

## Selected ionic components of the marine aerosol over the Gulf of Gdańsk

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### Abstract

Aerosol samples were collected in May 1997 at a routine off-shore measurement station in the Gdańsk Deep region and at Hel, the latter being a coastal station situated at the tip of the Hel Peninsula. Concentrations of  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  were measured simultaneously at both stations.

The sea influences the chemical composition of aerosols in the coastal zone of the Gulf of Gdańsk regardless of season, time of day or direction of advection. Sodium chloride was always present in aerosols in the form of large particles originating from seawater. Besides the marine chloride and nitrate, additional amounts of these ions could have been of terrigenous origin. Sodium and chloride concentrations were dominant in the total mass of aerosols at both stations; however, these concentrations were three times higher at the marine station. Similarly, the concentrations of ions originating from seawater, like magnesium and calcium, were, on average, three times higher at the marine station.

The chemical composition of aerosols and air over the Gulf of Gdańsk was modified through the evaporation of chloride from the marine salt particles in reactions with gaseous nitric and sulphuric acids. A certain deficit of chloride versus sodium ions was noted. At the marine station the  $\text{Cl}^-/\text{Na}^+$  ratio reached  $0.89 \pm 0.2$ , on average, while over the land station it was  $0.93 \pm 0.25$ , i.e. lower than the seawater standard.

## 1. Introduction

Aerosol particles perform various functions in the atmosphere. Absorption and scattering of radiation in the atmosphere depend on the number and type of aerosol particles. Such particles are responsible for various optical phenomena observed in the atmosphere and which are characteristic of colloidal solutions. Aerosols partake in such processes as particle electrification, and the formation of clouds, droplets and ice crystals, fog and smog. By reflecting and scattering solar radiation, aerosols participate in the Earth's heat balance. Because of their surface properties like adhesion, sorption and condensation, aerosols are active in various chemical reactions, aiding, for example, the neutralisation of acid in the atmosphere or in atmospheric precipitation.

According to the ideal size distribution pattern of particles, ammonia, and sulphate and nitrate ions are classified as small particles (diameter  $< 1 \mu\text{m}$ ). Fe, Ca, Si, Na, Cl and Al are included among the large particles (diameter  $> 1 \mu\text{m}$ ) (Seinfeld 1986, Hillamo & Kauppinen 1991). The ions form large or small aerosol particles, depending on the chemical reactions they are likely to participate in. The small particles are mainly of anthropogenic origin, while the large ones usually come from natural processes such as volcanic eruptions or sea-surface emission (Seinfeld 1986). As regards the atmosphere near the sea surface, the particle concentration depends to a great extent on wind speed and direction, also on the season, and even on the time of the day (Monahan 1986).

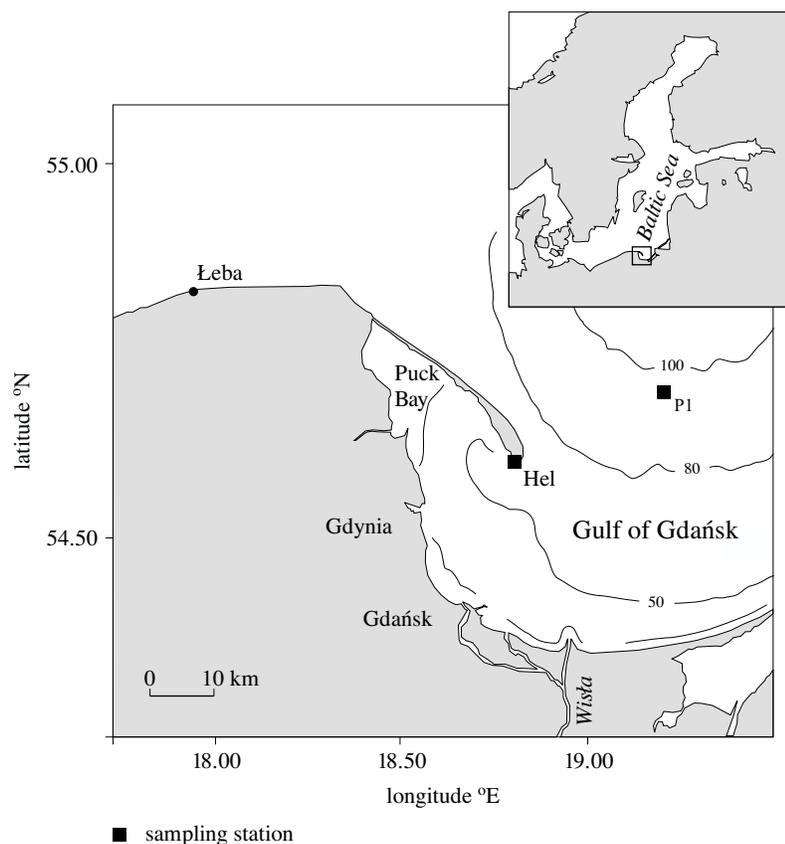
Maritime aerosols differ in their morphology and chemical composition from terrigenous aerosols. In wholly marine aerosols, the prevalent ions are chloride and sulphate (88.7% and 10.8% respectively). Other ions, like  $\text{NO}_3^-$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , make up only around 0.5% of the total aerosol mass (Parungo et al. 1986). However, depending on the sampling region, the proportions in the terrigenous aerosol may be different; for instance, in an urban area they may even be reversed in comparison with marine aerosols (Behlen 1996).

A considerable proportion of the aerosols over the open sea are of marine origin. However, the definition of the origin of an aerosol at such a land station like Hel is no longer certain. The aerosol components in the near-water layer of the atmosphere may be of both terrigenous/anthropogenic (ammonia and nitrate) and marine origin (the principal components of sea salt). In this project we have attempted to compare the concentrations of  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in aerosols in two areas: in the coastal region and over the open sea. To assess the origin of the ions, the relations between individual ion concentrations were determined. Additionally, possible interactions were defined.

The evaporation of gaseous components from aerosols is an important problem in chemical relations in the atmosphere. Assuming that sea salts are the main components of the marine aerosol, the ratio of these ions in aerosols should be of the same magnitude. In actual fact, however, there is a surplus of chloride ions over sodium or, conversely, a chloride deficit. The aim of the study was to test the hypothesis that chloride ions are lost from the aerosol as a result of partial evaporation of gaseous HCl produced in reactions of  $\text{HNO}_3$  with  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and  $\text{KCl}$ .

## 2. Experimental

Aerosol samples were collected at a routine measurement station located in the Gdańsk Deep region (P1,  $\varphi = 55^\circ 22' \text{N}$ ;  $\lambda = 19^\circ 10' \text{E}$ ) and at a land-based station situated at the tip of the Hel Peninsula ( $\varphi = 54^\circ 35.974' \text{N}$ ;  $\lambda = 18^\circ 48.858' \text{E}$ ) (Fig. 1). The measurements were



**Fig. 1.** Location of measurement stations

conducted during the period 5–10 May 1997. Aerosols were sampled at the same height of 20 m above sea level at both stations, which were 37 km apart. The samples were collected in a 12 h cycle at both stations simultaneously. Air flow, regulated by a critical orifice, was constant at  $2.2 \text{ m}^3 \text{ h}^{-1}$ .

Concentrations of the following ions were determined in samples from both stations:  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . Samples were collected on Whatman 41 filters:

- (i) impregnated with 5% phosphoric acid, to determine  $\text{NH}_4^+$  ions,
- (ii) washed with de-ionised water ( $3\times$ ), to determine  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and macro-components.

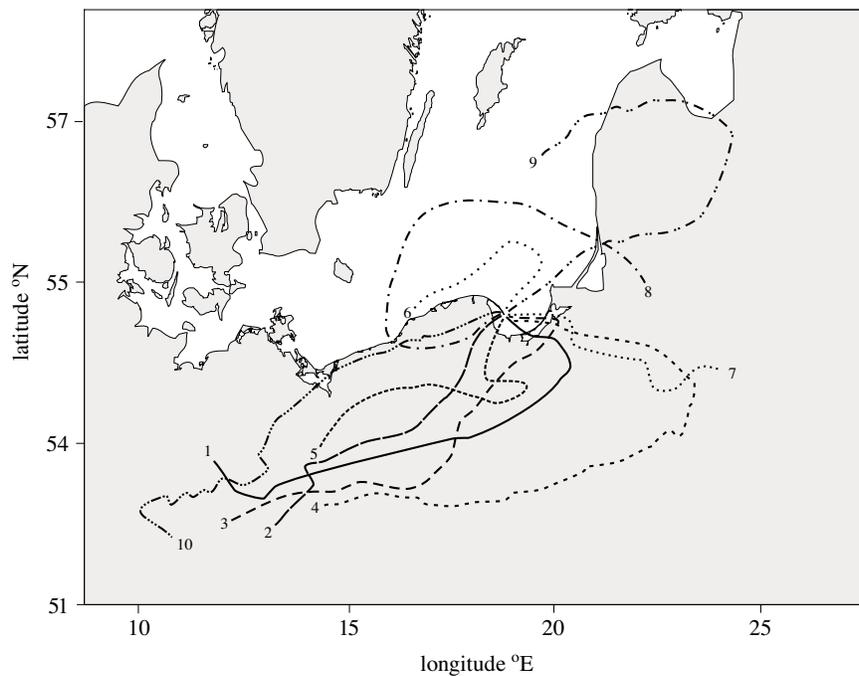
Each analysed parameter was determined in 10 samples. When exposure had come to an end, the filters were extracted in a sonicator bath for 45 min. The individual ions were analysed with colorimetric methods:  $\text{NH}_4^+$  – indophenol blue, according to Grasshoff et al. (1983),  $\text{NO}_3^-$  – reduction by hydrazine to nitrates and their determination in the Griess-Ilsovacy reaction, (Alfa 1992), and  $\text{Cl}^-$  – the reaction that yields the yellow  $\text{Fe}[\text{CSN}]_3$  complex in the presence of perchloric acid (EMEP 1977). Absorption was determined using a Perkin Elmer 103 spectrophotometer. Metallic macro-components were determined by flame atomic absorption spectrometry.

Within the low and high concentration ranges, the standard deviations of particular ion measurements are presented in Table 1. The calculation of SD took into account the air flow ( $24 \text{ m}^3$ ), the volume of solution used for ion extraction (14 ml) and the exposure time (12 h).

**Table 1.** Standard deviations of the measurements of particular ions in two concentration ranges

Ion	Low concentration range [nmol $\text{m}^{-3}$ ]	High concentration range [nmol $\text{m}^{-3}$ ]
$\text{Na}^+$	2.13	1.28
$\text{K}^+$	0.89	0.14
$\text{Mg}^{2+}$	0.17	0.10
$\text{Ca}^{2+}$	1.38	0.13
$\text{NH}_4^+$	0.68	0.22
$\text{Cl}^-$	2.35	1.19
$\text{NO}_3^-$	1.38	1.45

In addition, meteorological data were recorded, including the trajectories of the air masses over the measurement stations (Fig. 2).



**Fig. 2.** Trajectories of air masses over the measurement stations (the numbers of the sampling periods refer to Table 2)

### 3. Results and discussion

Salt emitted from the sea surface constitutes the main component of marine atmosphere, hence sodium and chloride ions were dominant in the aerosols analysed at both stations: at Hel and at sea (Table 2).

However, the concentrations of the main components were three times higher and much more variable at the marine station than on land. Sodium and chloride concentrations showed identical changes during the experiment. The strong correlation between the concentrations of these ions –  $r = 0.96$  at the marine station P1 and  $r = 0.98$  on land – supported by the  $\chi^2$  test, provided evidence of their marine origin. The sodium concentration was equal to or slightly exceeded the chloride content in all cases (Table 2).

The formation of compounds like  $\text{NaNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{HSO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  in aerosols has been extensively described in the literature (Pio et al. 1992, Plate & Schulz 1997).

The presence of large particles of sodium nitrate and magnesium nitrate at the marine station was demonstrated by the high correlation coefficients between  $\text{NO}_3^-$  and  $\text{Na}^+$  ions ( $r = 0.80$ ) and between  $\text{NO}_3^-$  and  $\text{Mg}^{2+}$  ( $r = 0.72$ ). Gaseous nitric acid is involved in surface reactions with large

**Table 2.** Concentrations of major ions at both stations during the May 1997 experiment [ $\text{nmol m}^{-3}$ ]

Location	Sampling periods	Beginning	End	Wind speed [ $\text{m s}^{-1}$ ]	Wind direction [ $^{\circ}$ ]	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{NH}_4^+$	$\text{Cl}^-$	$\text{NO}_3^-$
coastal station Hel	1*	5.05.97; 10:00	5.05.97; 22:00	$4.0 \pm 3.5$	S-SE	18.0	3.0	0.5	5.2	8.7	14.1	4.6
	2	5.05.97; 22:00	6.05.97; 10:00	$3.5 \pm 2.1$	S	150.4	85.7	6.1	17.7	17.0	116.8	8.6
	3	6.05.97; 10:00	6.05.97; 22:00	$4.0 \pm 1.4$	S	40.0	17.7	1.0	4.9	16.4	39.5	11.3
	4	6.05.97; 22:00	7.05.97; 10:00	$5.0 \pm 1.4$	S-SE	28.2	2.5	1.0	2.5	12.8	33.6	7.5
	5*	7.05.97; 10:00	7.05.97; 22:00	$3.8 \pm 2.8$	S	40.7	2.7	1.6	4.9	4.1	40.4	3.8
	6	7.05.97; 22:00	8.05.97; 10:00	$2.0 \pm 1.4$	N-NW	50.0	4.0	5.3	4.8	12.1	37.4	8.2
	7**	8.05.97; 10:00	8.05.97; 22:00	$4.3 \pm 1.6$	E-SE	49.3	0.3	1.6	4.9	6.4	59.4	8.4
	8	8.05.97; 22:00	9.05.97; 10:00	$3.3 \pm 2.1$	N-NW	93.7	23.1	17.8	29.5	15.8	5.9	21.6
	9	9.05.97; 10:00	9.05.97; 22:00	$4.3 \pm 3.5$	N-NE	344.5	21.5	13.1	4.9	1.9	284.6	3.9
	10	9.05.97; 22:00	10.05.97; 10:00	$4.6 \pm 1.4$	S-SW	83.1	38.7	6.4	12.9	20.1	93.0	11.9
$\bar{x}$						89.8	21.0	4.0	11.5	11.5	76.5	9.0
SD						97.6	25.7	5.3	8.3	6.1	78.7	5.3
sea station	1*	5.05.97; 10:00	5.05.97; 22:00	$6.5 \pm 3.2$	NE, SW	53.9	< LD	3.1	31.8	6.7	32.1	11.9
	2	5.05.97; 22:00	6.05.97; 10:00	$7.2 \pm 2.2$	SW	74.5	2.2	5.2	16.9	7.8	70.5	3.4
	3	6.05.97; 10:00	6.05.97; 22:00	$7.4 \pm 2.2$	SE	959.6	82.7	94.8	128.0	20.4	823.5	69.8
	4	6.05.97; 22:00	7.05.97; 10:00	$11.6 \pm 1.9$	SE	64.0	1.9	4.2	3.7	36.9	59.2	30.0
	5	7.05.97; 10:00	7.05.97; 22:00	$12.0 \pm 3.4$	W	54.0	2.0	8.6	< LD	14.2	50.0	24.2
	6	7.05.97; 22:00	8.05.97; 10:00	$3.6 \pm 0.9$	S-SE	10.8	0.4	2.2	3.0	19.4	10.9	11.0
	7	8.05.97; 10:00	8.05.97; 22:00	$8.2 \pm 1.3$	NE	74.3	2.9	9.6	3.2	39.2	66.2	24.0
	8*	8.05.97; 22:00	9.05.97; 10:00	$7.6 \pm 2.8$	E-NE	58.0	7.1	8.6	29.6	69.1	48.2	23.3
	9	9.05.97; 10:00	9.05.97; 22:00	$8.0 \pm 2.6$	S	19.7	1.0	4.9	1.5	55.3	24.0	16.1
	10	9.05.97; 22:00	10.05.97; 10:00	$7.1 \pm 2.5$	S	13.2	3.5	2.4	< LD	26.5	9.8	27.4
$\bar{x}$						138.2	11.5	14.4	27.2	29.5	119.4	24.1
SD						289.6	25.3	28.4	39.3	20.6	248.3	22.5

\* drizzle, \*\* heavy rain,  $\bar{x}$  – the mean value of N measurements,  $\overline{\text{SD}}$  – standard deviation, LD – limit of detection.

salt particles, and sodium nitrate is an example of a large molecule produced by these surface reactions (John et al. 1988, Wall et al. 1988, De Bock et al. 1994, Harrison & Msibi 1994, Ottlay et al. 1994). The probability of detecting  $\text{NaNO}_3$  and  $\text{Mg}(\text{NO}_3)_2$  in aerosols over the land station was negligible because of the generally lower nitrate concentrations and smaller contributions of the marine aerosol.

The correlation coefficients for calcium nitrate (Hel,  $r = 0.82$ ; P1,  $r = 0.79$ ) and ammonium nitrate (Hel,  $r = 0.87$ ; P1,  $r = 0.55$ ) were statistically significant according to the  $\chi^2$  test. This suggests that they could have a common source, especially as they are components of both large and small aerosol particles. Ammonium nitrate was independently determined and mostly dissolved in wet aerosol particles ( $\text{RH} > 40\text{--}60$ ), depending on solubility and hygroscopicity. Mészáros et al. (1991) calculated that c. 75% of the ammonia commonly present in aerosols reacts with sulphates to form  $\text{NH}_4\text{HSO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$ . However, sulphate and ammonium ions usually appeared at the land station at Hel as constituents of small aerosols ( $\text{NH}_4^+$ : 70–80%;  $\text{SO}_4^{2-}$ : 50–100%); this was supported by the results of simultaneous long-term measurements in a Berner impactor (Nadstazik 1999).

Ever present in the atmosphere, ammonia not only binds nitric acid but also reacts with gaseous HCl to produce ammonium chloride, which is three times as volatile as ammonium nitrate and dissociates to gaseous  $\text{NH}_3$  and HCl (Stelson & Seinfeld 1982, Pio & Harrison 1987, Plate & Schulz 1997). It is probably as a result of this process that gaseous  $\text{NH}_4\text{Cl}$  was not detected, either in the marine aerosol or over land, since no relation was found between these ions. The chloride ions may have been substituted by  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  (Pio et al. 1992). It is thus possible that a certain quantity of ammonia ions neutralised sulphate at both stations.

The diurnal fluctuations of particle concentrations in the atmosphere caused by the photo-oxidation of gases emitted by the ocean display daily maxima (Fitzgerald 1991). The highest concentrations of aerosols have been measured over the southern Atlantic and Indian Oceans at noon (Mészáros & Vissy 1974). However, during short-term experiments carried out at sea these daily maxima were not detected, possibly because of the extremely changeable directions of advection during a short period of measurements (Fig. 2). Under stable air masses over the Pacific Ocean, maximum particle levels were recorded at night (Parungo et al. 1987). Hoppel & Frick (1990) indicated diurnal changes in particle concentrations in relation to their size. Over the Pacific and Atlantic Oceans they recorded a daily cycle of small particles ( $\text{Ø} < 0.006 \mu\text{m}$ ).

During this short experiment, the lowest concentrations of aerosol components were measured during rainfall (Table 2). The purifying effect of rain was particularly noticeable at the land station during the 1st and the 5th measurement periods, and at the marine station on the very first day of the experiment. A brief but heavy shower only slightly depressed the concentrations of ionic components in the aerosol (7th and 8th measurement periods at the land and marine station respectively).

### **Origin of aerosols and evaluation of hydrogen chloride evaporation**

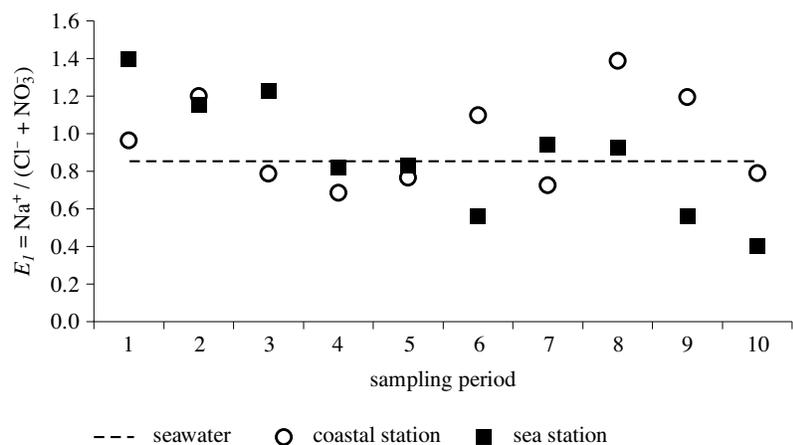
Over the open-sea area a considerable proportion of the aerosol is of marine origin. At the land station at Hel, it was very hard indeed to define the aerosol's origin unequivocally. In origin, the aerosol components in the near-water layer of the atmosphere can be both terrigenous (ammonia and nitrate) and marine (main components of sea salt). During the experiment, the relation between ion concentrations and direction of advection was clearly defined. Relatively low concentrations of all ionic components, such as nitrate and potassium, particularly from anthropogenic sources, were measured at both stations during advection from the Baltic Sea (6th measurement period).

Despite their definitely terrigenous origin, the air masses transported from the east (1, 3, 4, 7 and 9th measurement periods – Fig. 2), could have been modified by the sea (these air masses were carried from 50 to 160 km over the Gdańsk Basin, Fig. 2). Low concentrations of most ions, largely of terrigenous origin, were measured then. However, an increase in the wind speed (the 3rd measurement period at marine station and the 9th at the land one) caused a considerable rise in the concentrations of both marine and terrigenous ions. The 9th measurement period at the marine station was the only time that an excess of chloride (probably small particles) over sodium was recorded. A considerable proportion of terrigenous chloride ions in easterly air masses was determined in the coastal zone of the Gdańsk Basin during long-term measurements (Nadstazik 1999). In a 10-year study in the Kuronian Lagoon (Lithuania), Sopauskiene & Budvytyte (1994) suggested that chloride transportation over the Baltic Sea was highly likely with advection from the east. A surplus of mineral chloride was also observed in aerosols in other geographical regions, e.g. the Amazon Basin (Artaxo & Hansson 1995).

Southerly air masses (2nd, 5th, 8th and 10th measurement periods; Fig. 2) cause an increase in ammonium and potassium ions in aerosols. Very probably, a certain amount of these ions comes from terrigenous and specifically anthropogenic sources. The concentration ratios of potassium

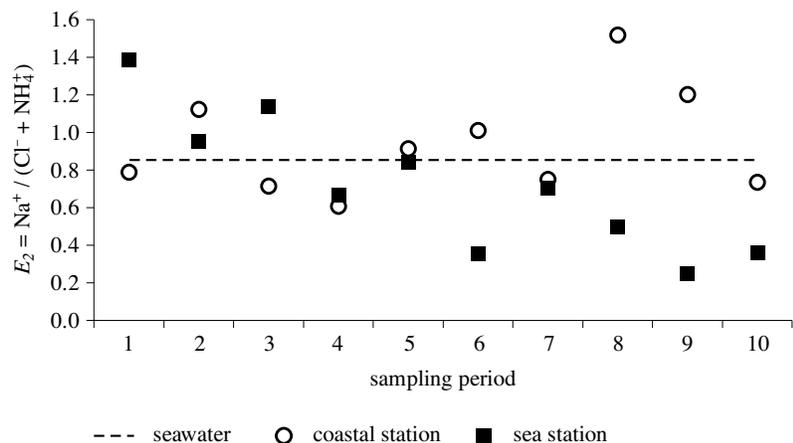
and calcium ions to sodium ions were usually higher by one order of magnitude than the respective values in seawater (mean  $K^+/Na^+$  at Hel = 0.22, at sea 0.8; mean  $Ca^{2+}/Na^+$  at Hel 0.14, at sea 0.24).

The origin of the ammonium and nitrate ions can be defined by the analysis of ratios  $E_1 = Na^+/(Cl^- + NO_3^-)$  and  $E_2 = Na^+/(Cl^- + NH_4^+)$ . In seawater the coefficient is simplified to  $Na^+/Cl^-$  and takes values up to 0.85 (Pakkanen 1995). In the atmosphere, nitrate and ammonium ions cannot be neglected because of their high contents and variety of sources. The respective nitrate (Fig. 3) and ammonia (Fig. 4) origin coefficients,  $E_1$  and  $E_2$ , were close to the seawater values (0.85) at both stations. Any deviation from this value was probably caused by additional quantities of chloride, nitrate and ammonium ions from terrigenous sources under prevailing southerly or easterly advection. Despite the commonly accepted idea of the terrigenous origin of nitrate and ammonium, their emission from the sea surface cannot be ruled out completely. However, the mean concentration ratios of nitrate and ammonium ions to sodium in seawater are less than  $10^{-5}$  (Riley & Skirrow 1975), whereas at Hel they were 0.17 and 0.23 for  $NO_3^-$  and  $NH_4^+$  respectively. In aerosols collected over the marine station they were also three orders of magnitude higher than in the seawater (0.59 and 0.94 for  $NO_3^-$  and  $NH_4^+$  respectively).



**Fig. 3.** Coefficients  $E_1 = Na^+/(Cl^- + NO_3^-)$  measured at the land station at Hel and in the Gdańsk Deep region in May 1997 (horizontal dashed line denotes the value in seawater; the numbers of the sampling periods refer to Table 2)

The spring phytoplankton bloom usually depletes the nitrate pool in the surface seawater, even to below the detection limit. However, nitrate was present in the sea surface microlayer during the entire measurement period in concentrations  $0.7\text{--}1.0 \mu\text{mol dm}^{-3}$ , while the ammonium concentration



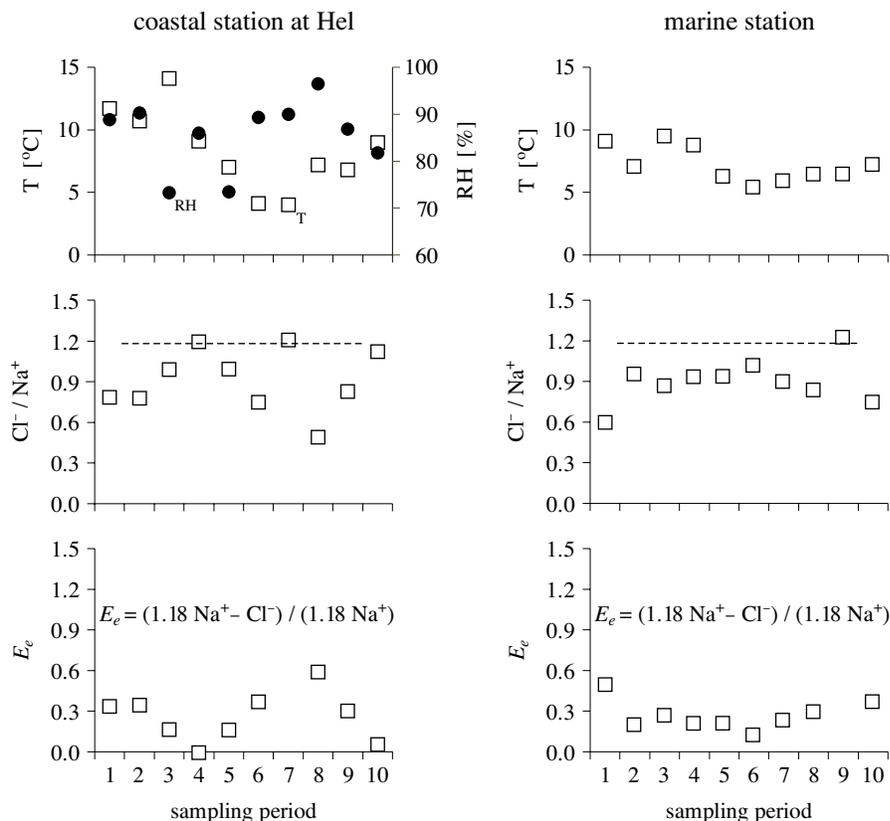
**Fig. 4.** Coefficients  $E_2 = \text{Na}^+ / (\text{Cl}^- + \text{NH}_4^+)$  measured at the land station at Hel and in the Gdańsk Deep region in May 1997 (horizontal dashed line denotes the value in seawater; the numbers of the sampling periods refer to Table 2)

rose even above  $7 \mu\text{mol dm}^{-3}$ . The wind speed also exerted a considerable effect on nitrate concentrations at the marine station ( $\text{NO}_3^- = 5.3 V_w + 26.4$ ;  $r = 0.7$ ,  $p < 0.05$ ).

High values of  $E_1$  were recorded a few times during the measurement period at both the marine and the land stations; this was attributed to low concentrations of  $\text{Cl}^-$  or high concentrations of  $\text{Na}^+$  (Figs. 3 and 4). Chloride ion evaporation seems to have been the most probable mechanism responsible for the high values of  $E_1$  on the first occasion.

The ratio between chloride and sodium ions in seawater is 1.18 (Pakkanen 1995, Plate & Schulz 1997). Assuming that sea salts are the main components of the aerosol, the ratio of these ions in aerosols should be of the same magnitude. In reality, however, one quite frequently observes a surplus of chloride ions over sodium (Suzuki & Tsunogai 1988) or, conversely, a chloride deficit is recorded (Plate & Schulz 1997). Several processes can determine the change in the  $\text{Cl}^- / \text{Na}^+$  ratio following salt emission into the atmosphere: (i) particulate Cl may be lost by atmospheric conversion to gaseous Cl species; (ii) Cl may be gained by adsorption of gaseous Cl species; (iii) the particles may gain Na from terrigenous dust; (iv) the composition may change as a result of selective wet or dry deposition of particles of a certain size or composition (MacIntyre 1974). Recently, some authors, e.g. Plate & Schulz (1997) have regarded the evaporation of gaseous chloride forms as the most important mechanism.

Chloride evaporation was found to occur during the short-term experiment at both the land and the marine stations. At the marine station the



**Fig. 5.** Coefficients  $\text{Cl}^-/\text{Na}^+$  and  $E_e = (1.18 \text{ Na}^+ - \text{Cl}^-)/(1.18 \text{ Na}^+)$  measured at the coastal station at Hel and at the marine station in the Gdańsk Deep in May 1997 (horizontal dashed lines denote values in seawater; the numbers of the sampling periods refer to Table 2)

$\text{Cl}^-/\text{Na}^+$  ratio reached  $0.89 \pm 0.2$  on average; over the land station it was  $0.93 \pm 0.25$ , hence lower than the seawater standard (Fig. 5). Elevated values were recorded during the 9th (1.22) and 4th (1.20) measurement periods at sea and during the 7th (1.22) measurement period on land. This coincided with easterly air masses (Fig. 2), which transported terrigenous material containing great quantities of chloride ions. Chloride loss due to evaporation was estimated at 23% over the marine station and at 22% over the land station.

Assuming that the total load of sodium in aerosols is derived from seawater ( $\text{Cl}^-/\text{Na}^+ = 1.18$ ), the real quantity of chloride emitted from the sea can be calculated from the ratio  $E_e = (1.18 \text{ Na}^+ - \text{Cl}^-)/(1.18 \text{ Na}^+)$  (Pakkanen 1995). At both stations,  $\text{Cl}^-/\text{Na}^+$  ratios lower than in seawater corresponded to elevated values of the chloride evaporation coefficient  $E_e$

(Fig. 5). It was only with easterly advection that the evaporation coefficient was close to or equal to zero. Additional amounts of chloride ions present in the aerosol replenished the losses resulting from evaporation and precluded a quantitative resolution of the process.

At the marine station, temperature could have exerted a certain influence on chloride evaporation ( $E_e = 0.05 T - 0.1$ ;  $r = 0.6$ ), while at the Hel station, no such effect was observed. However, a significant influence was attributed to the relative humidity ( $E_e = 0.02 RH - 1.3$ ;  $r = 0.7$ ). Chloride losses reached a maximum at over 90% humidity, when the reaction between gaseous nitric acid was possible on the surface of sodium chloride (Hillamo & Kauppinen 1991). In addition, it was found that chloride ions bound to  $K^+$ ,  $Mg^{2+}$  or  $Ca^{2+}$  from the sea salt may evaporate as a result of the reaction between these ions and  $H_2SO_4$  or  $SO_2$  from the aerosol (Harrison & Pio 1983, Sievering et al. 1991, Hillamo et al. 1993, De Bock et al. 1994). The chloride ions in the atmosphere over the Hel Peninsula and over the marine station were bound up in calcium, potassium and magnesium salts, the respective correlation coefficients at Hel and at sea being high:  $Ca^{2+}$  vs  $Cl^-$  –  $r = 0.96$  and  $0.82$ ;  $K^+$  vs  $Cl^-$  –  $r = 0.88$  and  $0.81$ ; and  $Mg^{2+}$  vs  $Cl^-$  –  $r = 0.92$  and  $0.87$ . According to Pakkanen (1995), chloride losses due to rising evaporation rise with the increasing size of aerosols originating from marine salts. Sievering et al. (1991) established that chloride evaporation in aerosols intensifies when the amount of nitrate from terrigenous sources increases. This observation was endorsed by the measurements at both stations. Analysis of the paths of air masses over the measurement stations (Fig. 2) indicates that regardless of their area of origin, these air masses must have come into contact en route with other air masses saturated with marine aerosols that modified them to various extents and increased the probability of reactions leading to the release of gaseous hydrogen chloride.

#### 4. Concluding remarks

Simultaneous measurements within the coastal zone, at Hel, and in the open-sea region, indicated considerable differences in the chemical composition of aerosols. Despite its location at the tip of the Hel Peninsula, the station at Hel cannot be regarded as a representative marine station in aerosol studies. Chloride and sodium concentrations predominated in the total aerosol mass over both stations, but were three times higher at the marine station. Similarly, the concentrations of ammonium, nitrate, magnesium and calcium ions were three times higher, on average, at this station as well.

During this short-term experiment, the relation between ion concentrations and advection direction was clearly defined. Despite the evident contribution of marine sodium chloride in the total aerosol mass, additional amounts of chloride and sodium ions of terrigenous origin were found.

From an analysis of the air mass trajectories it may be inferred that ammonium in aerosols over the Hel station originated mainly from the sea.

The high probability of salt formation between  $\text{Cl}^-$  and  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{NO}_3^-$  and  $\text{Na}^+$  ions was confirmed, while the reaction leading to  $\text{NH}_4\text{Cl}$  was highly unlikely. Ammonia most probably reacted with nitrate and sulphate ions.

The possible conversion of molecular Cl into the gaseous form was indicated by chlorine losses, calculated at 23% over the marine station and at 22% over the land station. Sodium chloride reactions with gaseous nitric acid and sea salt components ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$ ) with  $\text{H}_2\text{SO}_4$  or  $\text{SO}_2$  were probably responsible for chloride evaporation.

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