Ammonia and ammonium over the southern Baltic Sea. Part 2. The origin of ammonia and ammonium over two coastal stations: Gdynia and Hel

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Abstract

Ammonia concentrations in aerosols and ammonium concentrations in the air were measured in the coastal zone of the southern Baltic Sea. The main study area was the Hel Peninsula, where measurements were carried out from December 1997 to March 1998. There was a second such area in Gdynia, where the first measurement period extended from May to December 2000, and the second one lasted from February to May 2001. At the same time, chloride, sulphate and sodium concentrations in the aerosols were determined; meteorological parameters were also measured. Aerosol samples were collected with a filter pack, and the gaseous phase species were collected on denuders. At both stations, the ammonium concentration in aerosols was at least one order of magnitude higher than that of the ammonia in the air samples. It was found that the marine boundary layer always contained ammonium chloride and ammonium sulphate. The presence of ammonium nitrate was detected only when winds were slight and was attributed to local anthropogenic sources. The ammonia concentration related to nitrate increased with rising air humidity and a falling temperature. The contribution of marigenic ions in aerosols was noted at onshore wind of speeds > 3.5 m s^{-1}. In winter as in summer, conditions occurred facilitating light backscattering by a 'wet' aerosol, which contained ammonium nitrate and ammonium sulphate in proportions of 2.5:1 and 1:1.

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

1. Introduction

There is a good reason for the interest in atmospheric aerosols: it is their effect on climate and on our understanding of climate change (Houghton et al. 2001). A significant fraction of air pollutants, both natural and anthropogenic in origin, emitted into the atmosphere, ends up in the form of quite stable submicrometer aerosol particles, which are responsible for a variety of atmospheric phenomena. The transfer and transformation of solar radiation in the atmosphere is strongly dependent on its aerosol content (Girgždys et al. 1995). Inorganic species such as ammonium, nitrate, sulphate, chloride and sodium are an important part of the atmospheric particulate mass, and inorganic salts formed from these species are known to deliquesce and absorb water in a moist atmosphere (Day & Malm 2001). The light scattering properties of aerosols (especially of ammonium nitrate and ammonium sulphates can change significantly as a result of their uptake or loss of water as the ambient relative humidity changes (Horváth 1996, Tang 1996). The ammonium/nitrate/sulphate system consists of several liquid, solid and gaseous components and is thermodynamically complex (Hillamo & Kaupinen 1991).

Despite the importance of NH_3 for particle formation and climate, relatively little effort has been expended on trying to understand its sources and how it is removed from the atmosphere. Most of the work on atmospheric ammonia has focused on its role in eutrophication and acidification, while the transport and chemistry of NH_3 and NH_4^+ have taken a back seat. In the long term, representative and reliable measurements of ammonium, sulphate and nitrate are required in conjunction with measurements to estimate the ammonia budget. The main purpose of the present study was to determine changes in ammonia and ammonium concentrations over two coastal stations: the slightly urbanised Hel and the highly urbanised Gdynia. Additionally, the relations between ammonia and ammonium concentrations on the one hand and meteorological parameters on the other were determined to assess their origin. The study also aimed to determine the phase state of the aerosol with respect to the solar radiation backscattering problem.

2. Material and methods

Gas and aerosol samples were collected at 2 coastal measurement stations (Fig. 1) at Hel from December 1997 to March 1998, and at Gdynia from May to December 2000 and from February to May 2001. Each sample was collected for seven days.
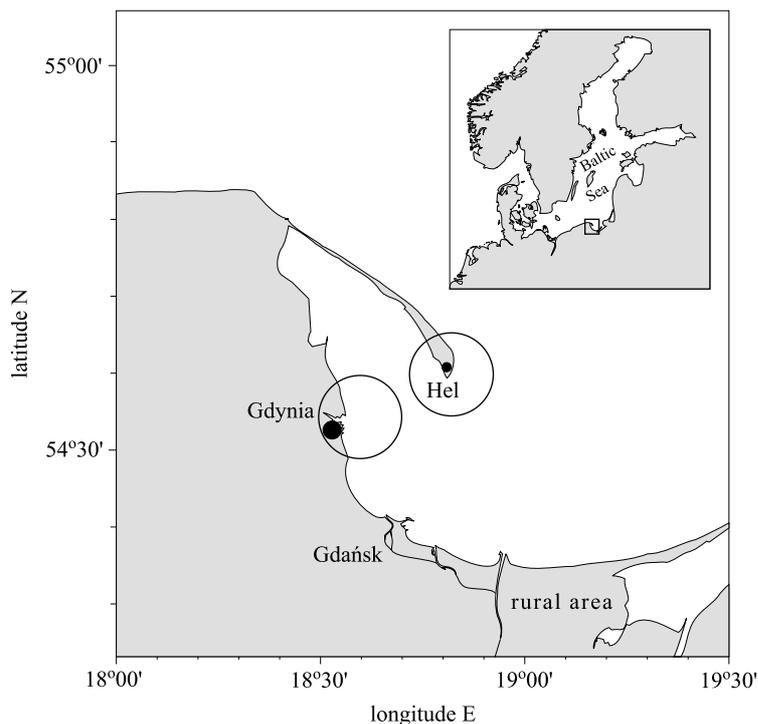
Fig. 1. The geographical location of the sampling stations at Hel and Gdynia

In Gdynia, the samples were collected on the roof of the building of the Institute of Oceanography of Gdańsk University ($\varphi = 54°31'$N, $\lambda = 18°48.86'$E). Gdynia is a city with a population of c. 250 000, located close to agricultural and industrial centres (shipyards, food-processing and chemical plants, port facilities etc.). In close proximity to Gdynia there are two other sizeable cities – Gdańsk and Sopot. Together with Gdynia, they make up the so-called 'Tri-city' agglomeration, which has nearly 1 million inhabitants.

The small town of Hel is situated at the very tip of the Peninsula (spit) of the same name ($\varphi = 54°36'$N, $\lambda = 18°49'$). A seaside resort with a population of just over 2000, it is not urbanised to any great extent.

At both sampling stations, samples were collected above the level of the tree crowns at a height of c. 20 m a.s.l. A total of 55 samples were collected for the determination of ammonia in air and ammonium in aerosols.

The aerosols were collected with filter packs. Each collector set contained two types of filter: a 5 μm mesh PTFE filter and a Whatman 41 filter impregnated with 5% orthophosphoric acid (p.a.). The sampled air first passed through the Teflon filter, which collected the larger suspended particles ($\phi > 1$ μm in diameter), and then through the Whatman filter,

which also adsorbed gaseous ammonia apart from a small fraction of suspended particles ($\phi < 1~\mu$m).

Ammonia was also collected with annular denuders. At the sampling site, filter pack and denuder were installed in parallel in a container protecting them from the weather (rain, strong wind) and connected to the air pump by polyethylene tubing. Air flow through the filter pack and denuder was regulated by the critical orifice and attained a rate of $3.2~\text{m}^3~\text{h}^{-1}$. Details of the sampling method, analytical procedures and measurement statistics (bias, precision and detection limit) are presented in part 1 of this article (Falkowska & Lewandowska 2004, in this volume). The sampling method and analytical procedures for the determination of chloride, nitrate and sulphate in aerosols are discussed at length in Nadstazik et al. (2000) and Nadstazik & Falkowska (2001).

3. Results and discussion

3.1. Ammonium concentrations in aerosols and ammonia in the air over Gdynia and Hel

The ammonium concentrations measured at the coastal station in Hel in 1997–98 and in Gdynia in 2000 and 2001 are presented in Table 1. At both stations the mean concentration of ammonium ions was always higher than the concentration of gaseous ammonia.

During the measurements at Hel at the turn of 1997, the weather was windy and the recorded mean wind speed was $4.3~\text{m s}^{-1}$, never falling below $3.2~\text{m s}^{-1}$ (Table 2). Under such conditions, the aerosols, which contained considerable amounts of ammonium, were of both marine and terrestrial origin, and ammonia concentrations were highest in easterly winds blowing at speeds $> 3.5~\text{m s}^{-1}$ (Fig. 2a).

During the measurements carried out at Gdynia in 2000, the estimated mean wind speed was $2.2~\text{m s}^{-1}$, and did not exceed $3.0~\text{m s}^{-1}$ (Table 2). The highest ammonium concentrations were found in aerosols arriving with onshore winds, while the highest concentrations of ammonia were found in air blowing off the land (Fig. 2b). No statistically significant relationships between these various concentrations and wind speeds were found. According to Ferm (1998), when winds are slight, with speeds no greater than $3.5~\text{m s}^{-1}$, it has to be anticipated that up to 50% of ammonia emitted into the atmosphere will be deposited locally, close to the emission source.

In 2001, Gdynia was under the influence of southerly and westerly winds from the land and the Gulf of Gdańsk, with mean speeds of $2.9~\text{m s}^{-1}$ (Table 2). These winds affected the concentration of ammonium (Fig. 2c) and were indicative of its terrestrial but also marine origins. It was an

Table 1. Monthly mean concentrations of ammonium in aerosols and ammonia in air at the measurement stations at Hel and Gdynia

| Month	Estimator	Hel [nmol m^{-3}]		Gdynia [nmol m^{-3}]			
		1997–98		2000		2001	
		$NH_4^+{}_{(a)}$	$NH_{3(g)}$	NH_4^+	$NH_{3(g)}$	NH_4^+	$NH_{3(g)}$
December	n	4	4				
	$\overline{x}\pm SD$	29.3±3.0	1.3±0.1				
January	n	4	3				
	$\overline{x}\pm SD$	22.5±7.5	0.8±0.6				
February	n	5	5			3	3
	$\overline{x}\pm SD$	23.6±8.1	2.5±1.5			31.5±5.2	0.3±0.1
March	n	4	3			4	4
	$\overline{x}\pm SD$	13.8±5.8	2.5±2.0			27.5±5.2	1.7±1.2
April	n					4	4
	$\overline{x}\pm SD$					30.0±4.3	1.8±2.4
May	n			3	3	3	3
	$\overline{x}\pm SD$			26.4±7.6	5.5±2.8	17.4±6.2	2.2±1.2
June	n			5	5		
	$\overline{x}\pm SD$			18.5±6.2	3.1±1.1		
July	n			4	4		
	$\overline{x}\pm SD$			21.2±12.4	0.7±0.8		
August	n			4	4		
	$\overline{x}\pm SD$			15.5±13.5	3.4±1.4		
September	n			3	5		
	$\overline{x}\pm SD$			11.6±0.8	4.8±2.7		
October	n			3	4		
	$\overline{x}\pm SD$			14.6±9.1	6.7±2.1		
November	n			2	2		
	$\overline{x}\pm SD$			15.0±11.4	4.8±1.3		

Symbols: n – number of samples, a – aerosol fraction (concentration calculated as the difference between the sum of concentrations determined from the Teflon and Whatman 41 filters and the concentration determined in the denuder), g – gaseous fraction (the concentration determined in the denuder), $\overline{x}$ – mean, SD – standard deviation.

isolated incident when the concentration of NH_3 displayed a significant negative relationship with the wind speed (r = 0.84, p < 0.05). This particular observation was made during easterly winds (Fig. 2c), which suggests that the ammonia was of marine origin. An increase in ammonium

Table 2. Statistics of air humidity (Rh), temperature (T) and wind speed (V_W) at the measurement stations at Hel and Gdynia

Estimator	Station											
	Hel				Gdynia							
	1997–98				2000				2001			
	$\overline{x}$	max	min	SD	$\overline{x}$	max	min	SD	$\overline{x}$	max	min	SD
RH [%]	88.1	98.2	51.0	6.2	83.5	99.8	40.9	6.6	75.2	97.0	24.0	7.0
T [°C]	2.8	10.0	−9.7	1.4	12.4	15.8	6.7	2.7	5.8	28.0	2.9	3.5
V_W [m s^{-1}]	4.3	6.4	3.2	1.0	2.2	2.8	1.5	0.4	2.9	12.3	0.3	0.4

Symbols: $\overline{x}$ – average value, SD – standard deviation, max – maximum, min – minimum.
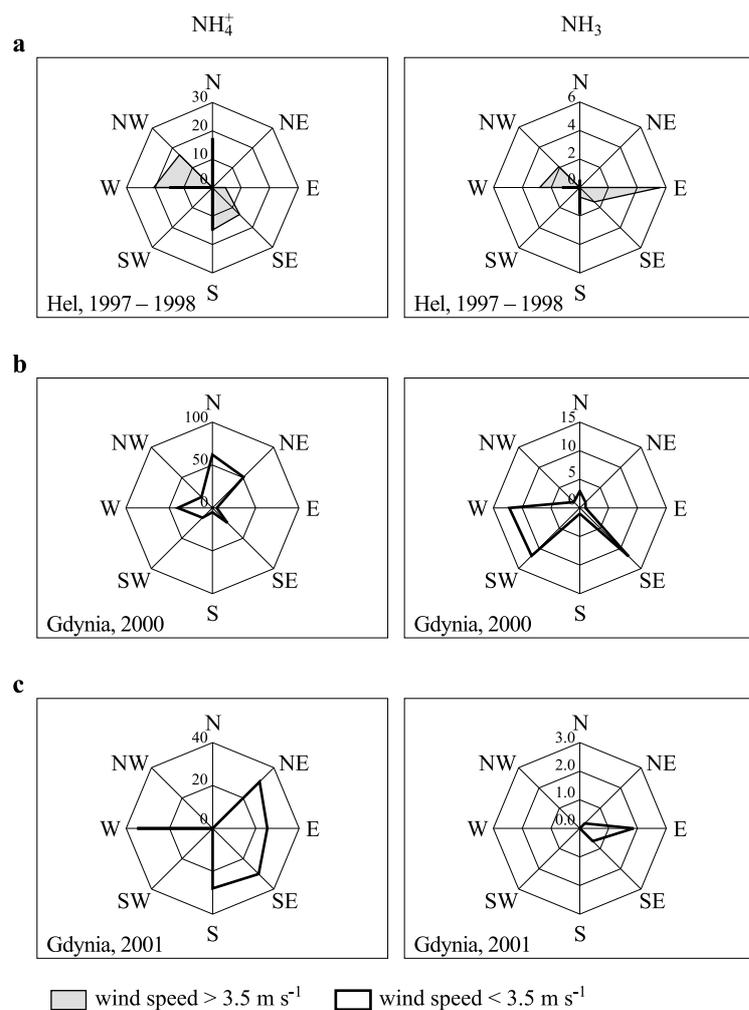
Fig. 2. The concentrations of ammonium and ammonia [nmol m^{-3}] over Hel and Gdynia taking into account wind direction in 1997–98 (a), 2000 (b), 2001 (c)

concentrations during easterly winds was recorded in winter 1997–98 over Hel and in 2001 in Gdynia, but the correlation showed only a low level of significance (r = 0.6).

3.2. Ammonia reactions with chloride, nitrate and sulphate ions in the atmosphere over Hel and Gdynia

Mineral salts emitted form the sea surface are the main components of the atmosphere over the sea. They are liable to react with the gaseous components of the air, i.e. the vapours of nitric and sulphuric acids, to

produce sodium sulphate or nitrate and hydrochloric acid (Ottley et al. 1994, de Bock et al. 1994, Harrison & Msibi 1994). Ammonia is ever present in the atmosphere and, besides binding nitric acid, may react with gaseous HCl to produce ammonium chloride, which is three times as volatile as ammonium nitrate. NH_4Cl can also decompose to gaseous NH_3 and HCl (Stelson & Seinfeld 1982, Plate & Schulz 1997).
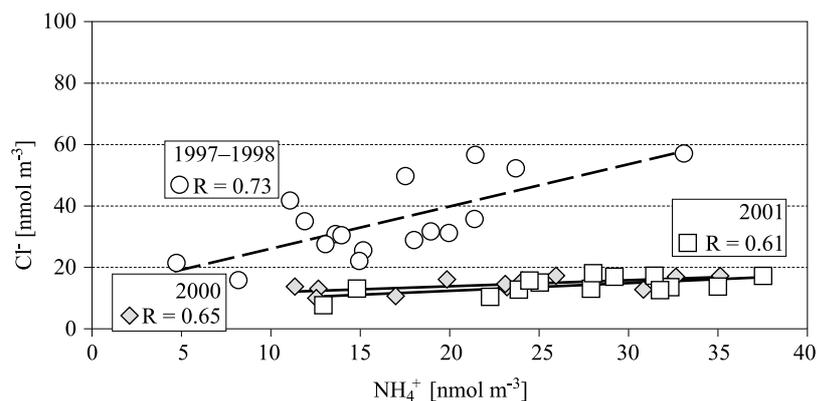
Ammonium chloride

Ammonium chloride was present in the aerosols at both Hel and Gdynia throughout the study period. The concentration of this volatile compound was influenced by the air temperature and humidity as well as by the concentration of chloride ions in the aerosols. The highest correlation coefficients were found between the concentrations of these ions in aerosols over the Hel station, when chloride concentrations reached maximum values (Table 3, Fig. 3). Because the sampling station at Hel is located close to the sea, the presence of sea salt in air has to be assumed as a result of generation by sea spray (Nadstazik et al. 2000). The measurements at the Hel station were carried out during the autumn-winter season (December

Table 3. Mean concentrations of nitrate, chloride, sodium and sulphate ions [nmol m^{-3}] in aerosols over Hel in 1997–98 and over Gdynia in 2000–01

Ion	Estimator	Hel	Gdynia	
		1997–98	2000	2001
chloride	$\overline{x}$	34.9	13.8	14.1
	max	57.1	17.3	18.1
	min	15.9	6.8	7.7
	SD	12.5	3.1	2.9
nitrate	$\overline{x}$	50.1	35.5	30.8
	max	114.0	73.6	52.5
	min	16.2	3.7	16.1
	SD	26.3	23.5	11.3
sulphate	$\overline{x}$	3.1	20.1	75.3
	max	13.6	32.3	116.4
	min	0.2	12.8	26.2
	SD	3.8	5.7	31.1
sodium	$\overline{x}$	25.2	22.9	1089.5
	max	99.6	32.9	1438.1
	min	7.3	18.1	780.6
	SD	21.1	7.5	219.7

Symbols as in Table 2.

Fig. 3. Relation between ammonium ion concentration and chloride concentration over Hel and Gdynia during the measurement periods

to March), when the temperature range is still relatively broad ($-9.7°$C to $+10.0°$C). However, the overall mean temperature was just $2.8°$C (Table 2). The relative humidity of the air was rather high (51.0–98.2%). Hillamo & Kaupaninen (1991) suggested that such meteorological conditions (cool, humid air) facilitate the formation of large aerosol aggregates from gaseous ammonia. This may explain the observed decline in the gaseous ammonia content and the increase in ammonium ion concentration during the study period (Table 1). A low correlation coefficient between the concentrations of ammonium and chloride ions was calculated from the measurements conducted in Gdynia in 2000 and 2001 (Fig. 3). In both instances the chloride ion concentration was c. 2.5 times lower than at the Hel station. Nevertheless, the probability of NH_4Cl evaporation from the aerosol surface was smaller in 2000 because the relative air humidity remained at a high level: av. 83.5%, min. 40.9%, max. 99.8%. The air temperature varied between 6.7 and $15.8°$C (mean $12.4°$C) (Table 2). These two meteorological factors probably determined the quite exceptional direct proportionality between the concentration of ammonium ions and air temperature ($r = 0.68$ and 0.62 for Hel 1997–98 and Gdynia 2000, respectively) and the inverse proportionality between the ion concentration and air humidity ($r = -0.7$ and -0.67 for Hel 1997–98 and Gdynia 2000, respectively) in the aerosols collected in Gdynia in winter 1997–98 and in spring, summer and autumn 2000. The high air humidity and low temperature (Table 2) prevented the rapid evaporation of ammonium chloride. A similar relation was found by Plate & Schulz (1997) in aerosols over the German Bight.

In 2001, chloride concentrations were similar to those measured in 2000, although the mean Rh of 75.2% reached its lowest recorded level in the study (Table 2). The measurements carried out during that year showed

that the contribution of ammonium chloride was declining as a result of meteorologically forced evaporation. This was facilitated by the low air humidity (min. 24%) and the continually rising air temperature (as high as 28°C in the final stage of the experiment). Hence, in 2001, the ammonium concentration was inversely proportional to the air temperature, but directly proportional to the air humidity (r = −0.76 and 0.6 for temperature and humidity, respectively). The measurements from 2001 also reflected the relation between ammonia concentration and these two meteorological parameters, indicating that rising air temperature (r = 0.78) and falling humidity (r = −0.72) could result in NH_4Cl evaporation. Burkhardt et al. (1998) in the atmosphere over southern Scotland, Yamamoto et al. (1995) over Yokohama in Japan, and Horváth & Sutton (1998) over a station in Hungary have all indicated the lack of a relationship between air temperature and ammonia (NH_3) concentration. These authors explained this finding by the combined effect of meteorological conditions and of anthropogenic sources – the close proximity of large cities, something we too were able to observe in Gdynia. The relation between ammonia concentration and the two meteorological parameters recorded in our study in 2001 was detectable probably because of the greater air temperature and humidity amplitudes occurring that year than in other periods (Table 2).

Ammonium nitrate

Besides ammonium chloride, ammonium nitrate was detected in aerosols over both measurement stations (Fig. 4), the compound being the product of the reaction between ammonia and gaseous nitric acid. The ammonia and ammonium ions ($NH_3 + NH_4^+$) as well as the nitric acid and nitrate ions ($HNO_3 + NO_3^-$) present in the aerosol are nutrients in seawater. Their air-to-sea deposition can occur in either particulate or gaseous form. Anthropogenic ammonium nitrates were detected in aerosols over the Hel station in winter 1997–98 as well as in Gdynia in 2001, when the wind was blowing off the land (from the south and west of Poland) (Fig. 2a, c). Nitric acid is constantly produced from nitrogen oxides, which are also present in the marine atmosphere (Plate & Schulz 1997). However, when offshore winds rich in nitric acid are blowing, the acid reacts with the sea salt. Its scavenging thus becomes significant in coastal regions (Pio et al. 1992).

In winter 1997–98, nitrate concentrations in aerosols over Hel were higher than in the other measurement seasons (Table 3). This has to be attributed to an increase in NO_3^- emission and the considerable stability of the atmosphere at this time (the 'heating season') (Ottley et al. 1994). Aerosols of anthropogenic origin were transported over the Hel Peninsula from land by strong winds at an average speed of > 3.5 m s^{-1} (Fig. 2a,
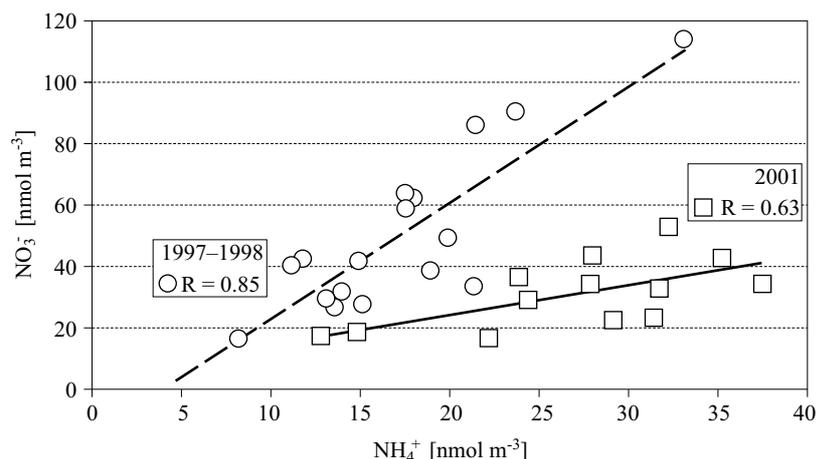
Fig. 4. Relation between ammonium and nitrate concentrations in the atmosphere over Hel and Gdynia during the measurement periods

Table 2). Similarly in Gdynia, in 2001, the aerosols again contained ammonium nitrate during offshore winds of mean speed 2.9 m s^{-1} (Fig. 2c, Fig. 4; Table 2). The high correlation coefficient between ammonium and nitrate concentrations in the air over Hel was the result of high air humidity and low temperatures. A relative humidity higher than 87% and lower air temperatures are the preferred conditions for the formation of this particulate aerosol component (Hillamo & Kaupinen 1991, Nadstazik et al. 2000). Particulate ammonium nitrate (NH_4NO_3) can evaporate under warm and dry conditions and form highly soluble gases like NH_3 and HNO_3, which deposit rapidly onto the water surface. Furthermore, nitric acid reacts with sea salt to form coarse particles of sodium nitrate ($NaNO_3$), which increases the deposition velocities even more.

In 2000, there were no observations of ammonium binding nitrate in aerosols over Gdynia. Ammonia reacted preferentially with sulphate to form $(NH_4)_2SO_4$ or NH_4HSO_4 (Quinn et al. 1988), but its concentration was probably too low to react with nitrate (Table 1). Moreover, the nitrate concentration was nearly 3 times lower than over Hel in winter 1997–98 (Table 3), when the presence of ammonium nitrate was detected in the aerosol. The low concentrations of nitrate in the air over Gdynia in 2000, as compared to other measurement periods, probably resulted from the lower emission of nitrogen oxides into the air in the warm part of the year on the one hand and the low speed (2.2 m s^{-1} on average) of the mainly onshore winds on the other (Table 2). The absence of ammonium nitrate in the atmosphere over the coastal zone of the North Sea was also reported by Quinn et al. (1988) and Fitzgerald (1991). Plate & Schulz (1997) explained

the absence of NH_4NO_3 in the air over the German Bight by its rapid dissociation into gaseous NH_3 and HNO_3. These compounds, in turn, may evaporate quickly or react with other substances. Because the contribution of onshore winds was quite considerable during the measurements in Gdynia in 2000, nitrate could have reacted with sea salt (de Bock et al. 1994, Harrison & Msibi 1994, Ottley et al. 1994).

Ammonium sulphate

The ammonia present in the air over Hel in 1997–98 and over Gdynia in 2000 and 2001, besides reacting with HNO_3 and HCl, also formed certain amounts of ammonium sulphate (Fig. 5). However, this compound was detected at Hel only in the second half of January 1998, when the concentration of sulphate ions fell to minimal values (Table 3, Fig. 5). The SO_4^{2-}/Na^+ ratio in the aerosol was then 0.045. This is a proportion very close to that in seawater (0.06). This observation seems to indicate a significant contribution of maritime particles and is supported by the low contribution of a sulphate fraction unrelated to seawater ($nssSO_4$) of less than 20% (Falkowska & Lewandowska 2004). Also in 2001, particles containing ammonium sulphate were formed in the aerosols over Gdynia (Fig. 5). The sulphate concentration then reached its maximum and the mean SO_4^{2-}/Na^+ ratio was 0.060, that is to say, identical to the proportion of these ions in seawater. The low contribution of sulphate unrelated
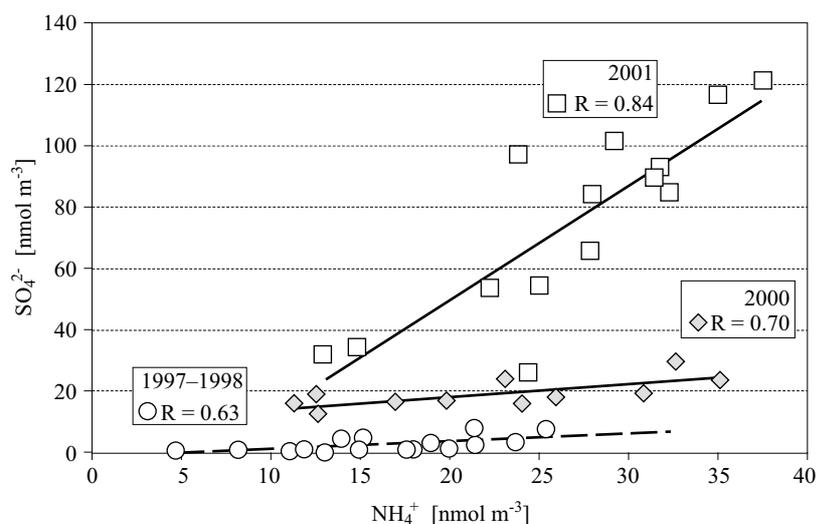
Fig. 5. Relation between ammonium and sulphate concentrations in the atmosphere over Hel and Gdynia during the measurement periods (in 1997–98 the data were selected from the second half of January 1998)

to seawater, of the order of 24%, and prevailing onshore winds (Fig. 2c) furnished additional evidence of the marine origin of the ammonium compounds in the aerosols over Gdynia in 2001.

In 2000, the ammonium sulphate in the aerosols over Gdynia could have originated from local sources (Fig. 2b, Fig. 5). At that time, the mean concentration of SO_4^{2-} was only marginally lower than the NH_4^+ concentration (20.1 and 22.4 nmol m^{-3}, respectively). Nevertheless, 90.2% of the sulphate belonged to the fraction unrelated to sea salt. The value 1.21 of the SO_4^{2-}/Na^+ coefficient in the aerosols indicates that the sulphate that bound ammonia was definitely of terrestrial origin. Wind speeds no greater than 2.8 m s^{-1} (Table 2) are also indicative of local sources of ammonium sulphate (Ferm 1998).

3.3. Ammonium nitrate and sulphate – the aerosols responsible for light backscattering within the southern Baltic Sea region

By being able to backscatter solar radiation, anthropogenic particles in aerosols, i.e. ammonium nitrate and ammonium sulphate, bring about a cooling of the climate. This cooling balances the climatic warming resulting from increased amounts of CO_2 (-1 W m^{-2}) (ten Brink et al. 1997, Dougle et al. 1998). Water-saturated aerosol particles are capable of backscattering up to twice as much radiation as 'dry' particles. When the aerosol contains ammonium sulphate as well as ammonium nitrate, it is mixed internally and the water saturation point is stable (ten Brink et al. 2000).

The form of the aerosol – wet or dry – is defined by the ratio of ammonium nitrate to ammonium sulphate present in the aerosol. When ammonium nitrate and ammonia dominated in the aerosols studied over Hel in winter 1997–98, the $NH_4NO_3/(NH_4)_2SO_4$ ratio was 2.5:1. Experiments carried out by Dougle et al. (1996) have shown that an aerosol can never be dry when the $NH_4NO_3/(NH_4)_2SO_4$ ratio exceeds a level of 2.5. During our studies, the air over Hel was always extremely humid (Table 2). A value of Rh below 80% was recorded only on 4 days (17–21 March 1998), after which it rose rapidly to 98.2%. High Rh values suggest an increase in the albedo, especially when the aerosol contains considerable amounts of ammonium nitrate. This observation is confirmed by such authors as Dougle et al. (1998) and ten Brink et al. (2000). Gebhart et al. (2001) are of the opinion that in regions where nitrate is the dominant chemical species, it is the principal compound responsible for light backscattering; the process becomes very intensive in winter.

In 2000, when nitrate and ammonium concentrations in aerosols over Gdynia were lower than over Hel (Table 3), it was not ammonium nitrate but ammonium sulphate that was detected in aerosols. The 90% contribution of $nssSO_4$ to the total mass of sulphate was confirmation of their anthropogenic origin. The air humidity during the measurements in Gdynia ranged from 40.9% to 99.8% (Table 2). According to ten Brink et al. (1997) and Gebhart et al. (2001), ammonium sulphate starts to crystallise at a humidity level of 40–42% in aerosols without ammonium nitrate. The process is accompanied by a decline in light backscattering by the aerosol. When the air humidity again increases to 80%, the 'dried-out' aerosol becomes saturated with water, and the backscattering intensity increases rapidly. This was the situation observed in Gdynia in 2000.

In 2001, the air humidity displayed the widest amplitudes, ranging from 24 to 97% (Table 2). The aerosols under investigation then contained both ammonium nitrate and ammonium sulphate, and the $NH_4NO_3/(NH_4)_2SO_4$ ratio reached 1:2. At this proportion, the aerosol becomes supersaturated with water at 61% humidity, i.e. at the level characteristic for ammonium nitrate (ten Brink et al. 2000). However, the minimum air humidity values at this time were at the 24% level, indicating that with a compound ratio of 1:2, crystallisation was bound to occur in the aerosol. Dougle et al. (1996) estimated that, under such conditions, nearly 50% of the aerosol is likely to be in the 'dry' form, hence the function of light backscattering may decrease by as much as three times.

4. Conclusions

- Ammonia present in the atmosphere over the coastal zone of the southern Baltic Sea reacted to produce a variety of compounds. Ammonium chloride and ammonium sulphate were the substances always detected in the aerosols, while the presence of ammonium nitrate was generated by the emission of nitrogen oxides and the wind speed.

- When strong winds brought onshore air masses over the coastal zone, the aerosols contained ammonium chloride, ammonium nitrate and ammonium sulphate. Both the cations – ammonium and sodium, and the anions – chloride and sulphate were of marine origin.

- With weak winds blowing from inland, nitrate and sulphate in the aerosols came from local anthropogenic sources. Nitrate and ammonia concentrations were directly proportional to the air humidity but inversely proportional to the air temperature. Under such conditions, the most stable compound NH_4NO_3 was detected in winter (the 'heating season') at the Hel station.

- Because ammonium nitrate and ammonium sulphate occurred in aerosols in variable proportions, it it suggested that this was a 'wet' aerosol, with ammonium nitrate, the dominant component, responsible for light backscattering in winter at Hel in 1997–98. In the warm part of the year (Gdynia 2000), ammonium sulphate present in the 'wet' aerosol was very probably responsible for the increase in light backscattering intensity. When both NH_4NO_3 and $(NH_4)_2SO_4$ were present in the aerosol in the ratio of 1:2, as recorded in Gdynia in 2001, the aerosol was presumably internally mixed and its backscattering intensity may well have been minimal.

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