JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 110, D15306, doi:10.1029/2004JD005403, 2005

Flux divergence of nitric acid in the marine atmospheric surface layer

Lise Lotte Sørensen,[1] Sara C. Pryor,[2] Gerrit de Leeuw,[3] and Michael Schulz[4]

Received 31 August 2004; revised 3 December 2004; accepted 9 March 2005; published 12 August 2005.

[1] It is hypothesized that removal of HNO_3 from the atmosphere close to the sea surface is due to two processes: dry deposition to the sea surface and chemical reaction with sea spray. The latter process invalidates the application of the constant flux layer assumption to calculate dry deposition based on concentrations of HNO_3 at, e.g., a reference height of 10 m. A field experiment was carried out to investigate this hypothesis, and the measured concentration profiles were found to differ dramatically from the log linear profiles, which would have been produced by turbulent transport only. Surface fluxes of HNO_3 were calculated from the measured profiles taking chemical reactions into account and were compared to surface fluxes calculated by the traditional resistance method. It was found that the surface fluxes could be a factor of two less when chemical reactions are taken into account, depending on the characteristics of the near-surface aerosols. HNO_3 loss rates due to heterogeneous chemistry are calculated by two independent methods and are compared.

Citation: Sørensen, L. L., S. C. Pryor, G. de Leeuw, and M. Schulz (2005), Flux divergence of nitric acid in the marine atmospheric surface layer, *J. Geophys. Res.*, *110*, D15306, doi:10.1029/2004JD005403.

1. Introduction

[2] During the past half century, there has been a growing body of literature dealing with air sea exchange of various trace gases [see, e.g., *Liss and Duce*, 1997]. Much of the attention has been placed on efforts to measure the climate relevant gases, e.g., carbon dioxide and dimethyl sulfide fluxes. Building on the theoretical base developed by *Monin and Obukhov* [1954], methods of estimating these fluxes have typically relied on the assumptions of horizontal homogeneity and steady state, and it has furthermore been assumed that the constant flux layer assumption applies to the lowest tens of meters over the sea, i.e., in the marine atmospheric surface layer.

[3] For momentum and/or heat fluxes, the assumptions supporting the Monin-Obukhov similarity theory are generally satisfied. However, the theory begins to break down when one examines the nutrient compounds of interest to marine ecosystems, such as the nitrogen gases. Unlike momentum or heat, ammonia (NH_3) and nitric acid (HNO_3) undergo reactions on fairly short timescales introducing a source/sink term, which must be taken into account both in the analysis of experimental data and in models. If the source/sink term is significant, a flux divergence will be introduced where one cannot simply assume that the flux measured at a given height above the surface is equivalent to the surface flux.

[4] To estimate the deposition/emission of reactive or nonconservative species, classical flux theory must therefore be modified in order to take a height-dependent sink/source term into account. *Lenschow* [1982], *Lenschow and Delaney* [1987], and *Duyzer* [1992] have each described the flux divergence for the chemical triad nitrogen dioxide (NO_2), nitric oxide (NO) and ozone (O_3) with the same general approach and conclusions, and *Kramm and Dlugi* [1994] have described the flux divergence for NH_3, HNO_3 and ammonium nitrate (NH_4NO_3). None of these previous studies have focused on the marine environment, but they have rather emphasized either terrestrial or idealized conditions. The few studies designed to estimate reactive trace gas fluxes between the atmosphere and the ocean [*Quinn et al.*, 1988; *Sørensen et al.*, 1994a; *Asman et al.*, 1995; *Geernaert et al.*, 1998], faced unresolvable problems as regards the estimation of the source/sink term with sufficient accuracy, given the uncertainties in either the chemistry or horizontal homogeneity. In the study by *Geernaert et al.* [1998], data were presented which suggest that reaction on sea spray may produce a flux divergence of HNO_3. The present paper extends that work with an analysis of the chemistry involved in the source/sink term based on the fundamental hypothesis that sea spray is an important scavenger in the marine atmosphere for highly soluble gases, specifically HNO_3.

[5] Because of technological limitations in high-frequency sampling for HNO_3, direct flux measurements using, e.g., the eddy correlation method, are not practical. Instead, indirect methods, such as the gradient technique, are often used for measurement of these gas fluxes. However, since the flux of chemically reactive compounds can be influenced by chemical reactions, the interpretation of the profile is often difficult.

---

[1] Department of Wind Energy, Risø National Laboratory, Roskilde, Denmark.

[2] Atmospheric Science Program, Department of Geography, Indiana University, Bloomington, Indiana, USA.

[3] TNO-Physics and Electronics Laboratory, The Hague, Netherlands.

[4] Laboratoire des Sciences du Climat et de l'Environnement, CEA/CNRS–LSCE, Gif-sur-Yvette, France.

0148-0227/05/2004JD005403$09.00

This paper will serve to demonstrate that the flux divergence can be both measured and predicted, using HNO_3 as an example. Such a demonstration requires that HNO_3, NH_3, and sea spray concentrations are measured over a variety of environmental conditions, and that the profiles are interpreted based on the inclusion of all terms in the budget equations (described in section 2).

[6] In the next section, we review the flux profile theory, which is followed in section 3 with a discussion of the nature of the source/sink term in the flux profile equations. Experimental details to test our hypothesis are summarized in section 4. In section 5, we provide results, which are followed by concluding remarks in sections 6 and 7.

2. Flux Theory

[7] The description of vertical fluxes of gases is based on the continuity equation

$$\frac{dc}{dt} = \frac{\partial c}{\partial t} + u_i \frac{\partial c}{\partial x_i} = D \frac{\partial^2}{\partial x_i^2} c + S, \qquad (1)$$

where c is the concentration of the gas; u_i is the wind velocity; D is the molecular diffusion coefficient of the quantity c in air; and S is an internal source (positive) or a sink (negative) term. Reynolds averaging and conservation of mass is applied. The averaging time must be sufficiently long that the mean vertical velocity is zero (e.g., on the order of half an hour or more), and the horizontal turbulent flux is small compared to the advection, and recognizing that molecular diffusion is insignificant with respect to turbulent transport, the continuity equation reduces to the following more practical form:

$$\frac{\partial \overline{c}}{\partial t} + \frac{\partial \overline{w'c'}}{\partial z} + \overline{u} \frac{\partial \overline{c}}{\partial x} = \overline{S}. \qquad (2)$$

In (2), the second term represents the flux divergence ($\overline{w'c'} = F$) and the third term the advection term in the downwind direction.

[8] To simplify the analysis, we assume that the concentration and reaction rates do not change significantly during the averaging interval. Also other removal and production processes are considered constant. With such conditions the physical and chemical attributes of the system are in steady state, where $\partial c/\partial t = 0$.

[9] In steady state any measured or assumed flux divergence term, $\partial F/\partial z$, can be attributed to some combination of $u\partial c/\partial x$ and S:

$$u \frac{\partial c}{\partial x} - S = \frac{\partial F}{\partial z}. \qquad (3)$$

[10] Since we want to relate measured flux divergence to internal sinks, we need to investigate the possible interference of the advection term. This applies to both the species of interest (HNO_3 in this case) and reactants that influence the concentration of HNO_3 (e.g., sea salt).

[11] The production of HNO_3 is due to photochemical reactions (HNO_3 is mainly formed from NO_2, with a conversion rate of less than 3% per hour) and may be considered constant giving rise to only small horizontal gradients, which are negligible on the scale of interest. One may assume that above the atmospheric surface layer, where no significant scavenging of HNO_3 by freshly produced sea spray is taking place, $\partial c/\partial x$ is negligibly small. Assuming that sea spray of a size that dominates uptake of HNO_3 and other constituents involved in the S term also are spatially homogeneous on the scale of interest, an obvious conclusion is that $\partial c/\partial x$ may also be neglected as one approaches the surface. The degree to which the constant flux layer assumption where $\partial F/\partial z \approx 0$ and thus $S = 0$ and $u\partial c/\partial x = 0$ can be employed for fluxes of sea spray is dependent on the size fraction in focus [*Petelski*, 2003], and the assumption is violated close to the coast, where sea spray production in the surf zone significantly affects the atmospheric composition [*de Leeuw et al.*, 2000]. The fetch at which surf-produced sea spray is well mixed throughout the MBL is dependent on atmospheric stability and wind speed but numerical models suggest vertical homogeneity is established within 5–10 km of the coast even with initial conditions of zero sea spray aerosol above 25 m and a very steep vertical profile below that level in the modeling conducted by *Vignati et al.* [2001]. Denmark has an aerosol burden that is heavily marine influenced and hence in modeling conducted with an equilibrium open-ocean sea spray profile the influence of the surf zone was even more rapidly dispersed. In these conditions the advection term $u\partial c/\partial x$ can be ignored for HNO_3 with respect to S, and $\partial F/\partial z$ will be equal to S, and thus for the examination of the flux divergence of HNO_3 only the chemistry involved in the source/sink function, S needs to be explored. The influence on the flux of horizontal sea spray production gradients, e.g., in a developing wave field in offshore wind, would be a subject for future research.

[12] With the following practical example, using realistic values for the various physical and chemical quantities will be shown that the effect of advection due to horizontal HNO_3 gradients may be neglected. Assuming that a few kilometers downstream from the coast the atmosphere is well mixed, a budget for the atmospheric surface layer (completed by entrainment fluxes) can be described by equation (4):

$$\underbrace{u\frac{\partial c}{\partial x}}_{\mathrm{I}} = -\underbrace{\frac{(v_d + w_e)c}{h}}_{\mathrm{II}} + \underbrace{\frac{w_e c_1}{h}}_{\mathrm{III}} + \underbrace{S_1}_{\mathrm{IV}} - \underbrace{S_2 \frac{\delta h}{h}}_{\mathrm{V}}. \qquad (4)$$

Term I is the advection term which we want to estimate. The flux out of the air parcel due to deposition (deposition velocity v_d) and entrainment (entrainment rate w_e), is described by term II. Term III describes the flux into the air parcel by entrainment from above the boundary layer. The terms IV and V are specific chemical source/sink terms, the former describes production and the latter describes scavenging of HNO_3 by sea salt. Since the scavenging only takes place in the lowest part of the boundary layer this term is also height-dependent. Rearranging equation (4) yields

$$hu\frac{\partial c}{\partial x} = -(v_d + w_e)c + w_e c_1 + hS_1 - S_2 \delta h. \qquad (5)$$

Table 1. HNO_3 *udc*/*dx* Measured in the Kattegat and in the Central Baltic at Coastal Stations[a]

udc/*dx*	Number of Samples	*Dx*, m	*U*, m s^{-1}	Mean ppb s^{-1}	Standard Deviation
Kattegat	8	30,000	7	-2.03×10^{-6}	4.00×10^{-6}
Central Baltic	5	200	2.5	2.82×10^{-4}	4.97×10^{-4}

[a] At both studies the advection term (*udc*/*dx*) is much smaller than the sink term (*S*), which in the present study is estimated to be 7.5×10^{-3} ppb s^{-1}.

Letting equation (5) describe the HNO_3 system, the advection term has been evaluated using the following quantities: [OH] = 5×10^{6} molecules cm^{-3} [*Seinfeld*, 1986]; [NO_2] = 1 ppb; the reaction rate for HNO_3 production is found in the work of *Seinfeld* [1986] to be $k_{HNO3} = 1.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}; hence from the parameters found in the work of *Seinfeld* [1986], S_1 can be estimated $S_1 = 5.5 \times 10^{-5}$ ppb s^{-1}; using further $S_2 = 1 \times 10^{-3}$ ppb s^{-1} (found in this study), $c_1 = 2$ ppb; *c* is 1 ppb; $v_d = 3 \times 10^{-2}$ ms^{-1} (estimated from pure turbulent transport); $w_e = 1 \times 10^{-2}$ ms^{-1}, the boundary layer depth h is chosen to be 500 m and $\delta h = 20$ m. The value for $u\partial c/\partial x$ calculated by equation (5) is found to be two orders of magnitude smaller than $|S|$ (= $S_1 - S_2$), which leads to the conclusion that the sink term is dominating and therefore the advection can be neglected with respect to the flux divergence. Data from two experiments where horizontal gradients of HNO_3 were measured support this analysis. One experiment was carried out at the island Östergarnsholm close to Gotland in the central Baltic [*Pryor et al.*, 1999] and one was carried out in the Kattegat strait between Denmark and Sweden [*Sørensen et al.*, 2003]. The data are shown in Table 1. The data show that $u\partial c/\partial x$ is 2–3 orders of magnitudes smaller than the estimated *S* this also suggest homogeneous horizontal distribution of the sea spray taking up HNO_3. According to the "constant flux layer assumption" flux divergence less 10% is acceptable [*Stull*, 1988], which for HNO_3 fluxes of magnitude 1×10^{-3} μg m^{-2} s^{-1} means that the influence from advection ($u\partial c/\partial x$) of the order 1×10^{-4} μg m^{-2} s^{-1} ($\approx 0.5 \times 10^{-5}$ ppb s^{-1}) or smaller is acceptable. This implies that for some cases the horizontal advection does violate the "constant flux layer assumption," however the sink term is still more dominating. Hence

$$\frac{\partial F}{\partial z} = \frac{\partial \overline{w'c'}}{\partial z} = S. \tag{6}$$

[13] It suggests that one must include processes such as chemical reactions between nitric acid and other gases and heterogeneous reactions involving aerosols and sea spray. The source/sink term and thus also the flux, depends on the rate of the chemical reaction. Applying similarity theory and using the traditional K closure for turbulent eddy diffusion yields

$$u_{*}\kappa \frac{\partial}{\partial z}\left(z \frac{\partial c}{\partial z} \phi^{-1}\right) - S = 0, \tag{7}$$

where u_* is the friction velocity, κ is the von Karman constant (≈0.4) and φ is the stability function. For simple first-order chemistry, *S* can be written as $k \cdot c$, where *c* (μg m^{-3}) is the concentration and *k* (s^{-1}) is a coefficient expressing the removal rate or production rate of *c*. Assuming near neutral conditions to avoid stability corrections, equation (7) can be solved analytically [*Geernaert et al.*, 1998]:

$$c(z) = AI_0\left(2\sqrt{az}\right) + BK_0\left(2\sqrt{az}\right), \tag{8}$$

where $a = k/u_*\kappa$, and I_0 is the modified Bessel function of the first kind of order 0, K_0 is the modified Bessel function of the second kind of order 0 [*Jeffrey*, 1995]. *A* and *B* are constants determined by the boundary conditions (here they are set to $c(z_o)$ and $c(z_{20})$ which are the concentration at z_0 and at 20 m) and then solving the two equations. From this solution the vertical concentration gradients influenced by chemical reactions can be calculated. It is assumed that the scavenging is constant with height in the lower part of the surface layer, i.e., in the lower tens of meters. This assumption is discussed further in section 5, however it seems valid for our study where measurements of particle size spectra in two heights using two independent instruments show only relatively small gradients.

3. Discussion of the Reactions Influencing the Flux of Nitric Acid

[14] To provide a physical-chemical basis for the appropriate evaluation of *k* and the magnitude of *S*, the set of governing chemical reactions is now investigated. The formation of HNO_3 is mainly due to the reaction between anthropogenic NO_2 and the OH radical formed from photochemical reactions:

$$NO_2 + OH \rightarrow HNO_3. \tag{R1}$$

Therefore the formation of HNO_3 is favored during sunny conditions. *Pruppacher and Klett* [1997] suggested that N_2O_5 would form HNO_3 aqueous droplets in the atmosphere from a heterogeneous reaction with water droplets in the atmosphere due to the high solubility of N_2O_5. This reaction is mainly important at night since N_2O_5 is rapidly photolyzed by sunlight to form NO_2 [*Logan*, 1983], however the reaction with N_2O_5 may be important in the marine atmospheric boundary layer where water vapor concentrations can be high:

$$NO_2 + NO_3 \rightarrow N_2O_5 \tag{R2}$$

$$N_2O_5 + H_2O(g, aq) \rightarrow 2HNO_3. \tag{R3}$$

The removal process for HNO_3 is considered to be mainly dry deposition, although reactions with NH_3 to form NH_4NO_3 can also act as a removal process. According to *Pruppacher and Klett* [1997] the reaction with NH_3 is suggested to be a gas-phase reaction but the same authors also propose that HNO_3 droplets can form from binary

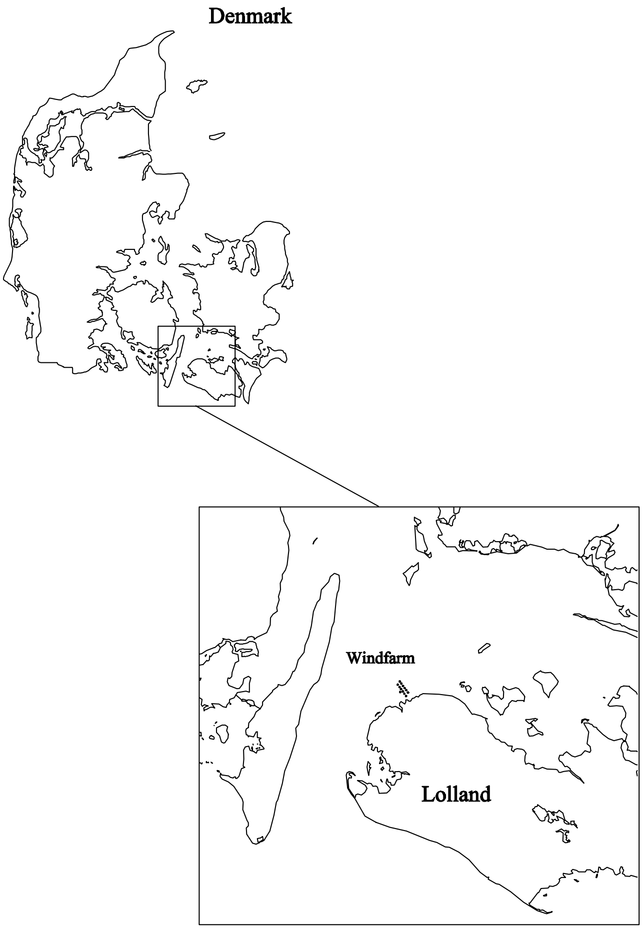

Figure 1. Measurement site in Lolland, Denmark.

nucleation in a HNO_3–water vapor reaction, and this droplet will react with available NH_3:

$$\text{(R4)} \qquad HNO_3\,(g, aq) + NH_3(g) \rightleftharpoons NH_4NO_3(s, aq).$$

The nucleation rate for the HNO_3 reaction with water vapor might even be enhanced by the presence of NH_3, as is suggested to be the case for the reaction between H_2SO_4 and water vapor [*Hoppel and Frick*, 1991]. The reaction between sodium chloride (NaCl) and HNO_3 to form sodium nitrate ($NaNO_3$) and hydrochloric acid (HCl) in the marine atmosphere has relevance for oxidant cycling and the chemical composition of marine aerosol [*Robbins et al.*, 1959; *Martens et al.*, 1973; *Harrison and Pio*, 1983; *Hillamo et al.*, 1993; *Pakkanen et al.*, 1996; *Plate and Schulz*, 1997; *Vignati et al.*, 2001]:

$$\text{(R5)} \qquad HNO_3(g) + NaCl(s, aq) \rightleftharpoons NaNO_3(s, aq) + HCl(g).$$

4. Experimental Design

[15] Two field experiments were designed and conducted to quantify the processes governing the flux divergence of HNO_3. The experiments took place at a coastal station near Vindeby, on the island Lolland in Denmark (see Figures 1 and 2). Most of the water near the station is rather shallow (depth: 0.5–15 m) except for a 20–55 m deep navigational channel to the west of the field site. The field experiments were conducted from 27 October to 10 November 1994 and 27 April to 10 May 1995.

[16] HNO_3 was sampled with denuders comprising a 3 mm inner diameter, 500 mm long (Duran) glass tube coated with NaCl (0.5 volume %) [*Perrino et al.*, 1990]. This method was chosen because of the good selectivity of this coating to HNO_3 [*Perrino et al.*, 1990] and the collection efficiency is close to 100%. The flow through the denuder is approximately 1–1.5 L min^{-1} driven by a pump which was connected to a manifold. From the manifold there was a polypropylene tube to each denuder, and in each tube a nozzle was placed to control the flow. The denuders were installed in a mast situated about 1 km offshore (the sea mast) (Figure 3) at elevations of 2.5, 5, 7, 10, 15 and 20 m above mean sea level. The sampling times were relatively long (minimum 3 hours, depending on the meteorological conditions).

[17] Two different types of devices were used for collection of NH_3, diffusion scrubbers and denuders. Diffusion denuders [*Ferm*, 1979] were used to collect NH_3 at the sea mast in the spring campaign. The denuder setup and design were the same as for the NaCl coated denuder, described above, except the tube was coated with oxalic acid (1.5 volume %). The diffusion scrubber measures NH_3 semicontinuously with a detection limit of 0.01 ppb [*Sørensen et al.*, 1994b]. During the fall 1994 experiment the diffusion scrubber systems were placed at three levels on the sea mast. For the spring experiment the diffusion scrubbers were mounted on a land mast (10 m from the water line).

[18] Filterpacks were used on the sea mast at heights of 2.5, 5, 7 and 10 m to measure the main water soluble aerosol constituents (sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), $\Sigma(NH_3, NH_4^+)$, $\Sigma(HNO_3, NO_3^-)$, sulfate (SO_4^{2-}) [*Plate*, 2000; *Tamm and Schulz*, 2003]. The filter pack consists of a PTFE particle filter with a pore size of 5 μm, and two back-up filters to collect gaseous species. The back-up filters were washed nylon filters with a pore size of 0.45 μm (for HNO_3) and washed $H_3PO_4^-$ impregnated paper filter (for NH_3). Owing to evaporation of NH_3 and possible HNO_3 from NH_4NO_3 at the particle filter it is not possible to separate the gases HNO_3 and NH_3 from the aerosols in a filterpack. They do provide, however, a reliable measure of the sum of NH_3 + NH_4^+ and HNO_3 + NO_3^-.

[19] Particle size distributions were measured at the sea mast using optical particle counters (Particle Measuring Systems, Boulder, Colorado, USA). A CSASP-200 probe was mounted at 7.5 m above the sea surface to sample particles in the 0.2–20 μm diameter range; a CSASP-100-HV probe was mounted on the grid at 3 m above the sea surface to sample particles in the 0.5–47 μm diameter range. For logistical reasons the particle counters were placed in a fixed position with the inlet aligned into the prevailing wind direction (west) during both experiments. This implies that at certain wind directions at high wind speeds the larger particles were likely undersampled.

[20] Equipment for measurement of mean wind speed and direction and temperature were mounted at several levels on both masts; in addition, sonic anemometers were

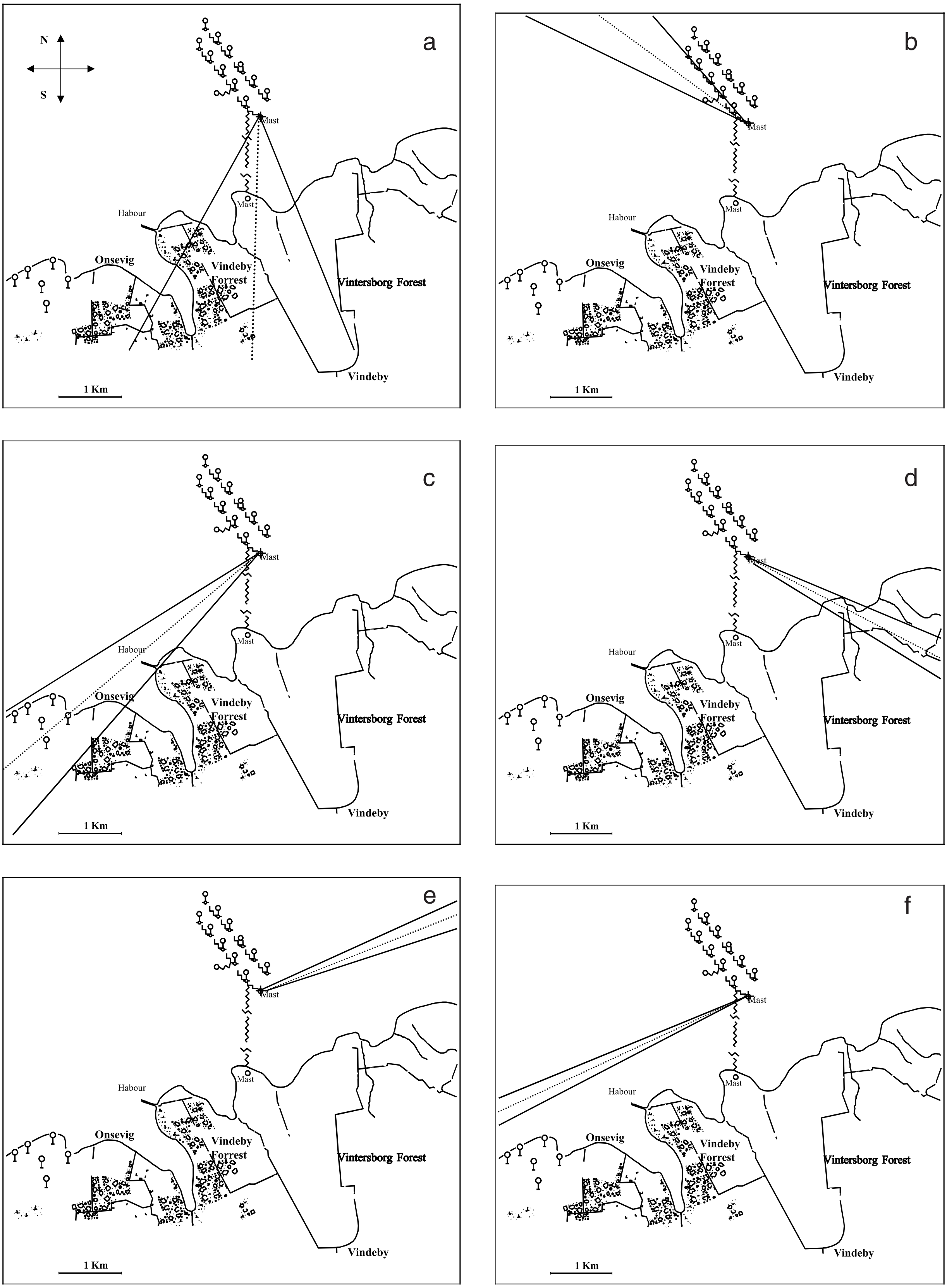

Figure 2. Maps showing the measurement site with the wind direction for the specific periods: (a) 94-3; (b) 94-4; (c) 94-6; (d) 94-13; (e) 95-7; and (f) 95-14.

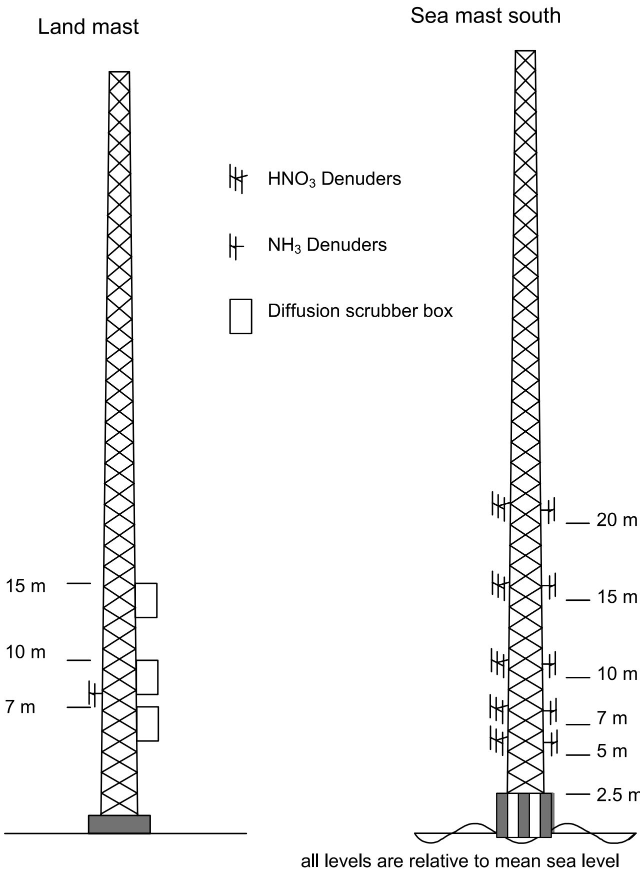

Figure 3. Measurement masts in Vindeby, Lolland, Denmark. The land mast was situated at the coast 10 m inland. The water mast was situated in the water about 1.5 km from the coastline.

mounted on the water mast at 15 and 40 m height to obtain measurements of turbulence intensity and the friction velocity.

5. Calculating the Surface Flux

[21] The measured profiles were used to derive the magnitude of the surface flux by extrapolation using equation (8) and compared to the flux obtained from the constant flux layer assumption. To avoid complications from stability corrections only cases in which the stratification was near-neutral ($1/L < |0.03|$) were selected for analysis. Further, to ensure uniform chemistry in time, sampling periods were chosen with relatively steady wind direction (within 30°) so that the fetch and the air mass composition could be treated as constants. Also periods were used with only small changes in wind speed ($\pm 1-2$ m s^{-1}) during the sampling time, so that the conditions could be assumed to be in a steady state. These criteria left us with only 6 useful profiles of HNO_3 from the two experiments. In Table 2 we summarize the profiles and concurrent environmental conditions. Only two of the profiles were associated with relatively high concentrations of NH_3 (the profiles from the spring experiment). As indicated in the introduction, only compounds newly introduced into the system and reacting at a timescale shorter than the timescale for turbulent transport will cause a flux divergence. We hypothesize that the major reason for flux divergence observed in the profiles from Vindeby is the interaction between HNO_3 and sea spray droplets and not reaction with NH_3 because NH_3 can only be invoked as an explanation if there is a local NH_3 source present.

[22] From equation (8) the vertical profiles of the chemical species can be calculated, but to carry out this calculation the coefficient k is needed, recalling k is the removal rate that occurs in the sink term in equation (7), involving reaction between HNO_3 and sea spray. Existing data on sea spray concentrations in the surface layer indicate that sea spray gradients are small except very close to the surface from the wave trough up to 1–2 times wave height [*de Leeuw*, 1986, 1993]. No significant trend with meteorological parameters or wave height is apparent from these data. Therefore aerosol measurements were conducted at two levels (7.5 and 3 m) in the fall Vindeby experiment. The observed particle surface area at the two heights (Figure 4) show that gradients between 3 and 7.5 m are generally small, and may result in part from differences in the accuracy and precision of the instruments deployed at the two heights. The only long fetch in the data set for 1994 was period 4, periods 3 had a short fetch (about 1–2 km) and in period 6 the fetch was along shore (Table 2 and Figure 2c). In view of these small gradients, and considering that the waves in the area are too small to create strong concentration gradients observed by [*de Leeuw*, 1986] or to otherwise significantly influence the concentration of sea spray aerosol at the levels where the HNO_3 concentrations were measured, the sea spray concentrations are assumed to be well mixed across the layer where the measurements are carried out. This assumption will allow for the reaction to be treated as a first-order reaction where the sea spray surface is constant in the vertical direction over the domain of interest, i.e., between 3 and 20 m above the surface and thus the analytical solution of equation (7) can be used.

[23] The concentrations of HNO_3 at different heights were determined using the boundary conditions $c(z_0) = 0$, $c(20)$ = "the concentration measured at 20 m" to estimate A and B from the two equations and then adjusting k in equation (8), in order to fit the calculated concentrations to the measured profile, by a least squares function. The measured and calculated profiles are shown in Figure 5.

[24] The surface fluxes were calculated by the following approach. Close to the surface where the turbulent eddies are small, the turbulent timescale is expected to dominate the chemical timescale. Hence the flux divergence close to the surface will be insignificant. Therefore it is assumed that there is no flux divergence at a level of 10 cm and the concentration at this height was calculated by equation (8). The calculated concentrations were then used to calculate the HNO_3 dry deposition by application of the resistance method [*Wesley and Hicks*, 1977] for the layer between the surface and 10 cm height.

[25] The Wesley-Hicks method is based on a deposition velocity, v_d (m s^{-1}) which is parameterized in terms of two resistances: r_a (m^{-1} s), the aerodynamic resistance governing the turbulent transport; and r_b (m^{-1} s), the sublayer resistance, governing diffusion through the laminar sublayer. A resistance, r_s (surface resistance) can express the transfer across the surface. Here we will consider $r_s = 0$

Table 2. Identification of the Sample Periods, Start and End Time of the Sampling, Averages and Standard Deviations of Wind Speeds (*ws*), Wind Direction (*wd*), Inverse Monin-Obukhov Length (1/*L*), Atmospheric Temperature (*T*), and Fetch (*F*)

Name	Start, UT	End, UT	*ws*, m s^{-1}	*wd*, deg	1/*L*, m^{-1}	*T*, °C	*F*, Km
Period 3-94	29 Oct. 1994, 1320	30 Oct. 1994, 0825	4.9 ± 0.7	184 ± 26	0.001 ± 0.021	8	~1
Period 4-94	30 Oct. 1994, 1310	30 Oct. 1994, 1605	3.9 ± 0.5	306.5 ± 10.7	0.003 ± 0.003	8.7	~20
Period 6-94	31 Oct. 1994, 0845	31 Oct. 1994, 1650	7.4 ± 1.1	230.6 ± 8	0.01 ± 0.006	13	~5
Period 13-94	4 Nov. 1994, 1617	5 Nov. 1994, 0907	4.7 ± 1.2	118.9 ± 5	0.012 ± 0.014	6	~2
Period 7-95	9 Jan. 1995, 0925	1 May 1995, 1425	6.4 ± 0.5	66.5 ± 4.6	0.008 ± 0.009	9.5	~40
Period 14-95	5 May 1995, 1435	5 May 1995, 1808	7.9 ± 0.5	244.6 ± 1.1	0.014 ± 0.004	17	~25

since HNO_3 is rapidly taken up by the surface. The flux can be calculated from

$$F = v_d(c - c_0), \tag{9}$$

where c_0 is the concentration of the constituent at the surface, for HNO_3 c_0 is 0, and

$$v_d = \frac{1}{r_a + r_b}, \tag{10}$$

where

$$r_a = \frac{1}{\kappa u_*} \ln\frac{z}{z_0} \tag{11}$$

$$r_b = \frac{1}{\kappa u_*} \ln\frac{z_0}{z_s}. \tag{12}$$

In equations (11) and (12), z_0 is estimated from [*Asman et al.*, 1994]

$$z_0 = \frac{0.13\nu}{u_*} + \frac{0.0144 u_*^2}{g}, \tag{13}$$

where ν is the viscosity of the air, *g* is gravity and z_s is the surface roughness length for the gas. The parameter z_s refers to the level where the concentration becomes zero or has reached the equilibrium concentration with the water phase. In *Joffre* [1988] and *Asman et al.* [1994], z_s was computed for smooth conditions ($Re < 0.13$) from

$$z_s = 30(\nu/u_*) \exp\left[-13.6\kappa Sc^{2/3}\right] \tag{14}$$

and for rough conditions ($Re > 0.13$) from

$$z_s = 20 z_0 \exp\left[-7.3\kappa Re^{1/4} Sc^{1/2}\right]. \tag{15}$$

Re is the Reynolds number and *Sc* is the Schmidt number:

$$F = u_* \kappa z \frac{\partial c}{\partial z}. \tag{16}$$

[26] The fluxes of HNO_3 were calculated for the 6 measurement periods by application of both methods, i.e., calculations were made with and without accounting for chemical reactions. Furthermore, the flux was calculated from equation (16) by fitting a linear regression to c versus log(*z*) and use the slope to compute the flux assuming steady state, no chemical sink or source and horizontal homogeneity.

[27] Comparison of the results in Table 3 using the case where chemical reactions are taken into account as the reference shows that the error in the flux estimates is large if we estimate the fluxes by simple extrapolation of the concentration profile to the surface. In some cases the fluxes may be overestimated by as much as a factor of 10. For the fluxes calculated taking chemical reactions into account and calculations with the resistance method, only in one case the

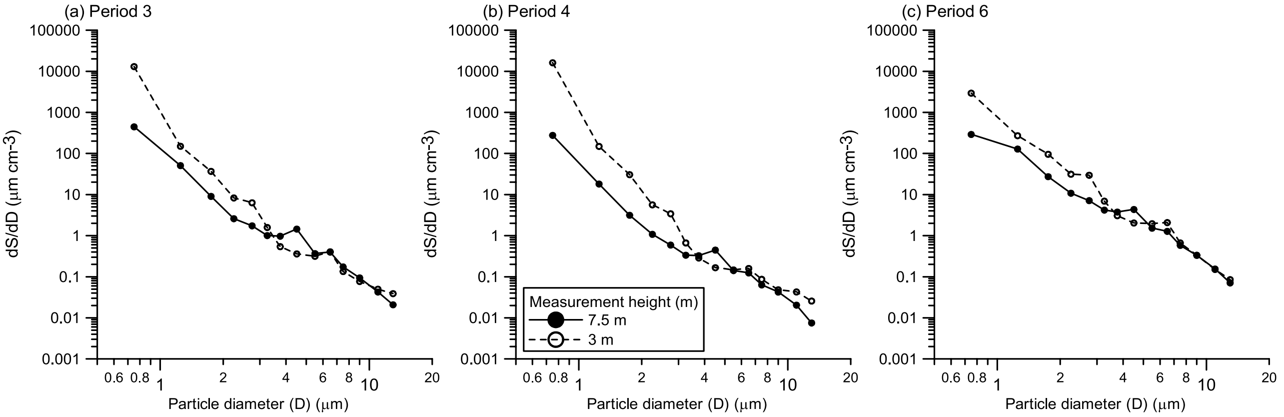

Figure 4. Comparison of particle size distributions shown as the surface area measured at 3 and 7.5 m for periods (a) 3, (b) 4, and (c) 6.

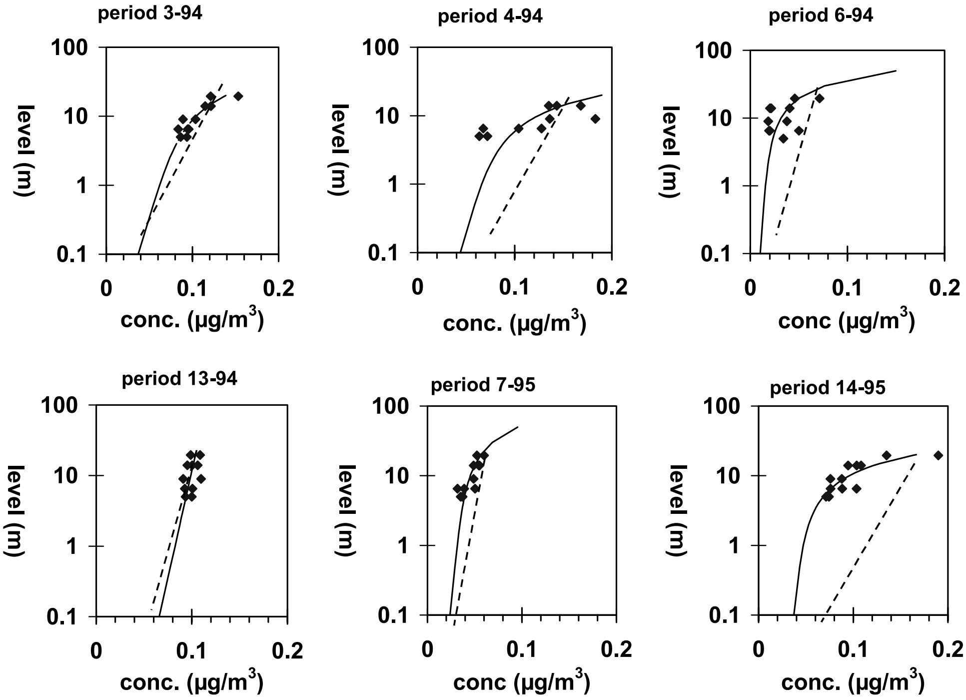

Figure 5. Measured vertical profiles of HNO_3 (diamonds) and the calculated profiles taking chemical reactions into account (solid lines) for the six measurement periods in the experiments in 1994 and 1995. The dotted lines show the profiles that would be expected if chemical reactions were not influencing the profiles. See color version of this figure in the HTML.

difference between the two calculated fluxes was more than a factor of two (period 4) and in another one the difference was close to a factor of two (period 6). For the measurement periods presented here, the calculation of surface fluxes using the resistance method traditionally used in atmospheric chemistry-transport models may be sufficient since the calculated fluxes here are very similar, however that may not be true for other cases. Large chemical removal rates can cause large differences in the surface flux estimations.

6. Discussion of the Heterogeneous Reactions

[28] In the present study the sink term ($S = k \cdot c$) in equation (8) describes the removal of HNO_3, where $c = [HNO_3]$ and k represents the removal rate, which we assume depends on the following four processes or parameters: (1) the surface area of the marine aerosol; (2) the transport in the atmosphere of the gas to the aerosol surface by molecular diffusion; (3) the adsorption or uptake at the surface; and (4) the conversion rate of HNO_3 to NO_3^-, which is a measure of available adsorption sites. Since it is assumed that the uptake/removal depends on sea spray, k derived using (8) and the measured profiles should correlate with the sea spray concentration. The chemical composition of the aerosols (Table 4) can be used as an indicator for the origin of the aerosols and enable us to identify sea spray aerosols and sea spray having reacted with nitric acid. $NaNO_3$ and NH_4NO_3 concentrations were calculated for the periods where data were available (see explanations in Table 4). *Geernaert et al.* [1998] suggested that the removal rate, k, could correlate with the NaCl concentrations. However, a scatterplot of k versus $[Na^+]$ (Figure 6) does not show a clear correlation. Nevertheless $[Na^+]$ was higher for the period (6–94), which had the largest flux divergence or k. Next a possible relation between k and $NaNO_3$ was investigated, with the rationale that $NaNO_3$ is produced from the reaction between HNO_3 and sea spray. The result in Figure 7 indicates increased k with increasing $NaNO_3$

Table 3. Surface Fluxes of HNO_3 Calculated for the Six Measurement Periods by the Three Different Approaches[a]

Period	Flux Using Equation (16) Fitting a Linear Regression to c Versus log (z), F (kg m^{-2} s^{-1}) × 10^{12}	Flux Calculated by the Use of the Resistance Method [*Asman et al.*, 1994], F (kg m^{-2} s^{-1}) × 10^{12}	Flux Using Equation (8) From 20 m to 0.1 m and Equation (9) From 0.1 m to the Surface, F (kg m^{-2} s^{-1}) × 10^{12}
3-94	3.49	0.99	0.77 ± 0.1
4-94	5.14	0.89	0.46 ± 0.19
6-94	1.94	0.39	0.24 ± 0.19
13-94	0.57	1.38	1.05–2.39
7-95	1.19	0.29	0.21 ± 0.03
14-95	1.69	0.27	0.16 ± 0.06

[a] The flux calculation in the last column is based on a calculated concentration at 0.1 m. The calculated concentration is derived from a measured profile, and the standard deviation on the measurements gives a standard deviation on the flux, which can be seen in the last column.

Table 4. Relative Humidity (RH), Rate Constant (*k*), and Chemical Concentrations During the Measurement Periods[a]

Period	Na^+, nmol m^{-3}	$NaNO_3$, nmol m^{-3}	NH_4NO_3, nmol m^{-3}	K^+, nmol m^{-3}	nss-SO_4^{2-}, nmol m^{-3}	NH_3, nmol m^{-3}	RH, %	*k*, s^{-1}
3-94	17.1	4.1	63.2	1.3	34.3	<10	~100	0.0028 ± 0.0087
4(+5)-94	5.0		50.3	0.8	44.4	<10	~100	0.0035 ± 0.029
6-94	57.9	8.9	3.1	0	7	<10	~100	0.0085 ± 0.014
13-94	14.3		83.4	3.4	77.2	<10	~90	0.00 ± 0.0057
7-95	9.0	3.5	28.2	0	35.0	~350		0.0017 ± 0.0052
14-95	7.6	5.2	347.7	4.7	302.4	~710		0.0057 ± 0.018

[a] The particle concentrations presented are averages of measurements at three/four different levels. The $NaNO_3$ concentration was calculated via the molar Cl^-/Na^+ ratio on the particle filter assuming that all Na^+ and Cl^- is sea salt derived, with a molar ratio of 1.166, and that any chloride loss is due to the reaction of HNO_3 with sea salt as suggested in data from the Baltic [*Pryor et al.*, 1999]. The NH_4NO_3 concentrations result from particulate NO_3^-, from which $NaNO_3$ is subtracted. Non-sea salt-sulphate (nss-SO_4^{2-}) was calculated using a mass ratio of $Na^+/SO_4^{2-} = 3.99$ in seawater. The estimated *k* is derived by making a best fit of the calculated profile to measured concentrations obtaining the least variance between measurement and calculated profile. The standard deviation reported in the last column is derived from the obtained variance.

concentration. However, since the data set is very small, this relation needs to be confirmed by more data obtained in different conditions. The lack of a strong correspondence between aerosol composition and *k* may be due to difficulty in relating local HNO_3 flux divergence as manifest in *k* with aerosol composition which is an integrated product of remote and local effects.

[29] Recent studies have shown that sea salt aerosol is produced over a very wide range of sizes from less than 100 nanometers to hundreds of micrometers [e.g., *O'Dowd et al.*, 1997; *Mårtensson et al.*, 2003], but measurements from impactors suggest that Cl^- depletion due to uptake of acidic gases is most pronounced for particle diameters of approximately 0.5–5 μm [*Martens et al.*, 1973; *Pryor et al.*, 1999, 2001], in the size range in which marine aerosols dominate the particle mass and surface area [e.g., *Harrison and Pio*, 1983]. For the present study, to estimate the sea spray surface that is available for accommodation of HNO_3, i.e., the surface of sea spray aerosol, the measured size distributions were integrated over the range from 0.75 μm to 5.25 μm diameter. It is assumed that this surface area is a reasonable surrogate for the total sea spray surface available for uptake, although it must be acknowledged that not all particles in this size range will be of marine origin, and the error in this assumption will depend on fetch and sources upwind other than sea spray, and further that some fraction of the sea spray surface will lie outside this range. Figure 8 shows a scatterplot of *k* versus (circles are the *k* estimated from measurements) surface area. In spite of the large scatter in *k* and the uncertainty in the surface area, the data indicate that the magnitude of *k* may increase with increasing surface. The statistical significance of such a speculation must be evaluated with more data to be collected in future studies.

[30] It is obvious from Figure 8 that the particles measured in period 3-94 and period 13-94 offer a larger surface area than the particles in period 4-94 and 7-95. However, since both periods 3-94 and 13-94 are sampled during short-fetch conditions (see Table 2), the large surface could be due to other types of particles which are either in equilibrium or do not react with HNO_3. In case 13-94 we expected to find $NaNO_3$ due to the presence of Na^+ (which concentration was similar to that in most of the other cases). However, consistent with a negligible removal rate and a wind speed decreasing during the sampling period, no $NaNO_3$ was measured, and indeed a surplus of chloride was found in the aerosol. Biomass burning was observed on the island and the concurrent highest observed potassium concentration, which is a good tracer for biomass burning, can explain the high chloride concentration, which could in part explain also the high Na concentration and the large amount of small particles. The easterly wind, which prevailed during that period, also causes the shortest possible marine fetch of only 2 km with very little sea salt production between the coastline and the measurement site. Thus also

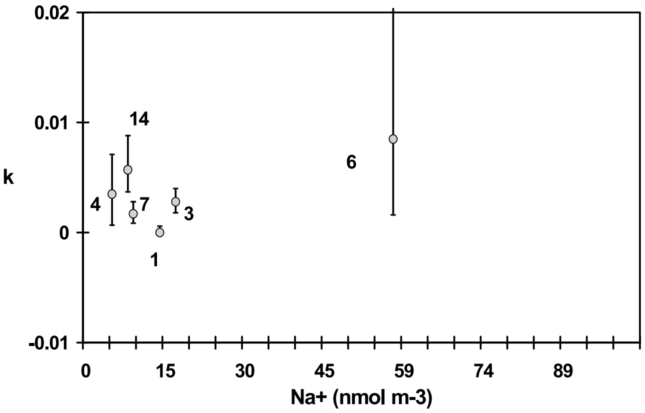

Figure 6. Estimated *k* versus Na^+. See color version of this figure in the HTML.

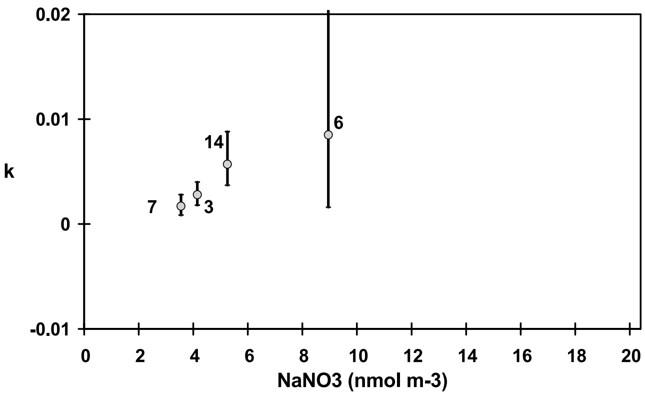

Figure 7. Estimated *k* versus $NaNO_3$. See color version of this figure in the HTML.

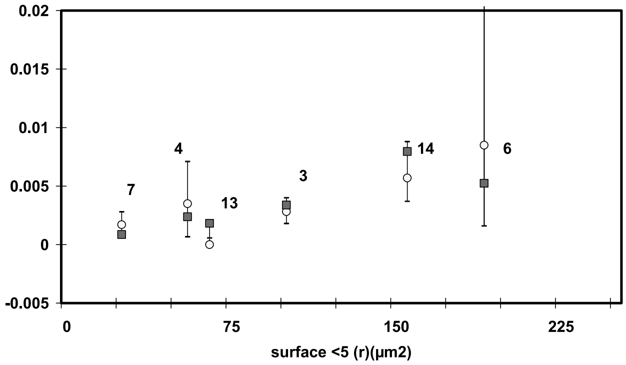

Figure 8. Values of k estimated from profile measurements (circles) and k values calculated from the model described in equations (17)–(19) (squares) versus the estimated sea spray surface. See color version of this figure in the HTML.

the influence of removal by heterogeneous reaction on the HNO_3 profile was expected to be smallest. Period 3-94 was also measured during short-fetch conditions but here we found slightly higher Na^+ concentrations than in case 13-94 for the same wind speeds. Also the removal rate for case 3-94 was higher than in case 13-94. The higher removal rate can be due to the higher relative humidity during period 3-94 (see Table 3). *Karlsson and Ljungström* [1994] measured the rate of replacement of Cl^- by NO_3^- on sea spray particles as a function of time and relative humidity, and showed that HNO_3 uptake is faster on wet particles and that the replacement rates are higher at higher temperature [*Hoffman et al.*, 2003].

[31] The highest removal rates are observed for the cases 14-95 and 6-94 (see Table 3), with case 6-94 having the highest sea salt concentration. We hypothesize that the chemical interaction profile can develop over the water to the southwest of the measuring site during high winds, due to the buildup of sea spray concentrations caused by breaking waves and surfs around the pier and the harbor in Onsevig (see Figure 3).

[32] With a much longer fetch but similar wind conditions, case 14-95 also shows considerable aerosol contributions from land based sources as is reflected by the high NH_4NO_3 and nss-SO_4 concentrations. *Pakkanen et al.* [1996] found that when 90% of the original Cl^- is released from the marine particles, the rate of replacement decreases, which indicates saturation. Despite reduced Na concentrations, $NaNO_3$ comprises 68% of the sea salt mass. Therefore the uptake of HNO_3 may be reduced in this case, resulting in a lower removal rate as deduced from the HNO_3 profile. This would imply that the sink term is not a first-order linear reaction since $\partial k/\partial z$ is not zero, however according to Figure 4 the vertical gradients of the aerosol surface are small.

[33] In order to investigate further the k values derived from the shape of the HNO_3 profiles and assess whether they can be caused by sea spray reactions we computed the expected uptake rate for HNO_3 on sea spray droplets using the model proposed by *Pakkanen et al.* [1996]. Using their relationship, under the assumption of spherical particles and surface-limited chemical reactions, the rate at which nitrate accumulates into a sea spray particle (I, in mol s^{-1}) is given by

$$I = \frac{2\pi D dp[\mathrm{HNO_3}]}{1+\beta}, \tag{17}$$

where

D diffusivity of HNO_3 ($m^2\ s^{-1}$);
dp particle diameter (m).

$[HNO_3]$ is concentration of HNO_3 (in this application we use the measured concentration from the uppermost measurement height) in mol m^{-3}:

$$\beta = \frac{2D}{k_s dp} \tag{18}$$

$$k_s = \frac{\gamma c}{4}, \tag{19}$$

where

γ reaction uptake coefficient;
c mean molecular speed of HNO_3 ($m\ s^{-1}$).

In this analysis we calculate the mean molecular speed according to sample temperature and diffusivity of HNO_3 according to the sample mean temperature based on the Fuller method [*Reid et al.*, 1987]. The particle size distribution is set according to the mean size distribution for each sample determined from the PMS data, and is confined to the size range 0.75–5.25 μm. Further following *Evans et al.* [2004] we assume the reaction uptake coefficient is 0.5 (as determined in the laboratory studies of *Guimbaud et al.* [2002]).

[34] The results (when normalized by concentration) are plotted in Figure 8 and demonstrate very good agreement with the values derived entirely independently from the HNO_3 profile. The discrepancies between the two estimates of k for any given sample may reflect variations in the particle size distribution during the sampling period, analytical uncertainties in the measurement of HNO_3 or possibly variations in the actual reaction uptake coefficient that in reality will vary according to the actual composition of the particles including the role of previous uptake of acidifying gases or the possible role of surfactants.

7. Conclusion

[35] It is shown that removal of HNO_3 from the atmosphere close to the sea surface is due to two processes: dry deposition to the sea surface and chemical reaction with sea spray. The latter process invalidates the application of the constant flux layer assumption to calculate dry deposition based on concentrations of HNO_3 at, e.g., a reference height of 10 m. Measured HNO_3 concentration profiles were found to differ from the log linear profiles, and hence surface fluxes of HNO_3 calculated from the measured profiles over estimate fluxes computed taking into account flux divergence due to uptake of HNO_3 on marine aerosol. HNO_3 loss rates to marine particles computed using the measured

profiles and a Bessel function compare very well with rates estimated from the observed particle size distribution and the model of *Pakkanen et al.* [1996]. The good agreement between the modeled and the measured *k* also supports the model parameterization of HNO_3 uptake on sea spray. It is important to note however that the data set used herein is small and more data, particularly fetch-dependent observations of sea spray profiles are needed to confirm our conclusions.

[36] The particles absorbing the HNO_3 will eventually deposit to the sea as well, thus implying that the nitrogen originating from the HNO_3 will still provide a contribution to the eutrophication of the marine waters. However, since the deposition velocities for particles are different from those for gases [*Pryor and Sørensen*, 2000] the amount of the deposited nitrogen to the water can be substantially different from model estimates on a local basis. This implies that more effort is needed to improve model performance when computing high-resolution variability of deposition.

[37] **Acknowledgments.** The field work received financial support from the U.S. Office of Naval Research, the Danish Environmental Research Program, and the Nordic Council of Ministers. We acknowledge support from the Nordic Centre of Excellence (BACCI), the E.U. contract MAST3-CT96-0058, and the E.U. contract EVK3-CT-1999-00014-MEAD for the data analysis; Sara Pryor also acknowledges support from NSF (ATM 0334321). Thanks are extended to Hans E. Jørgensen from Risø National Laboratory and Poul Hummelshøj from MetSupport Aps. for discussions on the flux calculations and the particle data interpretation. Measurements of the aerosol composition were performed by Elke Plate in the scope of her Ph.D. at the University of Hamburg. Measurements of HNO_3 and NH_3 were supported by Bjarne Jensen and Hanne Langberg, National Environmental Research Institute, Denmark. Meteorological measurements were supported by Jørgen Højstrup, Søren W. Lund, and Jan Nielsen from Risø National Laboratory, Denmark. Aerosol measurements were supported by Marcel Moerman, Leo Cohen, Gerard Kunz, and Lex Van Eijk from TNO-FEL, with financial support from ONR grant N00014-91-J-1948. Thanks to the technicians from NERI and RISØ for their helping hands every time it was needed and to Bent Christensen and "Inge" from Onsevig for sailing to the water mast in Vindeby.

References

Asman, W. A. H., R. M. Harrison, and C. J. Ottley (1994), Estimation of the net air-sea flux of ammonia over the southern bight of the North Sea, *Atmos. Environ.*, *28*, 3647–3654.

Asman, W. A. H., et al. (1995), Atmospheric nitrogen input to the Kattegat, *Ophelia*, *42*, 5–28.

de Leeuw, G. (1986), Vertical profiles of giant particles close above the sea surface, *Tellus, Ser. B*, *38*, 51–61.

de Leeuw, G. (1993), Aerosols near the air-sea interface, *Trends Geophys. Res.*, *2*, 55–70.

de Leeuw, G., F. P. Neele, M. Hill, M. H. Smith, and E. Vignati (2000), Sea spray aerosol production by waves breaking in the surf zone, *J. Geophys. Res.*, *105*, 29,397–29,410.

Duyzer, J. H. (1992), The influence of chemical reactions on surface exchange of NO, NO_2 and O_3, in *Precipitation Scavenging and Atmospheric-Surface Exchange*, edited by S. Schwartz and W. Slinn, pp. 1105–1114, Taylor and Francis, Philadelphia, Pa.

Evans, M., S. Campbell, V. Bhethanabotla, and N. Poor (2004), Effect of sea salt and calcium carbonate interactions with nitric acid on the direct dry deposition of nitrogen to Tampa Bay, Florida, *Atmos. Environ.*, *38*, 4847–4858.

Ferm, M. (1979), Method for determination of atmospheric ammonia, *Atmos. Environ.*, *13*, 1385–1393.

Geernaert, L. L. S., G. L. Geernaert, K. Granby, and W. A. H. Asman (1998), Fluxes of soluble gases in the marine atmospheric surface layer, *Tellus, Ser. B*, *50*, 111–127.

Guimbaud, C., F. Arens, L. Gutzwiller, H. W. Gäggeler, and M. Ammann (2002), Uptake of HNO_3 to deliquescent sea-salt particles, *Atmos. Chem. Phys. Disc.*, *2*(4), 739–763.

Harrison, R. M., and C. A. Pio (1983), Size differentiated composition of inorganic atmospheric aerosols of both marine and polluted continental origin, *Atmos. Environ.*, *17*, 1733–1738.

Hillamo, R. E., J. M. Pacyna, A. Semb, and J. E. Hanssen (1993), Size distributions of inorganic ions in atmospheric aerosol in Norway, in *Proceedings of the Workshop on the Development of Analytical Techniques for Atmospheric Pollutants, Rome, April 13–15 1992*, edited by I. Allegrini, *Air Pollut. Res. Rep. 41*, Comm. of the Eur. Commun., Brussels.

Hoffman, R. C., M. A. Kaleuati, and B. J. Finlayson-Pitts (2003), Knudsen cell studies of the reaction of gaseous HNO_3 with NaCl using less than a single layer of particles at 298 K: A modified mechanism, *J. Phys. Chem. A*, *107*, 7818–7826.

Hoppel, W. A., and G. M. Frick (1991), Effect of nonprecipitating clouds on the aerosol size distribution: Results of a cloud chamber study and atmospheric measurements, *Eos Trans. AGU*, *72*(44), Fall Meeting Suppl., 104.

Jeffrey, A. (1995), *Handbook of Mathematical Formulas and Integrals*, 401 pp., Elsevier, New York.

Joffre, S. M. (1988), Modelling the dry deposition velocity of highly soluble gases to the sea surface, *Atmos. Environ.*, *22*, 1137–1147.

Karlsson, R., and E. Ljungström (1994), Transformation and removal of N-compounds in the marine atmosphere, *Final Rep. ct90-0047*, Risø Natl. Lab., Roskilde, Denmark.

Kramm, G., and R. Dlugi (1994), Modelling of the vertical fluxes of nitric acid, ammonia and ammonium nitrate, *J. Atmos. Chem.*, *18*, 319–357.

Lenschow, D. H. (1982), Reactive trace species in the boundary layer from a micrometeorological perspective, *J. Meteorol. Soc. Jpn.*, *60*, 472–480.

Lenschow, D. H., and A. C. Delaney (1987), An analytical formulation for NO and NO_2 flux profiles in the atmospheric surface layer, *J. Atmos. Chem.*, *5*, 301–309.

Liss, P. S., and R. A. Duce (1997), *The Sea Surface and Global Change*, 519 pp., Cambridge Univ. Press, New York.

Logan, J. A. (1983), Nitrogen oxides in the troposphere: Global and regional budget, *J. Geophys. Res.*, *88*, 10,785–10,807.

Martens, C. S., J. J. Wesolowski, R. C. Harriss, and R. Kaifer (1973), Chlorine loss from Puerto Rican and San Francisco bay area marine aerosols, *J. Geophys. Res.*, *78*, 8778–8791.

Mårtensson, E. M., E. D. Nilsson, G. de Leeuw, L. H. Cohen, and H.-C. Hansson (2003), Laboratory simulations and parameterization of the primary marine aerosol production, *J. Geophys. Res.*, *108*(D9), 4297, doi:10.1029/2002JD002263.

Monin, A. S., and A. M. Obukhov (1954), Basic laws of turbulent mixing in the atmosphere near the ground layer of the atmosphere, *Trans. Geophys. Inst. Akad., Nauk USSR*, *151*, 163–187.

O'Dowd, C. D., M. H. Smith, I. E. Consterdine, and J. A. Lowe (1997), Marine aerosol, sea-salt, and the marine sulphur cycle: A short review, *Atmos. Environ.*, *31*, 73–80.

Pakkanen, T. A., V.-M. Kerminen, R. E. Hillamo, M. Mäkinen, T. Mäkelä, and A. Virkkula (1996), Distribution of nitrate over sea-salt and soil derived particles: Implications from a field study, *J. Atmos. Chem.*, *24*, 189–205.

Perrino, C., F. De Santis, and A. Febo (1990), Criteria for the choice of a denuder sampling technique devoted to the measurements of atmospheric nitrous and nitric acids, *Atmos. Environ., Part A*, *24*, 617–626.

Petelski, T. (2003), Marine aerosol fluxes over open sea calculated from vertical concentration gradients, *J. Aerosol Sci.*, *34*, 359–371.

Plate, E. (2000), Variabilität der Zusammensetzung anoorganischer Aerosole—insbesondere der reaktiven Stickstoffverbindungen—in küstennahen Gebieten der Nordsee und Ostsee, Ph.D. dissertation, Inst. of Inorg. and Appl. Chem., Univ. of Hamburg, Hamburg, Germany.

Plate, E., and M. Schulz (1997), Coarse nitrate formation in a coastal area of the North Sea, *J. Aerosol Sci.*, *28*, 333–334.

Pruppacher, H. R., and J. D. Klett (1997), *Microphysics of Clouds and Precipitation*, 976 pp., Springer, New York.

Pryor, S. C., and L. L. Sørensen (2000), Nitric acid-sea salt reactions: Implications for nitrogen deposition to water surfaces, *J. Appl. Meteorol.*, *39*, 725–731.

Pryor, S. C., R. J. Barthelmie, L. L. S. Geernaert, T. Ellermann, and K. D. Perry (1999), Speciated particle dry deposition to the sea surface: Results from ASEPS '97, *Atmos. Environ.*, *33*, 2045–2058.

Pryor, S. C., R. J. Barthelmie, J. T. Schoof, L. L. Sørensen, and D. J. Erickson (2001), Implications of heterogeneous chemistry of nitric acid for nitrogen deposition to marine ecosystems: Observations and modeling, *J. Water Air Soil Pollut.*, *1*(5/6), 99–107.

Quinn, P. K., R. J. Charlson, and T. S. Bates (1988), Simultaneous observations of ammonia in the atmosphere and ocean, *Nature*, *335*, 336–338.

Reid, R. C., J. M. Prausnitz, and B. E. Poling (1987), *The Properties of Gases and Liquids*, 741 pp., McGraw-Hill, New York.

Robbins, R. C., R. D. Cadle, and D. L. Eckhardt (1959), The conversion of sodium chloride to hydrogen chloride in the atmosphere, *J. Meteorol.*, *16*, 53–56.

Seinfeld, J. H. (1986), *Atmospheric Chemistry and Physics of Air Pollution*, 738 pp., John Wiley, Hoboken, N. J.

Sørensen, L. L., O. Hertel, B. Pedersen, M. Wagner, S. E. Larsen, J. Højstrup, M. Schulz, G. de Leeuw, and G. L. Geernaert (1994a), Horizontal transport modelling and exchange of atmospheric nitrogen gases with the coastal ocean, in *Proceedings of the 2nd International Conference on Air-Sea Interaction and Meteorology and Oceanography of the Coastal Zone*, pp. 208–209, Am. Meteorol. Soc., Boston, Mass.

Sørensen, L. L., K. Granby, H. Nielsen, and W. A. H. Asman (1994b), Diffusion scrubber technique used for measurements of atmospheric ammonia, *Atmos. Environ.*, *28*, 3637–3645.

Sørensen, L. L., S. C. Pryor, L. Spokes, and A. M. Sempreviva (2003), Air-sea fluxes of nitrogen compounds: Coastal Air Pollution Meteorology and Air-Sea Nutrient Exchange (CAPMAN), in *EUROTRAC-2 Subproject Final Report*, pp. 111–123, GSF-Nat. Res. Cent. for Environ. and Health, Munich, Germany.

Stull, R. B. (1988), *An Introduction to Boundary Layer Meteorology*, 666 pp., Springer, New York.

Tamm, S., and M. Schulz (2003), Open-ocean aerosol composition obtained during 15 months on a North Sea ferry, *Atmos. Environ.*, *37*, S133–S143.

Vignati, E., G. de Leeuw, and R. Berkowicz (2001), Modeling coastal aerosol transport and effects of surf-produced aerosols on processes in the marine atmospheric boundary layer, *J. Geophys. Res.*, *106*, 20,225–20,238.

Wesley, M. L., and B. B. Hicks (1977), Some factors that affect the deposition rates of sulfur dioxide and similar gases on vegetation, *JAPCA*, *27*, 1110–1116.

G. de Leeuw, TNO-Physics and Electronics Laboratory, P.O. Box 96864, 2509 JG The Hague, Netherlands. (deleeuw@fel.tno.nl)

S. C. Pryor, Atmospheric Science Program, Department of Geography, Indiana University, 701 E. Kirkwood Avenue, Bloomington, IN 47405, USA. (spryor@indiana.edu)

M. Schulz, Laboratoire des Sciences du Climat et de l'Environnement, CEA/CNRS–LSCE, L'Orme des Merisiers, Bat. 701, F-91191 Gif-sur-Yvette Cedex, France. (schulz@lsce.saclay.cea.fr)

L. L. Sørensen, Department of Wind Energy, Risø National Laboratory, Frederiksborgvej 399, DK-4000 Roskilde, Denmark. (lotte.geern@risoe.dk)