

Sulphates in particles of different sizes in the marine boundary layer over the southern Baltic Sea*

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Abstract

Concentrations of sulphate ions and particle size distributions were measured in the marine boundary layer using a ten-cascade Berner impactor at Hel between December 1997 and March 1998, and with a filter pack in Gdynia from February to May 2001. In the marine boundary layer over the Hel Peninsula the presence of natural sea-salt and non-sea-salt sulphate ions (nssSO_4^{2-}) was confirmed in the aerosols. The nssSO_4^{2-} were present in all size ranges only in December 1997 and in the first half of January 1998, making up an average of $83.7 \pm 2.4\%$ of the total sulphate content. In the other winter months, nssSO_4^{2-} were recorded only in aerosols of diameters from 0.4 to $1.5 \mu\text{m}$, and their average contribution dropped by over 20%. The extended growing season in the Southern Baltic resulted in the formation of fine particles that appeared in the marine boundary layer in early winter. At that time the proportion of nssSO_4^{2-} in ultra-fine particles ranged from 75.7% to 100%. The concentration of nssSO_4^{2-} , which varied from 0.8 to 2.3 nmol m^{-3} in particles $< 0.4 \mu\text{m}$ in size probably constituted the natural background aerosol population in the relatively clean coastal environment of the Southern Baltic Sea. In the coastal urbanised area of Gdynia, the sulphate

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concentration in aerosols was higher than at Hel (av. 75.3 nmol m^{-3}) but the proportion of nssSO₄ was low, of the order of 24%. Sea salt was then the dominant source of sulphate.

1. Introduction

Many sulphur-containing organic and inorganic compounds are involved in the global atmospheric cycle, and they are present in both gaseous and particulate forms. On land, volcanic eruptions and the decomposition of organic matter are very effective sources of this element in the atmosphere (Andres & Kasgnoc 1998). As a result of sea salt aerosol emission, the oceans and seas also contribute significantly to sulphur cycling in the atmosphere. Besides ssSO₄ aerosols, also gaseous compounds of sulphur originating from shore biota are released to the atmosphere, where they become the primary precursor of new particles, formed through gas-to-particle conversion processes (O'Dowd et al. 1999). These new particles can grow through collision coalescence and condensation processes to quasi-stable sizes of 50–100 nm, where they can directly and indirectly influence the radiative budget. Dimethylsulphide (DMS—(CH₃)₂S) is considered to be the compound with the strongest impact on the radiative budget, and hence the Earth's climate, of all the gaseous particles of natural origin (Haubert et al. 1994). Apart from seawater DMS, anthropogenic sulphur dioxide is also a precursor of submicronic aerosols, produced in particular by the combustion of fuel (Pszenny et al. 1998).

Sulphates 0.1 μm in diameter or larger occur most often in the marine boundary layer and in remote continental sites as (NH₄)₂SO₄, NH₄HSO₄, (NH₄)₃(SO₄)₂ and become very effective cloud condensation nuclei (CCN) in most atmospheric clouds. Moreover, observations from the last ten years indicate a close relationship between climate cooling and the presence of sulphates in aerosols (Bates & Scholes 2002).

Two environments have been identified as the most significant sources of gaseous sulphur emission to the atmosphere: the coastal zone and forested areas (Mäkelä et al. 1997).

The coastal boundary layer of the Southern Baltic appears to be an important source of fine particles of natural origin. Studies were therefore undertaken to determine the variability of sulphate concentrations in aerosols of different sizes. The influence of non-sea salt sulphate (nssSO₄²⁻) as a natural background aerosol population on a regional scale seems to be an interesting research topic not only with respect to climate change, especially in winter, but also to basic atmospheric chemistry.

2. Material and methods

The aerosol samples were collected at 2 coastal measurement stations from December 1997 to March 1998 at Hel and from February to May 2001 in Gdynia (Fig. 1).

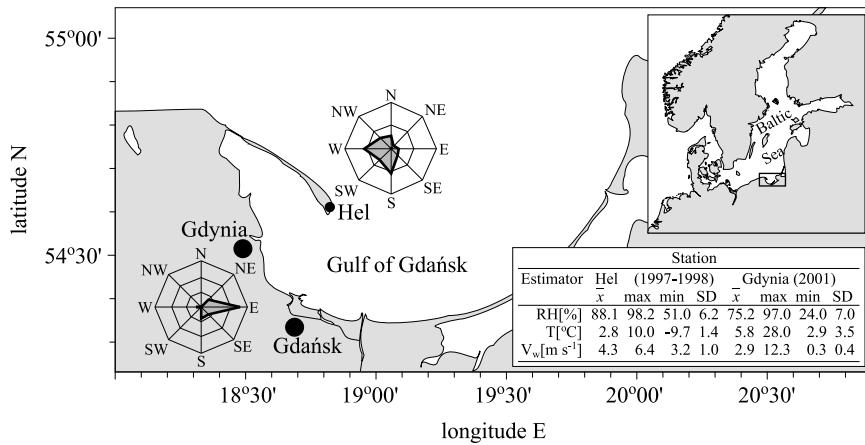


Fig. 1. Location of the sampling sites at the Hel (December 1997 – March 1998) and Gdynia sites (February – May 2001) (air temperature (T), humidity (Rh), wind speed (V_w))

Situated at the very tip of the Hel Peninsula (spit) ($\varphi = 54^{\circ}36'N$, $\lambda = 18^{\circ}49'E$), the small town of Hel is urbanised only to a slight extent. It is a seaside resort with a permanent population of just over 2000. The measurement site was located at the top of a disused 20-metre-high observation tower standing in coastal woodland. This allowed for continuous sampling almost undisturbed by local sources. The exception was the narrow north-west sector, where the incoming air had already passed over Hel. The site is located c. 20 km north-east of the Gdańsk, Sopot and Gdynia conurbation. Four- to seven-day cycle sampling was practised most of the time. To determine the size-fractionation of the aerosol a 10-stage Berner low-pressure impactor was used. The particle cut-off diameters in the impactor were: 0.02 μm , 0.05 μm , 0.1 μm , 0.2 μm , 0.4 μm , 0.8 μm , 1.5 μm , 3.0 μm , 6.0 μm and 12.0 μm respectively. The characteristics of this impactor are discussed in detail by Behlen (1996). Thin pre-washed aluminium foils were used as deposition surfaces. The flow was controlled by the critical orifice at $1.5 m^3 h^{-1}$.

At the Gdynia site, the samples were collected on the roof of the Institute of Oceanography building of Gdańsk University ($\varphi = 54^{\circ}31'N$, $\lambda = 18^{\circ}48'E$). Gdynia is a city of c. 250 thousand people, located close to agricultural

and industrial centres (shipyards, food-processing and chemical plants, port facilities, among others). There are two other large cities – Gdańsk and Sopot – in close proximity to Gdynia. Altogether, the population of the ‘Tri-city’ conurbation is nearly 1 million. Samples were collected above the tree crowns, at a height of c. 20 m a.s.l. Aerosols were collected with a filter pack. The collector set contained two types of filters: teflon and nylon. The sampled air first passed through the pre-washed teflon membrane filter (5 µm pore size), which collected the larger suspended particles ($\phi > 1 \mu\text{m}$), and then through the pre-washed nylon filters (0.45 µm pore size), which adsorbed fine particles ($\phi < 1 \mu\text{m}$) and gaseous acids. The PTFE-filter is made of non-flammable, high-quality material, resistant to mechanical breakage. Its surface is hydrophobic and chemically inactive, and aerosol adsorption by this material is 99.99% effective (Appel et al. 1984, Markaki et al. 2003). Air flow through the filter pack was maintained at $3.2 \text{ m}^3 \text{ h}^{-1}$ by the critical orifice.

After sampling, all filters were stored in airtight polypropylene bottles in a refrigerator. Immediately after desorption via agitation in an ultrasonic bath for 45 min., ions from the aluminium foils and from teflon filters were introduced into deionised water and from the nylon filter into a carbonate buffer (0.75 mM NaHCO₃ / 2.2 mM Na₂CO₃) (always 0.014 dm³).

All in all, 18 samples of every diameter range were taken at the Hel site and 14 samples for the determination of sulphates in aerosols at the Gdynia site. The number of samples was sufficient for statistical analysis.

The thorin calorimetric method recommended by HELCOM¹ was used to analyse SO₄²⁻ (Alfa 1992). Sulphates are precipitated from a barium perchlorate solution in the presence of ethanol, and the excess barium ions yield a yellow complex with thorin. The method gives precise and accurate results for concentrations measured in the ambient air. Absorbance ($\lambda = 520 \text{ nm}$) was determined on a Perkin-Elmer spectrophotometer. The mean blank value was deduced from the sample values. The detection limit was taken to be three standard deviations of blank values (EURACHEM 2000), and was calculated at $0.052 \text{ nmol m}^{-3}$. The standard deviation calculated for low SO₄²⁻ ions concentrations was 0.2 nmol m^{-3} , that for high SO₄²⁻ ion concentrations was 1.0 nmol m^{-3} . These values took account of the mean flow rate, mean deposition time and mean volume of solution. The relative standard error for daily concentration determinations, including random errors from both sampling and analysis is less than 20% at a typical concentration of 1 nmol m^{-3} (test range $0.1\text{--}3 \text{ nmol m}^{-3}$). The standard error values are, however, much smaller for monthly scales as a result of

¹Helsinki Commission – Baltic Marine Environment Protection Commission.

averaging over a larger number of samples. The sulphate concentration of nssSO_4 in an aerosol was calculated using the formula proposed by Sievering et al. (1990).

The atomic emission method was used to determine the sodium ion concentration in aerosols (Tables 1 and 2). The sampling method and analytical procedures for the determination of sodium in aerosols were discussed in detail in Nadstazik et al. (2000) and Nadstazik & Falkowska (2001).

The measurements were supplemented by meteorological parameters (Fig. 1). In addition, the trajectories of the air masses passing over the Hel Peninsula from December 1997 to March 1998 were obtained from the synoptic IMGW maps in 6-hour cycles, and 48-hour advance periods (Fig. 2). The trajectories were calculated per 4–7 days (depending on the sulphate sampling) at 925 hPa pressure, including the land and sea friction

Table 1. Concentration of sodium measured at different cut-off diameters in Hel during winter 1997–98

Month	Concentration dC/dlog AD [nmol m ⁻³ log μm]										Sum	
	Arithmetic diameter AD [log μm]											
	0.02	0.05	0.1	0.2	0.4	0.8	1.5	3	6	12		
December	\bar{x}	0.37	0.44	0.43	1.01	1.28	2.28	2.23	2.84	2.49	0.48 13.8	
	max	0.82	0.73	0.82	1.26	1.76	3.77	3.57	5.87	3.21	0.84 10.84	
	min	0.03	0.07	0.11	0.79	0.85	1.18	1.68	1.64	2.12	0.32 10.2	
	SD	0.39	0.3	0.29	0.22	0.39	1.20	0.89	2.02	0.49	0.24 20.59	
January	\bar{x}	0.24	0.25	0.22	0.43	1.17	1.59	4.39	5.7	4.06	0.72 18.77	
	max	0.58	0.71	0.39	0.79	1.84	2.33	9.02	8.32	5.58	0.90 21.89	
	min	0.01	<LoD	<LoD	0.16	0.89	1.25	1.99	3.31	2.67	0.48 11.74	
	SD	0.24	0.32	0.17	0.28	0.45	0.51	3.16	2.46	1.23	0.19 4.78	
February	\bar{x}	0.88	1.22	1.41	2.45	1.98	2.30	4.32	13.87	9.13	2.06 29.60	
	max	1.38	2.31	2.12	6.02	3.06	2.75	5.98	19.42	13.25	3.33 19.46	
	min	0.33	0.24	0.85	0.78	0.88	1.35	2.67	6.06	4.73	0.65 50.65	
	SD	0.43	0.85	0.64	2.40	0.95	0.64	1.47	5.83	4.47	1.23 46.44	
March	\bar{x}	0.57	0.91	1.79	2.12	2.35	2.23	4.50	7.93	5.01	1.31 44.84	
	max	1.17	1.48	4.38	3.86	3.37	2.98	5.74	11.63	7.10	1.85 30.63	
	min	0.34	0.43	0.60	1.08	1.56	1.80	3.47	4.94	3.27	0.70 24.39	
	SD	0.40	0.44	1.74	1.29	0.76	0.54	1.00	2.85	1.75	0.59 26.06	

Symbols: \bar{x} – mean, max – maximum, min – minimum, SD – standard deviation, LoD – limit of detection.

Table 2. Concentration of sulphates, sodium and nss SO_4^{2-} in Gdynia (2001)

Month	Concentration [nmol m ⁻³]		
			nss SO_4^{2-} [%]
	sulphates	sodium	
February	\bar{x}	93.2	811.0
	max	120.9	1222.6
	min	65.7	208.2
	SD	23.6	39.9
March	\bar{x}	80.1	1090.3
	max	96.9	1283.8
	min	53.8	780.6
	SD	23.1	4.1
April	\bar{x}	87.0	1201.5
	max	116.4	1438.1
	min	54.5	966.2
	SD	25.6	18.8
May	\bar{x}	30.9	895.6
	max	34.6	1065.6
	min	26.2	788.8
	SD	4.3	148.8

coefficient, wind speed and wind direction. The backward travel times were chosen according to the average lifetimes defined by Wojcik & Chang (1997), so that particulate SO_4^{2-} concentrations are associated with a 48–54 h back trajectory.

During the measurements at the Hel station at the turn of 1997, the weather was extremely windy. The recorded average mean wind speed was 4.3 m s⁻¹ and never fell below 3.2 m s⁻¹ (Fig. 1). At the Gdynia site, the mean wind speed was < 3 m s⁻¹, the value of 12.3 m s⁻¹ being an isolated incident (8–15 February 2001). 60% of winds over the Hel Peninsula were westerly to southerly, carrying sulphates from anthropogenic sources, while in Gdynia 64% of the winds directions were easterly to north-easterly, carrying either purely marine aerosols, or aerosols of terrestrial origin but subsequently modified by transport over the Baltic Sea (Fig. 1).

Relative humidity and air temperature also differed in the two periods. At the Hel station high air humidities (mean 88.1%) and low temperatures (mean 2.8°C) were recorded. In Gdynia the mean Rh was 75.2% (min. 24%). The air temperature in Gdynia was on average 3°C higher than at Hel, reaching as high as 28°C in the final stage of the experiment.

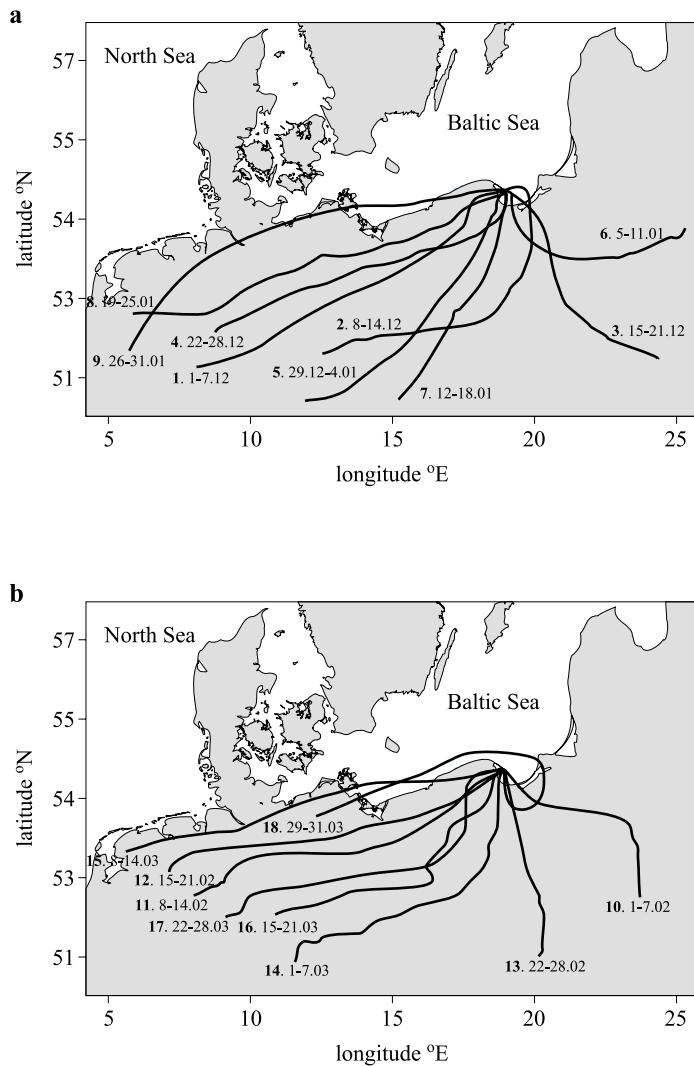


Fig. 2. Air mass trajectories over the Hel Peninsula in winter 1997–98: from 1 December 1997 to 31 January 1998 (a); from 1 February 1998 to 31 March 1998 (b)

3. Results and discussion

Although the pollution sources are clearly dominant in the samples from many coastal sites, natural sources are also important, especially in the atmospheric sulphur cycle. Sulphates are the main components of fine aerosol particles of diameters $< 1 \mu\text{m}$ (Behlen 1996). The sulphate concentration over the Hel station was the highest in the $0.2\text{--}1.5 \mu\text{m}$ diameter range (max. $0.8 \mu\text{m}$) (Table 3, Fig. 3). Similar sulphate concentrations in aerosols were recorded during the same period at Łeba

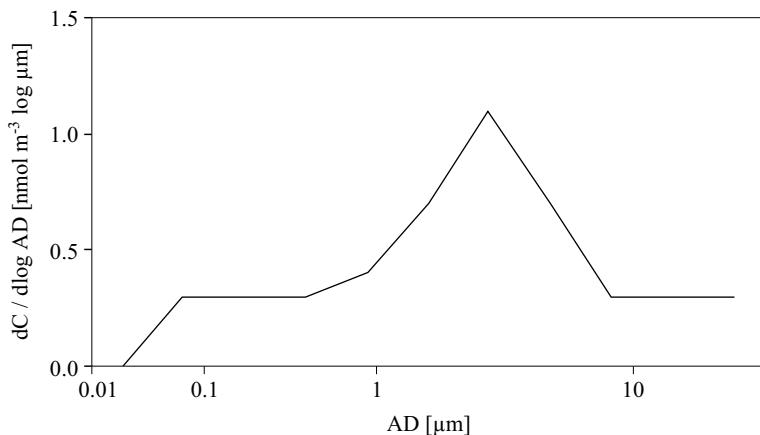


Fig. 3. Mean size distribution of sulphates determined for the samples collected at the Hel site (December 1997 – March 1998)

in the Southern Baltic coastal area (Woroń 1999). Leba and Hel are not very urbanised, as is the case in northern Finland, where winter and spring sulphate concentrations in particles $< 2.5 \mu\text{m}$ in diameter ranged from 1.35 to 3.6 nmol dm^{-3} (Mäkinen et al. 1995). In urbanised coastal areas, such as the Gdynia site, sulphate concentrations in aerosols are much higher (Table 2). The mean sulphate concentration measured over Gdynia in 2001 was 75.3 nmol m^{-3} (max. 120.9, min. 26.2 nmol m^{-3}) (Table 2) and was similar to that obtained by Lee et al. (1999) in England and by Prendes et al. (1999) in Spain (74.4 and 73.3, respectively). In Hong Kong too (Lam et al. 1997), the SO_4^{2-} concentration in aerosols was three times higher than over the Hel Peninsula during winter 1997–98.

Sulphates in the atmosphere at the Hel station were present at detectable concentrations in all size classes only in December 1997 and in the first half of January 1998 (Table 3). In February and March 1998 sulphates were present in three aerosol size classes, from 0.4 to $3.0 \mu\text{m}$, but not in larger and smaller particles (Table 3). The sizes of particles in which SO_4^{2-} ions are present are to a great extent dependent on the sources and the transformations occurring in the subsequent oxidation stages prior to the formation of S(VI) and its removal from the atmosphere (Penkett et al. 1994). Because they are generated from different sources, coarse and fine aerosol particles vary in their chemical compositions, residence times in the atmosphere and their removal mechanisms. The sulphate frequency of fine aerosols ($\phi < 0.4 \mu\text{m}$) in early winter varied from 12 to 45%. In late winter the sulphate contribution in fine aerosols fell to trace amounts (Fig. 4). This variability may be explained by the reaction of sulphate with sea salt components, the emission of which in coastal areas increases during storms

Table 3. Concentration of sulphates measured at different cut-off diameters in Hel during winter 1997–98

Month	Concentration dC/dlog AD [nmol m ⁻³ log μm]										Sum	
	Arithmetic diameter AD [log μm]											
	0.02	0.05	0.1	0.2	0.4	0.8	1.5	3	6	12		
December	\bar{x}	0.34	0.31	0.31	0.46	1.71	2.77	1.55	0.29	0.28	0.28	8.28
	max	0.56	0.43	0.46	1.00	3.10	4.15	3.10	0.41	0.37	0.35	13.55
	min	0.23	0.22	0.22	0.23	0.62	0.32	0.28	0.23	0.22	0.22	3.48
	SD	0.15	0.09	0.10	0.37	1.10	1.70	1.17	0.08	0.06	0.05	4.13
January	\bar{x}	0.22	0.22	0.23	0.22	0.72	0.73	0.35	0.32	0.21	0.22	1.76
	max	0.32	0.31	0.35	0.49	1.11	1.66	0.41	0.49	0.36	0.29	4.65
	min	0.10	0.11	0.14	0.12	< LoD	0.20	< LoD				
	SD	0.12	0.10	0.11	0.19	0.55	0.64	0.09	0.10	0.08	0.04	1.98
February	\bar{x}	< LoD	< LoD	< LoD	< LoD	0.28	0.55	0.32	< LoD	< LoD	< LoD	0.85
	max					0.38	0.89	0.35				1.27
	min					0.20	< LoD	< LoD				< LoD
	SD					0.07	0.24	0.04				0.38
March	\bar{x}	< LoD	< LoD	< LoD	< LoD	0.36	0.50	< LoD	< LoD	< LoD	< LoD	0.87
	max					0.57	0.78					1.10
	min					< LoD	< LoD					< LoD
	SD					0.19	0.28					0.39

Symbols as in Table 1.

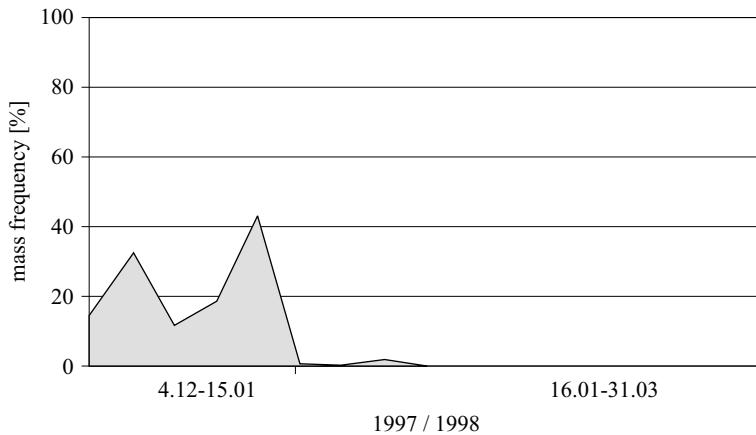


Fig. 4. The mass contribution of ultra-fine particles ($\phi < 0.4 \mu\text{m}$) to the total mass of sulphates in the aerosol during winter 1997–98 at the Hel station

(Pakkanen 1996). In the marine boundary layer gaseous sulphates react with sodium or other macrocompounds of marine or crustal origin, becoming part of both coarse and fine aerosols (Quinn et al. 1988). During the winter of 1997–98, there were no statistically significant correlations between sulphate and sodium in the aerosols over Hel. Sulphates reacted preferentially with ammonium to form $(\text{NH}_4)_2\text{SO}_4$ (Fig. 5), as was suggested by Quinn et al. (1988). However, this compound was recorded at Hel only after the second half of January 1998, when the sulphate concentration dropped to a minimum (Table 3). The $\text{SO}_4^{2-}/\text{Na}^+$ ratio in the aerosol was then 0.045, a proportion very close to that in seawater (0.06). This observation seems to

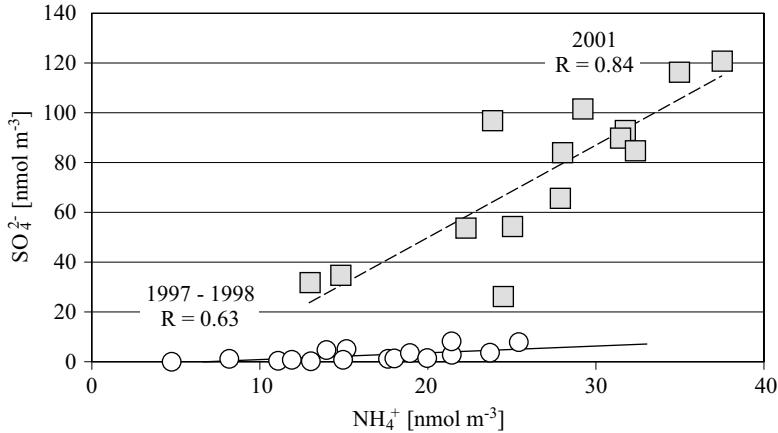


Fig. 5. Relation between sulphate ion concentration and ammonia ion concentration over Hel and Gdynia

indicate a significant contribution of marigenic particles, especially since the concentration of sodium ions was then at its highest (Table 1). Moreover, the high relative air humidity (Rh) recorded during winter 1997–98 at Hel (Fig. 1) is thought to have enhanced the aqueous- and aerosol-phase conversion of SO_2 to sulphate in the coarse mode. In addition, SO_2 or H_2SO_4 could have reacted with alkaline, carbonate-containing soil particles to form a coarse-mode sulphate, as observed by Zhuang et al. (1999a, b). Particles containing ammonium sulphate were also formed in aerosols over Gdynia in 2001 (Fig. 5). The sulphate concentration then reached its maximum value and the mean $\text{SO}_4^{2-}/\text{Na}^+$ ratio was 0.060, a figure identical to the proportion of those ions in seawater. Furthermore, a correlation ($p < 0.05$) between both sodium and sulphate ions was found (Fig. 6). At the end of the winter and in spring 2001, sea-salt-sulphate in aerosol was the dominant species over the Gdynia station. At low wind speeds, nssSO_4^{2-} made up 24% of the total sulphate concentration by mass and was presumably derived from both anthropogenic and marigenic sources.

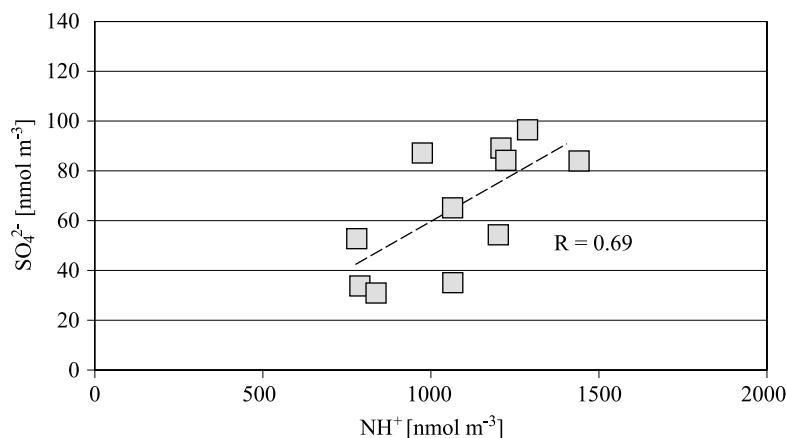


Fig. 6. Relation between sulphate ion concentration and sodium concentration over Gdynia

The presence of non-sea-salt sulphate (nssSO_4^{2-}) in fine marigenic aerosols is closely linked to the annual cycle of primary productivity in the oceans, which peaks in May – June and drops to a minimum in December – January (Penkett et al. 1994). In early winter 1997–98 in the coastal area of the Gdańsk Basin this was not the case, however. Non-sea-salt sulphates were present in almost all size ranges (Table 4), and their total concentration varied from 2.8 to 12.3 nmol m^{-3} , which is close to the values measured at five coastal stations in the North Atlantic by Penkett et al. (1994). In the fine particle fraction ($\phi < 0.4 \mu\text{m}$) the nssSO_4^{2-} concentration ranged from

Table 4. Proportion of nssSO_4^{2-} [%] in aerosols over Hel during winter 1997–98

Dates	Arithmetic diameter AD [log μm]									
	0.02	0.05	0.1	0.2	0.4	0.8	1.5	3	6	12
1–7.12.1997	83.3	85	83.3	74.8	95.2	95.5	93	57.3	53.4	91.3
7–14.12.1997	95.6	87.3	75.7	90	86.8	91.7	95.4		87.8	87.6
14–21.12.1997	99.3	98.1	97	79.7	94.8	97	91.6	51.7	42.9	90.8
21–28.12.1997	93.9	91.4	94.6	94.8	97.3	94.5	93.1		19.3	92.8
4–12.01.1998	99.6	100	100	95.6	95.2	95.5		25.8		76.7
12–18.01.1998						67	45			
18–25.01.1998					81	85.7	71.1			
25.01–3.02.1998						55				
7–11.02.1998					83.7	89.3				
11–15.02.1998					21.2	80.5	54.4			
15–19.02.1998					70	57.8				
19–23.02.1998					27.6					
23–27.02.1998					44.3	71.5				
27.02.–3.03.1998						41.9				
15–19.03.1998					70.7	8.7				
19–23.03.1998										
23–27.03.1998					64.2	78.8				
27–31.03.1998										

0.8 to 2.3 nmol m^{-3} , the highest values being recorded in the first ten days of January 1998 (even 100% – Table 4). Thereafter, however, until the end of winter there were no nssSO_4^{2-} in ultra-fine particles, as if the source had been eliminated. By contrast, nssSO_4^{2-} were present in aerosol particles of diameters from 0.4 to 3.0 m until the end of winter in concentrations ranging from 0.2 to 0.8 nmol m^{-3} .

The results from the Helsinki Commission monitoring programme for the Southern Baltic Sea in 1997 indicated a growing season extending into late autumn (Łysiak-Pastuszak 2000). At this time of year, the concentration of nutrients, including silicates, decreases in the surface waters of the Southern Baltic, which is indicated by a late-autumn bloom of diatoms. Even though in late autumn the primary production of diatoms is smaller than in spring, the contribution of the products of diatom biomass mineralisation in the formation of sulphate aerosols cannot be ruled out (Nguyen et al. 1988).

The formation of cloud condensation nuclei (CCN) can also be related to anthropogenic sulphur dioxide (Penkett et al. 1994, Pszenny et al. 1998); however, over the Gdańsk Basin the contribution of pollution sources in

winter 1997–98 could have been present only in aerosol particles $> 0.4 \mu\text{m}$. Otherwise, it would be difficult to explain why in the middle of January 1998 anthropogenic sulphur dioxide (mainly from fuel combustion) disappeared as it were, especially in view of the prevailing continental advection (Fig. 2).

4. Conclusions

- Through the emission of aerosols and gases to the atmosphere, the sea has a significant impact on the presence of both coarse and fine particles in the marine boundary layer over the coastal zone of the town of Hel and the city of Gdynia.
- The extended growing periods in the Southern Baltic resulted in the formation of fine particles which appeared in the marine boundary layer in early winter. At the same time, the contribution of nssSO_4^{2-} in ultra-fine particles varied from 75% to 100%. The concentration of nssSO_4^{2-} , which varied from 0.8 to 2.3 nmol m^{-3} in particles $< 0.4 \mu\text{m}$ in size, was probably a natural background aerosol population feature in the coastal environment of Southern Baltic Sea. Crustal sulphate and sea-salt sulphate particles also occurred in both the coarse and fine aerosols over the Hel station.
- Sea water seems to be the most important source of sulphate in the aerosol at the Gdynia site, since it is present in the form of sea-salt-sulphates. Even so, 24% of the total sulphate concentration by mass over Gdynia was present as nssSO_4 originating from both sea water and terrestrial sources.

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