

Characterization of aerosols at a coastal site near Vindeby (Denmark)

Elisabetta Vignati¹

Risø National Laboratory, Roskilde, Denmark
National Environmental Research Institute, Roskilde, Denmark

Gerrit de Leeuw

Physics and Electronics Laboratory, Netherlands Organization for Applied Scientific Research, The Hague

Michael Schulz and Elke Plate

Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Hamburg, Germany

Abstract. Aerosol particle size distributions and aerosol chemical composition were measured with optical particle counters and filter packs, respectively, on an offshore mast in the Danish coastal waters near Vindeby on the island of Lolland. The filter pack samples were analyzed for ions representative of marine and continental aerosol: Na^+ , Cl^- , SO_4^{2-} , NO_3^- , and NH_4^+ . The physical and chemical measurements are complementary, and the information on chemical composition, together with the local meteorological parameters, the synoptic situation, and air mass trajectories, is crucial for interpreting the observed variations in the particle concentrations. Considering these sets of data, four periods can be discerned during the experiment. Further, the aerosol concentrations vary with wind speed, as is expected for marine aerosols, depending strongly on the fetch. In the case of short fetch, the coarse aerosol fraction (diameter $>1 \mu\text{m}$) and the fine aerosol fraction ($0.2\text{--}1 \mu\text{m}$) decrease with wind speed. Processes like advection, diffusion, and dry deposition cannot explain the strong dependence of the concentrations on wind speed. Apparently, uncertainties in the source strength and origin of aerosol advected across the shore line, as well as processes affecting the aerosol concentrations over land, such as variability in the sources, washout by rain, and other removal and transport mechanisms, have much more influence than the transport and removal over water.

1. Introduction

Coastal aerosols consist of a mixture of particles and droplets of marine, anthropogenic, and rural origin. Besides sea spray, aerosols emitted over land, such as soil particles and anthropogenic aerosols, and long-range transported particles, contribute to the total aerosol content. Analyses of measurements performed at coastal sites have revealed a variety of aerosol size spectra [Jennings *et al.*, 1991; Van Eijk and de Leeuw, 1992], number concentrations [Smith *et al.*, 1991], and chemical contents [Savoie and Prospero, 1982], depending on particle origin and history.

Submicrometer aerosol particles can be formed from chemical reactions in the gas phase. In coastal areas, ammonia (NH_3), mostly resulting from agricultural activities, reacts with atmospheric acids such as sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl), which are mainly of anthropogenic origin, to produce ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), ammonium bisulfate (NH_4HSO_4), ammonium nitrate (NH_4NO_3), and ammonium chloride (NH_4Cl). H_2SO_4 can also be of marine origin as one of the final products of

dimethyl sulfide (DMS) oxidation [e.g., Barnes *et al.*, 1991; Hertel *et al.*, 1994]. HCl can be released from sea spray when HNO_3 is taken up in the droplets, typically in the coarse fraction, and subsequently dissociates.

Sea spray and soil particles, which are the most important groups of particles produced by dispersal of surface materials, are both present in the coarse aerosol fraction. Widely different formulations describe the generation of marine aerosols as a function of wind speed (see Andreas *et al.* [1995] for an overview). In coastal areas the development of the waves is fetch-dependent, and thus also the production of sea spray varies with the distance the air has traveled over water. Soil particles are advected over the sea and gradually disappear through several removal processes. Therefore both the particle size distribution and the chemical composition are variable, depending not only on the local meteorological parameters but also on those during transport to the site under investigation.

The chemical composition of aerosol particles is important for several reasons. It is of interest for the aerosol physics because the hygroscopic properties of the various species in the particles determine the equilibrium relative humidity over a solution and thus the condensation and evaporation of water vapor on the particles [Fitzgerald, 1975]. These processes, in turn, change the particle size and consequently also size-dependent transport processes such as removal by deposition.

The removal of aerosol particles from the atmospheric

¹Also at Joint Research Centre, Environment Institute, Ispra, Italy.

boundary layer takes place both in dry weather and through precipitation. During dry weather, particles can be transported to the surface by gravitational settling and turbulent diffusion. Dry deposition depends on wind speed and particle size [Slinn and Slinn, 1980], which in turn depends on relative humidity. The residence time of aerosols in the lower troposphere can be several days in the absence of precipitation. Entrainment, i.e., exchange between the boundary layer and the free troposphere, strongly affects the aerosol concentration in the boundary layer [Davidson and Schütz, 1983]. In addition, the role of clouds and precipitation is important. Clouds can be quite efficient in transporting aerosols from the boundary layer to the free troposphere [Flossmann and Wobrock, 1996]. Also, in-cloud processes can effectively remove aerosols from the boundary layer. Activation of condensation nuclei can efficiently remove background aerosols, such as ammonium sulfate and sulfuric acid particles. Particles that are too small to be activated can coagulate with cloud drops. Below cloud base, particles are quite efficiently removed from air by precipitation. This is an efficient deposition mechanism, especially for particles in the coarse mode.

Atmospheric pathways contribute considerably to the total inputs of chemical compounds such as ammonium and nitrate [Skov *et al.*, 1996] to the coastal seas. Atmospheric deposition increases the eutrophication problems of the sea, especially near the coast [e.g., Asman *et al.*, 1993].

Physical and chemical properties of aerosols, measured at a coastal site in Danish waters, were analyzed in terms of local meteorological conditions and synoptic situations. The aerosols were measured on an offshore mast near Vindeby on the island of Lolland during 2 weeks in fall 1994. For the data analysis, 96-hour air mass back trajectories were calculated, and weather maps were used. Local meteorological parameters, such as wind speed and direction and relative humidity determine the variations in particle size distributions and number concentrations. The relation between concentration and wind speed depends strongly on the fetch. Also wash out by rain affected the aerosol population. These effects are demonstrated in the analysis of the time series of the aerosol number concentrations.

The concentrations of ions such as sulfate, nitrate, ammonium, chlorine, and sodium in the aerosols are strong indications for the different geochemical origins of the particles. However, the local meteorological parameters and the air mass trajectories need to be taken into account to relate the aerosol chemical content to the source region of the particles. Analyzing the present data set shows that combining information on particle size distributions, chemical composition, synoptic situations, and local meteorological conditions is essential for understanding the aerosol behavior in a complicated coastal area.

2. The Vindeby Fall 1994 Experiments

The measurements described in this paper were made on an offshore mast in the Langeland Strait, 1.5 km NW of the island of Lolland (Denmark), near the village of Vindeby (Figure 1). They were made in fall 1994, from October 27 to November 10, as part of the Air-Sea Exchange Process Studies (ASEPS) experiments described by Sørensen *et al.* [1994]. The research mast is designed for meteorological measurements in support of the development of an offshore windmill park. The mast can be reached only with a small boat. The water around the mast

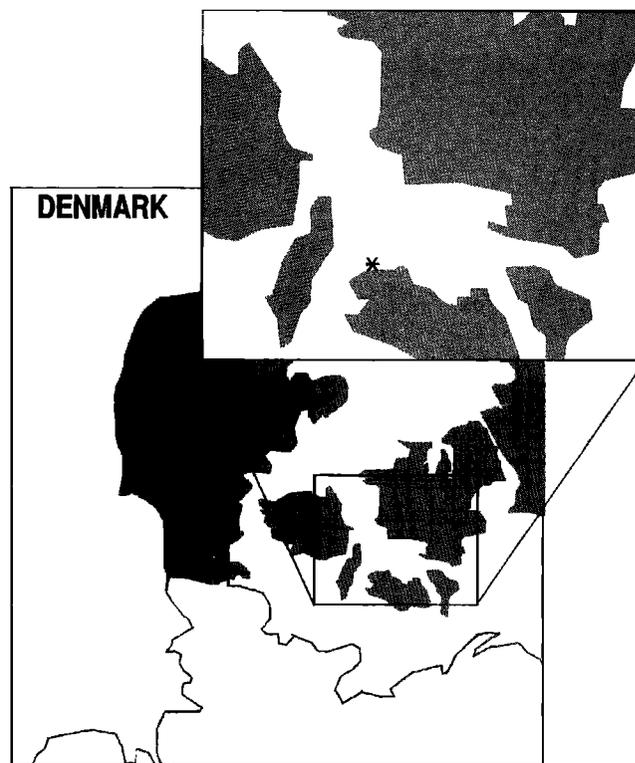


Figure 1. Location of the field study. The data were collected at an off-shore mast, indicated by the asterisk in the inset. The inset map encloses the area 54°20'–55°45'N, 10°16'–12°16'E.

is shallow, with a depth of ~2 m. As can be seen in Figure 1, a variety of fetches can be expected at this site, from about 1.5 km in the case of offshore winds, to more than 200 km in northerly winds. Nevertheless, even in high wind the waves are rather small owing to the limited water depth, the absence of swells, and the limited time available to develop the wave field. Hence the local production of sea spray aerosol will be rather small as compared to open sea conditions.

In this paper fetches will be referred to as either short or long. Short fetches at Vindeby are 1.5–2 km occurring in case of offshore winds; long fetches are larger than 15–20 km. Intermediate fetches are in fact alongshore, and the aerosol concentrations at these fetches may be influenced by surf effects.

Aerosol particle size distributions were measured with an optical particle counter, PMS-CSASP-200 (Particle Measuring Systems, Boulder, Colorado, U.S.A.). This instrument measures the diameters of single aerosol particles, in the range 0.2–20 μm , from the intensity of laser light scattered by each particle in the well-defined sample volume. Particle size distributions were stored as 20-min averages. The particle counter was mounted in the mast at a height of 7.5 m above the mean water level. The measurements were made continuously, 24 hours per day.

Chemical composition of the aerosol was determined from samples collected on filter packs mounted on the mast at different levels [Schulz *et al.*, 1995]. Here only the data from the filter pack mounted at 10 m above the mean water level are used. The filter pack consists of a particle filter with a pore size of 5 μm and two back-up filters to collect gaseous species. The back-up filters are a washed nylon filter with a pore size of 0.45

μm (for HNO_3) and a washed H_3PO_4 -impregnated paper filter (for NH_3). The particulate fraction of the aerosol is analyzed from the polytetrafluoroethylene (PTFE) filter, where negative artifacts for particulate ammonium nitrate can occur. However under humid marine conditions *Harrison and Kitto* [1990] found an underestimation of ammonium and nitrate from the particle filter of less than 13%. Chemical composition data are available for 18 samples. The sample times varied between 5 and 24 hours because of logistical problems.

Meteorological data used in this analysis were collected mainly with instrumentation mounted at the mast. These include wind speed and direction, air and water temperature, relative humidity, atmospheric pressure, and solar radiation. Rain data and significant wave height were also recorded. Atmospheric stability, an important mixing parameter, was derived from air temperatures measured at 10 m and at 2 m.

3. Analysis

Four periods can be discerned in the Vindeby experiment, according to meteorological situation, particle size distributions, and aerosol chemical composition. Obviously, the meteorological situation is responsible for the transition from one period to another. However, the response of the aerosol properties to changes in the meteorological conditions takes some time (see *Van Eijk and De Leeuw* [1992] for a description of the effect of frontal passages on the aerosol size distributions). Likewise, the chemical composition of the aerosol is not a sharp indicator of the time of the air mass change, not only because of the response time but also on account of the long sampling time.

The four periods are roughly as follows: period 1, October 28–30; period 2, October 31 to November 2; period 3, November 3–6; and period 4, November 7–9. The characteristic features of these periods are described in detail below. The large-scale characteristics, dominated by the synoptic situation, are described first. Air mass trajectories are also discussed because the recent history of the air mass is important for some of the general features in the aerosol distributions, especially concerning the influence of remote sources and the resulting chemical composition. However, other features in the aerosol concentrations, such as effects of the generation of the aerosol at the sea surface and the influence of local sources onshore, are mainly determined by local meteorological conditions. Examples of both situations, i.e., situations in which either the remote sources or the local sources were important, will be presented in section 3.3. The analysis shows that some care must be taken with a rigorous treatment of the data in terms of either the local meteorological parameters or the air mass history. Only the combination of local meteorology and large-scale characteristics can explain the observed features in a complicated coastal region such as that in which this campaign was carried out [*Vignati et al.*, 1997].

3.1. Synoptic Situations and Air Mass Trajectories

The different weather patterns encountered during the fall 1994 Vindeby campaign are illustrated in Figure 2. For each period a representative surface weather chart is shown. Four-day back trajectories of the air masses arriving at the Vindeby site were calculated using European Monitoring and Evaluation Programme (EMEP) meteorological fields and a program developed for the EMEP model [*Iversen et al.*, 1990]. The trajectories are calculated using meteorological data on a 150

$\text{km} \times 150 \text{ km}$ grid and with 6-hour time resolution. Representative examples, typical for each period, are presented in Figure 3. Only the last parts of the trajectories are shown. Time steps are indicated in the figures.

The four situations can be characterized as follows.

1. The weather situation typical for the first period is shown in Figure 2a. A deep low was situated over the North Atlantic, with a weak high over central Europe. The low-pressure systems moved steadily east while filling up and reaching Denmark on November 1. The air flow was from the south west, and the air masses were advected to the Lolland site from southern England over the North Sea and the Netherlands (trajectory A in Figure 3) or from France over Belgium, the Netherlands, northern Germany, and Denmark.

2. During the second period (Figure 2b) a new low-pressure system had developed over the North Atlantic. A trough of low pressure, consisting of a series of lows, stretched from Scandinavia over Russia. A high-pressure system was situated over central Europe stretching to SE Europe. This situation gave rise to a northwesterly flow in which the air masses reaching Vindeby were advected from the North Atlantic over northern England, the North Sea, and northern Denmark (trajectory B in Figure 3). The characteristic features were the maritime character of the air mass and the relatively high wind speed.

3. This situation was completely changed during the third period, when the pressure distribution was governed by a weak low situated west of Ireland and a strong high over eastern Europe (Figure 2c). The resulting southeasterly flow carried continental air from western Europe via central and eastern Europe to Vindeby (trajectory C in Figure 3). The frontal activity was low in this period, and there was only little precipitation. Important features are the gradually rising humidity and the decreasing wind speed that led to stagnant air, as will be discussed in section 3.3 in connection with the analysis of the aerosol particle size distributions.

4. The fourth period was characterized by a series of frontal systems bringing rain and showers, due to a deep low over the North Atlantic (Figure 2d), accompanied by some weaker depressions, while another deep low was situated over northern Europe. The air masses reaching Vindeby in this period were advected over France, the North Sea, and northern Denmark (trajectory D in Figure 3).

3.2. Aerosol Size Distributions

The aerosol particle size distributions measured during the Vindeby campaign changed according to air mass origin and in response to local meteorological conditions. Examples of such changes can be found in the literature [*Hoppel et al.*, 1990; *Smith et al.*, 1993]. To describe the evolution of the particle size distributions in terms of the meteorological situation, the simultaneous variations of the concentrations of particles in representative size ranges and meteorological parameters are analyzed.

For this analysis the aerosol concentrations have been grouped into two size classes: particles with diameters smaller than $1 \mu\text{m}$ and larger than $1 \mu\text{m}$, which will be referred to here as “fine” and “coarse” fractions, respectively. Subdividing the aerosol concentrations into fine and coarse fractions is a commonly used procedure [e.g., *Seinfeld*, 1986]. The division at $1 \mu\text{m}$ has been chosen to separate aerosols of mainly anthropogenic/rural origin (fine fraction) from those of mainly marine origin (coarse fraction), although from the particle size distri-

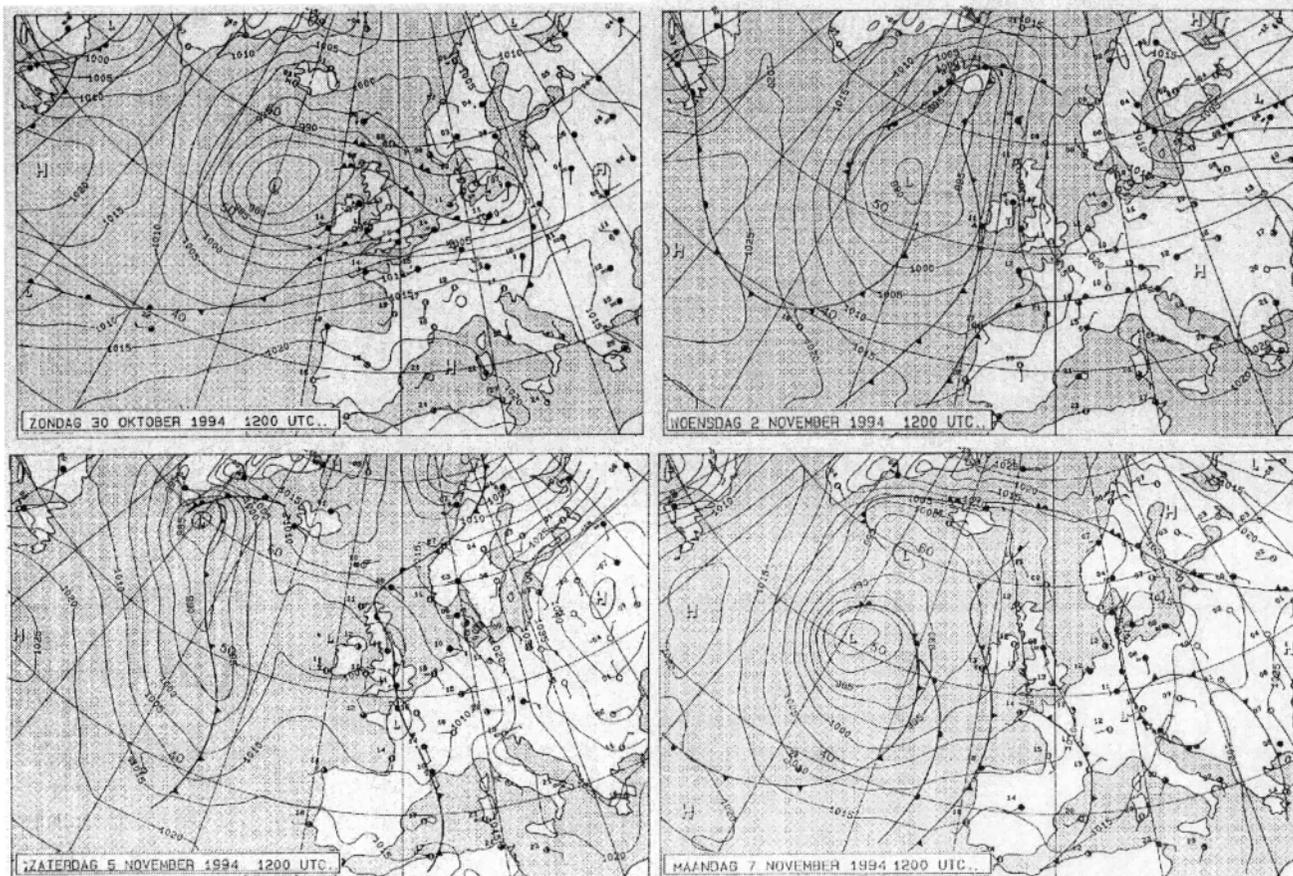


Figure 2. Typical weather maps representative for each of the four periods during the Vindeby fall campaign [Koninklijk Nederlands Meteorologisch Instituut (KNMI), 1994]: (a) period 1 (October 30, 1200 UTC), (b) period 2 (November 2, 1200 UTC), (c) period 3 (November 5, 1200 UTC), and (d) period 4 (November 7, 1200 UTC).

butions alone such a division cannot be justified. Rural particles such as soil dust occur in the coarse fraction. Therefore chemical analysis of the aerosol is required to identify the origin [Seinfeld, 1986; Wall *et al.*, 1988; Hillamo *et al.*, 1992; Pakkanen *et al.*, 1996]. Relative humidity changes may shift the particles into different size ranges. In addition, chemical reactions and other heterogeneous processes involving sea salt particles affect their chemical composition. Hence knowing the chemical composition is crucial to understanding the aerosol characteristics and their implications.

Obviously, the concentrations in each of the two fractions are dominated by the smallest particles in each fraction, i.e. the 0.2- to 0.3- μm particles in the fine fraction and the 1- to 2- μm particles in the coarse fraction, except in a few relatively short periods in which the shapes of the particle size distributions were changing. This is illustrated in the following example, with data collected on October 29. The situation on that day was dominated by the meteorological situation depicted in Figure 2a, but the air mass trajectories were shifting gradually west, i.e., from passage over the industrial Ruhr Gebiet in Germany, to a trajectory 6 hours later over the Rotterdam harbor area in the Netherlands, and finally to a more westerly trajectory mostly over the North Sea. All trajectories originated in the SW of the United Kingdom. As a result, the concentration of the small particles is large in all size distributions. As time evolved, the air masses were gradually influ-

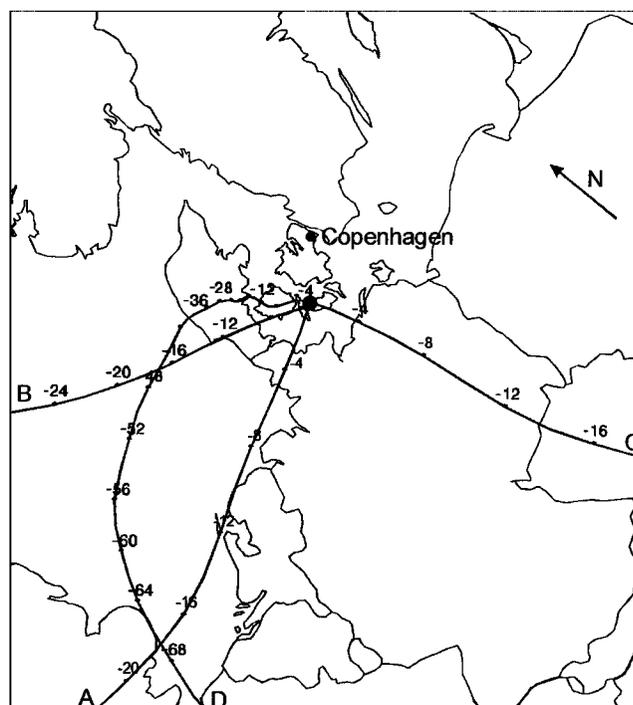


Figure 3. Representative trajectories of air masses reaching Vindeby during the campaign for each of the four periods.

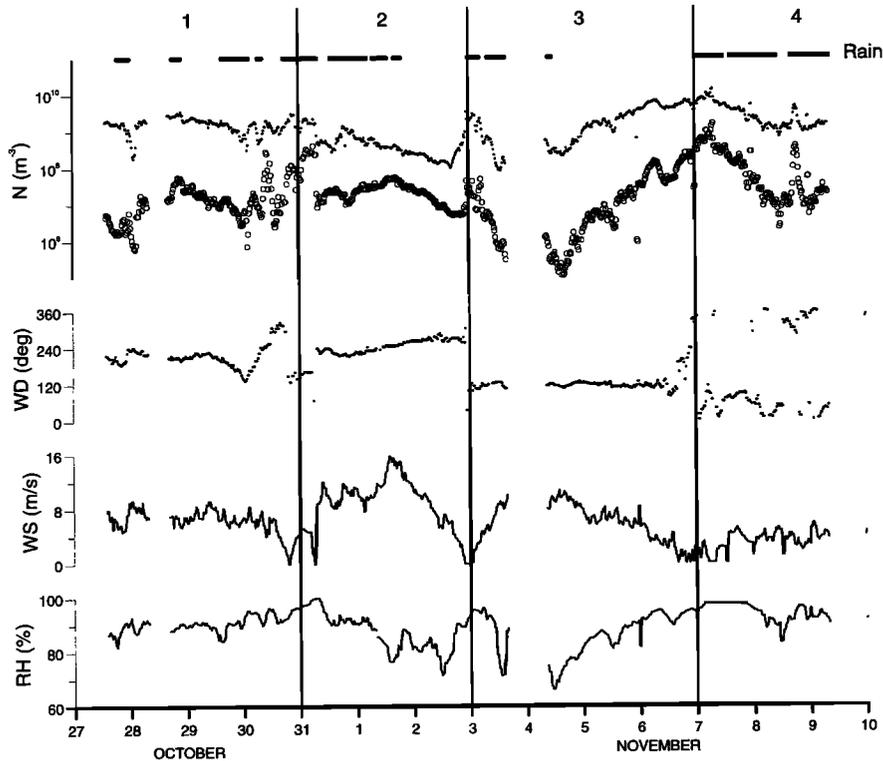


Figure 4. Time series of (from top to bottom) number concentrations (N) of the aerosols in the fine (solid dots) and coarse (open circles) fractions, rain, wind direction (WD), wind speed (WS), and relative humidity (RH). The vertical lines indicate division between the four periods of the campaign as discussed in the text.

enced less by production over the industrial areas in western Europe and obtained a more maritime character; the concentrations in the fine fraction thus gradually decreased (see Figure 4). However, Figure 5 shows that this decrease was mainly due to decreasing concentrations of particles larger than $0.4 \mu\text{m}$, which dropped by a factor of 2–3. The concentrations of the smallest particles did not change. Figure 4 also shows the decrease in concentrations of the coarse fraction, and the particle size distributions in Figure 5 show that this is mainly caused by particles of $1\text{--}2 \mu\text{m}$, while the concentrations of larger particles were relatively constant. The latter is ascribed to the constant wind speed (around 7 m s^{-1}) and direction (about 220°), resulting in a more or less constant but low

production of sea spray aerosol. Apparently aerosols from sources other than sea spray dominated the coarse fraction, except for the largest particles.

3.3. Variation of Aerosol Properties With Meteorological Conditions

The fine and coarse particle fractions are presented as time serial plots in Figure 4. Relative humidity is also plotted, and rain periods are indicated at the top of the graph. Clearly, in general, the variations in both aerosol fractions follow the trends in relative humidity. Specific features will be discussed below in more detail. Rain is indicated because its frequent occurrence may have a large influence on the aerosol concen-

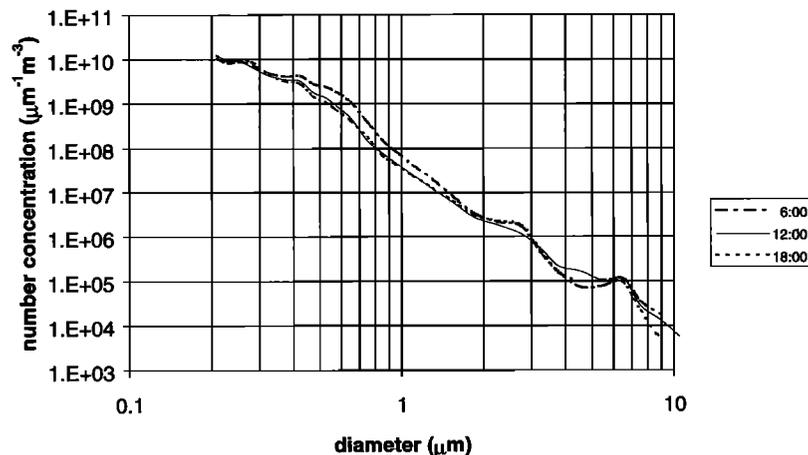


Figure 5. Particle size distributions measured on October 29 at 600, 1200, and 1800 UTC.

Table 1. Summary of the Chemical Samples

Sample	Period, UTC		Trajectory Type	Fetch*
	Start	End		
1	Oct. 27, 1720	Oct. 28, 1010	A	S/L
2	Oct. 28, 1640	Oct. 29, 0940	A	S
3	Oct. 29, 1232	Oct. 30, 0818	A	S
4	Oct. 30, 1255	Oct. 31, 0747	A	L/S
5	Oct. 31, 0838	Oct. 31, 1530	A	I
6	Oct. 31, 1626	Nov. 1, 1700	A	I/L
7	Nov. 2, 1035	Nov. 2, 1550	B	L
8	Nov. 2, 1638	Nov. 3, 0835	B	L/S
9	Nov. 3, 0938	Nov. 3, 1559	B	S
10	Nov. 3, 1709	Nov. 4, 0839	B/C	S
11	Nov. 4, 0945	Nov. 4, 1524	C	S
12	Nov. 4, 1615	Nov. 5, 0910	C	S
13	Nov. 5, 1017	Nov. 5, 1511	C	S
14	Nov. 5, 1607	Nov. 6, 1103	C	S
15	Nov. 6, 1145	Nov. 7, 1220	C/D	S
16	Nov. 7, 1421	Nov. 8, 0839	D	L
17	Nov. 8, 0943	Nov. 8, 1517	D	L
18	Nov. 8, 1601	Nov. 9, 0842	D	L

* L, long (>15 km); I, intermediate; S, short (1.5–2 km).

trations, due to removal by wet deposition. Only a qualitative assessment of the influence of this process will be given here. Wind conditions, speed and direction, are important parameters because they determine production, transport through advection, and vertical mixing (turbulence). In the discussion below, the samples are identified by the numbers in Table 1. The concentrations of the various ions are presented graphically in Figure 6.

As discussed above, the chemical sampling periods do not exactly coincide with the division into four periods as determined by both the synoptic and local meteorological situations and the aerosol size distributions. In general, however, the chemical properties follow these trends, and in some cases the chemical information turned out to be crucial for the final interpretation of the processes that determine the aerosol properties in this complicated coastal area. Therefore, the variations in the aerosol size distributions and their chemical content are discussed together for each period.

3.3.1. October 28–30. The first 2 days of the campaign (October 28–29) were characterized by high concentrations of small particles. A more accurate analysis of the particle size distributions (see also Figure 5) reveals that only the concentrations of particles with diameters smaller than $0.325 \mu\text{m}$ remained constant, while the particles with sizes between 0.325 and $1.85 \mu\text{m}$ decreased steadily. For larger particles the levels were more or less constant and low (10^7 particles m^{-3}). The latter reflects that at short fetches only little sea spray aerosol was generated. The wind speed was less than 8 m s^{-1} and mainly from land. Showers occurred at the end of both days.

On October 30 the concentrations in both the fine and the coarse fractions increased, but the concentrations of the coarse particles were rising faster. Thus also the shape of the size distributions changed. Both size fractions followed the trend of the relative humidity, and as a result of condensation, submicrometer particles were growing into the coarse size fraction. When it started to rain by the end of the day, the particles larger than $9 \mu\text{m}$ disappeared, while the others increased faster.

The trends in the particle size distributions are also present in the chemical composition of the filter pack samples (Figure

6). The small generation of sea spray is confirmed by the low concentrations of sea salt in samples 1–4. The high concentrations of NH_4^+ are as expected from the air mass trajectories (type 1), passing over rural areas in the Netherlands, Germany, and Denmark with much cattle breeding and high emissions of NH_3 . The mutual differences in the NH_4^+ concentrations in the four samples are likely due to local influences. The local wind direction was mainly from land, but in the first and fourth samples shifting to long fetch. Hence the concentrations of sulfate, nitrate, and ammonium of these two samples may have been reduced owing to a variety of processes, while there were no sources of these ions over water.

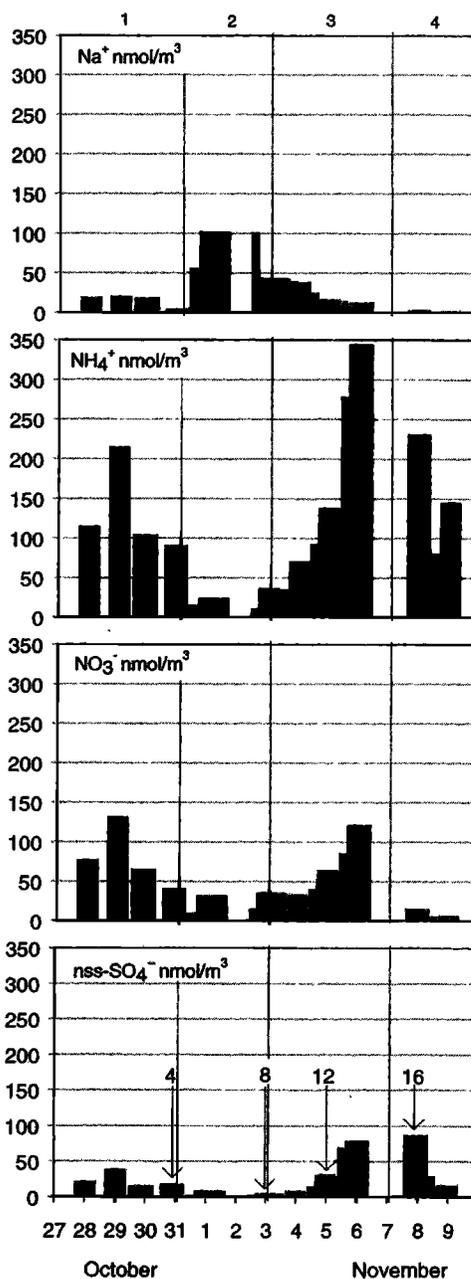


Figure 6. Concentrations of sodium, ammonium, nitrate, and non-sea-salt (nss) sulfate in the aerosol. Periods 1–4 are indicated and are the same as in Figure 4. The widths of the bars correspond with the sampling times.

3.3.2. October 31 to November 2. During the second period the wind was steady from the west (240° – 270°), resulting in intermediate and long fetches. Mean wind speed reached maximum values of almost 15.8 m s^{-1} in the afternoon of November 1. During the episodes of high wind speed, the waves were relatively high for this shallow water area, reaching values up to 0.75 m. Continuous rain occurred in the morning of October 31, followed by showers. In the evening of November 2 and all of November 3, it was dry. Relative humidity was high during the first rain period, but then the overall relative humidity decreased gradually with some daily variations. The stratification was stable during the whole period.

When the rain stopped on October 31, the concentrations of the fine fraction dropped by almost an order of magnitude, to increase again rapidly when the dry period ended with a series of showers. Following this rain period, the concentrations of the fine fraction decreased gradually in the next 2 days by 1 order of magnitude (see Figure 4). The behavior of the coarse fraction was initially contrary to that of the fine fraction, but after reaching their maximum concentration in the afternoon of November 1, the coarse fraction decreased steadily by one order of magnitude during about 1 day. Since the decrease in the coarse fraction was much faster than that in the fine fraction, the spectral shape of the particle size distribution also changed.

The variation of both small and large particles follows the behavior expected from the variation of the meteorological parameters. The chemical composition, samples 5–7, also shows these variations. Sample 5 was collected in a transition period while the air mass was changing. The fetch was intermediate, and the wind speed was 8 m s^{-1} . The sea salt concentrations were intermediate between those observed in the previous period (samples 1–4) and those for the long fetch with much surface generation (samples 6 and 7).

3.3.3. November 3–6. The third period was clearly marked by the sudden changes in wind direction at the beginning and at the end, when the synoptic situation was such that the flow near the site was negligible and only some local wind was generated. In the night of November 2–3, the wind turned from W (270°) to ESE (120°). The wind speed was variable in this period, with values between 0 and 12 m s^{-1} . Shower activity decreased in the morning of November 3, and during the rest of this period there was no precipitation. Relative humidity decreased, reaching a minimum of 65% in the middle of November 4, then increased steadily until the end of the period.

The ESE wind on November 3 brought cold continental air, with negative air-sea temperature differences during the night (-2 to -3°C) indicating unstable stratification and convective mixing. However, the lapse rates derived from the temperatures measured at 10 m and 2 m were positive, indicating stable stratification. Wind speed was very low in these situations, prohibiting turbulent mixing. It is likely that in this offshore flow with a very short fetch and radiative cooling, stably stratified cold air was advected from the land over a warmer layer adjacent to the water surface. At higher wind speeds, such as in the morning of November 3, the two layers were mixed, and the lapse rate was close to zero.

Both the fine and coarse particle fractions closely followed the trend of relative humidity. Initially, the concentrations dropped sharply, by >1 order of magnitude for the fine fraction and almost 3 orders of magnitude for the coarse fraction. Obviously, the changes in both synoptic and local meteorolog-

ical conditions influenced the aerosol concentrations. The change in the synoptic situation brought air from a completely different origin (central and eastern Europe versus Atlantic air in the preceding period). Other processes influencing the concentrations were the wash out by rain in the morning of November 3, the strong decrease in relative humidity, the cleaning by advection due to the increasing wind speed, and mixing over the water.

However, on November 4 the concentrations started to rise again, almost coincidental with the rise in relative humidity, while the wind speed decreased and the thermal stratification became stable in the afternoon of November 5. Hence transport by advection decreased, and turbulence mixing was prohibited, while at the same time the particles were growing on account of condensation. The synoptic situation (Figure 2c) and the air mass trajectories in Figure 3 show that the wind speed decreased during the transport of the air from central and eastern Europe to Lolland, resulting in accumulation of the aerosol. This is further discussed in section 3.3.4.

In general, the shape of the aerosol size distribution changes with the air mass characteristics. When the marine air mass is replaced by a continental one, the submicrometer particles increase significantly, whereas the concentrations of particles larger than $1 \mu\text{m}$ drop. As observed in period 3, the concentrations in both fractions rose on November 4–7, but faster for the coarse fraction. A simple calculation, using the equations of *Fitzgerald* [1975] (see section 3.4), shows that this can be ascribed to the effect of the increasing relative humidity. Owing to the growth of the particle sizes, the concentrations for a given size increase by up to 1–2 orders of magnitude, depending on the change in relative humidity. In the present representation of the particle concentrations in only two size fractions, particles grow from the fine fraction into the coarse fraction.

The chemical composition of the aerosol particles, samples 8–14, reflects the local conditions and the change in the synoptic situation. Sample 8 was collected while the wind was turning east (100°), and as a result the fetch changed from long to short. Sulfate, nitrate, and ammonium concentrations increased significantly, while those for Na^+ dropped. During collection of sample 10, the trajectory became continental. The concentrations of the particles of marine origin obviously decreased, as is reflected by the concentrations of Na^+ . In contrast, the concentrations of NH_4^+ , NO_3^- , and SO_4^{2-} increased exponentially. Exponential least square fits to the data in samples 10–14 show that the concentrations of sulfate rose with a rate that is about a factor of 1.8 larger than that for nitrate and a factor of 1.3 larger than for ammonium. The concentrations in the fine fraction increased overall at a rate close to that of sulfate.

3.3.4. November 7–9. The fourth period started with the passage of a cold front in the night of November 6–7, bringing rain and showers. Wind speeds in this period were low (2 – 3 m s^{-1}), from various directions, and relative humidity was high.

The aerosol concentrations initially increased. The following decrease is ascribed to washout and gravitation. The effect of the latter is evident in the stronger decrease of the concentrations of the large particles as compared to the decrease of the sub-micrometer aerosol. Also, the concentrations of sulfate and ammonium were initially rather high but decreased.

The fetch was long and the trajectories were of type 4 (see Figure 3). Therefore the high concentrations of continental aerosols were not expected. However, taking into account the

changing meteorological situation, the observed behavior can be understood. At the end of the foregoing period the air mass was advected from central Europe. During the transition into period 4 the wind turned, but the low wind speed implied that the air mass was initially driven slowly back and thus contained aerosols of the same origin as in the previous period. Since also there was little dispersion due to the low wind speed, the aerosol accumulated in the area (see Figure 4, and Figure 6, samples 14 and 16; it is noted that sample 15 is missing in Figure 6, but data collected at another level indicated that the concentrations of the continental aerosols reached their maximum values during the night of November 6–7. These aerosols were gradually removed by wet and dry deposition. Eventually, the “old” air mass was driven away and replaced by one that contained cleaner air. The latter is reflected in sample 17 (Figure 6), where the concentrations of all ions are significantly decreased.

This analysis clearly shows that the air mass trajectory, the synoptic situation, and the local meteorological condition together need to be taken into account to explain the observed aerosol behavior.

3.4. Dependence of Aerosol Concentrations on Wind Speed and Fetch

To quantify the aerosol properties, models are required with different degrees of detail. Large-scale transport-chemistry models may be used to explain the influence of remote source regions and transport over regional and global scales. Such models use emission inventories that have a coarse time resolution and thus cannot explain short-term variations such as those described above. This requires local-scale models. For the open ocean, some models are available that provide a reasonable description of the variations of the particle size distributions with local meteorological conditions, e.g., the Navy Aerosol Model [Gathman, 1989]. However, in coastal regions the situations are much more complicated than over the open ocean, and such models generally do not apply [de Leeuw, 1993]. Wind direction, indicative of sources at different fetches, including production of sea spray, needs to be taken into account [Van Eijk and de Leeuw, 1992]. This is confirmed in this section where the variations of the aerosol concentrations with wind speed are presented for different fetches.

In describing the dependence of the particle concentrations on wind speed, the effects of other meteorological parameters must first be considered. A major factor is relative humidity. Therefore, all data measured at relative humidity smaller than 97% were adjusted to a reference relative humidity of 80% using [Fitzgerald, 1975]

$$r_{0.8} = \frac{r_s}{g(S)} \quad (1)$$

where S is the saturation ratio, r_s is the particle radius at S , and $g(S) = 0.81 \exp[0.066S/(1.058 - S)]$. Data at relative humidity higher than 97% were excluded from the analysis, because at these high humidities the measurement uncertainty, combined with the steep growth curve, may lead to unrealistic corrections.

Fetch is a crucial parameter for developing the wave field and thus for producing sea spray aerosols. The removal of continental aerosols over water depends on the fetch as well. Therefore the data were divided into the three fetch categories indicated in section 2. The selection made by the previous

criterion on relative humidity restricts the data set to fetches of up to 100 km for the long fetch case. For wind directions between 108° and 127° the fetch was short. The latter limits the source regions. For intermediate fetch, the wind direction is only from WSW. No data are included with wind from ENE. Figure 7 shows the aerosol number concentrations as functions of wind speed for these three fetches. Fine and coarse particles behave similarly in either the short-fetch and long-fetch cases, while at intermediate fetches the two particle fractions behave differently. For long fetch (Figure 7a), the concentrations in both fractions increase with wind speed, for $u > 4\text{--}5 \text{ m s}^{-1}$. Air mass trajectories for this period were over the North Sea, then over rural Denmark (no industrial areas were crossed), and finally 80–90 km over sea between Germany and Lolland.

The increase of aerosol concentrations with wind speed over long fetches is expected because whitecapping increases with wind speed and thus also the surface production of aerosols. The data in Figure 7 suggest a logarithmic relation between the aerosol concentrations and wind speed, $\log c = a + bu$, where a and b are constants that are empirically determined. Values of a and b for the three fetch regimes and the two aerosol size classes are given in Table 2, together with the correlation coefficients. It is noted that for long fetch these values apply only to $u > 5 \text{ m s}^{-1}$. For lower wind speeds most of the data do not follow the general trend in the long-fetch wind speed dependence. These data are from one single day, with a different air mass history that affected particularly the concentrations of the fine particles.

The wind speed dependence of the concentrations of small particles at intermediate fetches indicates a balance between removal, advection, and production processes, resulting in relatively constant concentrations (Figure 7b). For the larger particles, production apparently was large enough to cause an increase in concentrations. This increase is even larger than for the long-fetch case. This may be caused by surf production in combination with turbulent lifting or by young waves at the shorter fetches, which break easier than aged waves, and thus can produce more aerosols.

Figure 7c shows that the concentrations in both fractions decrease at short fetch. Figure 4 shows that for this fetch the aerosols were mainly of continental origin (see also Figure 6). The atmospheric condition was predominantly close to neutral with no precipitation, except for a few hours. The data corresponding to these rain intervals are included, since the aerosol concentrations are not different from those for the dry situations, except for the small group of small particles with lower concentrations in the wind speed range between 7 and 10 m s^{-1} .

For both size fractions, especially for the coarse particles, the dependence of the concentrations on wind speed is too strong to be caused only by advection, diffusion and removal by dry deposition to the surface, as suggested in Van Eijk and de Leeuw [1992]. The latter is caused by gravitational and turbulent deposition, which is determined by wind speed (u_*). The dry deposition velocity of hygroscopic particles with diameter $d = 2 \text{ }\mu\text{m}$ on water surfaces can be roughly estimated as $v_d \cong C_D u = 1.3 \times 10^{-3} u$, when C_D is the drag coefficient and u is the wind speed [Slinn and Slinn, 1980]. Dispersion depends also on wind speed, causing the concentrations to decrease approximately as $1/u$. Furthermore, the removal of aerosol advected from sources over land apparently increases faster with wind speed than the production of sea spray aerosol, for the short fetch considered here, in which the wave field is not

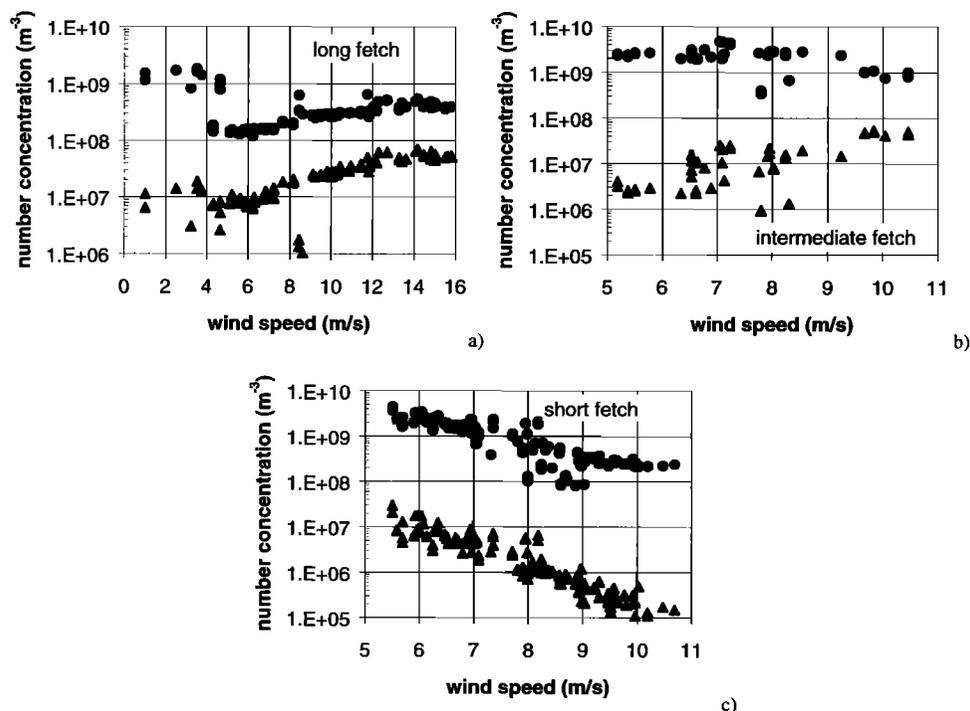


Figure 7. Wind speed dependence of the aerosol number concentrations (normalized to RH = 80%) for the fine (circles) and coarse (triangles) fractions: (a) short fetch (15–100 km), (b) intermediate fetch, and (c) long fetch (1.5–2 km).

developed enough to cause significant whitecapping. The effect of these processes, however, cannot explain the decrease of the concentrations, especially of large particles.

Apparently, other mechanisms play a role here. The surface stress depends on the wave age: for young waves the stress is appreciably enhanced with respect to a balanced wave field [Komen *et al.*, 1994], and thus deposition velocity will be also significantly larger. An important omission is information on the source regions and source strength. Variations may have occurred during the experiment that strongly influenced the concentrations already before they reached the Lolland coastline. Furthermore, the advection depends on the wind fields along the air mass trajectory. So not only the local wind field is important. In period 4, for example, wind speed decreased as the air mass came closer to the Vindeby site, and the stagnation led to a significant enhancement of the concentrations. Another important factor is the removal along the trajectory, which depends not only on local wind speed but especially on precipitation. Also atmospheric stability (mixing), entrainment at the top of the boundary layer, and other processes affecting boundary layer dynamics are important factors.

4. Discussion

The analysis presented is an attempt to better understand aerosol behavior in a complicated coastal region as encountered at the Vindeby site. Widely varying particle concentrations were observed with differences of several orders of magnitude and very different chemical composition with regard to the occurrence of chemical species as well as their concentrations. Combining data on aerosol particle size distributions and aerosol chemical composition with information on the synoptic situation (determining the air mass history) and the local meteorological condition shows that each of these parameters contributes to understanding the observed characteristics. It appears crucial to have access to all of these parameters to understand the observed aerosol behavior.

Quantitatively predicting the changes in the aerosol characteristics in response to changing synoptic and local meteorological situations requires a detailed knowledge of the upwind source strengths and the various processes that affect the particle size distributions and the chemical composition. A brief summary of the relevant processes was presented in the intro-

Table 2. Wind Speed Dependence of the Particle Concentrations Given by $\log c = a + bu$ and Correlation Coefficient R^2

	Long Fetch*		Intermediate Fetch		Short Fetch	
	$d < 1 \mu\text{m}$	$d > 1 \mu\text{m}$	$d < 1 \mu\text{m}$	$d > 1 \mu\text{m}$	$d < 1 \mu\text{m}$	$d > 1 \mu\text{m}$
a	7.8	6.5	10.0	5.3	11.0	9.6
b	0.053	0.090	-0.090	0.23	-0.28	-0.42
R^2	0.85	0.90	0.27	0.45	0.71	0.88

* For the long fetch the data for $u < 5 \text{ m s}^{-1}$ were not included in the fit.

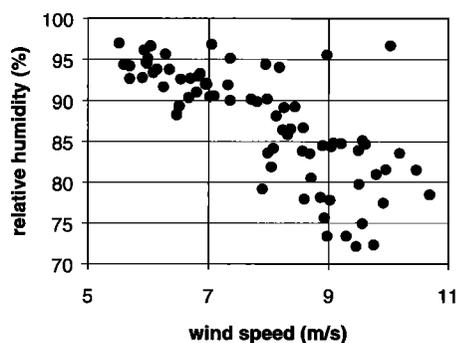


Figure 8. Variation of relative humidity with wind speed in the short-fetch case.

duction, and the data presented in section 3 were discussed in relation to these processes. A detailed assessment of their effects is outside the scope of this paper, as it requires not only a comprehensive transport-chemistry model but also detailed knowledge on the source strengths.

Parameterizing the various processes is required to avoid running complicated mathematical models for each of them. In an attempt to understand the various meteorological effects on the aerosol concentrations, the effect of wind speed was empirically determined. Different parameterizations are required for different fetches.

In the analysis of the wind speed dependence, the concentrations were normalized to a "standard" relative humidity of 80%. However, the relative humidity may be related to the wind speed. Figure 8 shows the anticorrelation of these parameters for short fetches. When the concentrations are normalized to a certain relative humidity, an "artificial" slope is introduced in the relationship between number concentration and wind speed. To quantify the effect of the normalization, $g(S)$ has been calculated for relative humidities of 95 and 75%, yielding values of 1.44 and 0.95, respectively. This means that the data are affected by, at most, a factor of 2, surely negligible compared with the orders of magnitude difference in concentrations over the wind speed interval. In fact, if instead of the normalized concentrations, the original data are used for correlation with the wind speed, the result is very similar. For the intermediate and long fetches, no correlation was found between relative humidity and wind speed.

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- G. de Leeuw, Physics and Electronics Laboratory, Netherlands Organization for Applied Scientific Research (TNO), P.O. Box 96864, 2509 JG The Hague Netherlands. (deleeuw@fel.tno.nl)
- E. Plate and M. Schulz, Institut für Anorganische und Angewandte Chemie (IAAC), Universität Hamburg, Martin-Luther-King Platz 6, 20146 Hamburg, Germany. (fcba001@chemie.chemie.uni-hamburg.de; michael.schulz@dkrz.de)
- E. Vignati, Department of Wind Energy and Atmospheric Physics, Risø National Laboratory, Frederiksborgvej 399, P.O. Box 49, 4000 Roskilde, Denmark. (elisabetta.vignati@risoc.dk)

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