

Sea salt in aerosols over
the southern Baltic.
Part 2. The neutralizing
properties of sea salt and
ammonia*

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Abstract

In 2001–2007 aerosols were measured in the coastal zone (11 campaigns) and over the open waters of the Gdańsk Basin (southern Baltic) (5 campaigns). The marine aerosols contained nitrogen and sulphur compounds, which increased their acidity. This situation intensified during the cool months of the year, when fossil fuel emissions were higher, proportionate to energy and heat requirements. Irrespective of the season, these acidic aerosols were neutralized in the reaction with sea salt. The likelihood of sodium nitrate being formed increased at air humidities > 80% and nitrate concentrations > 30 nmol m⁻³. Sodium sulphate was present in aerosols mostly in autumn and winter, with northerly advection, and at the highest wind speeds. The excess of free ammonia resulted in the formation of ammonium sulphate and ammonium nitrate in aerosols over the southern Baltic.

* Parts of this paper were originally published in Polish: Lewandowska A., 2011, *Chemizm aerozoli w rejonie Zatoki Gdańskiej*, Wyd. UG, Gdańsk, 184 pp.

The complete text of the paper is available at <http://www.iopan.gda.pl/oceanologia/>

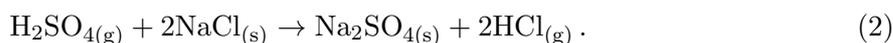
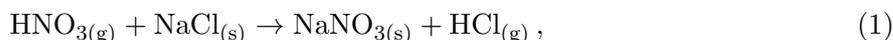
1. Introduction

A considerable proportion of aerosols is emitted directly into the atmosphere by the evaporation of droplets formed on the sea surface. Their main constituents are chlorides and sulphates, which make up nearly 99.5% of marine aerosols. The remainder consists of carbonates and other salts. In urban coastal regions, clean sea air becomes transformed as a result of fractionation and enrichment. This is demonstrated by the elevated contribution of ions related to anthropogenic aerosols (NO_3^- , NH_4^+ , SO_4^{2-}) and terrigenous aerosols (K^+ , Ca^{2+} , Cl^-) (Nadstazik et al. 2000).

Nitrates and ammonium are beneficial, even essential, for plant growth, but excessively high concentrations may lead to a loss of diversity. This problem has been encountered mainly in central and north-western Europe (Erisman 2004). In the mid-1980s, the eutrophication caused by nitrogen deposition in terrestrial and aquatic ecosystems was found to have adverse effects on the environment. Acidification and eutrophication are both caused by atmospheric deposition of pollutants, and the combination potentiates the effects.

Over Europe, aerosol NO_3^- is predominantly anthropogenic in origin and arises from the oxidation of NO_x (NO and NO_2), which is produced in the high-temperature combustion processes associated with vehicles and industrial activity (Seinfeld & Pandis 1998). NO is converted to additional NO_2 upon reaction with O_3 or peroxy radicals. Thereafter, HNO_3 is formed when NO_2 reacts with OH . At night, HNO_3 may also be produced by the reaction of aliphatic hydrocarbons and aldehydes with the nitrate radical (NO_3), which is rapidly photolysed during the day. In addition, NO_3 can react with NO_2 to set up an equilibrium with N_2O_5 . The subsequent heterogeneous dissolution of HNO_3 and N_2O_5 into water droplets gives rise to aerosol NO_3^- (Yeatman et al. 2001). NH_3 is generated primarily from the decomposition of agricultural livestock waste and to a lesser degree from fertilizer production. Other sources are thought to include emissions from the oceans as a result of biological activity.

In a polluted marine atmosphere the major marine salt component (NaCl) may react with sulphuric acid and nitric acid vapours to form sulphates and nitrates respectively (Chalbot et al. 2013):



This interaction may have important implications for halogen cycling and oxidation reactions in the marine atmosphere (Andreae & Crutzen 1997). It also results in a nitrate shift from the fine mode to the coarse

mode, and enhances deposition through more effective gravitational settling and increased precipitation scavenging to the marine ecosystem via inertial impaction (Jickells et al. 1998, Spokes et al. 2000). In marine air masses, over 80% of the nitrate occurs as coarse mode aerosol, greater than $1.0 \mu\text{m}$ in diameter (Spokes et al. 2000).

Aside from sea salt, the main chemical compound responsible for the reduction in aerosol acidity in the atmosphere is ammonia (Rastogi & Sarin 2005). Emitted at low levels, near the ground, this gas quickly becomes converted into NH_4^+ with dry aerosol precipitation and is removed from the atmosphere (Erisman et al. 2005). Aerosol NH_4^+ is produced when NH_3 undergoes gas-to-particle reactions with other acidic species. For instance, $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 aerosols are formed from gaseous NH_3 and H_2SO_4 (Ottley & Harrison 1992). Two environments have been identified as the regions with the most significant emission of gaseous sulphur into the atmosphere: coastal zones and forested areas. Besides seawater dimethyl sulphide, anthropogenic sulphur dioxide is also a precursor of submicron aerosols, especially those produced as a result of fuel combustion (Pszenny et al. 1998).

The purpose of the measurements described here was to determine the factors responsible for the formation of sodium nitrate and sodium sulphate in aerosols over the southern Baltic Sea. To understand fully the impact of atmospheric nitrogen depositions on the Baltic Sea ecosystem, we need more detailed knowledge of the temporal and spatial variations in atmospheric nitrogen concentrations and of changes in aerosol composition. Using a large data set (232 samples) collected at sea and at a coastal station, it has been possible to further consider the details of important interactions between sea salt and acidic gases. The roles of ammonia and ammonium must also be taken into consideration, as both are present in air and may react with nitric acid and sulphuric acid vapours to form ammonium salts (Dougle et al. 1998). Over north-western Europe, NH_4NO_3 represents the dominant form of both NO_3^- and NH_4^+ aerosols (Ottley & Harrison 1992).

2. Materials and methods

2.1. Measurement station locations and sample collection dates

Marine aerosol measurements were conducted in 2001–2007 in 12-hour cycles at a land station in Gdynia (11 campaigns) and a sea station, located in the Gdańsk Deep (P1) (5 campaigns). 164 samples were collected at the land station, i.e. the roof of the building of the Institute of Oceanography of Gdańsk University – IO UG ($\varphi = 54^\circ 31' \text{N}$, $\lambda = 18^\circ 49' \text{E}$). The sea station (P1, $\varphi = 54^\circ 52' \text{N}$; $\lambda = 19^\circ 10' \text{E}$), where 68 samples were obtained, lies 37 km

to the north-east of Gdynia. The measurement stations are described in detail in the first part of this paper (Lewandowska & Falkowska, Part 1, this volume).

The aerosols were collected using a filter pack. Each set contained three kinds of filters to correct for ammonium nitrate dissociation from the Teflon filter: Teflon, nylon and Whatman 41, impregnated with 5% orthophosphoric acid p.p.a. The sampled air was first passed through the pre-washed Teflon filter to collect the largest particles (diameter $> 1 \mu\text{m}$). Sodium, ammonium, chlorides, nitrates and sulphates were collected on this filter (Lewandowska & Falkowska, Part 1, this volume). The air was then passed through the nylon filter where, in addition to the particulate fraction of small aerosols (diameter $< 1 \mu\text{m}$), the gaseous constituents of air were retained. In those cases where an evaporated amount was analysed on the backup filters it was added to the particulate concentrations from the particle filter by calculating the sum of both. The gaseous ammonia fraction was chemically absorbed at the surface of the impregnating substance on the final Whatman 41 filter. Gaseous ammonia and nitric acid vapours were also chemically absorbed on annular denuders (Lewandowska & Falkowska 2004). 2% oxalic acid p.p.a. and 4% NaCl p.p.a. were used for impregnation. Glycerine (1%) was always added to the coating solution for better impregnation. Some silicon dioxide powder was added to both solutions to retain the coating solutions in the denuder under humid conditions.

At all sampling sites, filter packs and denuders were installed in parallel in a box to protect them from the elements (in particular, rain and strong wind) and connected to the pump by means of polyethylene tubing. The air flow through the filters and denuders, read from a gas meter, was regulated by a critical orifice to provide a constant value of $3.2 \text{ m}^3 \text{ h}^{-1}$.

After sampling, all filters were stored in airtight polypropylene bottles in a refrigerator at a temperature of $+4^\circ\text{C}$. Prior to analysis, the filter content was extracted in an ultrasonic bath for 45 min. Ions from the Teflon and Whatman 41 filters were transferred to deionized water, while those from the nylon filters were passed into a carbonate buffer (0.75 mM NaHCO_3 /2.2 mM Na_2CO_3) (constant volume = 0.014 dm^3).

The samples from the denuders were transferred to polyethylene vials, filtered and kept in a refrigerator until analysis.

2.2. Chemical analysis

Nitrate ions were analysed using ion chromatography in accordance with the Polish Standard prPN-EN ISO 10304-1 (PN 1995). The detection limit for nitrate ions was $0.2 \mu\text{g m}^{-3}$ and the standard error of estimation was

no higher than 5.5%. A certainty level of 99% was assumed. Each analysis took into account 20 blanks and an average air flow through the sampler.

In the chemical analysis of ammonium ions, corrections were made to the original indophenol method by Grasshoff et al. (1983). They resulted from the fact that the pH of the reaction was lowered by impregnating the Whatman 41 filters and the denuders with acids. They are described in detail in Nadstazik & Falkowska (2001) and Lewandowska & Falkowska (2004).

2.3. Meteorological conditions

Meteorological parameters such as rainfall, wind speed, relative air humidity and air temperature were measured during every sampling period by the Huger Weather Station on the roof of the Institute of Oceanography building. Data were based on a measurement duration of 30 s, and results were averaged according to the overall sampling duration: from 08:15 hrs to 20:00 hrs, and from 20:15 hrs to 08:00 hrs the next day. Measurements were carried out at a height of 20 m, so a correction had to be made to calculate the wind speed at 10 m above sea level u_{10} (Lewandowska & Falkowska, Part 1, this volume). The meteorological conditions during the measurements conducted in the southern Baltic zone in 2001–2007 were very variable. A detailed description of them, including a classification of incoming air masses divided into types 1, 2 and 3, is given in the first part of this paper (Lewandowska & Falkowska, Part 1, this volume).

3. Results and discussion

During measurements carried out in 2001–2007, the concentrations of all aerosol components varied considerably at both measurement stations. The concentrations of nitrate and ammonium ions are presented in Table 1. The concentrations of the remaining ions – sodium, chloride and sulphate – are listed in Table 2 in the first part of the present publication (Lewandowska & Falkowska, Part 1, this volume). The nitrate concentrations in the aerosols varied from 1.1 to 344.3 nmol m⁻³ over the Gdańsk Deep and from 0.9 to 246.0 nmol m⁻³ over Gdynia (Table 1). The concentration of ammonium ions was also highly variable, ranging from 0.3 to 368.4 nmol m⁻³ over Gdynia and from 1.7 to 68.0 nmol m⁻³ over the Gdańsk Deep. The mean HNO₃ concentration in the air over Gdynia was 13.1 ± 19.4 nmol m⁻³ and was less than half of the level measured over the Gdańsk Deep (30 nmol m⁻³ \pm 56.7 nmol m⁻³). Ammonia concentrations in the air over the southern Baltic varied from 1.2 nmol m⁻³ (Gdańsk Deep)

Table 1. Nitrate and ammonium ion concentrations in aerosols, and ammonia and nitric acid concentrations [nmol m^{-3}] at the land station (Gdynia) and over the open sea (Gdańsk Deep) in 2001–2007 (all concentrations of sodium, chlorides and sulphates were given in the first part of the publication – Lewandowska & Falkowska, Part 1, this volume)

Sampling period	Estimator	Gdynia				Gdańsk Deep			
		NO_3^-	HNO_3	NH_4^+	NH_3	NO_3^-	HNO_3	NH_4^+	NH_3
31.05–06.06.2001	min-max	40.5–92.3	0.5–17.9	12.9–35.3	1.6–13.9	7.9–161.1	2.0–30.0	2.9–16.3	1.2–18.9
	$\bar{x} \pm \text{SD}$	65.2 ± 13.5	5.4 ± 5.9	24.3 ± 6.6	4.2 ± 4.0	90.4 ± 47.3	10.2 ± 7.9	10.3 ± 7.6	12.7 ± 7.6
27.09–19.10.2002	min-max	3.3–181.7	3.7–74.4	0.3–47.2	8.3–195.0	101.7–344.3	64.6–229.0	3.6–68.0	7.9–60.4
	$\bar{x} \pm \text{SD}$	98.3 ± 51.4	31.9 ± 19.6	17.1 ± 13.1	45.4 ± 49.8	161.2 ± 72.0	133.7 ± 65.1	21.5 ± 22.8	36.6 ± 19.8
13.01–20.01.2003	min-max	151.9–246.0	1.1–9.7	0.4–220.7	24.3–58.4				
	$\bar{x} \pm \text{SD}$	205.7 ± 30.2	4.8 ± 3.1	87.8 ± 63.7	44.7 ± 10.2				
24.02–03.03.2003	min-max	65.2–246.0	1.2–10.3	38.8–368.4	30.6–76.8				
	$\bar{x} \pm \text{SD}$	174.9 ± 63.4	4.8 ± 2.4	163.6 ± 97.8	53.9 ± 15.7				
03.04–10.04.2003	min-max	16.2–85.5	2.9–15.8	16.9–331.8	46.8–115.9				
	$\bar{x} \pm \text{SD}$	54.7 ± 18.5	6.3 ± 3.2	105.2 ± 112.5	72.5 ± 20.0				
08.05–15.05.2003	min-max	3.7–45.8	3.5–100.0	0.5–30.3	1.6–13.9	1.1–44.6	0.1–9.0	1.7–51.3	9.1–20.5
	$\bar{x} \pm \text{SD}$	24.0 ± 14.8	43.6 ± 36.5	12.6 ± 9.7	4.2 ± 4.0	19.7 ± 12.7	2.2 ± 2.6	14.9 ± 15.4	14.3 ± 3.0
30.06–06.07.2003	min-max	27.7–112.8	1.1–15.9	2.8–92.3	8.3–195.0				
	$\bar{x} \pm \text{SD}$	49.7 ± 22.2	6.6 ± 5.6	26.9 ± 23.0	45.4 ± 49.8				

Table 1. (*continued*)

Sampling period	Estimator	Gdynia				Gdańsk Deep			
		NO ₃ ⁻	HNO ₃	NH ₄ ⁺	NH ₃	NO ₃ ⁻	HNO ₃	NH ₄ ⁺	NH ₃
23.04–27.04.2006	min-max	2.9–10.0	3.7–7.4	7.8–12.7	8.7–54.9	4.5–27.6	6.4–22.5	6.4–15.9	18.4–125.4
	$\bar{x} \pm \text{SD}$	5.4 ± 2.1	5.6 ± 1.5	9.4 ± 1.6	25.7 ± 14.9	14.7 ± 7.4	11.0 ± 5.9	10.4 ± 3.8	50.4 ± 36.3
27.07–04.08.2006	min-max	0.9–2.5	1.6–8.7	4.1–11.8	24.1–41.0				
	$\bar{x} \pm \text{SD}$	1.3 ± 0.5	4.6 ± 2.7	7.3 ± 2.8	34.7 ± 5.1				
17.04–5.04.2007	min-max					1.7–9.9	1.5–2.9	4.4–14.6	7.6–23.6
	$\bar{x} \pm \text{SD}$					3.6 ± 2.6	2.1 ± 0.5	8.4 ± 3.5	14.4 ± 5.3
17.08–28.08.2007	min-max	2.6–7.3	1.5–5.6	4.4–13.3	4.3–27.2				
	$\bar{x} \pm \text{SD}$	4.1 ± 1.3	3.9 ± 0.9	8.8 ± 2.5	15.17 ± 6.8				

Symbols: min-max – minimum and maximum value, $\bar{x} \pm \text{SD}$ – average plus/minus standard deviation.

to $195.0 \text{ nmol m}^{-3}$ (IO UG, Gdynia). In $> 80\%$ of cases, the concentration of this gas did not exceed 50 nmol m^{-3} over either land or sea.

3.1. Comparison of the aerosol chemical compositions at the sea and land stations

Based on the findings presented in Figure 1, the overall impression is that the chemical compositions of the aerosols in the different regions are not so different, in spite of the fact that the stations are situated tens of kilometres apart, one on land and the other at sea.

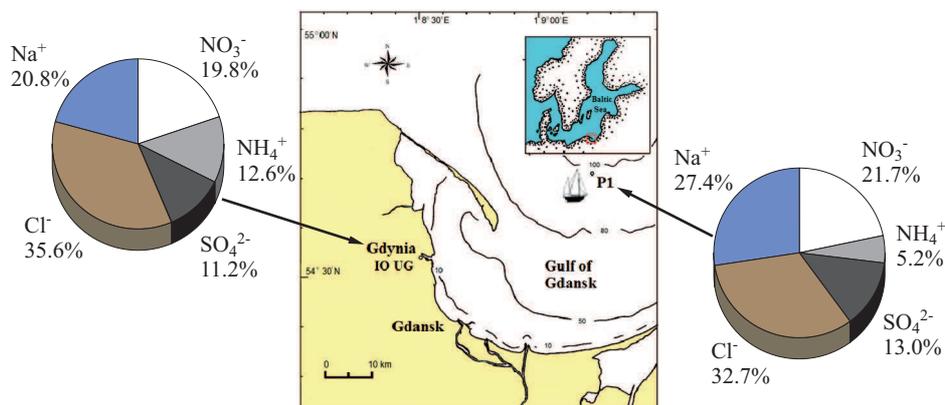


Figure 1. The proportions [%] of the chemical constituents of aerosols over the land station (Gdynia) and over the sea station in the Gdańsk Deep (P1) in 2001–2007 (Lewandowska 2011)

These results also indicate that polluted and clean air masses were present in both regions. As they are transported with air masses, the constituents of aerosols undergo chemical reactions that change their concentration, and even their phase of state or level of hydration (Raes et al. 2000). Over land, the formation of the chemical composition of aerosols was significantly influenced by the sea and this resulted in high proportions of chlorides and sodium (56.4%) (Figure 1). Over the Gdańsk Deep, clean air of marine origin was transformed on encountering aerosols from over the land. This fact was made manifest by the higher content of nitrogen and sulphur ions, which are largely attributed to aerosols of anthropogenic origin (40%).

The presence of sea salt in aerosols in the southern Baltic region both over land and at sea was confirmed by principal component analysis and classification (PCA) (Table 2). In each case two main factors were identified, which explained 78% of the variances found for the sea station and 64% for the land station. At the sea station the first factor (57% of variances)

Table 2. Results of principal component analysis and classification (PCA) in aerosols over the open sea (the Gdańsk Deep) and in the coastal zone (Gdynia) (Lewandowska 2011)

Gdańsk Deep			Gdynia coastal station		
Variable	Factor 1	Factor 2	Variable	Factor 1	Factor 2
Na ⁺	0.81	-0.36	Na ⁺	- 0.57	- 0.51
Cl ⁻	0.93	-0.17	Cl ⁻	- 0.76	-0.03
SO ₄ ²⁻	0.70	0.54	SO ₄ ²⁻	-0.08	- 0.86
NO ₃ ⁻	0.86	-0.05	NO ₃ ⁻	- 0.82	0.04
NH ⁴⁺	0.30	0.89	NH ⁴⁺	- 0.71	0.41
eigenvalue	2.64	1.26	eigenvalue	2.06	1.11
% of var. [%]	57	21	% of var. [%]	42	22
origin	marine and marine mo- dified	anthro- pogenic	origin	marine and anthropoge- nic	marine modified

Note: values in bold are > 0.5 and are treated as significant.

singled out chloride and sodium ions, as well as sulphates and nitrates. This indicates the presence of marine aerosols modified by nitrogen and sulphur compounds on their way from the source. The second factor (21% of variances) indicated the presence of secondary anthropogenic aerosols, rich in ammonium sulphate, carried over the sea with terrestrial air masses (Table 2).

Over land (Gdynia coastal station), the first factor (42% of variances) made it possible to identify sodium chloride of marine origin as well as ammonium nitrate, which is a basic component of anthropogenic aerosols. Factor 2 of the analysis, describing 22% of variances, explained the combinations of sea salt with sulphur-rich aerosols and the presence of sodium sulphate.

At both stations the first factor, characterized by high loadings of sodium, chlorides and nitrates, is most probably associated with the reaction of HNO₃ with coarse-mode sea salt particles and subsequent HCl volatilization. This result supplies evidence for the role of sea salt in the neutralization of nitric acid and should be taken into account when interpreting factor analysis results.

There is a difference in the levels of ammonium salts over land and sea. In Gdynia ammonium nitrate was present in anthropogenic aerosols (Factor 1). Over the sea the second factor, characterized by high loadings of ammonium and sulphate, may be attributed to continental anthropogenic sources of ammonium sulphate and suggests the partial neutralization of aerosols by ammonium in the measurement region.

3.2. Aerosol acidification

Higher concentrations of inorganic nitrogen compounds than of sulphur compounds were present over the stations located in the southern Baltic coastal area and at sea, regardless of the direction of advection. The concentrations of both compounds tended to be higher over land than at sea (Figure 2). These compounds are responsible for aerosol acidification (Yeatman et al. 2001), and their presence has even been discovered in acidified aerosols over the Arctic (Hara et al. 2002).

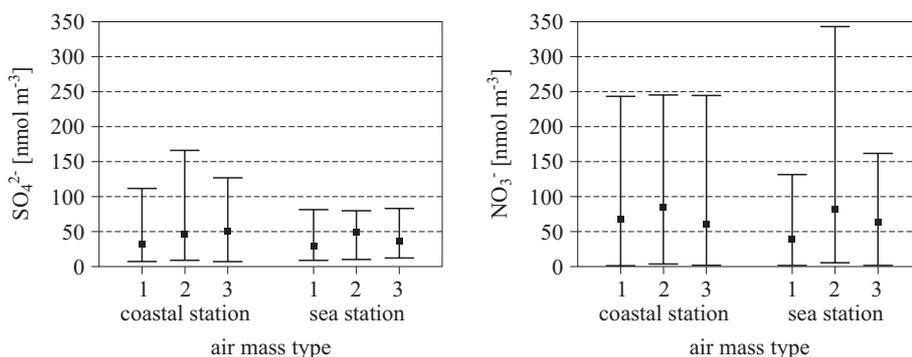


Figure 2. Concentration range of a) sulphate ions and b) nitrate ions [nmol m⁻³] in aerosols over land and sea in relation to advection type (1, 2 and 3)

No direct acidity estimations were made in the southern Baltic. However, taking into consideration the components responsible for acidity and the release of HCl during the reaction of nitric and sulphuric acid vapours with sea salt, aerosol acidity (α) was determined and expressed in nmol m⁻³ using the formula given by Yeatman et al. (2001):

$$\alpha = [\text{NO}_3^-] + 2[\text{nssSO}_4^{2-}] - \text{Cl}^-_{\text{loss}}, \quad (3)$$

where

$$\text{Cl}^-_{\text{loss}} = 1.2 [\text{Na}^+] - [\text{Cl}^-]. \quad (4)$$

Actual concentrations of non-sea salt sulphates (nssSO₄) in aerosols were calculated using the following equation (Sievering et al. 1990):

$$\text{nssSO}_4^{2-} = \text{SO}_4^{2-} - (0.06 \text{ Na}^+). \quad (5)$$

In eqs. (3–5) the concentrations of all ions, including non-sea salt sulphates (nssSO₄²⁻), are expressed in nmol m⁻³.

This study, which was conducted in 2001–2007 and embraced all advection types, aerosol acidification (α) over land (av. 205 nmol m⁻³)

was found to be almost double the value over the open waters of the Gulf of Gdańsk (av. $110.8 \text{ nmol m}^{-3}$) (Figure 3).

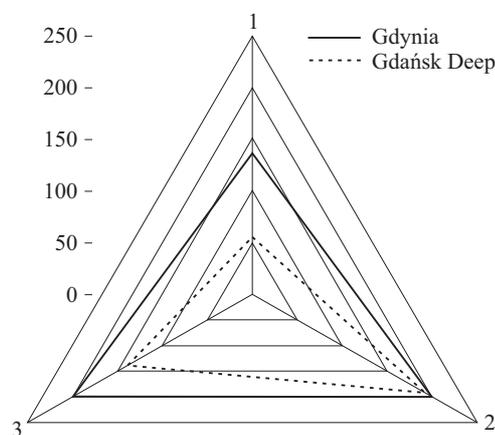


Figure 3. Aerosol acidification (α) [nmol m^{-3}] over land (Gdynia) and sea (Gdańsk Deep) in relation to the direction of air mass advection (1, 2 or 3) (Lewandowska 2011)

Measurements at sea were carried out only in spring and autumn when, regardless of wind speed, humid and warm air masses would blow over the station (Table 3, Lewandowska & Falkowska, Part 1, this volume). Taking into account only such air masses over land, the aerosol acidification at both measurement stations were comparable, amounting to $121.3 \text{ nmol m}^{-3}$ and $112.8 \text{ nmol m}^{-3}$ over land and sea respectively (Figure 4). The slightly higher values over land were due to local pollutants, mainly traffic-related, carried from the west and north-west.

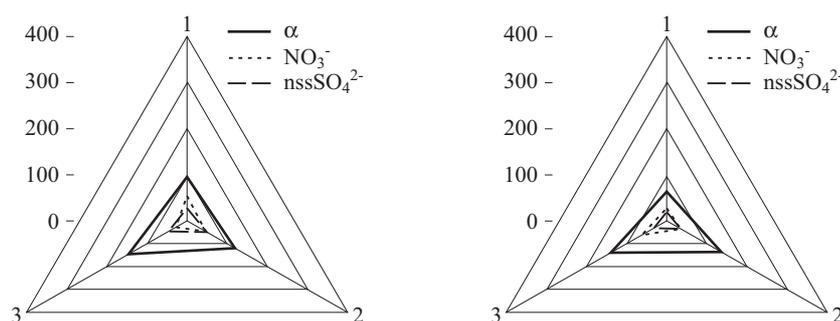


Figure 4. The effect of advection (type 1, 2 and 3) on the concentration of nitrates and non-sea-salt sulphates [nmol m^{-3}] and on the acidification of aerosols (α) [nmol m^{-3}] in the warm months a) over land and b) at sea (Lewandowska 2011)

The proportion of non-sea-salt sulphates was also of considerable significance. Aerosol acidification was comparatively high ($138.0 \text{ nmol m}^{-3}$ at sea and 148 nmol m^{-3} over land) when the proportion of nssSO_4^{2-} was 90%. With northerly advection, acidification was at its lowest, a fact that should be associated with the lowest levels of nssSO_4^{2-} , which were no higher than 80%.

Local sources over land also played an important role in acidification in winter, when the emission of nitrate precursors increased as a result of combustion processes. In situations when wind speeds were very low ($< 1 \text{ m s}^{-1}$) and air masses were coming from westerly and south-westerly directions, where the largest numbers of domestic heating systems and the busiest thoroughfares are located, nitrate concentrations increased to 405 nmol m^{-3} ($158.1 \text{ nmol m}^{-3}$ on average in winter) and aerosol acidity reached the value of $404.9 \text{ nmol m}^{-3}$ ($260.1 \text{ nmol m}^{-3}$ on average in winter) (Figure 5).

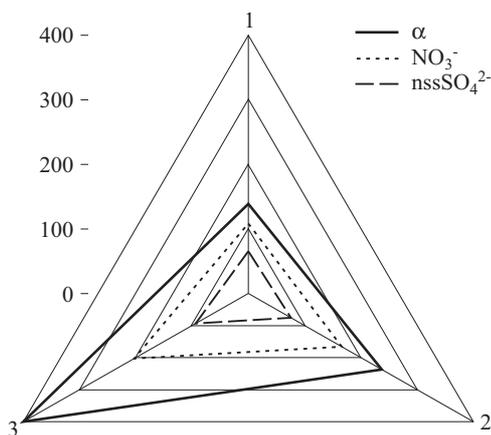


Figure 5. The effect of advection (types 1, 2 and 3) on concentrations of nitrate and non-sea-salt sulphates [nmol m^{-3}] and on aerosol acidification (α) [nmol m^{-3}] over land in the winter season (Lewandowska 2011)

At the same time, non-sea salt sulphate concentrations were 50% lower than the nitrate concentrations (Figure 5). Their proportion in the total sulphate fraction did not exceed 70% and was almost constant, irrespective of the direction of advection. This indicates the lesser significance of this ion compared to nitrates in the acidification of aerosols over land in winter.

According to Koçak et al. (2004), the concentrations of acidifying aerosol components, such as non-sea salt sulphates or nitrates, increase with the onset of winds carrying mineral dust. In such situations additional amounts of chlorides are generated in the atmosphere (Asman et al. 1994, Jickells

2006). In the present studies, excess chloride to sodium ($r\text{Cl}^-/r\text{Na}^+$) was found throughout the study period, regardless of the season. At low wind speeds ($< 3 \text{ m s}^{-1}$), both over land and at sea, the molar ratio $r\text{Cl}^-/r\text{Na}^+$ did not demonstrate any significant variability in relation to the direction of advection (Figure 6).

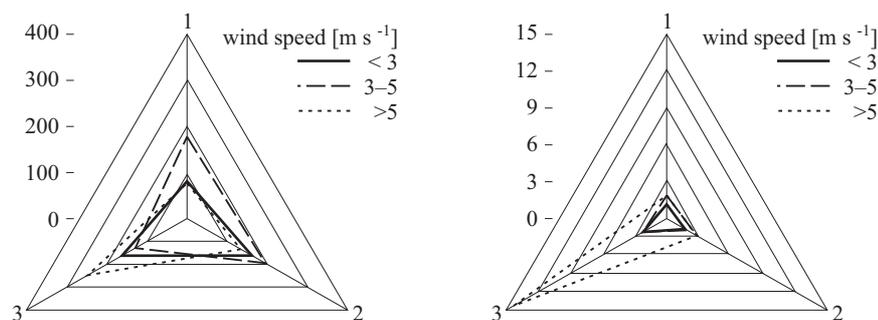


Figure 6. Variability of the molar proportion $r\text{Cl}^-/r\text{Na}^+$ for various air mass types (1, 2 and 3) in relation to wind speed a) at sea and b) over land (Lewandowska 2011)

At such times non-sea-salt chlorides were present in the Tri-city region in aerosols of local origin. In winter they resulted from increased emissions of hydrochloric acid vapour, which is formed during the combustion of chloride-rich coal in heating boilers, domestic heating systems or waste incinerators (Yao et al. 2003). At other times during the study period, these chlorides may have resulted from reactions between nitric and sulphuric acid vapours and sea salt.

As the wind speed increased, to $> 3 \text{ m s}^{-1}$ at sea and to $> 5 \text{ m s}^{-1}$ over land, the significance of local sources in the formation of chloride concentrations decreased, while the role of incoming air masses from distant sources became greater (Figure 6). At the same wind speeds as above, there was an increase in the proportion of aerosols generated from the sea surface (Table 4, Lewandowska & Falkowska, Part 1, this volume). Hence, these are the wind speed limits responsible for initiating aerosol transportation processes over longer distances from the source. Over the sea, at wind speeds varying between 3 and 5 m s^{-1} , the north-easterly sector was a possible source of non-sea salt chlorides (advection types 1 and 2). With strong winds ($> 5 \text{ m s}^{-1}$), the proportion of chlorides in aerosols increased noticeably with southerly advection (type 3), demonstrating the transport of chlorine compounds of terrestrial origin out to sea (Figure 6a). The situation was similar over the land station, where there was a pronounced increase in the proportion of non-sea salt chlorides with the third, southerly type of

advection (Figure 6b). Both over land and at sea, excess levels of chlorides were always at their highest in spring, suggesting a terrigenous (agricultural) source of these ions. The maximum value of the molar proportion $r\text{Cl}^-/r\text{Na}^+$ was recorded over land (12.9), at a time typical of increased agricultural activity (Raes et al. 2000). High proportions of terrigenous chlorides in the southern Baltic region, over the stations at Hel and Gdynia, were also noted by Nadstazik et al. (2000).

3.3. Neutralizing properties of sea salt

In the air of urbanized coastal areas, it is natural for a surface reaction to occur between sea salt and gases – the precursors of aerosol acidifying compounds (Kerminen et al. 1997, Hara et al. 2002). According to Seinfeld & Pandis (1998), more than half of the nitrates found in aerosols are related to sea salt. In the measurements conducted during the period 2001–2007, the neutralizing properties of sea salt manifested themselves in the presence of sodium nitrate over the sea during the warm months of the year, when wind speeds increased to as high as 14.4 m s^{-1} (Lewandowska & Falkowska, Part 1, this volume). However, this study shows that the formation of sodium nitrate was not directly related to either season or wind speed. The parameters that determined the production of this compound in aerosols over the sea turned out to be the concentration of nitrates and air humidity (Figure 7): the nitrate concentration required for sodium nitrate formation was $> 30 \text{ nmol m}^{-3}$ (Figure 7a) and the necessary air humidity was $> 80\%$ (Figure 7b).

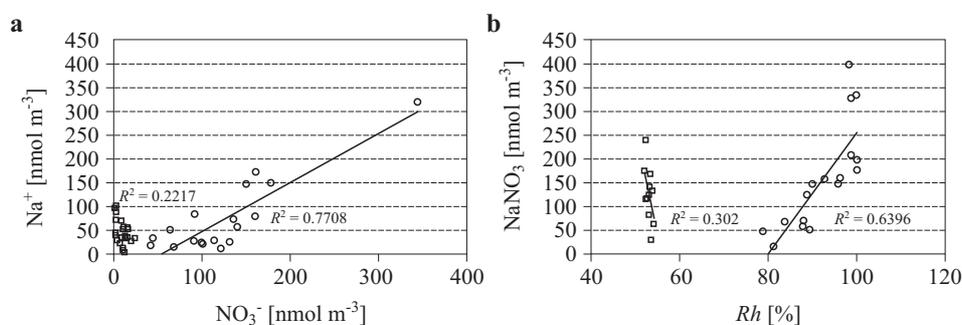


Figure 7. Relations between the concentrations of sodium and nitrates [nmol m^{-3}] (limiting nitrate concentration required for sodium nitrate formation = 30 nmol m^{-3}) (a), and between the concentration of sodium nitrate [nmol m^{-3}] and air humidity [%] (limiting humidity needed for sodium nitrate formation = 80%) (b) over the sea between 2001 and 2007 (Lewandowska 2011)

Because they have recrystallization point of 44% , sea salt particles can have a low liquid water content and may have a dry surface at low humidities

(< 30%). The modification of desiccated particles may be retarded by heterogeneous reactions with atmospheric acidic species. When the air humidity is 75.5–80% (deliquescence point), the water content of the aerosol increases, facilitating the highly efficient uptake of acidic gases, and the consequent decrease in aerosol pH (Hara et al. 2002). According to other authors (Katoshevski et al. 1999, Fridlind & Jacobson 2000), considerable amounts of chloride are liberated from sea-salt particles under such acidic conditions.

The conversion of gaseous nitric acid into an aerosol changes the deposition velocity of atmospheric nitrogen compounds, making this dependent on wind speed and air humidity (Zhuang et al. 1999, Kerminen et al. 2000, Lewandowska & Falkowska 2005, Jickells 2006). In the atmosphere over the Gdańsk Deep the reaction of sea salt with nitric acid constituted the basic means of nitrate removal from the atmosphere, and reduced aerosol acidification. Over land, where both wind speed and nitric acid vapour concentrations were less than half the values over the sea (the former 2.5 and 6.7 m s⁻¹, the latter 13.1 and 29.6 nmol m⁻³, over land and sea respectively), no sodium nitrate was found (Table 2). Irrespective of wind speed over land, sodium nitrate formation was limited by low air humidity, not exceeding 80% on average (Table 3, Lewandowska & Falkowska, Part 1, this volume).

Both over land and at sea the neutralizing properties of sea salt were manifested as a result of its reaction with gaseous nitric acid. In the southern Baltic zone, sodium sulphate was found to be present in aerosols (Table 2). The significance of the process was the most pronounced in autumn and winter with northerly advection, when the intensity of sea salt generation increased. At such times, the concentrations of non-sea salt sulphates increased to 43.4% at sea (autumn 2002) and to 33.2% over land (winter 2003) (section 3.5, Lewandowska & Falkowska, Part 1, this volume).

3.4. Neutralizing properties of ammonia

Ammonium salts were found to occur in aerosols over the southern Baltic (Table 2). The presence of ammonium nitrate over the land station only was established by factor analysis. The formation of ammonium nitrate requires nitric acid, created in photochemical reactions, and free ammonia. Other significant factors are temperature and air humidity, which influence phase changes or HNO₃ removal in the reaction with sea salt (Myhre & Grini 2006). In the coastal zone, ammonium nitrate concentrations were the highest during the cold months of the year (316.0 nmol m⁻³), when aerosol acidification was at its highest (Figure 5). The inflow of pollutants from combustion processes was constant at such times. In highly

urbanized areas such as Gdynia, NO_2 emitted into the atmosphere is converted to HNO_3 in the presence of hydroxy radicals or ozone. The resultant HNO_3 can be absorbed on aerosols and enter into reactions with gaseous ammonia, producing ammonium nitrate. The conversion of nitrogen oxides into nitrates is also possible owing to their conjugation with organic compounds in the atmosphere. Higher concentrations of ammonium nitrate over land during the cooler months of the year are typical across Europe (Jenkin 2006, Myhre & Grini 2006). The concentration of the NH_4NO_3 aerosol over Gdynia plotted against acidity demonstrates a clear relationship (Figure 8). Uptake of free NH_3 may alternatively explain the presence of coarse-mode NH_4^+ , a phenomenon that would partially neutralize the acidity of the coarse-mode aerosol (Yeatman 2001). In the warmer months aerosol acidification (Figure 4) and ammonium nitrate (80.1 nmol m^{-3}) levels decreased.

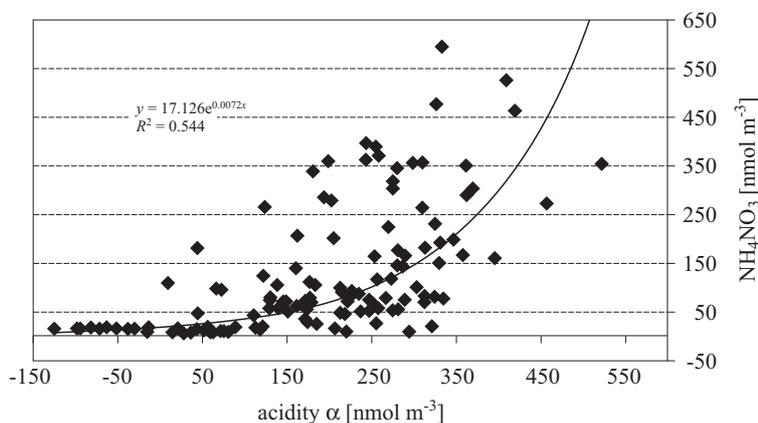


Figure 8. Acidity (α) [nmol m^{-3}] vs. NH_4NO_3 [nmol m^{-3}] concentration in the atmosphere over Gdynia (2001–2007)

The presence of hygroscopic ammonium sulphate was detected in aerosols in the coastal atmosphere (Table 2). This compound is typical of urbanized coastal zones, as long as gaseous ammonia exceeds its aerosol form (Matsumoto & Tanaka 1996, Seinfeld & Pandis 1998). In the period under discussion, the average concentration of ammonia in the air was 36.6 nmol m^{-3} , while that of ammonium ions was 21.5 nmol m^{-3} . In autumn 2002, when the air humidity over the Gdańsk Deep was $> 90\%$ (Table 3, Lewandowska & Falkowska, Part 1, this volume), the ammonium sulphate concentration dropped and the compound was efficiently removed by large hydrated aerosols (Figure 9).

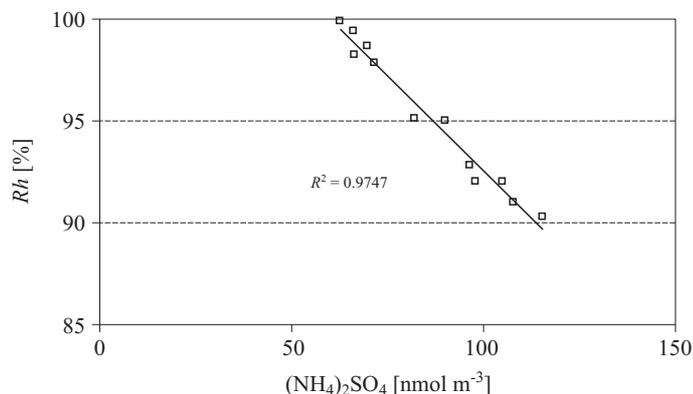


Figure 9. Relationship between the ammonium sulphate concentration [nmol m^{-3}] and air humidity [%] in autumn 2003 over the sea station (Lewandowska 2011)

With the predominance of the gaseous ammonia fraction over its aerosol form, ammonium sulphate was present in aerosols over land only during the warm period. At that time, air humidity dropped to 80.3% and the linear dependence of the ammonium nitrate concentration on this meteorological parameter was statistically not significant ($r = -0.27$).

4. Conclusions

The near-water layer of the atmosphere of the southern Baltic is almost homogeneous as regards the chemical composition of aerosols. Sea salt components were predominant in both the coastal area over land and over the open sea.

Over both stations marine aerosols became enriched with nitrogen and sulphur compounds emitted during combustion. The process intensified during the cool months of the year, when smoke emissions increased in proportion to the need for energy. In spring, the chemical composition of marine aerosols was modified by terrigenous particles, mostly due to agricultural activity at the beginning of the growing season in this part of Europe.

Aerosol acidification was higher over land than at sea. Acidification increased whenever nitrate concentrations rose and the proportion of nssSO_4^{2-} was $> 90\%$.

Irrespective of season, acidified aerosols in the coastal area were neutralized in reactions with sea salt. The likelihood of sodium nitrate being formed increased with air humidities $> 80\%$ and nitrate concentrations $> 30 \text{ nmol m}^{-3}$. Sodium sulphate formation in aerosols was of a seasonal

nature and took place mostly in autumn and winter. Strong winds and northerly advection were conducive to this reaction.

The neutralizing properties of ammonia manifested themselves by the presence of ammonium sulphate and nitrate in aerosols. The necessary requirement for the formation of ammonium aerosols in the coastal zone of the southern Baltic was the predominance of gaseous ammonia over the ionic form.

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