Nitrogen species and macroelements in aerosols over the southern Baltic Sea^{*}

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KEYWORDS

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Abstract

The annual cycle of atmospheric nitrogen species and macroelements (Na⁺, K⁺, Ca²⁺, Mg²⁺ and Cl⁻) over the south-eastern Baltic region was investigated. A one-year record enabled the variability of nitrogen species and macroelements in the aerosol over the coastal station at Hel to be traced.

The highest concentrations of sea salt components were recorded in summer, while anthropogenic nitrate concentrations were highest in winter. When the air masses were of mixed marine and continental origin, the nitric acid reacted with coarse sea salt particles to form stable, coarse sodium nitrate. This seems to be a permanent removal pathway for nitrate.

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Anthropogenic aerosol species like NH_4^+ or NO_3^- formed by gas-to-particle conversion were generally associated with fine particles (<1 μ m). Coarse particles like sodium or chloride resulted from resuspension from seawater.

1. Introduction

The European coastal zones are areas of great concern in view of the growing problems associated with increasing inputs of nutrients. Intensive agriculture and automobile traffic are the main sources of the high atmospheric concentrations of reactive N-species, mainly nitrogen oxides (NO_x) , but also HNO_3 , NH_3 and NH_4^+ . Nutrient deposition to seawater can cause eutrophication in the upper water layer. This is one reason why exchange of particles and gases at the air-sea interface are extremely important for the marine environment.

Not only ammonia and ammonium ions $(NH_3 + NH_4^+)$ but also nitric acid and nitrate ions $(HNO_3 + NO_3^-)$ in the aerosol act as nutrients once they have entered seawater. Their air-to-sea deposition may occur in particulate or gaseous form. Since particulate ammonium nitrate (NH_4NO_3) is volatile under dry and warm conditions, it may dissociate to form highly soluble gases like NH_3 and HNO_3 , which deposit rapidly onto the water surface. In addition, nitric acid reacts with sea salt to form coarse particles of sodium nitrate $(NaNO_3)$, which increases deposition velocities even more.

In order to understand ambient air concentrations of nitrogen compounds, sources within the marine environment itself must also be taken into account. Ammonia can be re-emitted from the sea surface when its partial pressure at the air-sea interface is insufficient to force its evaporation. Furthermore, nitric acid is continuously produced from nitrogen oxides in the marine atmosphere. However, with offshore winds, scavenging of nitric acid from the atmosphere seems to be the dominant process in coastal regions because of its high concentrations in continental air masses.

With respect to their sources, aerosol species are strictly divided into fine particles (mainly anthropogenic) due to particle condensation, and coarse particles resulting from re-suspension from seawater (Ten Brink *et al.* 1997). NH_4^+ and NO_3^- are therefore associated with fine particles, smaller than 1 μ m in diameter. However, interaction between sea salt and nitric acid should result in a shift in nitrate size distribution towards the coarse mode (Seinfeld 1986, Hillamo & Kauppinen 1991).

Estimates of nitrogen inputs are often based on measurements conducted over land or on a limited number of measurements made over the open sea. Therefore, the coastal effects on the total nitrogen depositions are included in a only simplistic way, if at all. However, the greatest changes in both the physical and chemical properties of an air mass advected from the land over the sea, and therefore also in the resulting processes, are expected in coastal regions. Since continental sources of atmospheric nitrogen species are dominant, sharp gradients in concentrations and associated fluxes across the coastal zone are expected. For example, ammonia concentrations in the German Bight were found to have been reduced by a factor of 4 after being transported 70 km out to sea (Plate *et al.* 1995), while 40% of the sea salt is transformed to sodium nitrate (Schulz in press).

2. Experimental

Samples of ambient air were collected from 28 February 1997 to 31 March 1998 at the top of a disused observation tower standing in a coastal woodland at the tip of the Hel Peninsula ($\varphi = 54^{\circ}35.974'$ N, $\lambda = 18^{\circ}48.858'$ E) (Fig. 1). The 20-meter-high tower allowed for continuous sampling almost undisturbed by local sources, except for the narrow north-west sector, where the air had to flow over the town of Hel. The observation site was located *ca* 20 km to the north-east of the Gdańsk, Gdynia and Sopot conurbation.

Samples were usually taken at one-week intervals. To avoid filter clogging, the sampling was shortened to 15 minutes per hour using an automatic clock. However, during two separate experiments in summer (16 June–10 August 1997) and in winter (3 February–31 March 1998), samples were collected every 4 days. 14 samples were taken during spring (March–May 1997), 19 during summer (June–August 1997), 12 during autumn (September–November 1997) and 23 during winter (December 1997 –March 1998). March 1998 was much colder than the same month a year earlier, which is why it is included in the winter period.

Two filter holders were deployed:

- (i) for ammonia (NH_4^+) ,
- (ii) for NO_3^- , Cl^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} .

Coarse aerosol particles were collected on Teflon membrane filters (0.5 μ m pore size), fine aerosol particles and gaseous acids on pre-washed nylon filters (0.45 μ m pore size). Ammonia was deposited on Whatman 41 filter papers, pre-washed and impregnated with 5% H₃PO₄. In addition, two denuders impregnated with 2% oxalic acid (for NH₃) and 4% sodium chloride (for HNO₃) were used.

Critical orifices at 2.2 m^3 h and a gas meter for the total air volume controlled the flow rate through the system.

A 10-stage Berner low-pressure impactor was used to determine the size fractionation of the aerosol. The particle cut-off diameters in the impactor were: < 0.05, 0.05-0.1, 0.1-0.2, 0.2-0.4, 0.4-0.8, 0.8-1.5, 1.5-3.0, 3.0-6.0, 6.0-12.0 and $> 12.0 \ \mu\text{m}$. Thin pre-washed aluminium foils were used as the



Fig. 1. The geographical location of the Hel sampling station (sectors describing air mass trajectories: 1 – from the west, 2 – from the south, 3 – from the east, 4 – from the north (Nadstazik 1999)

deposition surface. The exposure time was synchronised to that of the filter holders and denuders. The impactor data were taken during 8 months only (in summer – June–August 1997 and in winter – November 1997–March 1998). Altogether, 12 samples were taken during the summer and 20 samples during the winter period. The flow rate was maintained at 1.5 m³ h⁻¹ by the critical orifices.

After sampling, all filters were stored in airtight polypropylene bottles in a refrigerator. Colorimetric methods were used for analyses of Cl⁻ (EMEP 1977), NO₃⁻ (Alfa 1992) and NH₄⁺ (Grasshoff *et al.* 1983). These analytical methods were used for both the particulate material and gaseous acids as well as the segregated aerosol samples from the Berner impactor foils. Immediately after desorption via agitation in an ultrasonic bath, all ions from the Teflon and Whatman 41 filters were introduced into de-ionised water and from the nylon filters into a carbonate buffer (0.75 mM NaHCO₃/2.2 mM Na_2CO_3). The sodium, potassium, calcium and magnesium ions rinsed off the Teflon filters were analysed on a Perkin-Elmer 103 atomic absorption spectrometer.

The calculated standard deviations for low ion concentrations were: $\pm 2.4 \text{ nmol m}^{-3}$ for Cl⁻, ± 1.4 for NO₃⁻, ± 0.7 for NH₄⁺, ± 2.1 for Na⁺, ± 0.9 for K⁺, ± 0.2 for Mg²⁺ and ± 0.2 nmol m⁻³ for Ca²⁺. The standard deviations for high ion concentrations were: $\pm 1.2 \text{ nmol m}^{-3}$ for Cl⁻, ± 1.5 for NO₃⁻, ± 0.2 for NH₄⁺, ± 1.3 for Na⁺, ± 0.1 for K⁺, ± 0.1 for Mg²⁺ and ± 0.1 nmol m⁻³ for Ca²⁺. The mean flow rate, mean deposition time and mean volume of solution were included in the calculations of the standard deviation.

3. Results and discussion

As a first approach, a one-year time series of ion components in the aerosol is presented in Fig. 2. Formed by the reaction (e.g. Pakkanen 1996)

$$HNO_{3(g)} + NaCl_{(s)} \rightarrow NaNO_{3(s)} + HCl_{(g)},$$
(1)

coarse sodium nitrate is stable in the atmosphere and thereby serves as a permanent removal pathway for nitrate (Yoshizumi & Hoshi 1985). Potassium, magnesium and calcium chlorides can also react with free nitric acid (Ottley & Harrison 1994). However, reaction (1) is the favourable one and occurs especially when maritime and polluted continental air masses are mixed



Fig. 2. Monthly concentration of ions in the aerosol over Hel during the sampling period

(Harrison & Pio 1983). Such conditions were observed at Hel especially in June, September and November – December 1997, when Cl^- losses were highest (Fig. 2). However, the recorded highest losses of chloride are not directly dependent on the highest nitrate concentrations. This reflects the fact that the monthly means from a coastal site represent a complex sequence of transport and mixing conditions. Offshore winds contain high nitrate loads which, when transported over the sea, interact with the sea salt aerosol. Thus, the pure maritime air masses usually contain a limited amount of nitrate.

The sea salt aerosol compounds (Na⁺, Cl⁻) showed the highest concentrations in summer, while the highest NO₃⁻ concentrations occurred in the winter period (Fig. 3). In all probability, both elevated anthropogenic emissions of NO₃⁻ and increased atmospheric stability favour its higher winter concentrations (Ottley & Harrison 1994).



Fig. 3. The seasonal changes in aerosol and air components over the Hel station between 28 February 1997 and 31 March 1998 (g – gaseous fraction, a – aerosol fraction)

Aerosol species of both anthropogenic and marine origin can be found in different size fractions: in fine particles (<1 μ m) as a result of particle nucleation and condensation, and in coarse particles (>1 μ m) owing to resuspension from the seawater (Fig. 4). Therefore, when formed by gas-to-particle conversion, particulate NH₄⁺ and NO₃⁻ tend to be associated with fine particles, whereas sea salt compounds (Na⁺, Ca²⁺, Cl⁻) are found in the coarse mode.



Fig. 4. Mean size distribution of several ions associated with aerosols over Hel

Reaction (1) between sea salt and nitric acid should shift the nitrate size distribution towards the coarse mode. The sodium and chloride size distributions found at Hel displayed a less significant contribution to the mass of aerosol below 0.5 μ m (submicron size); the largest mass fraction was included in particles of 2–8 μ m diameter.

Nitrate shows a different size distribution with a peak at $1-4 \ \mu m$. This reflects the mixed nature of nitrate, which can occur both as ammonium nitrate and as sodium nitrate, depending on the air mass history.

Ammonium was more often present in the submicron aerosol particles $(0.5-2 \ \mu m)$ as a result of gas-to-particle formation processes. The seasonal variation in size distributions is shown in Fig. 5. The summer distribution of nitrate shows NO₃⁻ ions to have diameters larger than 4 μm , because of the low ammonia concentrations in the aerosols over the Hel Peninsula. Without ammonia, free atmospheric HNO₃ can react with sea salt to form



Fig. 5. The size distribution of several ions in the air during summer and winter over the Hel Peninsula

coarse nitrate. Furthermore, the chloride losses recorded in summer (Fig. 3) suggest that the reaction with sea salt might be more important at that time of the year (Wall *et al.* 1988).

In the autumn and winter, the concentrations of ammonia were one order of magnitude higher, but still most of the aerosol masses were associated with particles smaller than 1 μ m of diameter (Fig. 5). The ammonia was probably reacting with the sulphates present in fine aerosol particles or that was evaporating from ammonium nitrate (Plate & Schulz 1997). The heterogeneous size distribution is a reflection of the different particle formation processes (Fig. 4).

As regards the air mass trajectories over the Hel Peninsula, 48% of them originated from the westerly sector (Fig. 1) carrying oceanic input modified during transport over western Europe. About 18% of the air masses arrived from the south, carrying aerosols from mainly anthropogenic sources. 33% of air masses were from the east: these were either pure marine aerosols, or anthropogenic ones enriched with marine aerosol as they travelled along the Baltic (Nadstazik 1999).

Salt emitted from the sea surface is the main component of marine aerosols over Hel (Fig. 6). Sodium and chloride concentrations showed almost identical changes during the whole experimental period (Fig. 3). The strong correlation between the concentrations of these ions r = 0.96, supported by the χ^2 test, is indicative of their predominantly marine origin. The sodium concentration in all cases was equal to or slightly exceeded the chloride content (Fig. 3). The concentrations of calcium, potassium and magnesium ions also displayed a strong correlation with chloride ions (r > 0.80 in all cases), which again suggests their marine origin.



Fig. 6. The chemical composition of aerosols of different origin over the Hel Peninsula

The presence of large particles of sodium and magnesium nitrates at the Hel station (Fig. 6) was demonstrated by the high correlation coefficients between NO_3^- and Na^+ ions (r = 0.80) and between NO_3^- and Mg^{2+} (r = 0.82). Gaseous nitric acid is involved in surface reactions (1) with large salt particles, producing large molecules of sodium nitrate (John *et al.* 1988, Wall *et al.* 1988, de Bock *et al.* 1994, Harrison & Msibi 1994, Ottley & Harrison 1994). When the air masses originated from the west, the likelihood of detecting NaNO₃ in the aerosol was negligible, probably due to gravitational settling and wash-out effects.

Fine anthropogenic ammonium nitrates were detected in aerosols over the Hel station (Fig. 6) during the advection of air from the land (originating over southern and western Poland). In addition, a relative humidity higher than 87% and a lower air temperature are the conditions necessary for the formation of these particulate aerosol compounds (Hillamo & Kauppinen 1991).

Ammonia is ever-present in the atmosphere; besides binding nitric acid, it may react with gaseous HCl to produce ammonium chloride, which is three times as volatile as ammonium nitrate. It could also dissociate to gaseous NH₃ and HCl (Stelson & Seinfeld 1982, Pio & Harrison 1987, Plate & Schulz 1997). Gaseous NH₄Cl was detected in the marine aerosol only in the summer, when concentrations of nitrate ions were smallest. In other cases, ammonium ions could have been neutralised by NO₃⁻ or SO₄²⁻ (Pio *et al.* 1992). Further measurements are needed; they should either confirm the high seasonal variation of the chemical composition of the aerosol, or they will show that these results were typical only of the period 1997–98.

In order to compare the mean concentrations of aerosol species in the atmosphere over Hel as well as those collected over the North Sea (Ottley & Harrison 1994) and in Lithuania (Sopauskiene & Budvytyte 1994) Table 1 has been assembled. The comparison shows, for example, that the concentrations of marigenic aerosol components (Na⁺, Cl⁻) recorded at Hel (Poland) are slightly lower than those found at Preila (Kuronian Peninsula, Lithuania). The higher nitrate concentrations at Hel than at Preila or over the North Sea are a reflection of atmospheric transport from central European emission sources. The nitrate values seem comparable to the concentrations recorded in England or in Scandinavia, while the mean ammonium ion concentration recorded at Hel is similar to that measured over the sea or in Scotland. However, the concentrations of nitrate and ammonium were several times lower at Hel than those recorded in large urban agglomerations like Seoul or Leipzig (Table 1).

Sampling period	NO_3^-	NH_4^+	Cl^-	Na ⁺	Ca^{2+}	K^+	Mg^{2+}	References
1997-98	53.4	13.3	29.1	55.7	8.0	6.1	3.7	This study
1980–91	25.3	99.4	40.1	64.4	16.2	7.9	7.2	Sopauskiene & Budvytyte (1994)
1989–90	68.6	116.7						Ottley & Harrison (1994)
	26.9	40.6						
	42.4	86.7						
	22.9	24.4						
27.7–19.8.1994 east winds west winds	$96.9\\52.4$	$231.4 \\ 125.1$		$16.5 \\ 60.1$				Plate <i>et al.</i> (1995)
1993 1994 1995	$129.6 \\ 310.0 \\ 297.6$	$52.2 \\ 59.4 \\ 55.8$						Müller (1999)
	370.1	75.4						Hak Sung Lee <i>et al.</i> (1999

Table 1. The mean concentrations of NO_3^- , NH_4^+ , Cl^- , Na^+ , Ca^{2+} , K^+ and Mg^{2+} in the aerosol [nmol m⁻³]

Sampling site

Hel, Poland

England*

 $Scotland^*$

 $Scandinavia^*$

Westerheven

North Sea^{*}

Eiderstedt,

Germany

Leipzig,

Germany

Seoul, South Korea

Preila, Lithuania >4000

Number of samples

64

23

13

10

14

48

* All samples were taken with due regard for the transport co from a certain region.

4. Conclusions

- The aerosol concentration and size distribution over the southern Baltic Sea displayed high seasonal variability.
- The highest NO₃⁻ concentrations occurred in the winter period because of elevated anthropogenic emissions and atmospheric stability.
- The highest concentrations of sea salt aerosol compounds were recorded in summer.
- Chloride declined somewhat during the summer. The reaction between sea salt and nitric acid is prevalent when air masses are of both marine and continental origin.
- Anthropogenic and marigenic aerosol species may form different size fractions within fine and coarse particle modes. The nitrate size distributions reflect the two particle formation processes involved in creating large sodium nitrate and small ammonium particles.
- The sodium, potassium, magnesium, calcium and chloride over the Hel station were usually marigenic.
- Anthropogenic fine ammonium nitrates were found in aerosols advected from southern and western Poland, while ammonium chloride was advected from the north. The additional ammonia was probably neutralised by sulphates.

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