the North Sea/continental air-mass ranging up to 70 %.

The contribution of NH_4^+ to the N-flux from all the three particulate fractions was found to be higher than that of NO_3^- apart from the North Sea/continental influenced coarse aerosols, showing about 5-fold higher flux of NO_3^- (Table 2). The Atlantic/Channel/UK to North Sea and/or North Sea/continental ratios of total aerosol N flux were found to be 3.1 and 1.3, whereas the total dry N-fluxes were 2.5 and 2.2, respectively, indicating the significant contribution of UK/Atlantic/Channel air-masses to the N-loading of the Southern Bight of the North Sea.

During the late winter/spring campaign, the largest average daily deposition for total aerosol N was found for continental air-masses (1.8 mg/m^2 day), followed by lower values for the North Sea and Atlantic/Channel/UK air, 1.3 and 1.4 mg/m^2 day, respectively.

During continental influence, the average contribution of coarse fraction to the total aerosol N-flux is less significant (10%) than those of either the medium (58 %) or fine (32 %) fractions, due to enrichment of N in finer fractions by secondary aerosol formation, as well as combined with the coagulation of coarser particles in the medium fraction followed by their fall-out with wet air-masses. These led to the enrichment of N-species in the finer particulate fractions, and less abundance of N in the coarse fraction. On the other hand, during oceanic and North Sea air-mass movements the contribution was found to be very similar in all the three fractions, which is due to the less active secondary aerosol formation, and the coagulation of fine particles in medium and coarse mode by the assistance of the marine air of higher humidity (Table 3).

The contribution of NH_4^+ to the N-flux was found to be similar to that of NO_3^- in the coarse and medium fractions apart from the continental influenced aerosols, showing about 2-fold higher contribution. Somewhat higher contribution of NH_4^+ was also observed for the fine fractions. The percent of aerosol N-fluxes from the three diverse air-masses to the dry N-flux was around 50 % for all three air-masses. The continental to marine ratios of total aerosol, and total dry flux were found to be always higher, as expected by the more pollutants from continental air-masses (Table 3).

For the mid-summer campaign, the daily deposition flux of total aerosol N was found to be relatively similar for the three main air-masses. The contribution of coarse fraction to the total aerosol N-flux was a little bit more significant (30-40 %) than those of either the medium or fine fractions, due to the dry period, promoting the coagulation of particles in the coarse fraction (Table 4).

The contribution of NH_4^+ to the N-flux was found to be more intensive in the medium and the fine fractions, whereas NO_3^- was contributing more in the coarse fraction. The percent of aerosol-N to the dry N-flux was found to be around 41 % for Atlantic/Channel/UK air-masses, whereas lower values (32-35 %) were observed for continental and North Sea influenced air (Table 5). Surprisingly, the continental-to-marine ratios of total aerosol and total dry flux were found to be lower than unity, which is an indicative of the higher pollution content of the Atlantic/Channel/UK air-masses during the summer period. This is also a proof of the mixing of oceanic and continental air in the air-masses arriving from the Atlantic Ocean.

Comparing the average N-fluxes of aerosols over various seasons monitored, one can see an outstandingly high values for the late summer campaign, especially, with high deposition rates of 3.6 and 2.9 mg N/m^2 day for the Atlantic/Channel/UK and mixed-continental-North Sea air-masses, respectively. On the contrary, the other campaigns has shown average aerosol fluxes ranging between 0.9-1.9 mg N/m^2 day. The high level of nutrients at the late summer period, similar to that found for gaseous nitrogen (Table 2) can be associated with a typical eutrophication event in the coastal region studied.

When comparing the relative contribution of aerosols observed over various seasons/campaigns (Table 6), one can see a larger contribution during the late summer campaign from Atlantic/Channel/UK (48 %) and mixed continental/North Sea (37 %) air-masses, whereas the contribution from North Sea air was found to be low (15 %). For the late winter/spring campaign, continental air contributed more (41 %), while the Atlantic/Channel/UK and North Sea air-masses were contributing equally (~30 %). During the mid-summer campaign, all the three air-masses contributed similarly, each around 33 % (Figure 4).

5. Nitrogen deposition with atmospheric precipitation

In the autumn/winter campaign, the wet deposition flux was proved to be a more significant contributor (60 %) to the total N-deposition compared to the dry N-flux. Though on the representative day under continentally influenced air (1st October, 2004) its contribution was found to be lower (15 %). As a general observation for this campaign, its contribution was more emphasised for Atlantic/Channel/UK air-mass movements than for either continental, or North Sea air-masses.

During the late summer campaign in 2005, the Atlantic/Channel/UK air-masses contributed more to the wet N-flux (78 %) than those of North Sea (22 %) and North Sea-continentally influenced air (Table 2). The contribution of NO_3^- to the wet N-flux was found to be outstandingly high (12 mg N/m^2 day) than that of NH_4^+ for Atlantic/Channel/UK air-masses, whereas both species scored similar values (1.8-1.9 mg N/m^2 day) for the North Sea influenced air. Accordingly, the wet-to-dry ratios were found to be 2-fold higher for UK/Atlantic/Channel air-masses than that for North Sea, indicating the important N-contribution of (wet) N-fluxes from mixed air movements from the Atlantic passing through the UK and the Channel. For North Sea air-masses, a just about unity wet to dry ratio has been found.

Over the late winter/spring campaign, Atlantic air-masses generally more contributed to the wet N-flux (3.5 mg N/m^2 day) than those of continental and North Sea (Table 3). The contribution of NH_4^+ to the N-flux was found to be about 2-fold higher than that of NO_3^- for all the three air-masses. However, the wet to dry ratio was found to be higher than unity for Atlantic air-masses, indicating the more important contribution of dry N-fluxes from continental and North Sea air-masses.

The average DON content of rainwater samples was proved to be a less significant contributor to the N-flux, it amounted up to 0.4, 0.2 and 0.01 mg N/m^2 day, for continental, Atlantic and North Sea air-masses. It is to be mentioned here that the relevant literature generally associates DON with a large set of organic N-containing compounds present in the atmosphere, such as urea, peroxyacetyl nitrate (PAN), alkyl nitrates, aliphatic amines, amino acids, N-PAH, methyl cyanide, etc. (Cornell et al., 2003). Although the exact composition of DON in rainwater is not known, the listed species is to be investigated due to their bioavailability and/or toxicity. However, this is out of the scopes of the present study.

For the mid-summer campaign, despite the relatively low amounts of rain experienced, the wet deposition was found to be a considerable contributor to the total N budget of the sampling site (Table 4). For Atlantic air-masses, the wet deposition flux has been proved to be a more significant contributor (~80 %) to the total N-deposition flux compared to the dry N-flux.

On the other hand, an equal contribution of the dry and wet fluxes has been found for continental air-masses. As observed in the former campaigns, Atlantic/Channel/UK air-masses generally contributed more to the total N-flux than those of continental and North Sea.

The contribution of NO_3^- to the wet N-flux was found to be about 2-fold higher than that of NH_4^+ for Atlantic/Channel/UK air-masses, whereas for continental air, a similar contribution of these species has been observed. The wet-to-dry ratio was found to be higher than unity for Atlantic and continental air-masses, indicating that in the dry summer period the continental air-masses can also more significantly contribute to the N-flux than in the late winter/spring campaign.

In the mid-summer campaign, the average DON content of rainwater samples was also proved to be a significant contributor to the N-flux. It amounted up to 3.5, and 0.3 mg N/m^2 day, for continental and Atlantic/Channel/UK air-masses. The high contribution of the DON from continental air-masses was associated with the possibly high anthropogenic impact as well as the long and dry mid-summer period, which promoted the accumulation of pollutants in the ambient air. This certainly allows a higher DON content in rainwater samples, even during short, shower-like rain periods.

During each summer campaign, the relative contribution from NO_3^- was always found to be high (86 %) for the Atlantic/Channel/UK air-masses. In these air-masses, NH_4^+ was also high in the mid-summer campaign (72 %), whereas its lower contribution was found in the late winter/spring (28 %) and late summer campaigns (51 %).

The relative contribution of DON was observed to be high from continental air-masses during the late winter/spring campaign. It amounted up to 57 %, whereas the contribution was decreased for Atlantic/Channel/UK (32 %) and North Sea air-masses (11 %).

By comparing the relative contribution of wet deposition of diverse air-masses observed over various seasons/campaigns, a higher contribution (49-78 %) from the Atlantic/Channel/UK can always be seen, followed by the continental air-masses with contribution of (29-34 %), whereas the contributions from the North Sea air-masses were ranging up to 22 % only (Table 6).

6. Total (dry and wet) fluxes of nitrogen

In the late winter/spring, and the mid-summer campaigns, the relative contribution of diverse air-masses to the dry flux was found to be very similar, ranging between 28-39 %. However, for the late summer campaign, a high contribution was observed from Atlantic/Channel/UK air-masses (52 %), whereas similar contributions were found for continental and North Sea air (each 24 %) (see Figure 4 and Table 6).

In the late summer campaign, the relative nitrogen contribution to the total (dry plus wet) N-flux was the most considerable from the UK/Atlantic/Channel air-masses (65 %) followed by the North Sea (23 %) and the North Sea/continental (12 %) air-masses (Table 6). Compared to this campaign, the relative contributions for the mid-summer campaign in 2006 has only slightly been changed for Atlantic/Channel/UK (54 %) air-masses, but significantly for continental (34 %) and North Sea (12 %) air-masses. In the late winter/spring campaign, the relative contribution to the total flux of was significantly decreased for the Atlantic/Channel/UK air-masses (38 %), whereas it was increased for North Sea air-masses (28 %).

From the above data of individual fluxes, the overall average dry and wet fluxes for the coastal region of De Haan has been calculated, yielding 2.8 and 3.4 kg N/km^2 day, respectively. Comparing these results with the existing literature (model) values of 0.5 and 2.1 kg N/km^2 day in 1999 reported for the whole area of the sea as average dry and wet deposition, respectively (Hertel et al., 2002), an increased extent of N-deposition is evident at least for the Southern Bight of the North Sea.

Interestingly, due to the drier periods experiencing less precipitation during the seasons/campaigns, the dry to wet deposition ratio has been significantly increased. Nevertheless, it is to be noted that due to the intensive anthropogenic activities, the atmospheric N-contribution at a coastal sampling site is always higher than that of the northern part of the North Sea, it being rather opened to the Arctic and Atlantic waters.

Despite the relatively low amounts of rain experienced during the campaigns, the wet deposition was found to be a bit more considerable contributor to the total N budget of the North Sea.

The calculated annual dry and wet fluxes for De Haan are 1010 and 1357 kg N/km^2, respectively, which corresponds to a total deposition of 2.4 t N/km^2 (Table 7). This data is in the range of the predicted values by the ACDEP model for 1999 (Hertel et al., 2002), reporting 1.8-3.0 t N/km^2 for this coastal region of Belgium.

The calculated average atmospheric fluxes (wet and dry), extrapolated for the area of the North Sea excluding the British Channel, corresponds to a total flux of 1624 kt N/yr, while for the Greater North Sea area including the Channel a flux of 1832 kt N/yr. These are rather higher values for the annual flux, due possibly to the characteristic of the sampling site in De Haan, which is much influenced by anthropogenic activities. This certainly implies higher average fluxes observed at this site.

Model data of EMEP on oxidized (i.e., nitrates) and reduced (ammonia, and ammonium compounds) nitrogen depositions were also reported (Bartnicki and Fagerli, 2006) for the years between 1990-2004, they being calculated in nitrogen units consists of the sum of peroxyacetyl nitrate (PAN), NO_2 and HNO_3, while reduced nitrogen deposition as has been calculated to be as a sum of ammonia and ammonium in (ammonium nitrate and ammonium sulphate).

The annual fluxes of oxidized and reduced nitrogen are observed to be 834 and 1310 kg N/km^2. These data are higher by some 20-30 % than the flux ranges, i.e., 400-600 and 1000-1200 kg N/km^2, obtained for the oxidized and reduced N, respecitively, from model calculations for 2004 in the region of De Haan (Bartnicki and Fagerli, 2006).

This difference can be explained by a higher anthropogenic emission during the sampling years, thus a higher rate of deposition of nitrogen, particularly, due to the presence of more industry, as well as intensified terrestial and/or ship traffic around this region. Annual survey of the NO_2 emission data for international shiptraffic over the North Sea from 1990 till 2004 shows an increasing trend from 508 to 721 kt N/year (Bartnicki and Fagerli, 2006), and thus, it supports these assumptions. As well as increased NO_2 emissions has been reported for Russia, and an increased annual NH_3 emission strarting from 2003 has been reported for the UK and the Netherlands.

Comparing the obtained total annual atmospheric fluxes with the riverine inputs, one can seen that the formers are more intensive than the riverine N-input reported either for the German Bight for the 1990s (150 kt N/year; Beddig et al., 1997), or for the total North Sea catchment area (745 kt N/year, Spokes and Jickells, 2002).

According to the latest observation of OSPAR contracting parties on waterborne (direct and riverine) inputs, a total waterborne input of 807 kt N/yr has been reproted for 2004 (Bartnicki and Fagerli, 2006). This value is rather commensurable with the presently observed data on atmospheric inputs, even the latters are more intesive.

7. Characterization of single particles and related atmospheric processes

In this study, TW-EPMA has been utilized to characterize the morpohology and constitution of atmospheric single particles obtained from diverse air-masses. The results for the selected marine and continental samples after clustering are illustrated in Figure 5. The relative abundance of the obtained particle types, combined groups, in size fraction of the sampling days has been shown in Table 8. It can be seen that NaCl (sea salt) particles are abundant on the coarse stage in both samples, which is indeed a fingerprint for the important marine influence on the sampled aerosol. The so-called bubble bursting or sea spray process transports water drops from bursting white caps into the air, after which crystallization takes place and some salts remain airborne. Therefore, sea-salt should be the main constituent among the coarse particle fractions in marine aerosols, except during episodes of continental dust transport (Fitzgerald, 1991). Sodium and magnesium chlorides are known to react with other compounds in the atmosphere like nitric and sulphuric acid. This result in chloride loss, since the resulting hydrochloric acid evaporates, while the formed nitrates and sulphates stay behind as sodium nitrate and sulphate salts (together with some remaining chloride, when the particle did not react completely).

Since TW-EPMA is able to detect nitrogen and oxygen, it was possible to clearly identify sodium nitrate (Ro et al., 2001, 2002, 2005). Although only the name “$NaNO_3$” has been mentioned for the particle type identification, small sodium sulphate crystals were often observed to be connected to the surface of larger sodium nitrate particles. A possible reason for this effect is the inhomogeneous crystallization at the impacting surface, since sodium sulphate crystallizes at higher relative humidity (Storms et al., 1984).

Nitric and sulphuric acids in the air find their origin in transformations and reactions of nitrogen and sulphuric oxides. In urban environments, these compounds are mostly found as exhaust gases from combustion processes (domestic heating, industrial processes, traffic).

Since the sea is a continuous source of fresh sodium chloride, and this sea salt in air travelling over land has more chance to react with anthropogenic nitrogen and sulphur species, we could say that relatively high abundances of (progressive) sea salt aging is an indication for continental influences.

The presence of aged or completely transformed sea salt, like sodium nitrate, was also significant in the continentally influenced sample. A considerable amount of aged sea salt particles has been observed in the continental sample (as “$NaCl+NaNO_3$” group). This result is somewhat puzzling while considering that this air mass spent most of its time above the continent.

Organic particles and biogenic particles (recognized by their relatively higher potassium or phosphorus content) were detected with TW-EPMA in the coarse and fine fractions. However, we must mention that these particles are difficult to characterize more in detail, since only elemental concentrations can be determined with TW-EPMA (for elements with $Z>5$, excluding hydrogen).

For the samples influenced by marine sources, one can see a lower abundance of organic / biogenic particles, whereas they are also abundant in continental sample. The amount of organic and biogenic particles is considerably higher in continental samples, which seems logical taking into account the possible continental sources of these particle types (traffic, industrial processes, domestic heating; vegetation, other bioactivity). In urban aerosols, most organic particles originate from combustion processes, so these sources must certainly be involved.

The marine bubble bursting process might contribute to the organic fraction, since it also causes (bio)organic materials from the sea water to be transported into the atmosphere. The fact that numerous sea salt particles also appeared to contain certain amounts of carbon and oxygen (maybe as an organic layer on top of the sodium chloride crystals) is probably a result of this process. Even a mixed particle type of sea salt and organic compounds was found in these samples (“NaCl+Organic” or “$NaSO_4$+Organic”).

The presence of organic coatings was demonstrated earlier for particles suspended in seawater by using an indirect method, i.e. Ru-staining method for organic carbon (Jambers, 1997), but with TW-EPMA one could determine the existence of these layers directly in the X-ray spectra.

Ammonium sulphate and nitrate particles originate from transformations and reactions of nitrogen and sulphur oxides in the air and, like for sea salt aging, the presence of ammonium particles can be related to continental influences. With TW-EPMA, it was possible to specify the origin of sulphur-rich particles “Organic+S”.

Aluminosilicates frequently encountered in the continental samples are expected to have their origin from soil dust. Large soil dust particles are not often transported over large distances because of their fast deposition rates, and, therefore, their abundance is expected to be only very high on coarse stage if the analysed samples would have been strongly influenced by continental sources as observed in our case. This is indeed not the case for the marine samples, although the coarse stage contains other soil dust particles like metal oxides, but to a lesser extent. The contribution of mineral particles, like aluminosilicates, or oxides to the aerosol composition was much higher for the continental sample, which again proves that soil dust is more abundant above the continent. Iron oxide and other metal oxides showed to be more abundant than in the more marine samples, which could also partly be explained by the presence of the intense metallurgic industry over Europe (Van Malderen et al., 1992).

8. Elemental content of size-segregated aerosols

The variations in the elemental content of size-segregated aerosol samples observed under diverse air-masses has been measured with XRF and evaluated with the assisstance of air-mass trajectories and clustering. The relative abundance of the elements in each fraction is represented for the different air-influences during the autumn/early winter (e.g., Figure 6). For the Atlantic (oceanic) influences, Cl is always found to be highly abundant in the coarse fraction. Sea-salt is a very important source of Cl in atmospheric aerosols. These particles are usually present in the coarse fraction. In the samples with continental and industrial influence, the Cl becomes less abundant in the large fraction and seems to be concentrated in the medium fraction. NaCl is usually reacting with acidic gases such as SO_2 and NO_2, resulting in the formation of sodium-sulphate and -nitrate particles through the exchange of Cl. NO_2 and SO_2 are mainly from anthropogenic origin, especially from traffic, industry and domestic heating, the original NaCl particles are probably mostly replaced with nitrates and sulphates.

For all samples, the concentrations of Fe, Si, and Ca are sharply decreasing with decreasing particle size. This can be explained by the fact that they usually originate from soil-erosion, and therefore, they occur in the coarse particulate fraction. S is mostly present in the smaller fractions, which can be explained by secondary aerosol formation resulting in smaller particles. Other elements do not reveal a typical pattern and their distribution seems different in all four air-masses.

The main conclusion from the relative abundance data is the same throughout all the campaigns: Cl from sea-salt and soil dust elements are more abundant in the coarse fraction.

In the autumn/early winter campaign, the most abundant elements were found to be the low-Z elements for each fraction (see e.g., Figures 7-8). Toxic heavy metals, like Se, Cr, Cd, and Sb were analyzed, but their concentrations were found to be below the detection limit of the method (few ng/m^3). Cl is clearly the major constituent of coarse fraction of the oceanic samples, and the Cl content is the highest for the samples with air masses coming from the North Pole.

The Al, Si, Ca, and Fe content in the coarse fraction are the lowest in the oceanic air-masses, since these elements are the main components of soil dust and, therefore, they would be more explicitly present in the air-masses travelling over land.

The aerosol sample influenced by industries in the coarse fraction has the maximum S content. Also, the metal content is elevated for samples with air mass over land (industrial and continental). The concentrations for Pb and Ti in the “industrial” sample are very high.

For the medium fraction, it can be seen that Cl is equally abundant in all four samples. As expected from an industrial area, the S content is also significantly higher than in the other samples. Pb and Zn concentrations are also considerably higher in the continental and industrial samples, which suggests an anthropogenic source. For the fine fraction, sulphur is the dominant element. Contrary to the other fractions, the oceanic samples have the higher S content. Like in the medium fraction, Zn and Pb are the dominant metals.

In the late summer campaign, the level of S in the air-masses crossing the UK is very low in each fraction compared to the other air-masses studied. Another remarkable difference is the low concentration of Cl in the coarse fraction of the oceanic sample. The level of Cl in the industrial sample is extremely high; both compared to the other samples and to the highest levels of Cl found in the autumn/early winter campaign (Figure 8).

Although it was expected differently, Si, Ca, and Fe in the coarse fraction are most elevated in the case of the oceanic samples. These elements are the main constituents of soil dust and, therefore, the highest levels are expected in air masses travelling mostly over land. On the other hand, the air-mass trajectories clearly shows that this did not happen, but 10 days before the sample was taken.

The concentrations for all elements in the medium and fine fraction are smaller than in the autumn/early winter campaign. In the coarse fraction, however, they are comparable to that campaign, except for Cl. For the medium fraction, it can be noticed that the industrial and the North Sea influenced sample have similar pollutant concentrations.

During the late winter/spring campaign, no Cl is noticed in the coarse fraction of the sample with influence from the British Channel and France. This is somewhat unexpected since this air-mass is still strongly influenced by the Atlantic Ocean. On the contrary, the aerosol sample passing over the UK has a substantial Cl content. Inspection of the other samples in the cluster to which the sample crossing France belongs show an average Cl concentration of 134 ng/m^3, which is definitely lower than expected.

The sample with aerosols crossing Scotland shows the expected pattern, with Cl being the most abundant element. In the two other samples, from air-masses crossing England (Channel-England and Oceanic England), Cl and S have approximately the same abundance. Similar behaviour has been found in the autumn/early winter campaign (Figure 8) for the continental sample and in the late summer campaign in case of the oceanic sample. The concentration for this campaign, however, over 700 ng/m^3 , whereas lower levels were found for the former two campaigns (60 and 150 ng/m^3).

Except for S, Cu and Zn the concentrations of the oceanic sample are every time the lowest in the coarse fraction. In the sample crossing Scotland, the concentrations are every time the highest, except for Fe, Ti, Mn, and Al (the latter being only present in the continental sample).

For the mid-summer campaign, in the coarse aerosol fraction, sulphur was found to be the most abundant element in most cases, followed by Cl, similar to those in the other campaigns. The lowest Cl level was not in the continental sample as expected, but the sample passing The Netherlands, which is still severely influenced by the ocean. Additionally, the continental sample does not have the highest concentration of soil dust elements, but the sample with The Netherlands. As a matter of fact, the continental sample has usually an average concentration for all elements in the coarse fraction. For the medium fraction, contrary to the coarse fraction, the Cl concentration in the sample crossing The Netherlands is the highest of all samples in the medium fraction, so is the case for S, the soil dust elements and most metals. Especially, the Al level is much higher than the other elements.

The fact that Pb is also high combined with the high amount of soil dust elements (both in the medium and the coarse fractions) rises the suspicion that this sample is much more influenced by the continent than one could expect just by checking the BWT. After all Pb turned out to be an excellent tracer for continental air masses in all other campaigns. In the fine fraction, no Cl is present as usual. Also here, the highest concentration seems to be coming from the sample crossing The Netherlands. Especially, for the metals this is pronounced: V and Ni are twice as high as in the other samples, but for Cu and Ni the difference is much smaller. The concentrations of the metals are for most samples, however, lower than 10 ng/m³.

9. Alkyl nitrates in the ambient air: concentrations and fluxes

Alkyl nitrates (ANs) are of particular interest within the ozone/nitrogen oxide system, because their formation and degradation plays an important role in the tropospheric ozone production (Roberts, 1990). Within the framework of the present project, aiming also at the characterisation of organic nitrogen compounds in the marine environment, it appeared to be necessary to develop a sensitive and robust analytical procedure to the determination of ANs, particularly with the application of GC-MS to replace the routine application of GC-ECD. The latter method provides intrinsically high sensitivity and easy operation, but it is hampered by interferences (Glavas, 2001) to be identified with the aid of the highly specific MS detection. Several steps of the analytical method from sampling to extraction, clean-up and instrumental analysis have been systematically optimised for ANs with 3 to 9 carbons detected from gaseous air samples.

In the summer campaigns, 11 ANs have been identified and quantified, but only 8 ANs were detected to be present in the late winter/spring samples. Figure 9 shows the summed concentrations of ANs detected for each sample. It is to be noted, however, that the distribution over the different analogues and isomers is largely fluctuating between samples. The nomenclature for diverse AN analogues are listed in Table 9.

During the late summer campaign, the highest average daily deposition has been observed for 3C5 as can be expected from the concentration data (Figure 10), especially, for Atlantic/Channel/UK air-masses (1.8 ng N/m^2 day), followed by lower values for the North Sea/continental (0.76 ng N/m^2 day), but below the detection limit for the North Sea air-masses (0.18 ng N/m^2 day).

The contribution of 2C4 was also significant from the UK/Atlantic/Channel air-masses (1.7 ng N/m^2 day), whereas lower fluxes were found from 1C3, 1C4, 2C5, 1C5, 3C6, 2C6, 1C6 and 1C8 alkyl nitrates with similar fluxes (0.25 ng N/m^2 day). For the North Sea influenced air-masses, the contributions from 2C4 and 2C5 were found to be significant, both with a deposition value of 0.44 ng/m^2 day. Moreover, the 1C4, 1C5, 3C6 and 1C6 ANs also contributed to the flux, each with ~0.2 ng N/m^2 day.

Under mixed continental-North Sea influence, the contribution was significant from 1C4, 3C5, and 2C5 compounds, with deposition rates of 0.35, 0.76, and 0.46 ng N/m^2 day, respectively. The 1C5, 1C6, 1C7, 1C8, and 1C9 compounds also contributed to the N-flux, each with a flux of around 0.2 ng N/m^2 day.

The average fluxes of ANs for the UK/Atlantic/Channel, North Sea, and the mixed continental-North Sea air-masses were found to be 5.3, 1.4, and 2.9 ng N/m^2 day, respectively, corresponding to an overall average AN flux of 9.6 ng N/m^2 day for this late summer campaign.

Over the early winter/spring campaign, a high average daily flux of 3C5 has also been found for all the three main air-masses, ranging from 3.8 to 10.7 ng N/m^2 day. For the Atlantic/Channel/UK air-masses, the contributions of 3C5 was about 55 % of the total AN-flux, followed by the contribution from 2C5 (0.98 ng N/m^2 day), 2C6 and 1C8 (each with 0.5 ng N/m^2 day), whereas the fluxes of 1C4, 1C5, 1C6, and 1C9 were observed to be much lower, i.e., 0.15, 0.22, 0.37, and 0.34 ng N/m^2 day, respectively.

For continental air-masses, intensive fluxes of 3C5, 1C6, and 1C7 AN compounds, i.e., 4.4, 5.7, and 4.6 ng N/m^2 day, respectively, have been observed. The 2C5 has also shown a fairly high value of 1.5 ng N/m^2 day. The 1C8 and 1C9 ANs has only contributed with negligibly low fluxes of 0.37 and 0.15 ng N/m^2 day, respectively.

For air-masses, arriving from the North Sea, the flux of 3C5 was extremely high, i.e., with an average value of 10.7 ng N/m^2 day, corresponding to about 80 % of the total average AN-flux. The other ANs, characteristic for this air-mass, were 2C5, 1C5, 2C6, and 1C6 with low fluxes, ranging between 0.5-0.73 ng N/m^2 day. Negligibly low fluxes of 1C4, 1C8 and 1C9 ANs were also found with values of 0.16-0.27 ng N/m^2 day.

The average fluxes of ANs for the Atlantic/Channel/UK, continental and North Sea air-masses were found to be 6.9, 15.6, and 13.8 ng N/m^2 day, corresponding to an overall AN-flux of 36.3 ng N/m^2 day for this campaign. It can be concluded that the most contribution of AN-fluxes originate from air-masses approaching from the continent and the North Sea.

In the mid-summer campaign, similarly to the late summer campaign, the AN-fluxes were the most significant from the Atlantic/Channel/UK air-masses. The highest N-flux was observed again by 3C5 with an average value of 12.9 ng N/m^2 day, although the 1C4 flux was also very pronounced (6.5 ng N/m^2 day). The 1C6, 1C7, 1C8 and 1C9 ANs also contributed to the N-flux, but to a much lower extent than the former two ANs, i.e., with depositions ranging between 1.0-1.2 ng N/m^2 day. The fluxes of 2C5, 1C5, and 2C6 were negligibly low, amounting only up to 0.38, 0.6, and 0.57 ng N/m^2 day, respectively.

For continental air-masses, the daily average fluxes of 1C4, 3C5 and 1C8 were found to be the most significant contributors, i.e., 1.0, 2.8 and 2.0 ng N/m^2 day, respectively. The fluxes of 1C5, 2C6, 1C6, and 1C7 were lower, ranging between 0.34-0.46 ng N/m^2 day. For the North Sea air-masses, also the flux of 3C5 was the most decisive with an average value of 4.5 ng N/m^2 day, followed by the 1C5 flux (0.9 ng N/m^2 day). The 1C4, 2C6, 1C6, 1C7, 1C8 and 1C9 compounds contributed to the N-flux to a low and varying extent, i.e., 0.5, 0.3, 0.67, 0.36, 0.45, and 0.18 ng N/m^2 day, respectively.

The average fluxes of ANs for the Atlantic/Channel/UK, continental and North Sea air-masses were found to be 25.3, 7.5, and 7.9 ng N/m^2 day, corresponding to an overall AN-flux of 40.7 ng N/m^2 day for this campaign. Comparing this campaigns data with those observed for the late winter/spring campaign, a much higher percentage of AN contribution to the N-flux by the Atlantic/Channel/UK air-masses can be experienced (i.e. ~60 % of the total average AN-flux), whereas in the late winter/spring campaign the fluxes from the North Sea and the continental air-masses were prevailing (i.e., 38 % and 43 %, respectively).

The fluxes of alkyl nitrates have been found to be more pronounced for the summer periods than for the winter/spring months. Although the contribution of ANs to the total (inorganic and organic) N-flux has been found to be low, i.e., ranging between 10-40 ng N/m^2 day, it was amounting up to around 10 % of the NO_2 deposition observed for sea-surfaces.

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Tables

Table 1 Average and representative individual (daily) oceanic and continental nitrogen fluxes of inorganic nitrogen compounds during the autumn/ early winter campaign in 2004

	Deposition (mg N/m^2 day)			***Ratio of fluxes***
	Average (over season)	Oceanic (21st Sept., 2004.)	Continental (1st Oct., 2004.)	(Continental to Oceanic)
Gaseous compounds –				
N (HNO_2)	0.17 ± 0.12	0.08	0.16	2.0
N (HNO_3)	0.05 ± 0.04	0.04	0.11	2.7
N (NH_3)	1.98 ± 0.83	1.72	2.94	1.8
Total gaseous N –	**2.12 ± 0.89**	**1.83**	**3.21**	**1.8**
Aerosols –				
Coarse (AD > 10 µm)				
N (NO_3^-)	0.40 ± 0.24	0.37	0.98	2.7
N (NH_4^+)	0.16 ± 0.14	0.03	0.33	11
total	*0.55 ± 0.36*	*0.40*	*1.32*	*3.3*
Medium (10µm>AD>2µm)				
N (NO_3^-)	0.14 ± 0.14	0.18	0.26	1.4
N (NH_4^+)	0.35 ± 0.34	0.03	0.85	28
total	*0.49 ± 0.45*	*0.21*	*1.11*	*5.3*
Fine (2 µm>AD>0.4 µm)				
N (NO_3^-)	0.01 ± 0.009	0.006	0.02	3.0
N (NH_4^+)	0.06 ± 0.03	0.035	0.14	4.0
total	*0.07 ± 0.03*	*0.04*	*0.16*	*4.0*
Total aerosol N –	**1.09 ± 0.76**	**0.65**	**2.6**	**4.0**
Total dry N flux –	**2.75 ± 1.60**	**2.5**	**5.8**	**2.3**
Ratio of aerosol to total dry N (%)	***40***	***26***	***45***	**-**
Total wet flux	**3.6 ± 2.9**	**0**	**0.92**	**-**
Ratio of wet to dry fluxes	**1.3**	**0**	**0.16**	**-**

Table 2 Average nitrogen fluxes and fluctuations, expressed as standard deviation (±SD) of inorganic nitrogen for the late summer campaign in 2005

	Deposition (mg N/m^2 day)			**Ratio of fluxes**	
	(a) UK/Atlantic/ Channel	(b) North Sea	(c) North Sea/ Continental	(a) to (b)	(a) to (c)
Gaseous –					
N (HNO_2) (denuder)	0.20 ± 0.05	0.12 ± 0.06	0.17 ± 0.06	1.6	1.14
N (HNO_3)	0.13 ± 0.06	0.19 ± 0.14	0.08 ± 0.003	0.7	1.73
N (NH_3)	4.48 ± 1.49	2.37 ± 1.97	0.77 ± 1.34	1.9	5.8
N (NO_2) (diffusion tube)	0.0002 ± 0.00005	0.00025 ± 0.00004	0.00031 ± 0.00005	1.5	1.2
Total gaseous N –	***4.80 ± 1.45***	***2.68 ± 2.06***	***1.02 ± 1.37***	***1.8***	***4.7***
Aerosols –					
Coarse (AD > 10 µm)					
N (NO_3^-)	0.12 ± 0.07	0.39 ± 0.35	0.58 ± 0.08	0.3	0.20
N (NH_4^+)	1.47 ± 0.08	0.45 ± 0.72	0.11 ± 0.03	3.2	13.4
total coarse	*1.59 ± 0.14*	*0.84 ± 0.40*	*0.69 ± 0.06*	*1.9*	*2.3*
Medium (10µm>AD>2µm)					
N (NO_3^-)	0.74 ± 0.68	0.08 ± 0.04	0.55 ± 0.16	9.4	1.36
N (NH_4^+)	1.08 ± 0.87	0.11 ± 0.04	1.19 ± 0.23	10	0.90
total medium	*1.82 ± 1.55*	*0.19 ± 0.04*	*1.74 ± 0.38*	*9.8*	*1.04*
Fine (2 µm>AD>0.4 µm)					
N (NO_3^-)	0.09 ± 0.03	0.06 ± 0.02	0.15 ± 0.13	1.6	0.62
N (NH_4^+)	0.14 ± 0.05	0.07 ± 0.02	0.27 ± 0.24	2.0	0.52
total fine	*0.23 ± 0.08*	*0.13 ± 0.05*	*0.42 ± 0.36*	*1.8*	*0.56*
Total aerosol N –	***3.63 ± 1.72***	***1.16 ± 0.43***	***2.85 ± 0.40***	***3.1***	***1.3***
Total dry flux –	**8.44 ± 3.1**	**3.84 ± 2.47**	**3.87 ± 1.23**	**2.5**	**2.2**
Wet flux –					
N (NO_3^-)	12.2 ± 22.2	1.79 ± 2.84	0.0 ± 0.0	6.8	-
N (NH_4^+)	0.72 ± 0.92	1.89 ± 4.54	0.0 ± 0.0	0.4	-
Total wet flux	**13.1 ± 23**	**3.68 ± 7.38**	**0.0 ± 0.0**	**0.5**	**-**
Total flux	**21.5 ± 26**	**7.52 ± 9.8**	**3.87 ± 1.23**	**2.9**	**5.6**
Percent of aerosols in dry flux (%)	***43***	***30***	***74***		
Wet to dry ratio	**1.55**	**1.1**	**0**		

Table 3 Average nitrogen fluxes and fluctuations (±SD) of inorganic nitrogen for the early winter/spring campaign in 2006

	Deposition (mg N/m^2 day)			**Ratio of fluxes**	
	(a) Atlantic/ Channel*	(b) Continental	(c) North Sea	(b) to (a)	(b) to (c)
Gaseous –					
N (HNO_2) (denuder)	0.05 ± 0.04	0.11 ± 0.05	0.06 ± 0.05	2.3	2.0
N (HNO_3)	0.05 ± 0.04	0.07 ± 0.04	0.08 ± 0.04	1.2	0.85
N (NH_3)	1.12 ± 0.75	1.44 ± 1.46	1.35 ± 0.98	1.3	1.1
N (NO_2) (diffusion tube)	0.00014 ± 0.0001	0.00008 ± 0.00002	0.00007 ± 0.00003	1.5	1.2
Total gaseous N –	***1.22 ± 0.77***	***1.62 ± 1.48***	***1.49 ± 1.02***	***1.3***	***1.1***
Aerosols –					
Coarse (AD > 10 µm)					
N (NO_3^-)	0.25 ± 0.16	0.08 ± 0.04	0.19 ± 0.11	0.34	0.43
N (NH_4^+)	0.28 ± 0.23	0.10 ± 0.07	0.24 ± 0.23	0.36	0.41
total coarse	*0.53 ± 0.32*	*0.18 ± 0.11*	*0.44 ± 0.34*	*0.35*	*0.42*
Medium (10µm>AD>2µm)					
N (NO_3^-)	0.19 ± 0.11	0.38 ± 0.21	0.23 ± 0.12	2.0	1.7
N (NH_4^+)	0.21 ± 0.18	0.67 ± 0.36	0.31 ± 0.21	3.0	2.2
total medium	*0.41 ± 0.26*	*1.05 ± 0.56*	*0.54 ± 0.32*	*2.5*	*2.0*
Fine (2 µm>AD>0.4 µm)					
N (NO_3^-)	0.10 ± 0.14	0.23 ± 0.20	0.15 ± 0.15	2.2	1.5
N (NH_4^+)	0.21 ± 0.21	0.35 ± 0.25	0.25 ± 0.14	1.7	1.4
total fine	*0.31 ± 0.34*	*0.58 ± 0.45*	*0.40 ± 0.29*	*1.9*	*1.5*
Total aerosol N –	***1.25 ± 0.70***	***1.81 ± 0.66***	***1.37 ± 0.53***	***1.5***	***1.3***
Total dry flux –	**2.5 ± 1.5**	**3.4 ± 2.1**	**2.9 ± 1.6**	**1.4**	**1.2**
Wet flux –					
N (NO_3^-)	1.00 ± 1.9	0.57 ± 1.2	0.56 ± 2.1	0.6	1.0
N (NH_4^+)	2.35 ± 5.5	1.25 ± 2.6	0.98 ± 3.2	0.5	1.3
DON	0.20 ± 0.6	0.36 ± 1.1	0.07 ± 0.3	1.8	5.2
Total wet flux	**3.50 ± 7.2**	**2.10 ± 3.7**	**1.61 ± 5.3**	**0.5**	**1.2**
Total flux	**6.0 ± 8.7**	**5.5 ± 5.8**	**4.5 ± 6.9**	**0.9**	**1.2**
Percent of aerosols in total dry flux (%)	***50***	***53***	***47***		
Wet to dry ratio	**1.4**	**0.62**	**0.56**		

Table 4 Average nitrogen fluxes and fluctuations (±SD) of inorganic nitrogen for the mid-summer campaign in 2006

	Deposition (mg N/m^2 day)			**Ratio of fluxes**	
	(a) Atlantic/ Channel*	(b) Continental	(c) North Sea	(b) to (a)	(b) to (c)
Gaseous –					
N (HNO_2) (denuder)	0.07 ± 0.05	0.08 ± 0.07	0.04 ± 0.05	1.2	2.0
N (HNO_3)	0.09 ± 0.05	0.14 ± 0.10	0.11 ± 0.04	1.5	1.3
N (NH_3)	1.20 ± 0.95	1.63 ± 1.13	1.63 ± 0.97	1.4	1.0
N (NO_2) (diffusion tube)	0.00018 ± 0.00034	0.0002 ± 0.00007	0.00023 ± 0.00003	0.8	1.1
Total gaseous N –	***1.36 ± 0.96***	***1.85 ± 1.09***	***1.78 ± 0.99***	***1.4***	***1.0***
Aerosols –					
Coarse (AD > 10 µm)					
N (NO_3^-)	0.26 ± 0.19	0.24 ± 0.14	0.20 ± 0.16	0.9	1.2
N (NH_4^+)	0.20 ± 0.17	0.08 ± 0.12	0.17 ± 0.16	0.4	0.5
total coarse	*0.46 ± 0.30*	*0.32 ± 0.19*	*0.38 ± 0.16*	*0.7*	*0.8*
Medium (10µm>AD>2µm)					
N (NO_3^-)	0.09 ± 0.08	0.04 ± 0.03	0.05 ± 0.05	0.4	0.8
N (NH_4^+)	0.16 ± 0.20	0.23 ± 0.16	0.23 ± 0.25	1.4	1.0
total medium	*0.25 ± 0.26*	*0.27 ± 0.18*	*0.28 ± 0.26*	*1.1*	*0.9*
Fine (2 µm>AD>0.4 µm)					
N (NO_3^-)	0.08 ± 0.16	0.04 ± 0.05	0.07 ± 0.11	0.5	0.5
N (NH_4^+)	0.16 ± 0.14	0.24 ± 0.06	0.20 ± 0.15	1.1	1.2
total fine	*0.29 ± 0.28*	*0.27 ± 0.09*	*0.27 ± 0.23*	*0.9*	*1.1*
Total aerosol N –	***0.99 ± 0.65***	***0.86 ± 0.37***	***0.93 ± 0.52***	***0.9***	***0.9***
Total dry flux –	**2.4 ± 1.3**	**2.7 ± 1.5**	**2.7 ± 1.4**	**1.1**	**1.0**
Wet flux –					
N (NO_3^-)	6.67 ± 20	1.1 ± 2.8	0.0 ± 0.0	0.6	-
N (NH_4^+)	3.04 ± 8.6	1.2 ± 2.6	0.0 ± 0.0	0.5	-
DON	0.27 ± 0.9	3.5 ± 12	0.0 ± 0.0	12	-
Total wet flux	**10.0 ± 29**	**5.1 ± 15**	**0.0 ± 0.0**	**0.24**	**-**
Total (wet+dry) flux	**12.4 ± 29**	**7.8 ± 16.5**	**2.7 ± 1.4**	**0.63**	**2.9**
Percent of aerosols in total dry flux (%)	***41***	***32***	***35***		
Wet to dry ratio	**4.2**	**1.9**	**0**		

Table 5 Relative contribution (%) of various N-species to the nitrogen deposition in gases, aerosols, and rainwater samples for major air-masses observed over diverse campaigns

	Relative contribution (%)								
	Late summer campaign			Late winter/spring campaign			Mid-summer campaign		
	Atlantic/ Channel/ UK	**North Sea**	**Continental/ North Sea**	**Atlantic/ Channel/ UK**	**Continental**	**North Sea**	**Atlantic/ Channel/ UK**	**Continental**	**North Sea**
Aerosol N									
(>10 µm)									
N (NO_3^-)	3.2	33.7	20.4	19.6	4.6	14.1	26.1	27.6	22.0
N (NH_4^+)	40.3	39.2	3.8	22.4	5.5	17.7	19.7	9.7	18.8
(2-10 µm)									
N (NO_3^-)	20.4	6.8	19.2	15.6	21.0	16.7	8.7	4.2	5.1
N (NH_4^+)	29.6	9.2	41.8	17.6	36.9	22.4	16.3	26.6	25.3
(0.4-2 µm)									
N (NO_3^-)	2.5	5.1	5.1	8.1	12.6	11.2	8.1	4.2	7.4
N (NH_4^+)	3.9	6.0	9.5	16.6	19.4	17.9	21.2	27.5	21.5
Total N									
(>10 µm)	43.6	72.9	24.3	42.1	10.1	31.8	45.7	37.4	40.8
(2-10 µm)	50.0	16.0	61.1	33.2	57.9	39.1	25.0	30.9	30.4
(0.4-2 µm)	6.4	11.1	14.7	24.8	31.9	29.1	29.3	31.8	28.9
Rainwater N									
N (NO_3^-)	94.0	48.6	0.0	28.6	27.1	34.8	66.7	17.1	0.0
N (NH_4^+)	6.0	51.4	0.0	67.1	59.5	60.9	30.4	18.5	0.0
DON	n.a.	n.a.	0.0	5.7	17.1	4.3	2.7	65.6	0.0
Total N									
Gaseous N	22.3	35.6	26.4	20.4	29.4	32.9	11.0	23.7	66.1
Aerosol N	16.9	15.4	73.6	20.8	33.0	30.5	8.0	11.1	34.4
Rainwater N	60.9	48.9	0.0	58.3	38.2	35.8	80.6	65.4	0.0
Gaseous N									
N (HNO_2)	4.1	4.6	16.9	4.0	6.9	3.8	5.0	4.4	2.3
N (HNO_3)	2.8	7.0	7.5	4.4	4.1	5.2	6.8	7.5	6.1
N (NH_3)	93.2	88.4	75.6	91.6	89.1	91.0	88.2	88.1	91.6

n.a. – not analysed

Table 6 Relative contribution of N-fluxes for various air-masses to the nitrogen deposition over each season/campaign

	Relative contribution (%)								
	Late summer campaign			Late winter/spring campaign			Mid-summer campaign		
	Atlantic/ Channel/ UK	**North Sea**	**continental/ North Sea**	**Atlantic/ Channel/ UK**	**Continental**	**North Sea**	**Atlantic/ Channel/ UK**	**Continental**	**North Sea**
N (HNO_2)	40	25	35	23	51	26	36	42	21
N (HNO_3)	33	47	19	27	33	39	27	41	32
N (NH_3)	59	31	10	29	37	34	27	36	37
Total gaseous N	**56**	**31**	**12**	**28**	**37**	**34**	**27**	**37**	**36**
(> 10 µm)									
N (NO_3^-)	11	36	53	47	16	37	37	34	29
N (NH_4^+)	72	22	5	45	16	39	43	19	38
Total N	51	27	22	46	16	38	39	28	33
(2.0-10 µm)									
N (NO_3^-)	54	6	40	24	47	28	51	21	28
N (NH_4^+)	45	4	50	18	56	26	26	37	37
Total N	49	5	46	21	52	27	31	33	35
(0.4-2.0 µm)									
N (NO_3^-)	31	20	49	21	47	32	44	20	37
N (NH_4^+)	29	14	56	26	44	31	32	37	31
Total N	30	17	54	24	45	31	35	33	32
Total aerosol N	**48**	**15**	**37**	**28**	**41**	**31**	**36**	**31**	**33**
Total dry N	**52**	**24**	**24**	**28**	**39**	**33**	**31**	**35**	**35**
N (NO_3^-)	87	13	0	47	27	26	86	14	0
N (NH_4^+)	28	72	0	51	27	21	72	28	0
DON	n.a.	n.a.	0	32	57	11	7	93	0
Total rainwater N	**78**	**22**	**0**	**49**	**29**	**22**	**66**	**34**	**0**
Total N (wet+dry)	**65**	**23**	**12**	**38**	**34**	**28**	**54**	**34**	**12**

n.a. – not analysed

Table 7 Annual deposition of nitrogen in De Haan and extrapolated values for the North Sea with and without the British Channel

	Annual N-flux		
	De Haan (kg N/km^2 yr)	**North Sea without Channel (kt N/yr)**	**Greater North Sea (kt N/yr)**
N (HNO_2)	25	17	19
N (HNO_3)	33	22	25
N (HNO_2 + HNO_3)	57	39	44
N (NH_3)	509	349	394
Total gaseous N	**566**	**389**	**438**
(PM > 10 µm)			
N (NO_3^-)	74	51	58
N (NH_4^+)	66	45	51
Total N	*140*	*96*	*108*
(PM 2.0-10 µm)			
N (NO_3^-)	59	41	46
N (NH_4^+)	111	76	86
Total N	*170*	*117*	*132*
(PM 0.4-2.0 µm)			
N (NO_3^-)	41	28	31
N (NH_4^+)	88	61	68
Total N	*129*	*89*	*100*
Total aerosol N	**439**	**301**	**340**
Total dry (gas+aerosol) N	**1010**	**693**	**782**
N (NO_3^-)	602	413	466
N (NH_4^+)	537	368	415
DON	268	184	207
Total rainwater N	**1357**	**931**	**1050**
Total (wet+dry) N	**2366**	**1624**	**1832**
Oxidized N	*834*	*572*	*645*
Reduced N	*1310*	*899*	*1014*

Table 8 Relative abundance (%) of the particles types (combined groups) obtained by EPMA on representative days

	Al-Si	**NaCl**	**Org + S**	**FeOx**	**$NaNO_3$**	**SiOx**	**Biogenic**
September 22, 2004							
0.2 - 2.0 µm	52.1	9.4	14.1	9.0	9.8	3.4	2.1
2.0 - 8.0 µm	55.2	9.1	16.1	7.7	7.0	3.5	1.4
October 18, 2006							
0.2 - 2.0 µm	68.4	0.5	1.5	19.5	10.0	n.d.	n.d.
2.0 - 8.0 µm	38.0	22.8	22.2	10.4	6.6	n.d.	n.d.

n.d. – not detected

Table 9 Nomenclature of alkyl nitrates

Alkyl nitrate	
Methyl	1 C1
Ethyl	1 C2
1-Propyl	1 C3
1-Butyl	1 C4
2-Butyl	2 C4
1-Pentyl	1 C5
2-Pentyl	2 C5
3-Pentyl	3 C5
1-Hexyl	1 C6
1-Heptyl	1 C7
1-Octyl	1 C8
1-Nonyl	1 C9

Figures

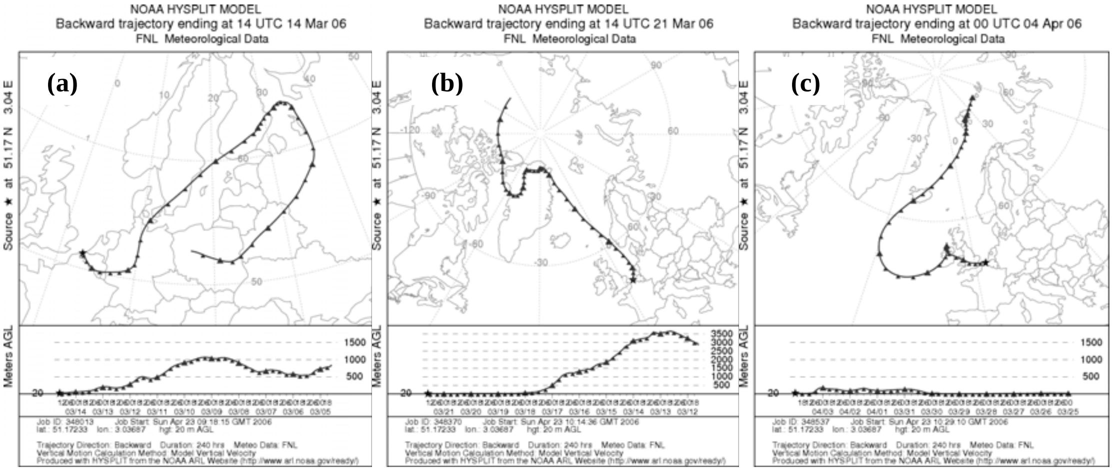

Fig 1 Typical Backward Trajectories (BWTs) for the three main air-masses, (a) Continental, (b) North Sea, and (c) Atlantic/Channel/UK

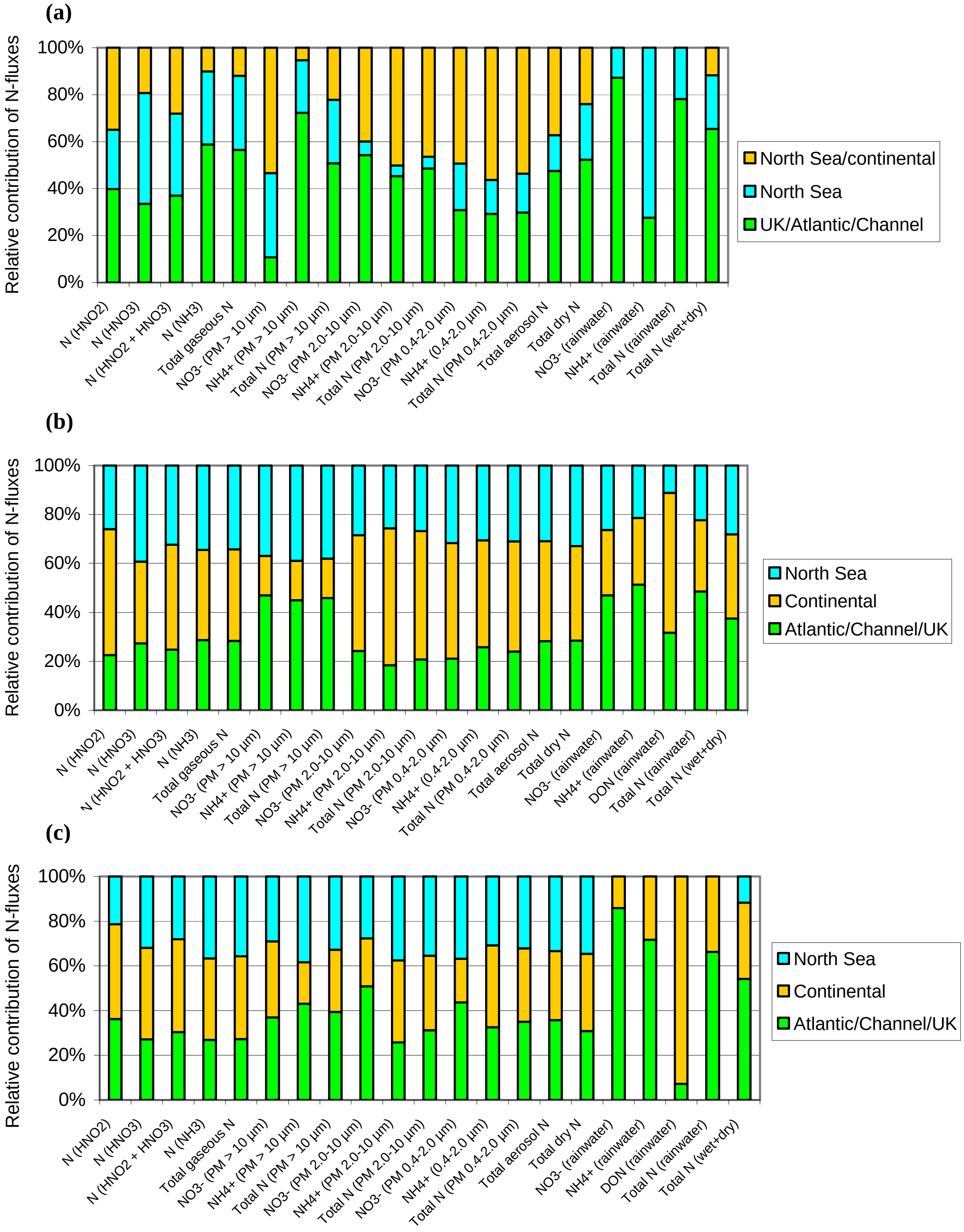

Fig 2 Relative contributions of N-fluxes of various species/air-masses in (a) the late summer campaign, (b) the late winter/spring campaign, and (c) the mid-summer campaign

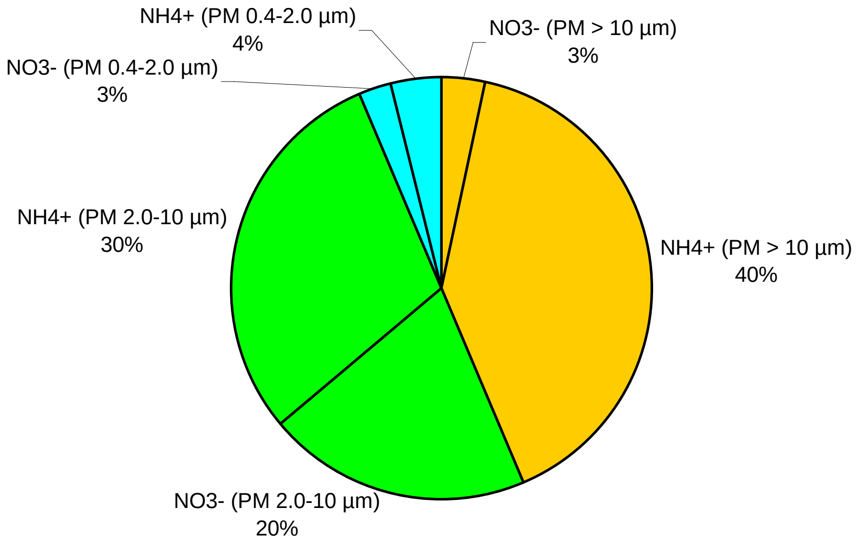

Fig 3 Relative contributions of inorganic N-species in the three aerosol fractions to the total N-flux for Atlantic/Channel/UK influenced air-masses during the late summer campaign

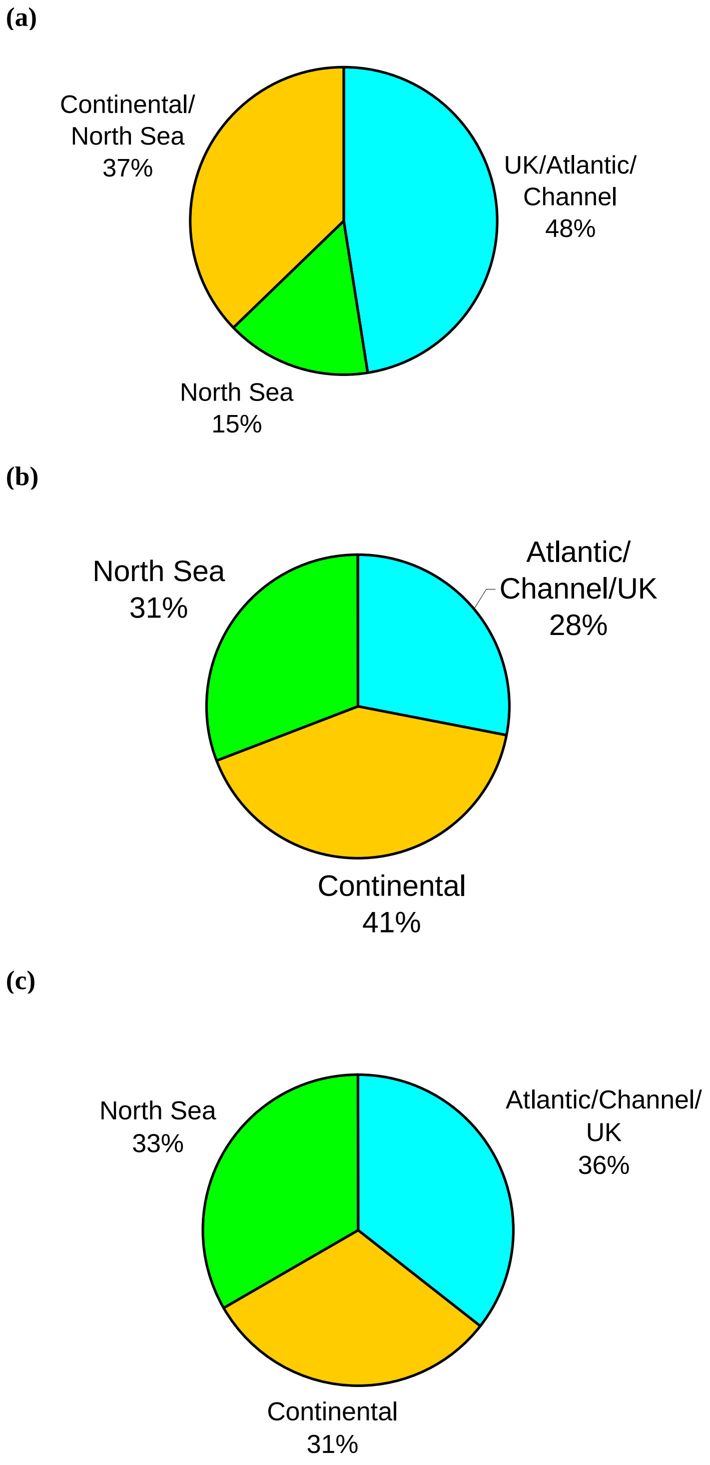

Fig 4 Relative contributions of various air-masses to the total inorganic N-flux in (a) the late summer campaign, (b) the late winter/spring campaign, and (c) the mid-summer campaign

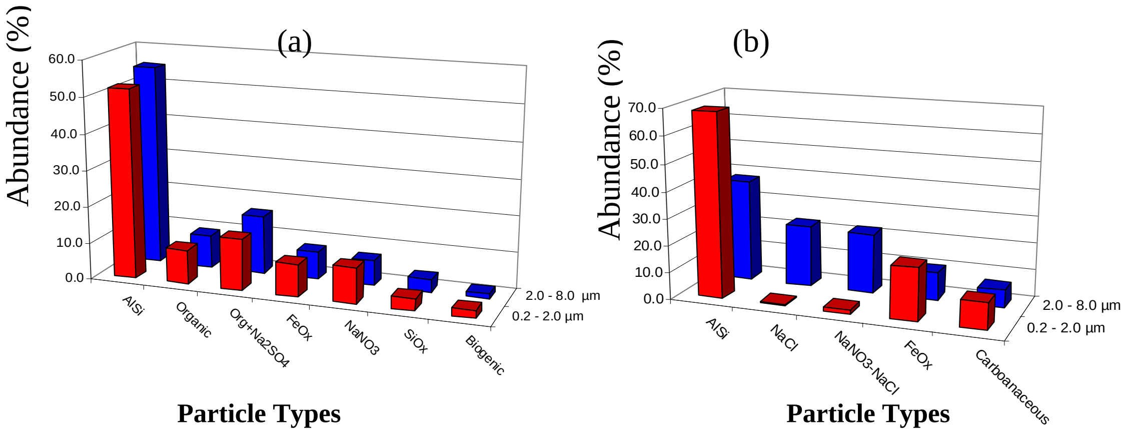

Fig 5 TW-EPMA results for a selected (a) marine, and (b) continental air-mass for the autumn/early winter campaign

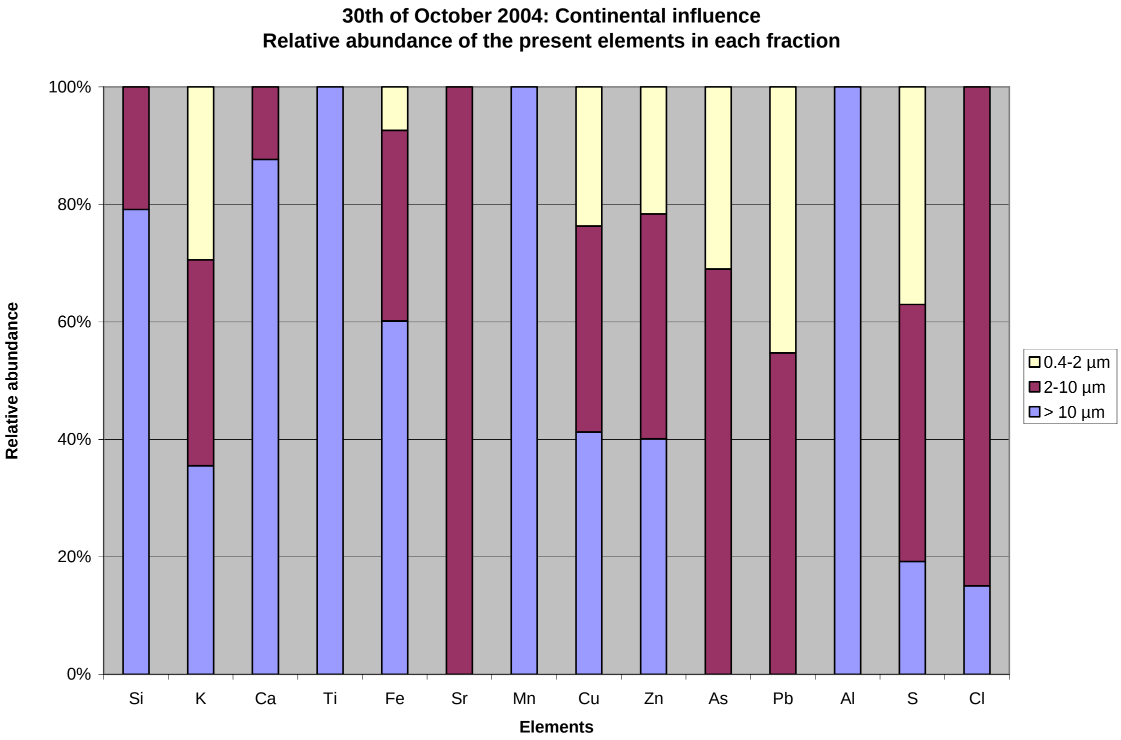

Fig 6 Relative abundance of several elements in the three size-fractions for the continental aerosol sample during the autumn/early winter campaign

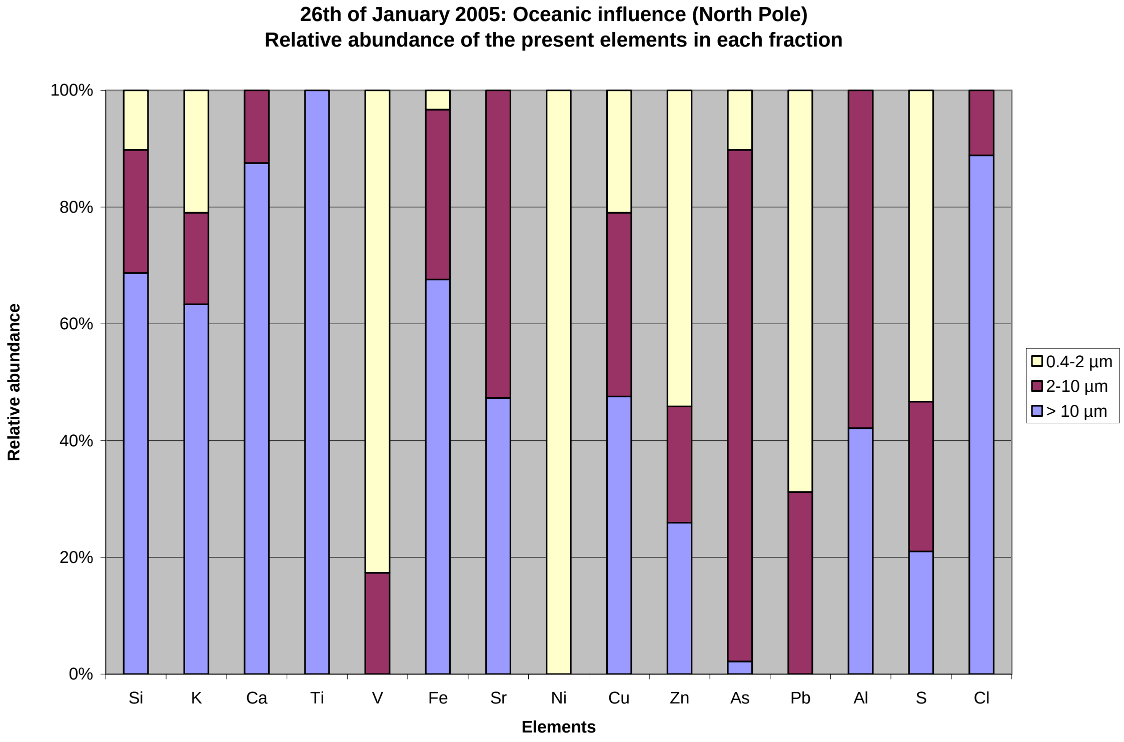

Fig 7 Relative abundance of several elements in the three size-fractions for the oceanic aerosol sample (origin: North Pole)

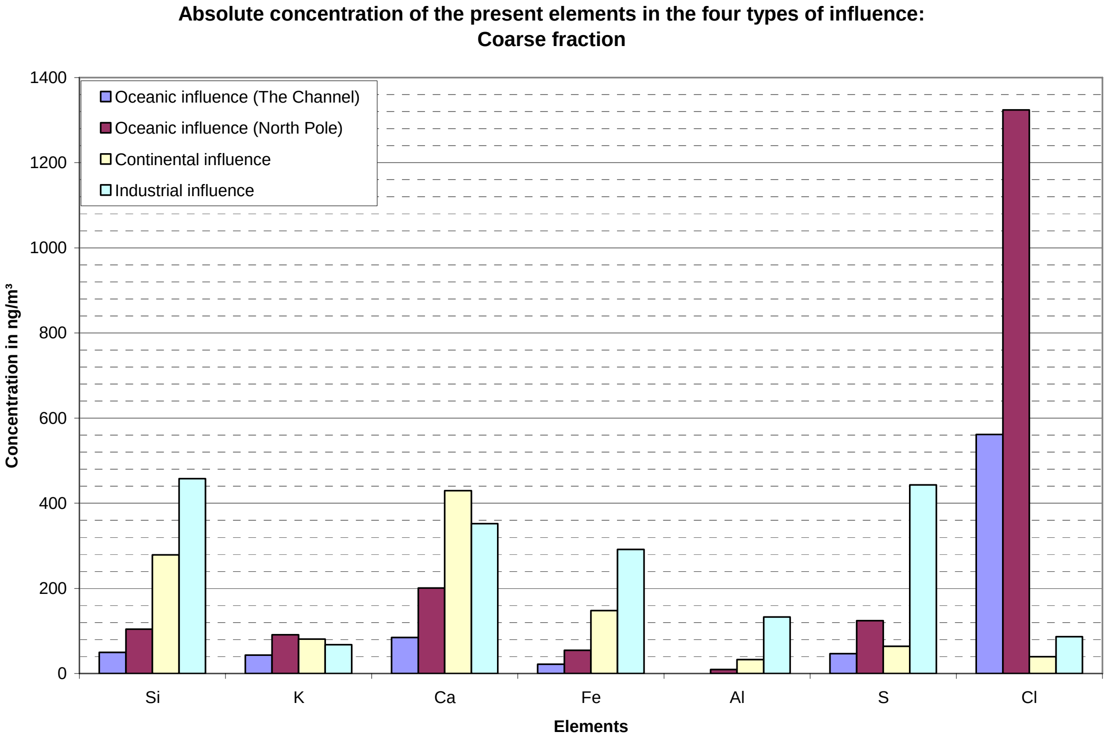

Fig 8 Absolute abundance of Si, K, Ca, Fe, Al, S, and Cl for the coarse aerosol fraction as a function of the four air-mass influences during the autumn/early winter campaign

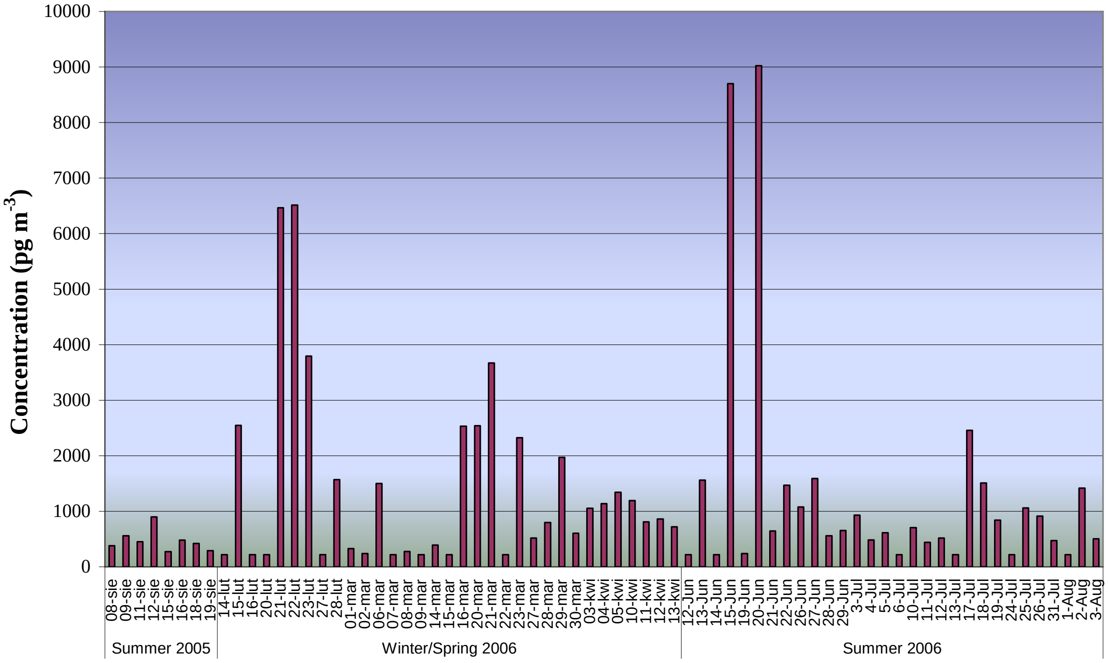

Fig 9 Variation in the sum of AN concentrations during various sampling campaigns

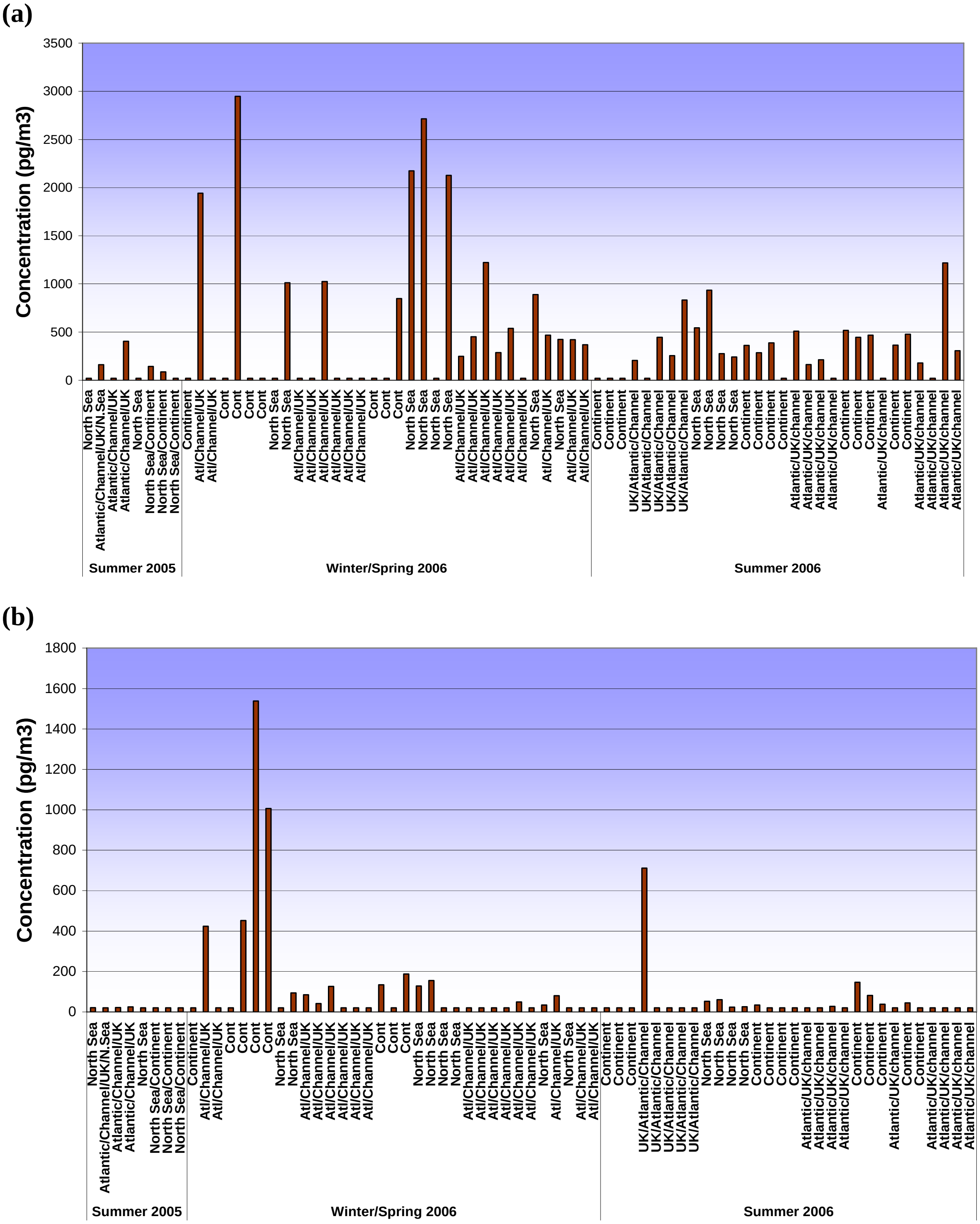

Fig 10 Variation in the concentrations of individual AN-analogues during the sampling campaigns; (a) 3C5, and (b) 2C6