

Full Length Research Paper

Preliminary studies of aerosol composition in coastal areas

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The wind speed and turbulence in the atmospheric surface layer are key parameters in the air-sea exchange processes. The turbulent structure of the marine atmospheric boundary layer (MABL) is very much influenced by the state of the sea (Panin and Krivickij, 1992). The aerosol composition in the MABL is influenced by air-sea gas exchange and subsequent atmospheric gas-gas and particle-gas reactions, sea spray and long range transported particles (Hasse et al., 1983; Quinn et al., 2001). The mixing and vertical transport of the particles will be influenced by the turbulent structure of the atmosphere in addition to aerosol dynamics and chemistry. The sea-salt particles are a significant fraction of the sub-100 nm particles in the MABL but quantification of the sea-salt flux is difficult, and estimates vary by an order of magnitude. The main goal of the studies was to recognize the patterns in the ion transfer over the coastal zone, which can be useful when determining the onshore transfer fluxes of pollutants. The data collected indicated that anthropogenic pollution was dominant among all sources. At onshore winds these ratios were similar to the ratios of seawater. The major ions in aerosols were probably formed by sea spray or air bubbling.

Key words: Marine aerosol, particle concentration, chemical composition, coastal area, lidar

INTRODUCTION

In the marine boundary layer aerosols comprise of a mixture of components, each varying in number, size distribution and composition. The two major components to aerosols in the marine environment are: continental and locally generated sea-spray droplets and, therefore, they include both natural and anthropogenic material which may be transported over vast distances (Littfin and Gathman, 1999; Smith et al., 1991). The contribution of these particles to moisture and energy exchange processes at the sea surface, to the global salt flux, their role in cloud droplet formation processes and their influence both upon the maritime atmospheric radiation balance and propagation at visible and infra-red wavelengths or visibility assessment are of increasing concern. A thorough understanding of such phenomena is essential to an accurate assessment of many processes important for the development of coupled ocean-atmosphere global circulation models, including the pollution problem (Fairall et al., 1983; Fitzgerald, 1991; Gong et al., 1997).

Pollution generated in the coastal and inland regions is advected into the coastal region as well as being injected into the local land-sea circulation. This is an important problem in remote sensing studies since information on refraction index of aerosol particles should be included in atmospheric correction algorithms.

MEASUREMENTS AND METHODS

The effective exchange of mass and energy between the sea and the atmosphere depends on the vertical temperature distribution, wind velocity and other meteorological phenomena as well as on the hydrological state of water masses which touch the air (Bortkovskii, 1983). The wind causes the sea surface to become wavy which leads to the distortion of its aerodynamic roughness and, furthermore, to the turbulent mixing of the air above the sea. Such a turbulently mixed atmosphere layer above the sea surface allows for the intense transmission of momentum, moisture and heat between the sea and the atmosphere. A significant role in such processes is played by the exchange of mass, momentum and energy transferred with aerosol particles which are produced on the sea surface.

The lidar system FLS-12 used in aerosol concentration measurements was installed in a van and stationed on the top of the dunes at a fixed distance from the sea. The inclination of the lidar was easily changed, which allowed for sounding of the marine boundary layer at

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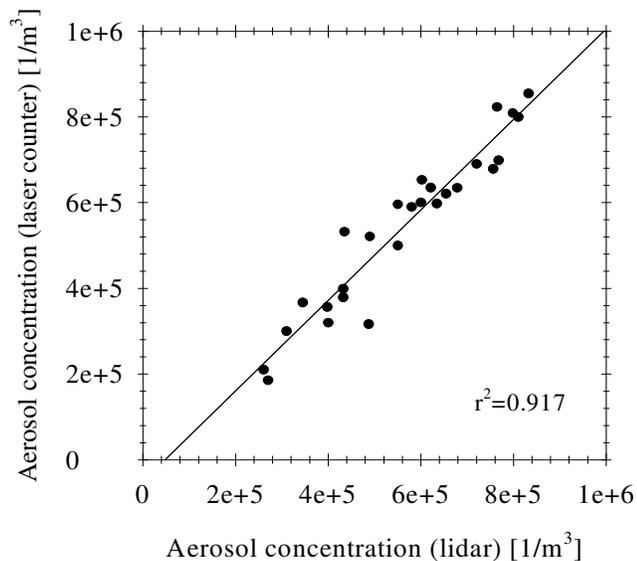


Figure 1. Aerosol concentrations obtained from simultaneous measurements with FLS-12 lidar and CSASP-100-HV-SP laser counter.

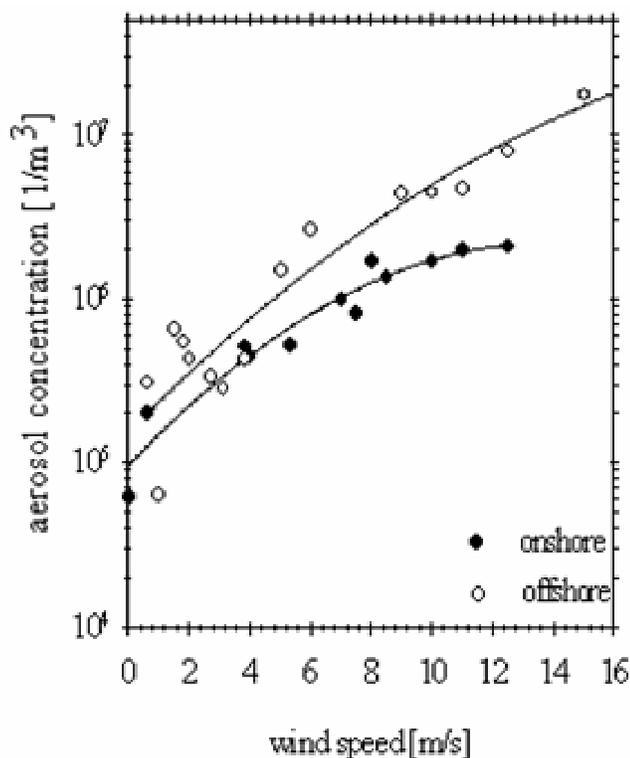


Figure 2. Variations of aerosol concentration with wind speed and direction derived using the FLS-12 lidar.

various altitudes. The vertical measurements were made using a reflecting mirror.

The lidar FLS-12 is a tunable laser system designed for remote sensing of the air in the VIS spectrum range (320 - 670 nm). The source various altitudes. The vertical measurements were made of

of UV pumping for the dye laser is a XeCl excimer laser (308 nm). During the experiments the lidar collected aerosol backscattered data every 50 ns, that is every 7.5 m on the optical path, and three wavelengths of 430 nm, 560 nm and 670 nm were employed. The lidar measurements were calibrated by simultaneous measurements with six stage cascade impactors and a laser particle counter (CSASP-HV-100) (Zielinski and Zielinski, 1994; Zielinski, 2004).

The comparison of the FLS-12 lidar concentrations with those obtained simultaneously using the CSASP-HV-100-SP at different coastal stations of the southern Baltic coast between 1993 - 2000 are presented in Figure 1.

The results presented in Figure 1 show good correlation of data obtained from both instruments - ($r^2 = 0.917$). Detailed information regarding the calibration of measurements made with FLS-12 lidar and CSASP-100-HV-SP laser counter are given in (Zielinski and Zielinski, 1994).

Measurements were taken from several stations on the Polish coast of the Baltic Sea (17-9° E and 54.4-55° N). All stations are located from approximately 25 to 60 km away from the urban area of Gdansk. There are over a million people living in this area and a significant number of industries are located there. The measurements were carried out in different seasons in order to detect the influence of the urban area on the level of aerosol concentrations and fluxes in the coastal zone. Therefore, wind speed and direction as well as wet and dry-bulb temperatures were recorded, together with other supporting information. The air temperature varied from 278°K to 293°K, while the wind speed fluctuated from 0 to 19 m/s and the wind direction varied from NE to SW.

Aerosol samples were collected to survey temporal variations of particle concentration, size distribution and chemical composition. The lidar FLS-12 and the particle measurement system provided data on aerosol size distribution and concentration (Zielinski, 2004). Aerosol samples were collected using a filter pack with teflon, nylon and Whatman 44 filters. Air was pumped through at 2.2 m³/h for 4 h. The filters were weighed and then extracted with de-ionized water. The solutions were analyzed for NH₄⁺, Cl⁻, HCl, HNO₃, NO₃⁻, by means of colorimetric methods while, Na⁺, K⁺, Ca²⁺, Mg²⁺ were analyzed by means of the flame atomic absorption method.

PRELIMINARY RESULTS

The average total aerosol concentrations derived as a function of wind speed and direction at an altitude of 4 m over the sea surface and an offshore distance of c. 110 m (surf zone) are shown in Figure 2.

The data presented in Figure 2 show that the average total aerosol concentration, increases with the increase of wind speed independently of wind direction. However, aerosol concentrations for offshore winds are 2 to 2.5 times higher in comparison with those of onshore winds of the same or similar speed. In the case of onshore winds, the aerosol ensemble was comprised mainly of particles of marine origin (salt and water droplets), while the aerosol ensemble with offshore winds was composed of both natural and anthropogenic material. For wind speeds below about 6 m/s the marine aerosol production is mainly determined by biological and chemical processes. At wind speeds exceeding 6 m/s the dynamic processes (wave breaking) start to dominate in the marine aerosol production (Zielinski, 2004). In both cases presented in Figure 2, the optical properties of the aerosols are different, which has a direct impact on atmospheric correction algorithms. at altitudes of $h = 4$ m and $h = 30$ m for wind speeds of $v = 9$

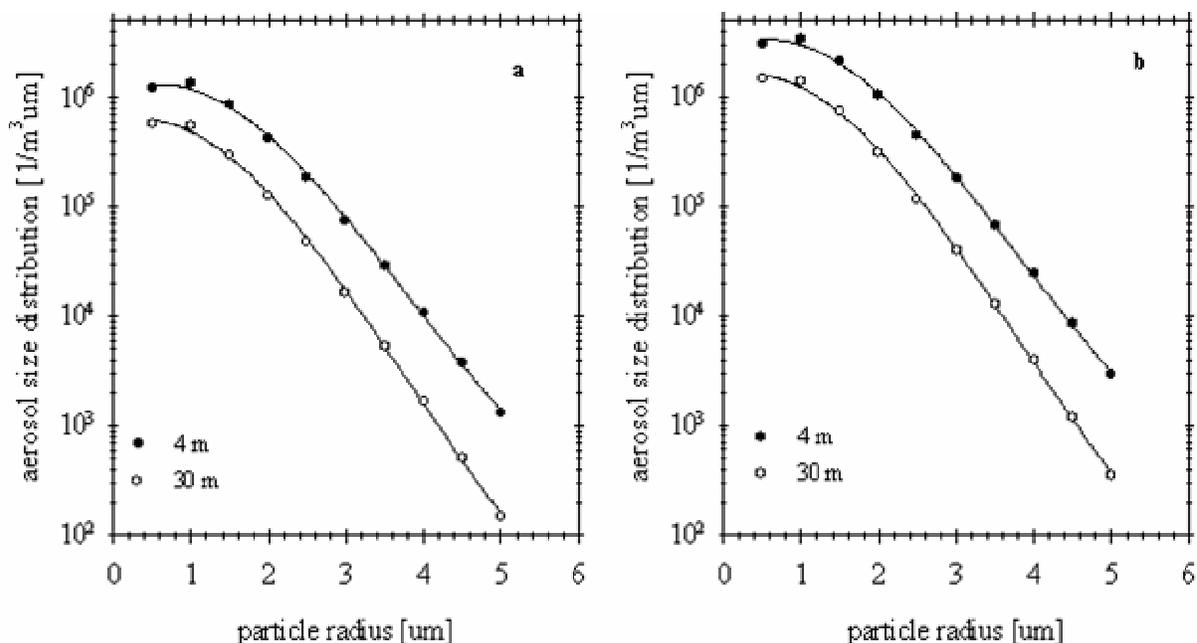


Figure 3. Variations of aerosol size distribution at two altitudes of 4 m and 30 m for two wind directions: a) onshore and b) offshore.

Table 1. Exemplary concentrations of chosen ions in sea water (nm/m^3).

DAY 1							
	NH_4^+	Cl^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}
Micro-layer	18.850	332.9	0.806	5.5478	1.323	3.690	7.708
Sub-layer	20.213	293.5	0.387	108.608	2.692	6.502.5	17.250
DAY 2							
	NH_4^+	Cl^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}
Micro-layer	19.169	307.2	0.629	17.391	428.2	1.325	2.625
Sub-layer	20.169	300.3	0.242	1.304	382.1	1.015	716.7

Table 2. Exemplary concentrations of chosen ions in aerosols (nm/m^3).

DAY 1									
	NH_4^+	Cl^-	HCL	NO_3^-	HNO_3	Na^+	K^+	Ca^{2+}	Mg^{2+}
Total	26.6	24.9	26.0	3.0	5.5	17.5	3.1	8.6	1.9
DAY 2									
Total	NH_4^+	Cl^-	HCL	NO_3^-	HNO_3	Na^+	K^+	Ca^{2+}	Mg^{2+}
	16.3	20.7	24.7	3.1	4.4	11.3	2.9	7.9	1.4

optical properties of the aerosols are different, which has a direct impact on atmospheric correction algorithms. at altitudes of $h = 4 \text{ m}$ and $h = 30 \text{ m}$ for wind speeds of $v = 9 \text{ ms}^{-1}$ (continental aerosol) and $v = 9.2 \text{ ms}^{-1}$ (marine aerosol). With an increase of altitude particle radii, at which maximum aerosol concentrations occur are as follows: for marine aerosols, $r_m = 0.787 \text{ }\mu\text{m}$ at $h = 4 \text{ m}$ and $r_m = 0.7 \text{ }\mu\text{m}$

Figure 3 presents exemplary plots of size distribution functions derived using the lidar for both types of aerosols at $h = 30 \text{ m}$ and for continental aerosols, $r_m = 0.778 \text{ }\mu\text{m}$ at $h = 4 \text{ m}$ and $r_m = 0.694 \text{ }\mu\text{m}$ at $h = 30 \text{ m}$. Chemical composition studies were made. The exemplary concentrations of chosen ions in sea water and aerosol from one experiment are presented in Tables 1 and 2.

Despite the fact that marine particles dominate the total mass of atmospheric aerosols their composition and sizes change with latitude and offshore distances. The composition is modified by land and especially anthropogenic advections. Another process which has impact on aerosol ensemble composition, especially in coastal areas, is salt fractioning due to ejection of air bubbles from the surface micro layer.

The enrichment factors in the air were calculated as follows:

Where: C_x – element X concentration, C_r – indicator concentration (Na^+).

For two exemplary days the following enrichment factors in

$$EF(X) = \frac{\left(\frac{C_x}{C_r}\right)_{\text{air}}}{\left(\frac{C_x}{C_r}\right)_{\text{microlayer}}} - 1$$

the air were obtained:

DAY 1	DAY 2
EF (Cl^-/Na^+) = 240.7	EF (Cl^-/Na^+) = 103.1
EF ($\text{NH}_4^+/\text{Na}^+$) = 3.60	EF ($\text{NH}_4^+/\text{Na}^+$) = 0.34
EF ($\text{NO}_3^-/\text{Na}^+$) = 11,332.3	EF ($\text{NO}_3^-/\text{Na}^+$) = 7,776.8
EF (K^+/Na^+) = 6.43	EF (K^+/Na^+) = 9.42
EF ($\text{Ca}^{2+}/\text{Na}^+$) = 6.39	EF ($\text{Ca}^{2+}/\text{Na}^+$) = 8.18
EF ($\text{Mg}^{2+}/\text{Na}^+$) = -0.22	EF ($\text{Mg}^{2+}/\text{Na}^+$) = -0.18

The enrichment factors in the micro layer were calculated as follows:

$$EF(X) = \frac{\left(\frac{C_x}{C_r}\right)_{\text{microlayer}}}{\left(\frac{C_x}{C_r}\right)_{\text{subsurface}}} - 1$$

Where: C_x – element X concentration, C_r – indicator concentration (Na^+).

For two exemplary days the following enrichment factors in the micro layer were obtained:

DAY 1	DAY 2	EF
EF (Cl^-/Na^+) = 1.20	EF (Cl^-/Na^+) = -0.92	
($\text{NH}_4^+/\text{Na}^+$) = 0.83	EF ($\text{NH}_4^+/\text{Na}^+$) = -0.93	
EF ($\text{NO}_3^-/\text{Na}^+$) = 3.08	EF ($\text{NO}_3^-/\text{Na}^+$) = -0.81	
EF (K^+/Na^+) = -0.04	EF (K^+/Na^+) = -0.92	
EF ($\text{Ca}^{2+}/\text{Na}^+$) = 0.11	EF ($\text{Ca}^{2+}/\text{Na}^+$) = -0.90	
EF ($\text{Mg}^{2+}/\text{Na}^+$) = -0.13	EF ($\text{Mg}^{2+}/\text{Na}^+$) = -0.73	

DISCUSSION

The ensemble of aerosol particles is dominated by particles of sizes smaller than 1 μm . The contribution of

large particles ($r = 5 \mu\text{m}$) is significant to some extent at small altitudes, c. 25 m a. s. l., while at greater altitudes their contribution is very small, and at altitudes above 40 m a. s. l., these particles are practically non-existent.

The particle number concentrations at exemplary wind speeds of 7.5 m/s varied from $\approx 10^6$ [$1/\text{m}^3$] to $\approx 10^5$ [$1/\text{m}^3$] for winds of continental origin and from over the sea, respectively.

With offshore winds at slow speeds the ratios $\text{Cl}^- / \text{Na}^+$ and $\text{Mg}^{2+} / \text{Na}^+$ varied from the ratios of seawater. The data indicated that anthropogenic pollution was dominant among all sources. At onshore winds these ratios were similar to the ratios of seawater. These major ions in aerosols were probably formed by sea spray or air bubbling. Similar studies need to be repeated in order to extend the data base. Additionally, such studies should be carried out in different areas in order to study the temporal variations of the measured parameters.

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