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Sea salt in aerosols over the southern Baltic. Part 1. The generation and transportation of marine particles*

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Abstract

During five campaigns at sea and 11 on land in 2001–2007, aerosols were measured in the coastal zone and over the open sea in the Gdańsk Basin (southern Baltic). Sea salt concentrations were high both over Gdynia (2.0–12.2 μg m^{-3}) and at sea (1.3–14.5 μg m^{-3}). The intensity of the generation and transport of marine aerosols increased exponentially with wind speeds > 5 m s^{-1} over land and > 3 m s^{-1} over the Gulf of Gdańsk, this being most noticeable with Baltic and oceanic advection. Sea breezes were conducive to the transport of marine aerosols over land areas. The sea was also the origin of both sea salt and non-sea salt sulphate aerosols. An interesting increase in the proportion of non-sea salt-related sulphates (86.7%) was observed in spring, when the biological processes in the sea were more intense.

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1. Introduction

Large amounts of aerosols are emitted into the atmosphere indirectly through the evaporation of sea surface spray. These spray droplets, regarded as the largest aerosols, have a considerable mass and are readily deposited on the ground. The marine aerosol consists predominantly of chlorides ($\sim 88.7\%$) and sulphates ($\sim 10.8\%$), whereas other chemical substances make up a mere 0.5% of the total mass. A typical component of the chlorides is sodium chloride, which can constitute up to 85% of all sea salt emitted into the atmosphere (Gustafsson & Franzén 2000).

The chemical composition of aerosols generated over the sea varies depending on the latitude, distance from the coastal zone, and the salinity of the sea water. The intensity of changes in the chemical composition of aerosols is also governed by meteorological factors such as convection, thermal inversion, air humidity, wind speed and direction, as well as the occurrence of sea or land breezes (Seinfeld & Pandis 1998, Rastogi & Sarin 2005).

In an urbanized coastal zone anthropogenic nitric acid reacts with sea salt to form coarse particles of sodium nitrate ($NaNO_3$), which increases the deposition velocities of particles and cleanses the atmosphere of acidic gaseous aerosol precursors. Another reaction, often occurring in the atmosphere along coasts, is the surface reaction between sulphuric acid and sodium chloride, producing sodium sulphate. This is thought to be one of the most efficient mechanisms of primary NaCl particle transformation into sulphate particles, the latter being very active condensation nuclei (Falkowska & Lewandowska 2004, Chalbot et al. 2013).

Because of its coastal location and the proximity of urbanized areas to farmland, the Tri-city provides highly interesting material for studies of atmospheric chemistry. The contact zone between atmosphere and water is of key significance in the extraction of chemical substances from the sea and their subsequent transport over adjacent urban and recreational areas, thus influencing air quality in the region. Apart from the sea salt emitted from the sea, however, the aerosols of the southern Baltic contain a large amount of substances that are harmful to human health, such as benzo(a)pyrene, mercury and other anthropogenic trace metals (Bełdowska et al. 2006, Staniszewska et al. 2009). They are readily absorbed by halide-rich aerosols under the specific conditions of the land-sea contact zone, which are due, among other things, the considerable dynamism of the atmosphere and the greater levels of humidity. In this context, the aim of the present research was to identify the factors influencing the concentrations of sea salts in aerosols, as well as their abilities to participate in chemical reactions and be transported in various synoptic situations. Knowledge of the chemical composition of the aerosol also helps to estimate the deposition rate of terrestrial material and pollutants over the ocean surface and the transfer rate of particulate matter from ocean to air.

2. Material and methods

2.1. Locations of measurement stations and sample collecting times

The measurements of marine aerosols were carried out in 2001–2007 in 12-hour cycles at the land station in Gdynia (11 campaigns – 164 samples) and the sea station in the Gdańsk Deep (5 campaigns – 68 samples). In Gdynia, the samples were collected on the roof of the building of the Institute of Oceanography of Gdańsk University ($\varphi = 54°31'$N, $\lambda = 18°49'$E). Gdynia is a city with a population of ca 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' conurbation, which has nearly 1 million inhabitants. The routine measurement station in the Gdańsk Deep region (P1, $\varphi = 54°52'$N; $\lambda = 19°10'$E) was located 37 km to the north-east of Gdynia (Figure 1).

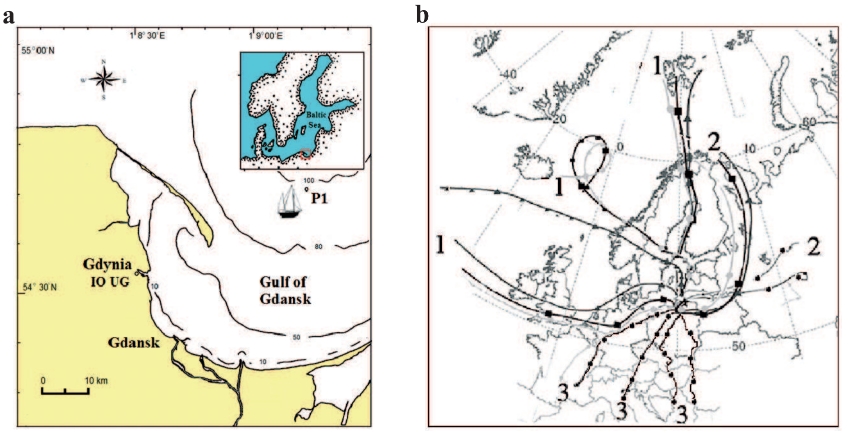

Figure 1. The location of measurement stations in Gdynia (IO UG) and the Gdańsk Deep (P1), where the samples were collected in 2001–2007 (a); back trajectory classification according to source region and pollution state. For a full description, see Table 1, Lewandowska et al. (2010) (b)

At both stations, samples were collected at a height of ca 20 m above sea level, and in Gdynia additionally above tree crown level. The aerosols were collected with the use of a filterpack. Large suspended particles (diameter

> 1 μm) were collected on the first, pre-washed, Teflon membrane filters (5 μm pore size). The PTFE-filter is made of non-flammable, high-quality, mechanically resistant material with a hydrophobic and chemically inactive surface. The effectiveness of aerosol adsorption by this material is as high as 99.99% (Markaki et al. 2003). The other two filters – nylon, and impregnated Whatman 41 – are described in detail in the second part of this article (Lewandowska & Falkowska, Part 2, this volume). Air flow (3.2 m^3 h^{-1}) through the filterpack was regulated by the critical orifice diameter. Immediately after desorption via agitation in an ultrasonic bath for 45 minutes, the ions from the Teflon filters were passed into deionized water (always 0.014 dm^3) and chemically analysed.

2.2. Chemical analysis

Chloride and sulphate ions were analysed by ion chromatography in accordance with the Polish Standard prPN-EN ISO 10304-1 (PN 1995). The detection limit for chloride ions was 0.2 μg m^{-3} and the standard error of estimation was no higher than 5.5%. The detection limit for sulphate ions was 0.1 μg m^{-3} and the standard error of estimation was 4.7%. The detection limit of sodium ions as determined by atomic absorption spectroscopy was 0.1 μg m^{-3} and the standard error of estimation was 4.3%. In all cases a certainty level of 99% was assumed. Each analysis took into account 20 blanks and an average rate of air flow through the sampler.

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 to 20:00 hrs and from 20:15 to 08:00 hrs the next day.

As these measurements were carried out at a height of 20 m, the wind speed at 10 m above sea level u_{10} had to be adjusted accordingly (Schwarzenbach et al. 1993):

$$u_{10} = \frac{10.4\ u_z}{\ln(z) + 8.1}\ \ [\mathrm{m\ s^{-1}}], \tag{1}$$

where u_z – wind speed at the height of measurement z [m s^{-1}], z – the height at which the wind speed was measured [m].

The meteorological conditions during the samplings carried out in the southern Baltic between 2001 and 2007 were very changeable. At the land station the air temperature T varied between −3.6°C in winter (24.02–03.03.03) and 25.3°C in summer (17–28.08.2007). At the sea station the lowest temperature was 2.3°C and the highest was 12.1°C. Both values were recorded in spring (2006 and 2003 respectively).

Like temperature, relative air humidity Rh was more variable at the land station than at station P1 in the Gdańsk Deep, ranging from 31.1% (3–10.04.2003) to 99.5% (31.05–6.06.2001) in Gdynia, and from 52.1% (31.05–6.06.2001) to 100% (29.09–3.10.2002) at sea.

Wind speeds V_w were lower on land than at sea. At the land station, mean wind speeds ranged from 1.3 m s^{-1} (23–27.04.2006) to 4.6 m s^{-1} (3–10.04.2003) with a maximum of 12.4 m s^{-1} (8–15.05.2003). At sea the corresponding mean values were twice as high: from 3.5 m s^{-1} (23–27.04.2006) to 11.7 m s^{-1} (29.09–3.10.2002); the maximum speed of 14.4 m s^{-1} was recorded between 8 and 15.05.2003.

In addition, the aerosol prehistory was profiled by conducting 48-hour air-mass backward trajectories at 3 h intervals using the atmospheric HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory) (Draxler & Rolph 2003, Rolph 2003). HYSPLIT is a complete system for computing simple air parcel trajectories to complex dispersion and deposition simulations (http://www.arl.noaa.gov/ready.html). Starting heights were set at the collection height (20 m AGL) in order to interpret sodium, chloride and sulphate concentrations in coarse particles. Heights of 500 m 1000 m and 1500 m were also used, depending on the boundary layer height at the sampling site for a given period. All the trajectories were then divided into three types (Table 1, Figure 1b) according to Lewandowska et al. (2010). Aerosols reaching Gdynia and station P1 from the north and north-west

Table 1. Aerosol classification according to the back trajectories (Lewandowska et al. 2010)

Classification	Pollution state	Source region	Regions crossed by back trajectories
maritime-continental	clean and moderately polluted	1	Atlantic, North Sea, Baltic Sea, Arctic Ocean, northern Europe, Scandinavia, Finland, Denmark, British Isles
continental	clean and moderately polluted	2	Polar regions, northern and eastern Russia, Baltic States, Belarus
	polluted	3	western and central Europe, southern Russia, Ukraine, southern Poland

were always influenced by the maritime environment (Type 1), whereas aerosols from other directions were influenced by continental environments (Types 2 and 3). The second type of air mass describes clean or partially polluted aerosols, mainly of terrigenous origin, and the third type indicates rather polluted aerosols, influenced by continental areas, that were carried to Gdynia station from the south and south-west (Table 1).

3. Results and discussion

The southern Baltic region is an area of convergence of clean air masses of marine origin and air masses, containing various levels of pollution, coming from over land. Sodium is commonly assumed to be a typically marine component of aerosols; chlorides and sulphates, on the other hand can also be related to terrigenous and/or anthropogenic aerosols (Yeatman et al. 2001). During the measurement period, the concentrations of all marine aerosol components varied dramatically at both test stations: sodium ions ranged from 2.7 nmol m^{-3} to 496.5 nmol m^{-3}, chloride ions from 10.9 nmol m^{-3} to 340.1 nmol m^{-3}, and sulphate ions from 5.8 to 165.3 nmol m^{-3} (Table 2).

As sodium chloride was always present in the aerosols ($r > 0.5$, $p < 0.05$), irrespective of the time and location of the measurement, the concentration of sea salt (Ass) expressed in μg m^{-3} was arrived at according to the equation of Quinn et al. (2002):

$$\mathrm{Ass} = \mathrm{Cl}^- + (\mathrm{Na}^+ \times 1.47)\,, \tag{2}$$

where 1.47 is the seawater ratio of $(\mathrm{Na}^+ + \mathrm{K}^+ + \mathrm{Mg}^{2+} + \mathrm{Ca}^{2+} + \mathrm{SO_4}^{2-} + \mathrm{HCO_3}^-)/\mathrm{Na}^+$. This approach prevents the inclusion of non-sea salt K^+, Mg^{2+}, Ca^{2+}, $\mathrm{SO_4}^{2-}$ and $\mathrm{HCO_3}^-$ in the sea salt mass and allows for the loss of Cl^- mass due to Cl^- depletion. It also assumes that all measured Na^+ is derived from seawater (Quinn et al. 2002). The studies conducted between 2001 and 2007 showed that there was considerable variability in the mean sea salt concentrations of the aerosols over Gdynia (2.0–12.2 μg m^{-3}) and the Gdańsk Deep (1.3–14.5 μg m^{-3}) (Figure 2). The maximum values both over land and sea were > 20 μg m^{-3}. No seasonal variability was found, although the lowest concentrations occurred in summer (1.0 and 1.1 g m^{-3}, over Gdynia and the Gdańsk Deep respectively).

3.1. Factors influencing the generation, interactions and transport of aerosols in the southern Baltic region

The use of various statistical tests made it possible to classify the data according to meteorological conditions. The statistical analysis of the data,

Table 2. The concentrations of sodium, sulphate and chloride ions in aerosols [nmol m^{-3}] in the coastal zone (Gdynia) and over the open sea (Gdańsk Deep) between 2001 and 2007

Sampling period	Estimator	Gdynia			Gulf of Gdańsk		
		Na$^+$	Cl$^-$	SO$_4{}^{2-}$	Na$^+$	Cl$^-$	SO$_4{}^{2-}$
31.05–06.06.2001	min-max	13.5–191.4	44.3–102.5	45.1–165.3	10.2–83.2	10.9–21.3	8.8–15.9
	$x \pm \mathrm{SD}$	98.4 ± 63.0	68.3 ± 17.9	93.1 ± 33.1	35.2 ± 24.9	15.9 ± 3.9	11.4 ± 2.4
27.09–19.10.2002	min-max	6.9–233.0	80.1–199.3	14.4–73.4	25.0–496.5	148.1–340.1	48.4–80.0
	$x \pm \mathrm{SD}$	41.9 ± 54.8	132.6 ± 38.7	32.6 ± 16.9	225.1 ± 174.8	215.3 ± 68.3	66.1 ± 11.7
13.01–20.01.2003	min-max	77.3–319.7	109.1–336.2	13.8–87.7			
	$x \pm \mathrm{SD}$	151.2 ± 76.9	192.6 ± 76.3	33.8 ± 24.7			
24.02–03.03.2003	min-max	70.2–208.2	115.9–388.6	10.2–81.5			
	$x \pm \mathrm{SD}$	120.8 ± 47.5	236.2 ± 90.4	33.9 ± 24.7			
03–10.04.2003	min-max	28.8–142.3	48.2–334.1	13.9–23.8			
	$x \pm \mathrm{SD}$	83.1 ± 32.2	217.2 ± 91.7	19.2 ± 3.1			
08–15.05.2003	min-max	5.9–92.9	76.3–281.0	39.1–78.0	2.7–136.6	57.9–177.2	30.0–81.4
	x ± SD	33.2 ± 24.1	157.3 ± 63.0	64.1 ± 11.8	33.8 ± 33.8	102.8 ± 35.5	56.6 ± 16.8
30.06–06.07.2003	min-max	18.0–137.9	31.2–338.8	56.5–123.7			
	$x \pm \mathrm{SD}$	73.6 ± 43.7	102.6 ± 79.5	93.9 ± 19.1			
23–27.04.2006	min-max	112.5–168.5	36.2–84.3	10.7–17.0	28.0–56.7	66.0–130.8	21.0–27.9
	$x \pm \mathrm{SD}$	138 ± 24.3	63.6 ± 18.3	13.6 ± 2.5	40.4 ± 11.4	89.2 ± 26.4	23.5 ± 2.6
27.07–04.08.2006	min-max	5.1–19.9	21.5–67.8	5.8–7.7			
	$x \pm \mathrm{SD}$	10.1 ± 4.8	43.8 ± 16.4	6.7 ± 0.7			
17–25.04.2007	min-max				12.0–101.0	30.1–63.5	6.9–33.0
	$x \pm \mathrm{SD}$				64.9 ± 30.9	40.5 ± 11.7	16.1 ± 8.2
17–28.08.2007	min-max	15.8–131.4	26.3–77	7.2–77.2			
	$x \pm \mathrm{SD}$	47.1 ± 32.3	56.6 ± 12.2	21.2 ± 17.0			

Symbols: min-max – minimum and maximum value, $x \pm \mathrm{SD}$ – average value and standard deviation.

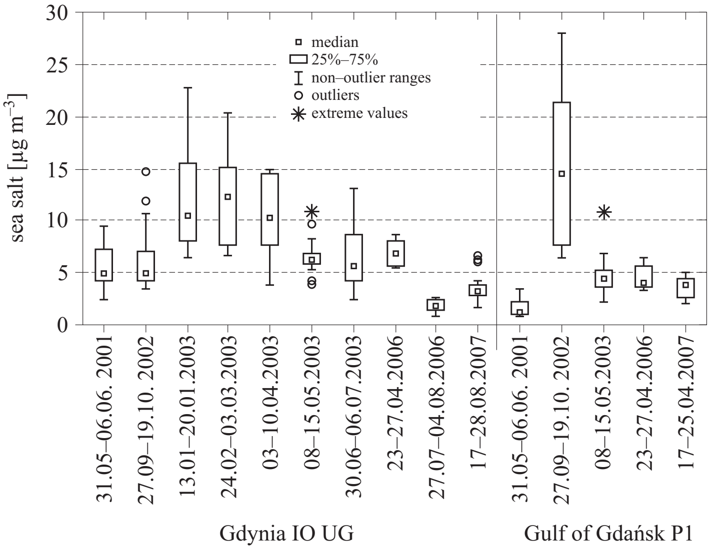

Figure 2. Sea salt concentration [μg m^{-3}] in aerosols over land (Gdynia IO UG) and sea (Gulf of Gdańsk)

performed using Statistica 8.0 software, included data from the entire study period (2001–2007) from the land station in Gdynia and the sea station in the Gdańsk Deep. Wind speeds, air temperatures and air humidities were standardized, after which cluster analysis was performed (Figure 3).

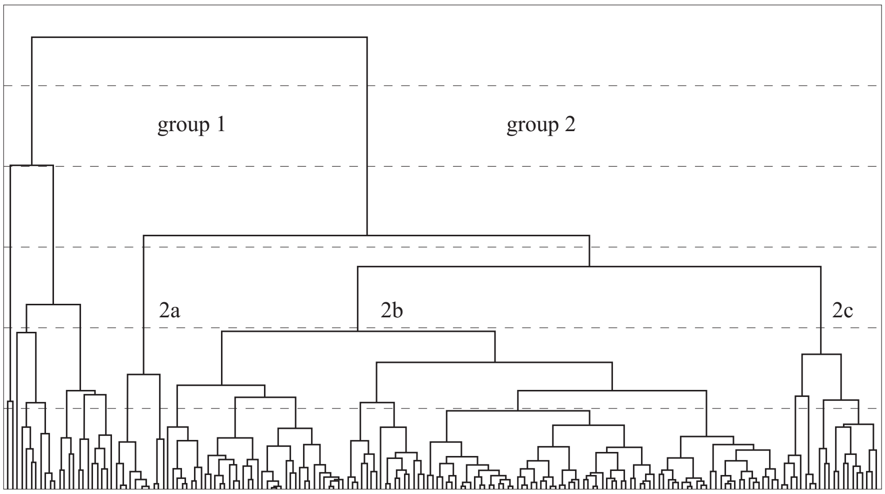

Figure 3. Associations between the meteorological parameters (temperature – T, air humidity – Rh and wind speed – V_w) that influence the chemical composition of aerosols over land and at sea (Lewandowska 2011)

Table 3. The characteristics of the groups of results singled out on the basis of cluster analysis (Figure 3) in measurements performed over land and sea (Lewandowska 2011)

Group	Group 1	Group 2		
		2a	2b	2c
meteorological parameter (median, range of mean values)	V_w =3.6 (0–7.4) T = 0.6 (−2.1– 3.7) Rh = 60.1 (37.6–92.6)	V_w =12.0 (10.5–12.7) T = 9.2 (2.1–11.5) Rh = 98.7 (89.3–100)	V_w =2.4 (0.7–14.4) T = 11.3 (2.4–25.3) Rh = 80.3 (31.1–100)	V_w =1.0 (0–2.9) T = 4.4 (−3.6–6.7) Rh = 79.4 (34.5–99.3)
characterization of air masses	dry and cool	humid and warm	humid and warm	humid and cool
station	Gdynia	Gdańsk Deep	Gdynia and Gdańsk Deep	Gdynia
	high wind speeds		low wind speeds	

Symbols: T – air temperature [°C], V_w – wind speed [m s^{-1}], Rh – air humidity [%].

The first group singled out by the cluster analysis (group 1) relates to the high wind speeds over Gdynia (Table 3). Three sets of data were revealed in the second group (Figure 3, Table 3). The Kruskal-Wallis ANOVA test was performed on them ($p = 0.00$ for air humidity, air temperature and wind speed), and air masses characterized by low wind speeds (< 2.5 m s^{-1}) over the sea and over Gdynia (groups 2b and 2c) were separated from the air masses of high speeds over the Gdańsk Deep (where the median was 12.0 m s^{-1}) (group 2a) (Table 3).

The Mann-Whitney U test showed that all three meteorological parameters affected the chemical composition of the aerosols in the southern Baltic region (Figure 4).

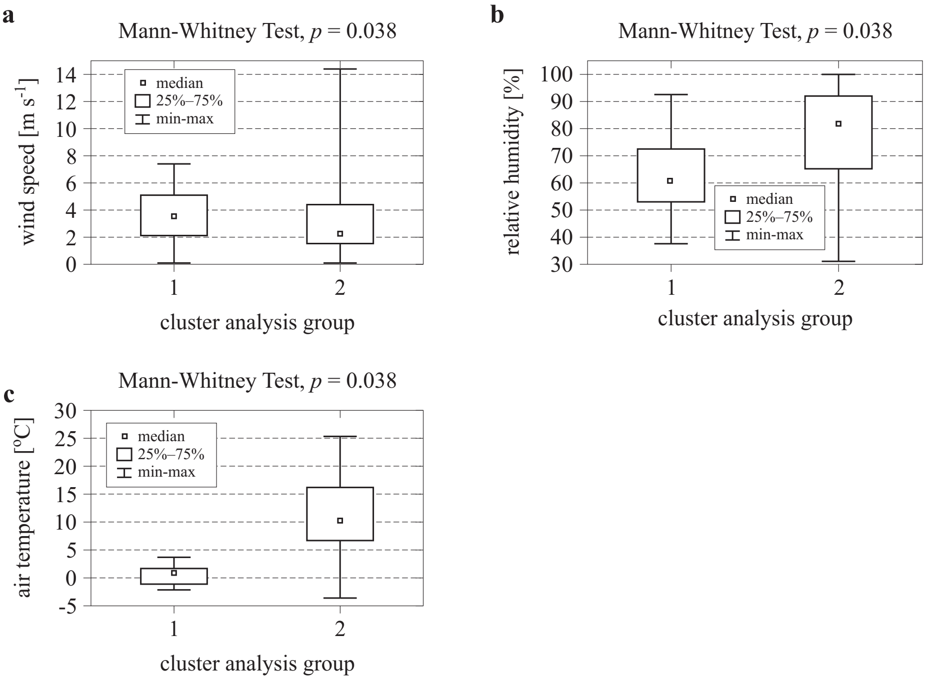

Figure 4. Variation of a) wind speed [m s^{-1}], b) air humidity [%] and c) air temperature [°C] for two groups singled out by cluster analysis (Figure 3) in measurements conducted between 2001 and 2007 (Lewandowska 2011)

At the same time, a separate group of results was obtained for humid and warm (groups 2a and 2b) and dry and cool air masses (group 2c). The influence of these meteorological conditions on marine aerosol transformations in the atmosphere of the southern Baltic is described in detail in part two of this publication (Lewandowska & Falkowska, Part 2, this volume).

3.2. The generation of marine aerosols

The cluster analysis performed for the data collected in the southern Baltic between 2001 and 2007 showed wind speed to have a great influence on the concentrations of marine aerosols (Figure 3, Table 3). The effectiveness of seawater droplets generating and dispersing large sea salt nuclei from the surface of breaking waves increases with square of the wind speed V_w and, if whitecaps occur ($V_w > 10$ m s^{-1}), increases with the cube of the wind speed (Nair et al. 2005, O'Dowd & Hoffmann 2005). The increase in wind speed is thus directly related to the increase in sea salt concentrations in aerosols. The effect is the most noticeable when the wind speed reaches a certain limiting value. Earlier publications suggested the range of 3–7.1 m s^{-1} (Spiel & De Leeuw 1996, Piazzola & Despiau 1997). However, recent studies have shown that a wind speed over 3 m s^{-1} is sufficient for the described effect to take place (Meira et al. 2007). In the study area, detailed regression analysis showed that the concentration of sodium and chloride ions in aerosols increased exponentially with the wind speed (Table 4).

The amount of sea salt transferred into the near-water layer of the atmosphere increases exponentially at wind speeds > 3 m s^{-1}. In the coastal zone, a statistically significant correlation between sea salt concentrations in aerosols and wind speed occurred only at wind speeds > 5 m s^{-1}. The limiting value over the sea was the same as that given in the literature (Nair et al. 2005, Meira et al. 2007) but indicated a stronger dependence on wind speed of the amounts of sea salt generated there than over land. This contradicts earlier observations made by Garbalewski (1999) in the Baltic Sea. A conceivable explanation for these discrepancies might be the distance between the land station and the coastline (over 1 km). The sea salt concentration in the aerosols was the resultant of wind speed and deposition; it was the highest at a distance of 1100 m from the wave surf zone (Meira et al. 2006).

Over land, the average wind speed was lower (2.5 m s^{-1}) than over the open sea (6.7 m s^{-1}), but the mean sea salt concentration in the coastal zone (7.5 ± 4.4 μg m^{-3}) exceeded that obtained over station P1 in the Gdańsk Deep (5.7 ± 5.9 μg m^{-3}). Marine aerosol production takes place either over the open sea or in the surf zone (McKay et al. 1994, Petelski & Chomka 2000), but it is in the surf zone, due to the movement of breaking waves, where aerosol production incorporates more and larger sea salt particles (O'Dowd et al. 1997, Hara et al. 2002). It was established that both values were higher than the concentrations regarded by Garbalewski (1999) as typical for the air circulation over the Baltic (3–5 μg m^{-3}). Over land, the average wind speed was lower (2.5 m s^{-1}) than over the open

Table 4. Correlation coefficients r and equations describing the dependence of the concentrations of basic sea salt components [nmol m^{-3}] on wind speed [m s^{-1}] over land and at sea (Lewandowska 2011)

Wind speed [m s^{-1}]	Sea		Land	
	Na^+	Cl^-	Na^+	Cl^-
>3	**r = 0.63**; $y = 8.4\ e^{0.24\ x}$	**r = 0.55**; $y = 15.7\ e^{0.19\ x}$	$r = 0.39$; $y = 3.8\ e^{0.0015\ x}$	$r = 0.24$; $y = 4.0\ e^{0.0006\ x}$
>4	**r = 0.64**; $y = 8.2\ e^{0.24\ x}$	**r = 0.57**; $y = 13.6\ e^{0.20\ x}$	$r = 0.44$; $y = 4.5\ e^{0.0008\ x}$	$r = 0.28$; $y = 4.6\ e^{0.0004\ x}$
>5	**r = 0.67**; $y = 4.3\ e^{0.30\ x}$	**r = 0.61**; $y = 11.7\ e^{0.22\ x}$	**r = 0.68**; $y = 5.0\ e^{0.0005\ x}$	**r = 0.71**; $y = 4.2\ e^{0.0015\ x}$
>7	**r = 0.90**; $y = 0.3\ e^{0.55\ x}$	**r = 0.68**; $y = 5.9\ e^{0.28\ x}$		
>10	**r = 0.98**; $y = 5E^{-5}\ e^{0.55\ x}$	**r = 0.77**; $y = 0.1\ e^{-0.64\ x}$		

Symbols: r – correlation coefficient, x – wind speed [m s^{-1}], y – sodium and chloride ion concentrations [nmol m^{-3}]. Statistically significant values are marked in bold ($p < 0.05$).

sea (6.7 m s^{-1}), but the mean sea salt concentration in the coastal zone (7.5 ± 4.4 μg m^{-3}) exceeded that obtained over station P1 in the Gdańsk Deep (5.7 ± 5.9 μg m^{-3}). Marine aerosol production takes place either over the open sea or in the surf zone (McKay et al. 1994, Petelski & Chomka 2000), but it is in the surf zone, due to the movement of breaking waves, that aerosol production incorporates more and larger sea salt particles (O'Dowd et al. 1997, Hara et al. 2002). It was established that both values were higher than the concentrations regarded by Garbalewski (1999) as typical for the air circulation over the Baltic (3–5 μg m^{-3}).

3.3. The transport of marine aerosols

Apart from being responsible for the intensity of marine aerosol generation, vertical and horizontal movements of air masses account for the transport of particles in the atmosphere. Both natural and anthropogenic aerosols are subject to transport (Hara et al. 2002). In our study in the southern Baltic, the direction of advection was of less significance to the sea salt concentration over land than over the sea (Figure 5). This resulted from the fact that wind speeds were nearly three times less over Gdynia than over station P1 (2.5 and 6.7 m s^{-1} respectively).

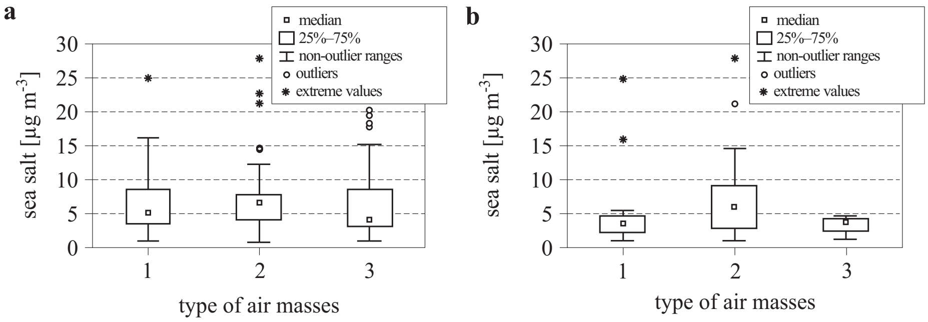

Figure 5. Sea salt concentration a) over land and b) over sea in relation to the direction of advection

A specific situation, where the sea salt concentration increased with a sudden rise in wind speed (on average 11.7 m s^{-1}), was recorded in autumn 2002. At this time clean air from the north (Figure 6a) and modified oceanic masses (Figure 6b) were blowing over the station in the Gdańsk Deep (P1). The average sea salt concentration (Ass) in aerosols at that time was 14.1 μg m^{-3}, occasionally reaching 27.9 μg m^{-3}. No precipitation was recorded then (Figure 6). In medium latitudes, which are where the measurement stations were located, aerosol transportation takes place predominantly from west to east. These are typical situations

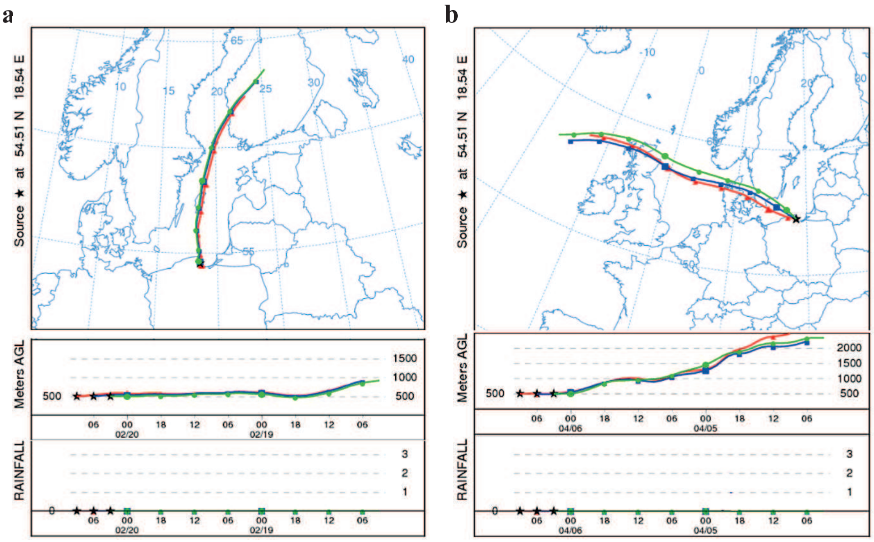

Figure 6. Some situations where in autumn over the sea station (P1) a high wind speed determined the increase in sea salt concentration in aerosols due to advection from a) the north (20.5 μg m^{-3}) and b) the west (12.5 μg m^{-3})

where aerosols from ocean regions are transported in the lower troposphere (Garbalewski 1999). High sea salt concentrations in the air were recorded even at low wind speeds, so long as oceanic advection was intense (Meira et al. 2008).

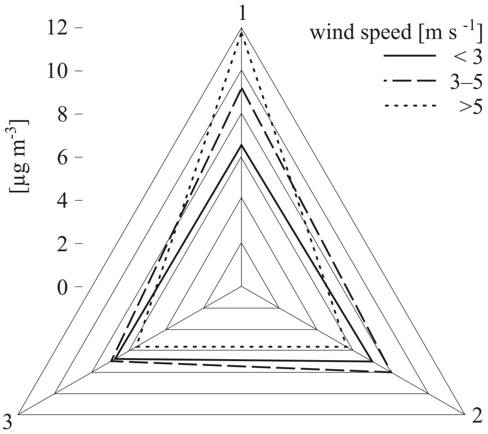

Figure 7. The effect of wind speed (<3, 3–5 and >5 m s^{-1}) on sea salt concentrations [μg m^{-3}] in aerosols over land in relation to the type of air mass advection (1, 2 and 3)

Over land for wind speeds of 3.0 m s^{-1} the average sea salt concentration was 6.8 μg m^{-3}; this figure doubled when the incoming air masses (advection Type 1) were characterized by wind speeds > 5 m s^{-1} (Figure 7).

It was discovered that in the coastal zone advection increased sea salt concentrations to a noticeable extent only when the wind speed increased. The highest Ass concentration over Gdynia, 22.7 μg m^{-3}, was recorded in January 2003, with the advent of clean air masses of the first type, carried from the north-west, at an average wind speed of 5.8 m s^{-1}.

3.4. Sea breezes

Sea breezes played an important role in the formation of high sea salt concentrations in the aerosols over Gdynia. Because the land heats up faster than the sea during the day, the warm air rising above the land is replaced by cooler, moister air blowing in from over the sea. In this sea breeze circulation, which starts up when the temperature difference between the land and sea surfaces reaches a certain value, low-level winds bring sea salt particles and fresh air over the coast from the sea, while high-level winds, blowing in the opposite direction, transport terrestrial aerosols out to sea (Rodríguez et al. 2008). In the southern Baltic coastal zone the effect of the sea breeze carrying sea salt landwards was the most pronounced in the warm season. Then, the average sea salt concentration was higher during the day (8.1 μg m^{-3}) than at night (6.7 μg m^{-3}). This tendency was observed in both spring (10.4 μg m^{-3} (day) 8.5 μg m^{-3} (night)) and in summer (6.3 nmol m^{-3} (day) 5.2 nmol m^{-3} (night)). In both seasons the daytime land temperatures were higher (6.3°C (spring) and 16.9°C (summer)) than at sea (5.9°C (spring) and 9.9°C (summer)). Since sea breezes usually blow in from over the Gdańsk Basin in the summer, the stronger landward transport of sea salt in the spring, as observed during this study, could have been due to other breeze-related mechanisms (Garbalewski 1999). Another reason could have been the lack of occasions when the wind speed over land rose to > 3 m s^{-1}.

3.5. Other components of marine aerosols

It was established during this research that during the generation of the marine aerosol several other sea salt components, besides sodium chloride, were released into the atmosphere. The presence of sodium sulphate was detected ($r > 0.5$, $p < 0.05$) over both the sea and land stations. The proportion of sea salt sulphates ($ssSO_4^{2-}$) was on average higher over land (20.5%) than over the sea (16.1%). In both cases, their frequency grew in the cool months of the year when wind speed increased, bringing marine and oceanic air masses over the study region (Figure 6, Table 5).

Table 5. The average seasonal proportion [%] of sea salt sulphates ($ssSO_4{}^{2-}$) at the land station and at the sea station in relation to the type of incoming air masses

Season	Air mass type					
	Land station			Sea station		
	1	2	3	1	2	3
autumn	3.9	16.6	6.3	32.2	16.9	n.d.
summer	21.6	17.5	9.4	21.8	17.6	16.7
spring	37.6	10.0	2.7	20.9	6.9	6.6
winter	43.2	25.6	733.4			
average [%]	28.8	17.4	13.2	22.2	12.0	10.4

Symbols: n.d. – no data; numbers 1, 2 and 3 – incoming air masses.

The remaining fraction of sulphates consisted of non-sea salt sulphates ($nssSO_4{}^{2-}$) and could have originated from anthropogenic sources. The proportion of sea salt sulphates decreased in aerosols particularly when the air arrived over the stations from the south (Table 5). The precursor of sulphur-rich aerosols in such situations could have been sulphur dioxide, the concentration of which depended directly on the volume of anthropogenic emissions, caused mostly by the burning of fossil fuels (Falkowska & Lewandowska 2009).

With advection from the north a certain proportion of the non-sea salt sulphates could have been due to dimethyl sulphate emission (DMS) from the sea surface (Huebert et al. 1994, Spokes & Jickells 2005). Most DMS particles remain in the water and are transformed by bacteria or become oxidized to dimethyl sulphoxide (DMSO). However, a certain proportion of them penetrates into the atmosphere, a process which intensifies with increasing wind speed (Spokes et al. 2006). Earlier studies conducted in winter (1997–1998) on the Hel peninsula had shown that a certain fraction of non-sea salt sulphates ($nssSO_4{}^{2-}$) were due to DMS emission into the atmosphere (Falkowska & Lewandowska 2004). No studies of DMS concentrations in the atmosphere were carried out in the southern Baltic coastal zone, but the results of studies conducted by HELCOM point to a seasonal prolongation of the growing season until late autumn (Łysiak-Pastuszak 2000). At that time in southern Baltic surface waters there is a marked drop in the concentrations of nutrients, including silicates, which indicates a late autumn bloom of diatoms. Despite the fact that the primary production of diatoms at the end of autumn is much lower than in spring, one cannot rule out their participation in the production of dimethyl sulphate and the consequent formation of sulphate aerosols in the near-water layer of the atmosphere (Nguyen et al. 1988, Falkowska

& Lewandowska 2004). High concentrations of DMS in the atmosphere in winter and its proportion in the production of small sulphate aerosols were also determined in the temperate zones of the Atlantic and the Pacific (Ledyard & Dacey 1994, Huebert 1996). An increase in the proportion of non-sea salt-related sulphates (86.7%) over the Gdańsk Deep was also noted in the warm months of the year, particularly in spring, when the biological processes in the sea were more intense. This would suggest that DMS participated in the formation of the sulphate aerosol concentration over the sea station in the time period under investigation (Kloster et al. 2006, Türküm et al. 2008).

4. Conclusions

Sea salt concentrations in the coastal zone were higher than those recorded over the Gdańsk Deep, as aerosol production in the surf zone incorporated more and larger salt particles as a result of the movement of breaking waves.

The main factor governing the generation of marine aerosols and their transport over both land and the open waters of the southern Baltic was the wind speed. Over the sea the concentration of marine aerosols grew exponentially with wind speeds > 3 m s^{-1}, whereas over land the limiting value speed was 5 m s^{-1}. The process was intensified by Baltic and oceanic advection.

The proportion of sea salt components in aerosols was particularly high during the warm months. With higher daytime temperatures, transport of sea salt over land was assisted by sea breezes.

The sea was the origin of both sea salt and non-sea salt sulphate aerosols. The frequency of sea salt sulphates rose in the cool months of the year with increasing wind speeds, when marine and oceanic air masses were carried over the study region. In spring, when the biological processes in the sea water intensified, there was an increase in the proportion of non-sea salt sulphates, probably originating from DMS emissions into the atmosphere.

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