*Tellus (1998), 50B, 111–127*
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**TELLUS**
*ISSN 0280–6495*

# Fluxes of soluble gases in the marine atmosphere surface layer

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(Manuscript received 9 April 1996; in final form 6 November 1997)

ABSTRACT

Fluxes of $HNO_3$ and $NH_3$ to the sea-surface have been obtained from measurements of vertical concentration profiles. The obtained fluxes have been compared to fluxes calculated by the use of the resistance method, and the fluxes calculated from measurements based on the extrapolation of a log-linear profile were found to be an order of a magnitude higher than the fluxes obtained from the resistance method. The difference between these two calculated fluxes is explained by scavenging of the gases by sea-spray and chemical reactions. A simple model is constructed to calculate the vertical profiles for $HNO_3$ in the case of high chemical reactions. The high fluxes and the measured profiles are explained by the calculated profiles of $HNO_3$ where chemical reactions are taken into account. Since both sink/sources and horizontal inhomogeneity are influencing the $NH_3$ flux, it has not been possible to calculate profiles for this component by taking chemical reactions into account.

## 1. Introduction

The air-sea exchange of trace gases plays an integral rôle in coastal biogeochemistry, ecosystem dynamics, aerosol generation, cloud microphysics, air quality and climate. The nitrogen gases (e.g. $NH_3$ and $HNO_3$) can act as nutrients to the biomass in the sea. Nitrogen is often the limiting nutrient in the ocean for algae which very quickly take up $NO_3^-$ and $NH_4^+$. Input of atmospheric nitrogen to the sea is responsible for much of the increase in the growth of the algae mass (Paerl, 1985; Paerl et al., 1990). During periods of decay of the biomass $NH_3$ will be released again and at low atmospheric concentrations it will be emitted to the atmosphere (Quinn et al., 1988). The emitted $NH_3$ in turn, is suspected to react with HCl or $HNO_3$ in the marine atmosphere and form $NH_3Cl$ or $NH_3NO_3$ aerosol particles (Pruppacher and Klett, 1997). Furthermore $HNO_3$ can through reactions on the surface of NaCl particles contribute to changing the chemical composition of marine aerosols into $NaNO_3$ (Martens et al., 1973; Harrison and Pio, 1983; Finlayson Pits and Pits, 1986; and Pruppacher and Klett, 1997). Other gases, e.g., sulphur dioxide, participate in the formation of cloud condensation nuclei (ccn) (Pruppacher and Klett, 1997).

The problem of correctly parameterizing air-sea gas exchange can be generally categorized by two levels of difficulty. The simplest is the exchange of those gases which are dominated by physical processes only, i.e., they are not very soluble in water and have long life times compared to the scales of marine boundary layer turbulence, i.e., much longer than one minute. These gases, e.g., oxygen and carbon dioxide, can be considered as conservative constituents and classical Monin-Obukhov similarity theory may be readily

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employed. The second level of complexity includes gases which undergo chemical reactions in such a way that the vertical concentration profiles are modified depending on the reactions, and a vertical divergence of the gas flux is introduced. In this class, care must be taken in interpreting profile measurements when computing fluxes or deposition velocities (Lenschow and Delaney, 1987). Air-sea fluxes of those gases which have high affinity for water and are very reactive, e.g., ammonia and nitric acid, are difficult to handle, due to scavenging by and uptake involving seaspray and/or chemical reactions. While there has been some theoretical advance in understanding the important processes governing fluxes over land surface (Lenschow, 1982; Lenschow and Delaney, 1987; Brost et al., 1988; Duyzer, 1992, Kramm and Dlugi, 1994), there has been no significant advance in examining the role of sea spray and chemistry on the exchange of gases with the ocean. Vertical flux divergences introduce difficulties in estimating surface fluxes ($F_0$) of chemically reactive species from flux measurements in the boundary layer at elevations significantly above the surface.

In this work we report measurements of concentration profiles of two reactive gases using the traditional profile technique described by Monin-Obukhov similarity theory to estimate their surface fluxes. We focus on ammonia and nitric acid. We explain our findings of higher than expected fluxes by considering chemical processes in order to adjust both the profile and the magnitude of the surface flux.

In the next section we summarize the classical similarity theory supporting gas transfer, and follow with a presentation of the field data and discussion of processes taking place in the marine atmosphere. This is followed by a simple model which incorporates chemical reactions in order to explain our observations. We summarize thereafter with a set of recommendations for research required to close the problem of generalized air-sea gas exchange of chemicals.

## 2. Governing flux theory

Using the concept of conservation of a scalar quantity, and applying the conservation of mass and Reynolds averaging, the transport equation may be written as:

$$\frac{\partial \bar{c}}{\partial t} = -\bar{u}_i \frac{\partial \bar{c}}{\partial x_i} - \frac{\partial \overline{u_i' c'}}{\partial x_i} + D \frac{\partial^2 c}{\partial x_i^2} + S, \tag{1}$$

where $c$ is the concentration; $u_i$ is the wind velocity; $D$ is the molecular diffusion coefficient of the quantity $c$ in air; and $S$ is a source (positive) or a sink (negative) term which is an expression for the production or destruction rate of the chemical component.

The horizontal flux gradient term ($\partial \overline{u'c'}/\partial x$) is neglected since it is small compared to the advection term ($\bar{u}\partial\bar{c}/\partial x$). Assuming horizontal homogeneity for the flux term and noting that the vertical velocity becomes zero when averaging over a sufficiently long time ($>1/2$ h) and assuming that the molecular diffusion is insignificant when compared to turbulence processes, the vertical transport of the scalar quantity in the turbulent part of the atmospheric surface layer can now be expressed by:

$$\frac{\partial \bar{c}}{\partial t} + \frac{\partial \overline{w'c'}}{\partial z} + \bar{u}\frac{\partial \bar{c}}{\partial x} = S \tag{2}$$

In (2), the 2nd term on the left hand side is the flux divergence and the third term represents the advection term in the downwind direction.

We will assume that at any given point in space the concentration is not changing with respect to time. This does not mean that chemical reactions cannot take place, only the chemical reactions are to be treated as constant (at a constant removal/production rate or/and at equilibrium) over a relatively short averaging interval, like all other removal or production processes. A relatively short interval refers to a period where variabilities are not expected to naturally occur, e.g., typically less than a few hours. When the removal, dilution and production processes for c as well as meteorological conditions are constant there will be a steady state situation. We will hereafter assume steady state where $\partial\bar{c}/\partial t = 0$.

To simplify the equation, horizontal homogeneity is usually assumed so $\partial\bar{c}/\partial x$ can be neglected and eq. (2) is simplified to:

$$\frac{\partial \overline{w'c'}}{\partial z} = S. \tag{3}$$

When we apply the Monin–Obukhov similarity theory, where physical processes dominate, the vertical flux, $F$, of a conservative gas (where $S=$

0), can be written as:

$$F = \overline{w'c'} = -\frac{u^* \kappa z}{\phi_c} \frac{\partial c}{\partial z} = \text{constant}, \quad (4)$$

where $u^*$ is the friction velocity, $\kappa$ is the Von Karman constant ($\approx 0.4$), and $\phi_c$ is the stability function for a trace species. Because the function $\phi_c$ is not well known, it is assumed that $\phi_c$ can be expressed by $\phi_h$ (Businger, 1986; and Businger and Delaney, 1990).

The flux at the surface, $F_0$, can now be estimated from concentration profile data and micrometeorological measurements, using eq. (4), because the flux is assumed to be constant with height, i.e., $F_0 = F$. We will see in later sections that the term $S$ becomes important in characterizing the profiles and fluxes of $NH_3$ and $HNO_3$, and eq. (4) is an over-simplification for these 2 gases.

## 3. Experimental setup

As a part of the Danish Marine Research Programme, field experiments were carried out in order to estimate the dry deposition velocities of $NH_3$ and $HNO_3$ to Danish coastal waters. The experiment took place at the island Anholt in the Kattegat strait between Denmark and Sweden (Fig. 1) (Asman et al., 1994b; Asman et al., 1995). In order to estimate fluxes of $HNO_3$ and $NH_3$ vertical concentration profiles of $HNO_3$ and $NH_3$ were measured in a tower placed on the beach during three different field experiments: June 1991; March–April 1992; and June 1992. The measurement equipment were installed in a 10 m tower at different levels: $NH_3$ at heights of 2 m and 9 m, where only one instrument for measurements was located at each height, and $HNO_3$ at 2, 4, 6 and 8 meters height (Fig. 2), where two samples of $HNO_3$ were taken at each height. Using a mast

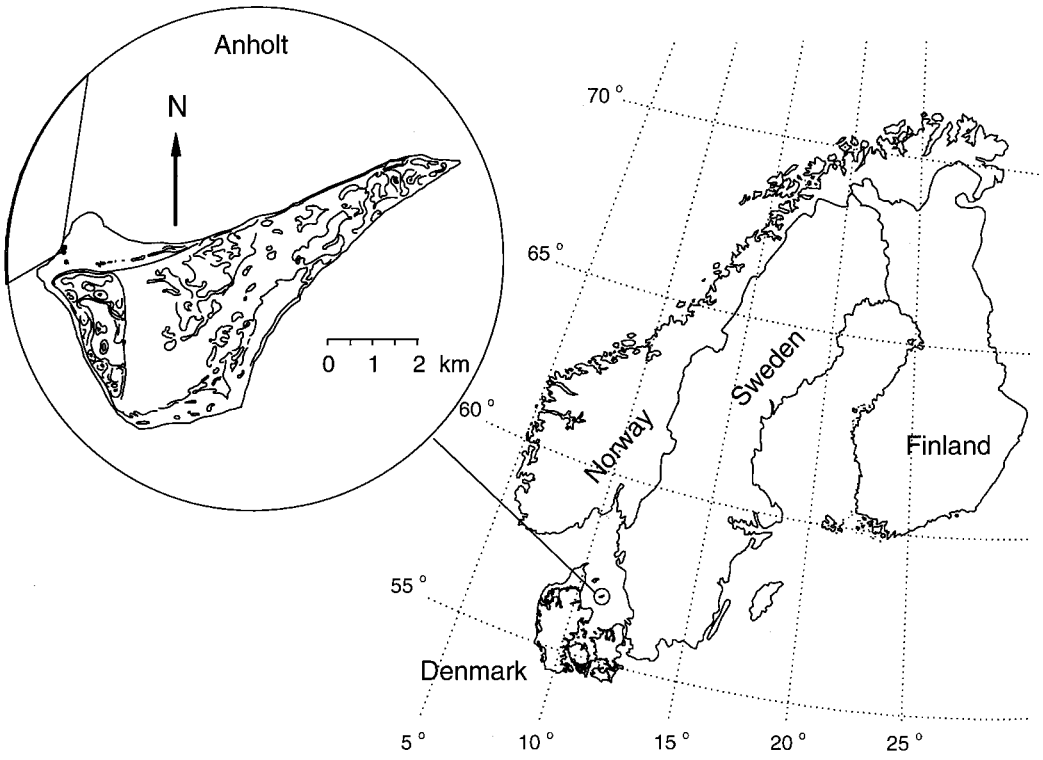


*Fig. 1.* Map showing Anholt placed in Scandinavia. The wind directions used for measurements are showed on the Anholt map.

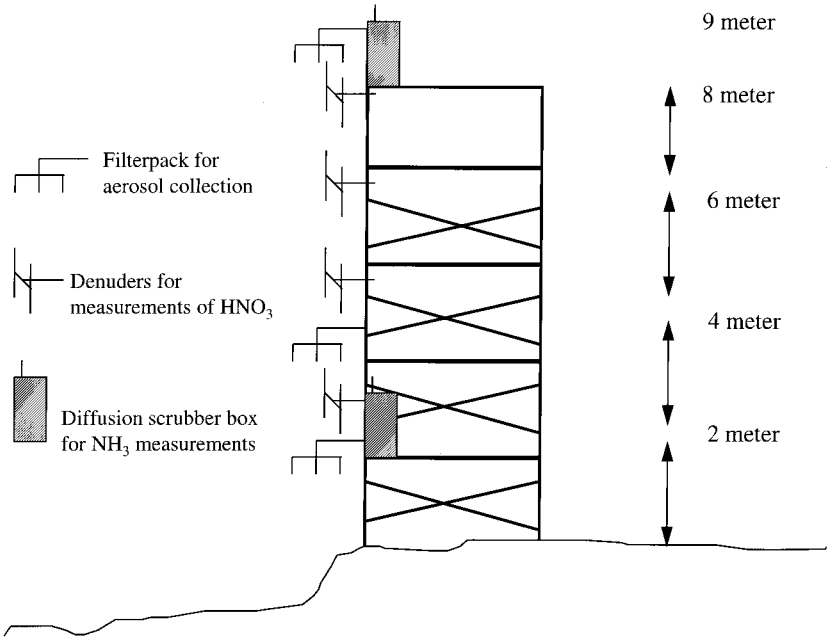


*Fig. 2.* The measurement tower including equipment at the island Anholt.

located 10 m from the tower in which the chemical measurements were collected, meteorological data including wind speed at three levels (4, 10 and 22 m) were obtained with cup anemometers, and temperature measurements at 2, 9.5 and 19.5 m, a vane was used for wind direction. Fluctuations in wind velocities and temperatures and their statistical characteristics were measured using an ultrasonic anemometer which was placed at the 22 m level (Gryning, 1993; Batchvarova and Gryning, 1994). $HNO_3$ was collected in NaCl coated denuders, with a collection flow of $1.5\,l\,min^{-1}$ (Perrino et al., 1990; Asman et al., 1994b) and the sampling time ranged from 3 to 6 h, depending on the meteorological conditions. The sampling time was manually controlled, which means that the denuders were taken down if the wind direction changed. The sampling time during night measurements were in general longer for practical reasons. $NH_3$ was measured using diffusion scrubbers (Sørensen et al., 1994a, 1994b; Asman et al., 1994b; Genfa et al., 1989) having 10 min sampling time. This is an automatic collection and measurement device which operates continously. The limit of detection for the $HNO_3$ denuder method differed between $0.06\,\mu g\,N\,m^{-3}$ and $0.19\,\mu g\,N\,m^{-3}$ over the three experiments and the relative standard deviation on the reproducibility was 15%. For the $NH_3$ diffusion scrubber the limit of detection was measured to be in the range $0.007\,\mu g\,m^{-3}$ to $0.07\,\mu g\,m^{-3}$, and the relative standard deviation on the reproducibility was 10%. The $NH_3$ data were collected in two different field experiments, spring 1992 and summer 1992. Only the measurements for wind directions between 230° and 30° were used in order to measure air of marine origin (Fig. 1). Samples of $NH_4^+$ and $NH_3$ concentrations in the water were also collected to complement the atmospheric measurements.

## 4. Data analysis

By focussing on near neutral conditions, only measurements from sampling periods with numerically large values of the Monin-Obukhov length are used in order to avoid uncertainties introduced by stability corrections. The fluxes obtained from profile measurements using eq. (4) were compared to fluxes calculated from parameterization by the resistance method.

The flux is defined by a transfer velocity (Weseley and Hicks, 1977; Joffre, 1988; and Kramm, 1989)

$$F = v_t(c - c_s), \tag{5}$$

where $v_t$ is parameterized by resistances terms: $r_a$, the aerodynamic resistance governing the turbulent transport; and $r_b$, the surface resistance, governing the diffusion transport over the laminar sublayer. By definition,

$$v_t = \frac{1}{r_a + r_b}. \tag{6}$$

The aerodynamic resistance is derived from the flux-gradient relationship (eq. (4)):

$$r_a = \int_{z_0}^{z_r} K^{-1}\,dz = \frac{1}{\kappa u^*}\left[\ln\frac{z_r}{z_0} - \psi_h\left(\frac{z_r}{L}, \frac{z_0}{L}\right)\right], \tag{7}$$

where $z_r$ is the height of the reference level, $z_0$ is the roughness height, $K$ denotes the turbulent diffusivity ($K = u^* z\kappa/\Phi$), $\psi_h$ is the integrated stability function and $L$ is the Monin–Obukhov length.

The 2nd term, based on the underlying thin molecular turbulent sublayer is (Kramm, 1989; Kramm et al., 1991; and Kramm and Dlugi, 1994) given by:

$$r_b = \int_{z_s}^{z_0} (D_i + K)^{-1}\,dz = \frac{1}{u^*}\left(\frac{u_{z_0}}{u^*} + B_i^{-1}\right), \tag{8}$$

where $z_s$ is the surface, $u_{z_0}$ is a characteristic velocity for the layer $z_s < z < z_0$, $D_i$ is the diffusion coefficient for the gas $i$, and $B_i^{-1}$ is the sublayer Stanton number, which is a function of the roughness Reynolds number, $\mathrm{Re}^* = u^* z/v$ and the Schmidt number, $\mathrm{Sc}_i = v/D_i$, which include the kinematic viscosity of the air, $v$. The Stanton number can be estimated from the following equation:

$$B_i^{-1} = a Sc_i^b\,\mathrm{Re}^{*c} + \varepsilon, \tag{9}$$

where the following values are suggested for smooth surfaces $a = 13.6$, $b = 2/3$, $c = 0$ and $\varepsilon = -15.5$; and for rough surfaces, $a = 7.3$, $b = 0.5$, $c = 0.25$ and $\varepsilon = -5$ ((Kramm and Dlugi, 1994).

The transfer over the surface can also be expressed by a resistance $r_s$ (surface resistance). Here we will consider $r_s \sim 0$ since $HNO_3$ and $NH_3$ are both very soluble and rapidly taken up by the surface. Therefore $r_s$ is considered to be low compared to $r_b$ and $r_a$.

Joffre, (1988) and Asman et al. (1994a) also used the resistance approach. Again from integration of eq. (4) over 2 sets of ranges the following is obtained:

$$r_a(z) = \frac{1}{\kappa u^*}\left[\ln\frac{z}{z_0} - \psi_h\left(\frac{z}{L}\right) + \psi_h\left(\frac{z_0}{L}\right)\right], \tag{10}$$

and

$$r_b = \frac{1}{\kappa u^*}\ln\frac{z_0}{z_{0_c}}. \tag{11}$$

In (11), $z_0$ is after Asman et al. (1994a) estimated from:

$$z_0 = \frac{0.13v}{u^*} + \frac{0.0144u^{*2}}{g}, \tag{12}$$

and $z_{0_c}$ is here defined as the surface roughness length for the gas. The parameter $z_{0_c}$ refers to the level where the gas concentration becomes zero or has reached equilibrium concentration with the water phase as, i.e., $NH_3$. In Joffre (1988) and Asman et al. (1994a) $z_{0_c}$ was computed for smooth conditions ($\mathrm{Re}^* < 0.13$) from:

$$z_{0_c} = 30(v/u^*)\exp[-13.6\kappa\,\mathrm{Sc}^{2/3}], \tag{13}$$

and for rough conditions ($\mathrm{Re}^* > 0.13$) from

$$z_{0_c} = 20 z_0 \exp[-7.3\kappa\,\mathrm{Re}^{1/4}\,\mathrm{Sc}^{1/2}]. \tag{14}$$

The parameterization using the resistance approach has been described in detail in several papers i.e., Weseley and Hicks, (1977), Kramm (1989), Müller et al. (1993) and Kramm and Dlugi (1994). The reader is referred to these papers for specifics on the various parameterizations. In this study, we will use the two parameterizations described here for comparison to the measurements.

The fluxes during the experiments were determined in two ways: first from use of the resistance method, which is presented above in eqs. (5)–(9), and second from the profiles of concentration measurements. We compute the fluxes by using eq. (4) and the measured profiles. Eq. (4) can be rewritten as:

$$c(z) = bX + a, \tag{15}$$

where

$$b = \frac{-F_c}{\kappa u^*} \tag{16}$$

$$X = \ln z, \tag{17}$$

and

$$a = b[-\ln z_{0_c}] + c_s. \tag{18}$$

The flux can be estimated from the linear slope of the profile (eqs. (15) and (16)) when the concentration $c(z)$ is plotted against $X$.

To be able to estimate the surface flux it is necessary to know the equilibrium concentration at the surface, $c_s$. The equilibrium between the gasseous and dissolved phase of a compound in water can be expressed by the Henry's law coefficient,

$$[G(\text{aq})] = H_G[G(g)], \tag{17}$$

where $[G(\text{aq})]$ is the concentration of the equilibrium amount of dissolved gas $G$ in solution, $[G(g)]$ is the equilibrium concentration in the gas phase, and $H_G$ is the Henry's law coefficient (mole $l^{-1}$ $atm^{-1}$), which is an equilibrium coefficient. The solubility of $HNO_3$ is very high and the Henry's law coefficient for $HNO_3$ dissolving in liquid water at 298 K is $2.1 \times 10^5$ (Seinfeld, 1986), which is much higher than the Henry's law coefficient for $NH_3$ (Henry's law coefficient = 62) and $SO_2$ (Henrys law coefficient = 1.24). The Henrys law coefficient depends on temperature, and the ionization of the compound in water depends on pH and salinity (Asman et al., 1994a). This surface concentration is the same as the equilibrium concentration:

$$NH_4^+(\text{aq}) + OH^- \Leftrightarrow NH_3(\text{aq})H_2O \Leftrightarrow NH_3(\text{g}). \tag{20}$$

Emission of $NH_3$ from the sea will take place, if the actual atmospheric $NH_3$ concentration is less than the gas phase concentration calculated from the equilibrium eq. (20). If the concentration in the atmosphere is higher than the equilibrium concentration the flux will be downward to the surface. Asman et al. (1994a) have computed $NH_3$ fluxes over the southern bight of the North Sea, and they used the following equation to estimate the $NH_3$ concentration at the surface:

$$c_{eq} = \frac{M_{NH_3}[NH_{xs}]}{RTH_{NH_3}\left[\dfrac{1}{\gamma_{NH_3}} + \dfrac{10^{-pHs}}{\gamma_{NH_4} K_{NH_4}}\right]}, \tag{21}$$

where $c_{eq}$ is the $NH_3$ concentration in the atmosphere at the surface in equilibrium with $[NH_{xs}]$, which is $[NH_3 + NH_4^+]$ in the sea water. $M_{NH_3}$ is the molecular mass of $NH_3$, $K_{NH_3}$ is the activity coefficient of $NH_3 \cdot H_2O$, $K_{NH_4}$ is the activity coefficient of $NH_4^+$ in sea water, $R$ is the gas constant, $H_{NH_3}$ is the Henry's law constant for $NH_3$, $pH_s$ is the pH of sea water, and $K_{NH_4}$ is the dissociation constant for $NH_4^+$. The Henry's law constants and dissociation constants are described in Asman et al. (1994a). For the calculation of the equilibrium concentration we used the same approach as Asman et al. (1994a).

Since the uptake of $HNO_3$ in water is irreversible it is safe to assume that the surface concentration, $c_s$, of $HNO_3$ is zero for flux computations. This assumption will generally not hold for $NH_3$ therefore measurements of $NH_4^+$ in the sea water were collected to estimate $c_{eq}$.

We assume $NH_3$ emissions to be related to algae growth and decay and therefore related to the season. As a consequence the data base of $NH_3$ fluxes has been divided into two different subsets for evaluation, a spring and a summer data set. In the spring season data set, the surface concentration for $NH_3$ is on the average $0.02\ \mu g \cdot m^{-3}$, and it is $0.2\ \mu g \cdot m^{-3}$ on average for the summer data set. Note that these averages of $c_s$ for $NH_3$ were determined from estimations of the equilibrium concentration obtained from water measurements. These average values are used as a surface concentration to compare seasonal fluxes in our study.

Examples of 4 measured typical $HNO_3$ profiles, with different slopes, are shown in Fig. 3. Two measured concentrations are shown for each height which give an impression of the scatter in the measurements of the chemical concentration. The dashed line in Fig. 3 shows the extrapolated profile using the measurements and the dotted line shows the expected profile which corresponds to similarity flux theory in the absence of source/sink processes (i.e., eqs. (15–16)).

First the two parameterizations based on the resistance method are compared and the results

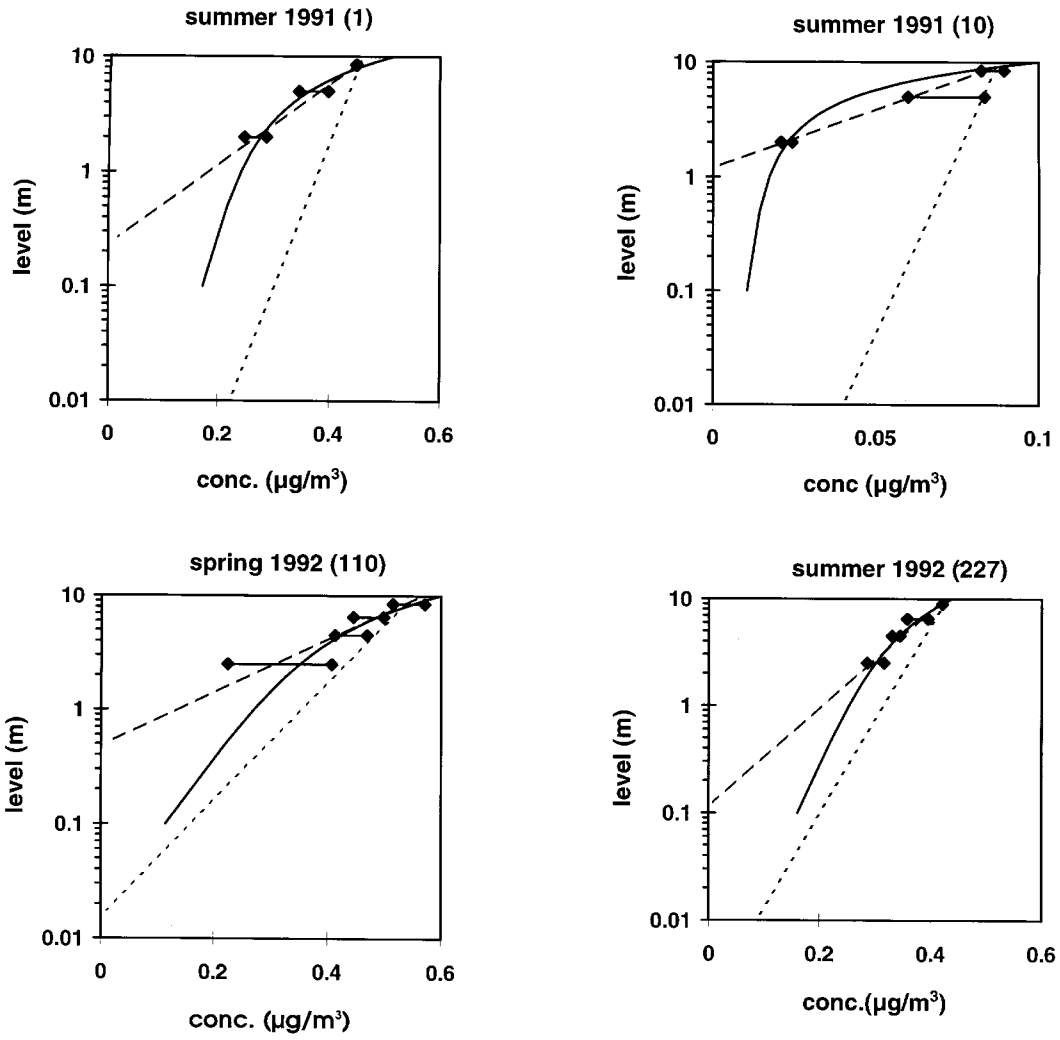


*Fig. 3.* Examples of the measured and calculated $HNO_3$ profiles. Two samples of HNO3 were taken at each hight at each measurement period. The measurements are shown by the diamonds.

| | |
|---|---|
| dashed line: | gradient from extrapolation of the measured concentrations |
| diamonds: | measured concentration of $HNO_3$ |
| dotted line: | gradient calculated from the resistance theory |
| full line: | gradient caculated when a sink term is taken into account |

are plotted in Fig. 4. The comparison shows that there is close agreement between the two parameterizations, which was expected, since they both are based on the resistance approach, but use two different approach to estimate $z_0$.

The flux estimated from chemical profile measurements is plotted in Figs. 5, 6, and 7, against the flux calculated from the resistance method. For $HNO_3$, the flux estimation from profiles are 4 times higher than the fluxes calculated from the resistance method assuming negligible surface resistance and extrapolation of a log-linear profile. It is clear that an upward flux for $NH_3$ exists, and the fluxes for $NH_3$ estimated from profiles are on the average 10 times higher in both field experiments, than expected from the resistance para-

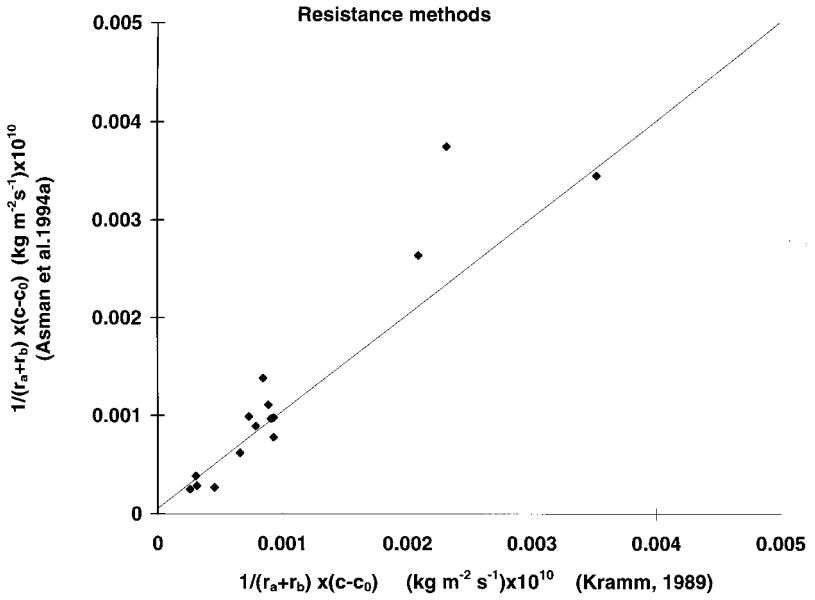


*Fig. 4.* Comparison of $HNO_3$ fluxes calculated by thee use of the two different parameterizations described in eqs, (5)–(9) and eqs. (10)–(14).

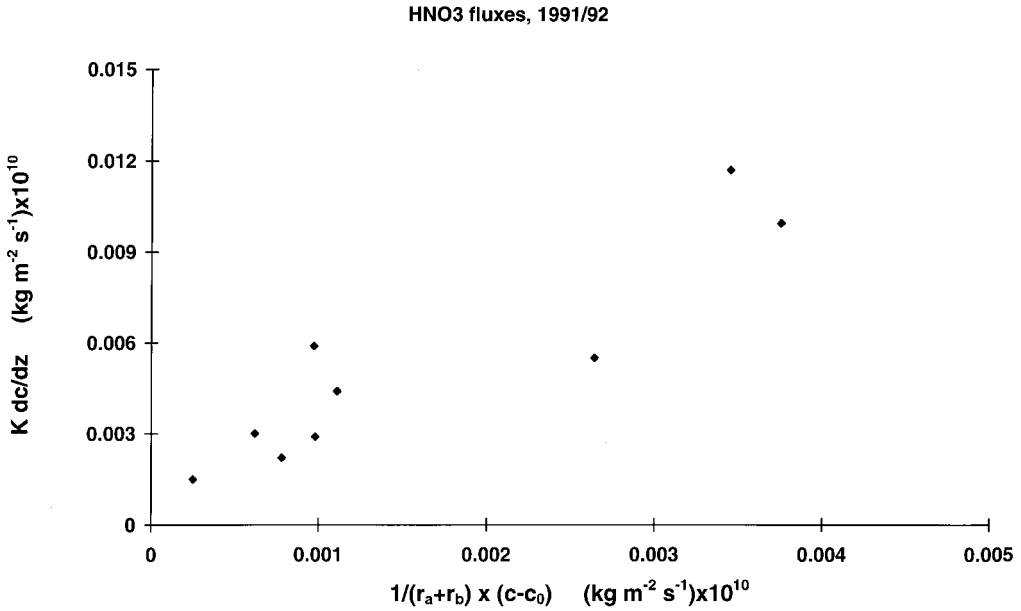


*Fig. 5.* Comparison of $HNO_3$ fluxes caculated from the resistance method and calculated from the gradients (chemical reactions are not taken into account). The measured gradients used for the caculation are taken from the experiments in 1991 and 1992.

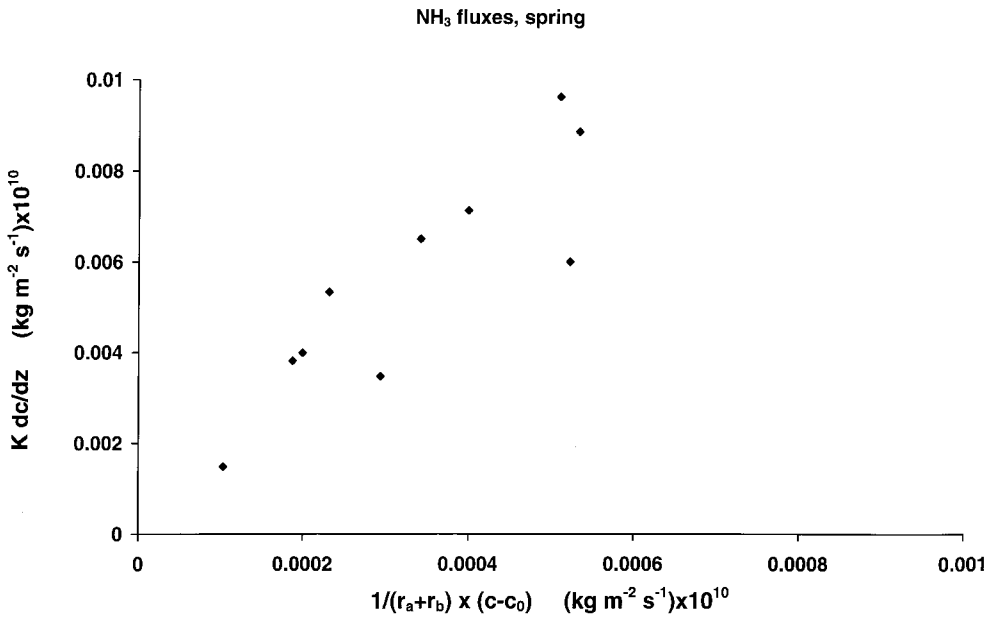


*Fig. 6.* Comparison of $NH_3$ fluxes caculated from the resistance method and calculated from the gradients (chemical reactions are not taken into account). The measured gradients used for the caculation are taken from the experiment in spring 1992.

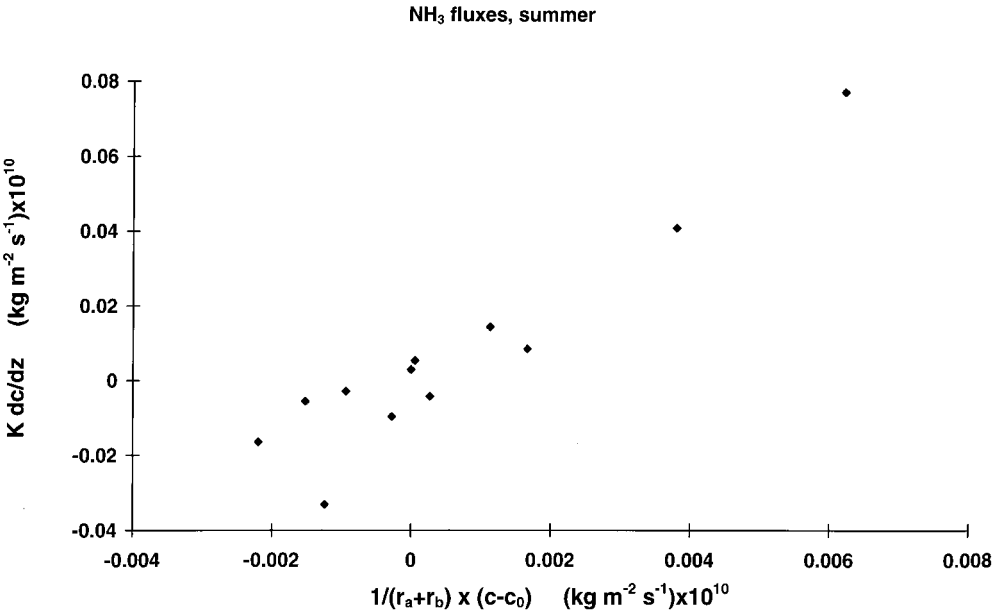


*Fig. 7.* Comparison of $NH_3$ fluxes caculated from the resistance method and calculated from the gradients (chemical reactions are not taken into account). The measured gradients used for the caculation are taken from the experiment in summer 1992.

Table 1. Comparison of estimated fluxes and deposition velocities for $HNO_3$ and $NH_3$ to sea surfaces

| | Reported by Lenschow and Hicks (1989) | | Calculated from parameterization | | Calculated from measured gradient | |
|---|---|---|---|---|---|---|
| | $V_d$ (cm s$^{-1}$) | $F$ (kg m$^{-2}$ s$^{-1}$) $10^{12}$ | $V_d$ (cm s$^{-1}$) | $F$ (kg m$^{-2}$ s$^{-1}$) $\times 10^{12}$ | $V_d$ (cm s$^{-1}$) | $F$ (kg m$^{-2}$ s$^{-1}$) $10^{12}$ |
| $HNO_3$ | 0.3–0.7 | | 0.4–1.1 | 0.2–3.7 | 1.1–6.9 | 1.5–11.7 |
| $NH_3$ | | $\pm$(0.1–1.0)[a] | | −0.2–0.6 | | —3.3–7.7 |

[a] Flux data for oceans are not reported. This flux is for tropic area.

Table 2. Roughness lengths ($Z_0$), $Z_{0_c}$ calculated from eqs. (13) and (14) and $Z_{0_c}$ calculated from the measured concentration profiles at different friction velocities

| $U^*$ (m s$^{-1}$) | $Z_0$ (m) | $Z_{0_c}$ calculated (m) | $Z_{0_c}$ measured (m) |
|---|---|---|---|
| 0.241 | 0.000056 | 0.000045 | 0.44 |
| 0.337 | 0.000093 | 0.000038 | 0.76 |
| 0.189 | 0.000204 | 0.000054 | 1.85 |
| 0.252 | 0.000045 | 0.000029 | 1.41 |
| 0.099 | 0.00052 | 0.000062 | 1.05 |

meterization. One is reminded that the flux computations using concentration profile measurements were based on the assumptions of no flux divergence and $S=0$. The two flux calculations are both based on similarity theory and the same set of assumptions. Due to chemical reactions the profile differ from the expected log-linear profile and when extrapolating the concentration profile in a log-linear way, the concentration reaches zero high above the surface (Table 2), which leads to an overestimation of the flux. The deposition velocities ($v_d = v_t$ for highly soluble gases) and fluxes for $HNO_3$ and $NH_3$ estimated from the two different methods are compared to reported fluxes and deposition velocities (Lenschow and Hicks, 1989) in Table 1. There is a very good agreement between the $v_d$ estimated by the resistance method and the reported $v_d$ by Lenschow and Hicks (1989).

## 5. Chemical reactions

It is hypothesized that the steeper profiles and higher fluxes are due to chemical reactions affecting the profiles. The estimation of the flux based on eq. (4) is valid for conservative compounds only. For reactive trace gases a source or sink in the air will exist and $S$ must be parameterized. We will soon see that a non-zero value of $S$ will produce a non log-linear extrapolation of the concentration profiles towards the surface, resulting in smaller $Z_{0_c}$ and smaller flux.

The source/sink term includes processes such as sea spray evaporation, chemical reactions between the gas of interest and other gases, and heteorogeneous reactions between particles and gases. Depending on the reaction rate for the chemical reaction the source/sink term will cause the flux to vary with height as is shown in eq. (3) (Lenschow, 1982; Fitzjarrald and Lenschow, 1983; Lenschow and Delaney, 1987; Brost et al., 1988; Duyzer, 1992; Kramm and Dlugi, 1994). Combining eq. (3) with eq. (4) one obtains:

$$-u^*\kappa \frac{\partial}{\partial z}\left( z \frac{\partial c}{\partial z} \phi^{-1} \right) - S = 0 . \qquad (22)$$

If we consider the case where $S$ is governed by chemical processes only, then at equilibrium the produced amount of the compound will be the same as the amount of the compound removed so $S=0$. On the other hand if a net production or net removal of the compound takes place $S \neq 0$. A

removal will take place if a specie which reacts fast with the component of interest is introduced into the system. If the reaction time scale is comparable to or less than the turbulent mixing time scales, significant departures from chemical equilibrium can occur, as has been shown by Lenschow (1982), Fitzjarrald and Lenschow (1983) and Vilá-Guerau de Arellano et al. (1995).

The following set of chemical reactions is important to the fluxes of $NH_3$ and $HNO_3$ in the marine atmospheric surface layer:

(I) $HNO_3 + NH_3 \Leftrightarrow NH_4NO_3$
(II) $NO_2 + OH \Rightarrow HNO_3$
(III) $HNO_3 + NaCl \Rightarrow HCl + NaNO_3$
(IV) $2NH_3 + H_2SO_4\ (<) \Rightarrow (NH_4)_2SO_4$
(V) $NH_3 + HCl \Leftrightarrow NH_4Cl$

For the flux of $HNO_3$ and $NH_3$, the source/sink at height $z$ will be:

$$S = [NO_2][OH]k_2 - [HNO_3][NaCl]k_3 - [HNO_3][NH_3]k_1$$

$$S = -[HNO_3][NH_3]k_1 - [NH_3]^2[H_2SO_4]k_4 - [NH_3][HCl]k_5$$

where $k_1$, $k_2$, $k_3$, $k_4$ and $k_5$ are reaction rates for the five reactions.

Kramm and Dlugi (1994) have specifically examined reaction (I) which produces or reduces $HNO_3$ and $NH_3$, and they compared the time scales for this reaction. They found that the chemical time scale is comparable to the turbulent time scale so this reaction must be taken into account.

Reaction (II) constitutes the main production of $HNO_3$ which depends on the photochemical conditions. Reaction (IV), which is a second order reaction, is considered to be irreversible, and $NH_3$ is believed to be taken up by the $H_2SO_4$ very quickly (Seinfeld, 1986). Referring to reaction (III) the reaction between NaCl and $HNO_3$ is known to be fast (Fenter et al., 1994), but there is no reaction rate reported for the reaction with wet NaCl particles. The reaction between the NaCl and the $HNO_3$ takes place on the NaCl particle surface (i.e., Martens et al., 1973, Mamane and Gottlieb, 1992 and Pakkanen et al., 1996) and as a consequence the total aerosol surface is more important than the mass. Due to a high number of NaCl particles introduced by sea spray to the marine atmosphere, reaction (III) is hypothesized to be very important for the removal of $HNO_3$ in this domain. The reaction rates and the concentrations are not well known for any of the three reaction equations (III), (IV) and (V).

## 6. Sea spray effects: hypotheses and assumptions

Sea spray is produced mainly by bursting bubbles at the sea surface, which eject sea spray into the air, but bubbles are not the only source of droplets. When the wind speed reaches 9 m $s^{-1}$, the wind is strong enough to tear off the wave crests and propel spray directly into the air. The sea spray produced by the second mechanism contains typically the largest sea spray droplets with radii greater than 10 μm. Sea spray droplets are saline; when a droplet evaporates, it leaves behind a microscopic sea-salt particle that the wind can easily carry long distances.

At wind speeds in excess of 13 m $s^{-1}$, there is a rapid increase in the observed sea salt aerosol concentration of large sizes (Monahan et al., 1983; Fairall et al., 1983). As the wind speed increases beyond 13 m $s^{-1}$, the number of spray droplets produced increases by several order of magnitude. As a result, in high winds, sea spray droplets effectively increase the oceanic surface area. Spray thus has the potential for enhancing the transfer of all constituents that are exchanged at the air-sea interface (Andreas, 1989).

As mentioned in Section 5, $HNO_3$ reacts with NaCl. Therefore NaCl flux or fluxes of sea spray from the water surface may lead to a significant violation of the constant flux layer hypothesis for $HNO_3$ due to the important role of the sink function in this case.

To complicate the problem more, $NH_3$ may also be influenced by sea spray. $NH_3$ does not react with the NaCl, but it will react with the water drops. Due to the lower solubility of $NH_3$ when compared to $HNO_3$ it is hypothesized that $NH_3$ will not be influenced by the sea spray to the same extent as $HNO_3$. However formation of HCl from the reaction between $HNO_3$ and NaCl may result in reactions between $NH_3$ and HCl which likely influence the $NH_3$ flux, but also reactions between $HNO_3$ and $NH_3$ may be important (Kramm and Dlugi, 1994). Many of the hypotheses posed above are beyond the scope of this paper, but they will serve as assumptions

supporting the present study and also subjects for future study.

## 7. Flux profile relationship including chemistry

There was insufficient information on the concentrations of many of the chemical constituents involved in reactions with $NH_3$, and the measured profiles of $NH_3$ were not sufficiently detailed; therefore, for the analysis of the concentration profiles we focus our analysis in this paper exclusively on $HNO_3$. Reaction (I) is in this case considered to be neglectable since we found low concentrations of $NH_3$ for all the measurements as is shown in Fig 8. Here it is assumed that the production of $HNO_3$ is vertically and horizontally homogeneous and in steady state. With these assumptions, we may write:

$$S_{NHO_3} = \frac{d[HNO_3]}{dt} = -[HNO_3][NaCl]k_3 . \quad (23)$$

Here, we use a very simple description for the reaction between $HNO_3$ and the sea spray particles. Ideally [NaCl] must be described in terms of particle or sea spray surface area. Also the reaction rate $k_3$ depends on several parameters, i.e., diffusivity of the gas and the accomodation coefficient, (refer to Martens et al, 1973; and Luther and Peters, 1982, for more details).

Using eq. (22) and assuming that the stability correction (since we consider neutral conditions only) can be neglected we get the following equation:

$$\int \frac{\partial}{\partial z}(\kappa u^* \left(z + z_0\right)\frac{\partial c}{\partial z}) = k \cdot c \quad (24)$$

Here $k_c = k_3[NaCl][HNO_3]$, since for simplicity we assume that the size distribution of the sea spray (here [NaCl]) is constant in the vertical direction up to at least 10 m, so that $k_3[NaCl]$ can be denoted by a constant $k$, which here is defined as a scavenging rate. This will enable us to find an analytical solution to the eq. (24). We are aware of the fact that the assumption of the sea spray size distribution being constant in vertical direction might not always be valid. Measured NaCl concentrations, which give an

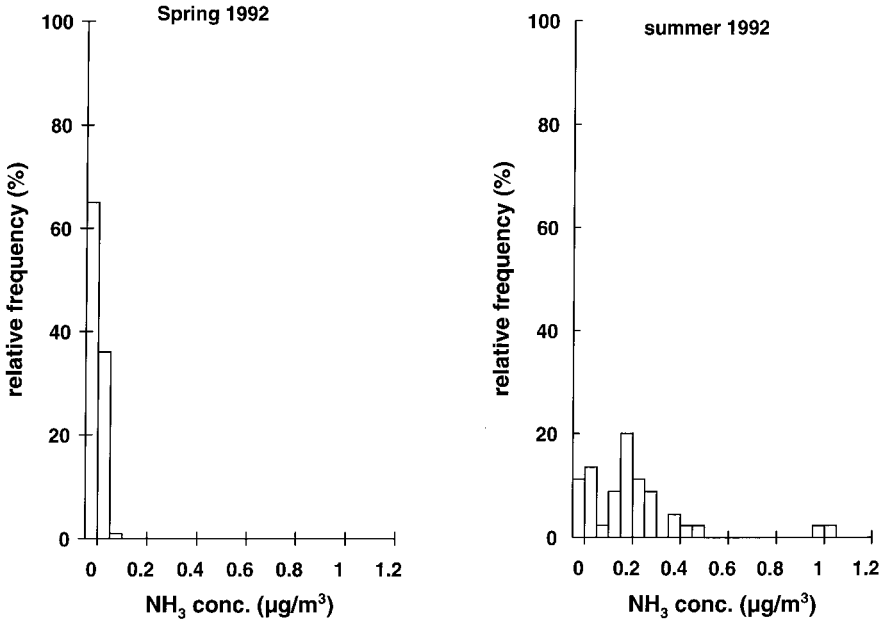


*Fig. 8.* The concentration of $NH_3$ measured in spring 1992 and summer 1992. The plots show the relative frequency of occurence of the concentration.

indirect estimate of the sea spray profiles are shown in Fig. 9. It is clear that the concentration at the lowest level (2–3 m) is higher than the concentration at higher elevation even at low windspeeds. The high concentration at the lowest elevations can be explained by upwind wave breaking at the beach.

The concentration of $c$ (in this case $HNO_3$) is assumed to be zero at the surface. This equation can be solved analytically by letting $Z = z + z_0$ and following is obtained:

$$\frac{\partial}{\partial Z}\left(\kappa u^* Z \frac{\partial c}{\partial Z}\right) = k \cdot c \tag{25}$$

Letting $Z = x^2$, $a = k/u^*\kappa$ and $\partial Z = 2x\partial x$;

$$\frac{1}{x}\frac{\partial}{\partial x}\left(x \frac{\partial c}{\partial x}\right) = 4ac\,, \tag{26}$$

which gives

$$x^2 c''(x) + c'(x) - 4ax^2 c(x) = 0\,. \tag{27}$$

This has the same form as a modified Bessel equation:

$$x^2 c'' + xc' - (\lambda^2 x^2 + n^2)c = 0\,, \tag{28}$$

with the solution:

$$c_1(x) = AI_0(\sqrt{4a}x)\,, \tag{29}$$

$$c_2(x) = BK_0(\sqrt{4a}x)\,, \tag{30}$$

which leads to

$$c(z) = AI_0(2\sqrt{az}) + BK_0(2\sqrt{az})\,, \tag{31}$$

where $I_0$ is the Bessel function of first kind of order 0, $K_0$ is the modified Bessel function of second kind of order 0, and $A$ and $B$ are constants to be determined by the boundary conditions. From this solution the vertical profiles influenced by chemical reactions can be calculated keeping in mind that the estimation of the boundary conditions is critical and that it is assumed that the production/scavenging is constant vertically and that $K$-closure can be used.

From eq. (31) the vertical profiles of the gaseous $HNO_3$ influenced by chemical reactions can be calculated. To calculate the profile the scavenging rate k is needed. Since this is not known we use the measured profiles and estimate $k$ so the calculated profile fits the measured profile. The boundary conditions for the calculated profiles are set such that $c = 0$ at the surface and $c = c_{\text{measured}}$ at

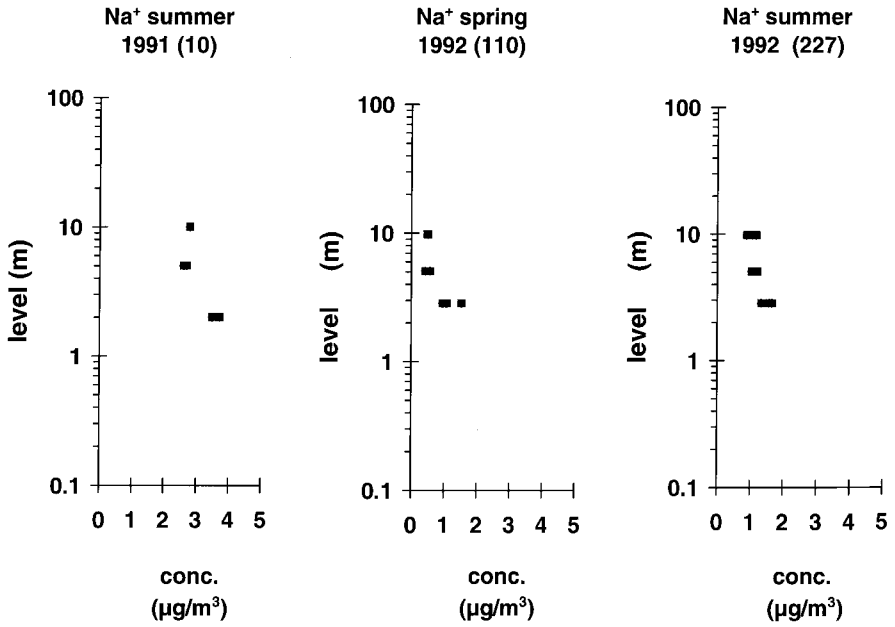


*Fig. 9.* Examples of NaCl gradients measured at Anholt in different experiments.

Table 3. The variable $k$ found at different sample periodes compared to the NaCl concentration and windspeed at 10 m in the period

| Season | $u$ (10 m)(m s$^{-1}$) | NaCl (μg m$^{-3}$) | $k$ (s$^{-1}$) |
|---|---|---|---|
| June 1991 | 7.1 | | 0.005–0.007 |
| | 5.8 | | 0.002–0.005 |
| | 9.4 | 2.4 | 0.04 |
| April/March 1992 | 7.4 | 0.5 | 0.005 |
| | 3.5 | 0.4 | 0.003–0.005 |
| | 2.1 | 0.2 | 0.005 |
| | 2.07 | 0.4 | 0.003 |
| June 1992 | 3.3 | 0.9 | 0.003 |

10 m. Examples of the measured and calculated profiles are shown in Fig. 3.

The measured profiles, the profiles calculated from Monin–Obukhov similarity theory where the scalar is passive (the resistance parameterization) and the profiles calculated from the eq. (31) where chemical reactions influence the profiles and produce a flux divergence are shown in Fig.3.

The surface flux can now be estimated from the "fitted" profiles, this is explained in Section 8. The $k$'s which are found from fitting the calculated profiles to the measured profiles can be used to support the hypothesis of sea spray scavenging of $HNO_3$ and thereby changing the vertical log-linear profiles. If the hypothesis is true we will expect to find a correlation between the sea spray ([NaCl]) and $k$. The estimated $k$'s are shown in Table 3. The $k$'s are the same for most of the measurements except for one period measured in summer 1991. Here the $k$ is an order of a magnitude higher than for other measurements. The NaCl concentration in this particular event is also significantly higher than NaCl concentrations found in the other measurement periods.

## 8. Comparison of surface fluxes

To calculate the surface flux from eq. (31) we use the following approach. Close to the surface the turbulent time scale will dominate in comparison to the chemical time scale. First the concentration at a level very close to the surface, i.e., at 10 cm height, is calculated from eq. (31). This lower level in principle is the level where the turbulent time scale is much larger than the chemical time scale, yet in practice we recognise that we have no adequate means to estimate the chemical time scale. We assume as a starting point that this criteria is satisfied at $z = 10$ cm. Then the resistance method is used for the rest of the path below this level.

First the flux is calculated from the extrapolated profile, then the flux is estimated from the resistance method described in eqs. (5)–(9) and finally the flux is calculated from the approach where chemical reactions are taken into account and the resistance parameterization is applied for the last few centimes over the surface. The following boundary conditions are used: $[HNO_3]$ at $10 = c_{\text{meassured}}$; and $[HNO_3]$ at the surface $= 0$ (due to 100% uptake). The three different flux estimation methods have been applied to the same measurement periods and the results are shown in Table 4. It is clear that the extrapolation of the profile down to the surface, if treated like a log-linear profile, will lead to a big overestimation, but also the flux calculated from resistance parameterization will for some periods be overestimated by a factor of 4 or 5.

## 9. Discussion and conclusion

Looking at the flux data from the field experiment we see that the high $z_{0_c}$'s found from profile measurements are obtained by extrapolation assuming that the concentration profile is log-

Table 4. Fluxes calculated by 3 different methods: by extrapolation of a log linear profile, by the resistance method, and by taken chemical reactions into account

| Period no. | Flux calculated by extrapolation of the measured profile | Flux calculated by the resistance method (Kramm, 1989) | Flux where chemical reactions are taken into account |
|---|---|---|---|
| | $F\ (\mathrm{kg\,m^{-2}\,s^{-1}}) \times 10^{12}$ | $F\ (\mathrm{kg\,m^{-2}\,s^{-1}}) \times 10^{12}$ | $F\ (\mathrm{kg\,m^{-2}\,s^{-1}}) \times 10^{12}$ |
| 1–1991 | 11.72 | 3.45 | 2.09 |
| 3–1991 | 2.17 | 0.78 | 0.61 |
| 10–1991 | 5.89 | 0.97 | 0.19 |
| 105–1992 | 1.49 | 0.25 | 0.17 |
| 107–1992 | 3.04 | 0.62 | 0.41 |
| 108–1992 | 4.42 | 1.11 | 0.49 |
| 109–1992 | 2.85 | 0.96 | 0.83 |
| 110–1992 | 9.96 | 3.75 | 2.07 |
| 227–1992 | 5.54 | 2.64 | 1.95 |

linear. If the concentration of the component is influenced by chemical reactions the measured profile will not be log-linear, which is illustrated by the full line in Fig. 3. Only a very small part of the profile has been measured during the experiment. Measurements in this limited section will, in the case of chemical reactions, give a locally steep gradient, which will result in an overestimation of the flux if the extrapolation does not account for flux divergence nearer to the surface. We find that the calculation of profiles taking chemical reactions into account seems to explain the measured profiles and overestimated fluxes using classical Monin–Obukhov similarity theory. The different $k$'s obtained from the data analyses are hypothesized to be due to differences in the size of the sea spray surface. Since we do not have measurements of the size distribution of the sea spray aerosols we use [NaCl] as an indirect measure of the sea spray. For the single period with the very high $k$, we find that the concentration of NaCl is only 3–4 times as high as the NaCl concentration in the other measurement periods. The uptake of $HNO_3$ is related to the aerosol surface, which can be large relative to the mass, thus an increase in mass can correspond to an even larger increase in surface. Referring to the wind history of the measurement periods, we find that the wind speed had been much higher, i.e., around $13\ \mathrm{m\,s^{-1}}$, during the time prior to the sampling period where we found a high $k$. This finding supports the hypothesis that a high sea spray production and large aerosol surface area occur at high windspeeds. Information of the reactant surface is needed to make a more qualified guess of the scavenging rates.

The $NH_3$ measurements showed steeper profiles than the $HNO_3$ profiles. If one only considers that $HNO_3$ is more soluble than $NH_3$, then one would have expected steeper $HNO_3$ profiles. However, there are a number of chemical processes which are influencing these profiles and affect their steepness. It is likely that $NH_3$ reacts with $HNO_3$ and the HCl formed from the $HNO_3$ reaction with NaCl and/or with water vapour and/or $NH_3$ have chemical pathways that we have not yet discovered. If chemical reactions and seaspray influence the profile, the assumption of a constant flux layer is not valid, and the profiles are not formed by turbulent fluxes only but also by chemical scavenging.

Table 4 shows that for some of the periods (10–91 and 108–92), the estimation of the surface flux is too large when using the traditional resistance parameterization compared to the surface fluxes obtained from calculations where chemical reactions are considered. The flux in period 10 in 1991 is overestimated by a factor of 5 using the resistance parameterization. During this period the windspeed was high causing a large sea spray production. It is an important conclusion to make that some of the modeled fluxes of soluble and reactive gasses are estimated to be too large during conditions when large scavenging rates occur.

To fully understand the processes and model the deposition of constituents to the sea it is necessary to distinguish between the different processes (chemical scavenging and dry deposition) which take place in the marine boundary layer Therefore the reaction and/or uptake rates and chemical pathways must be well understood. Still there is a lack of understanding of which parameterizations are required to describe the atmospheric chemistry of $NH_3$, $HNO_3$, $H_2SO_4$, HCl and their related aerosols. While this paper introduces the sea spray effects on flux divergence using data from Anholt, a following paper will focus on the processes of reactions between $HNO_3$, and seaspray using data emerging from a newly designed study conducted in Vindeby, Denmark, i.e., ASEPS (Air Sea Exchange Process Study) (Sørensen et al., 1994c).

## 10. Acknowledgements

The meteorological data for the experiment were provided by Sven-Erik Gryning and Anna Maria Sempreviva, Risø National Laboratory, Denmark. We are grateful for useful comments and assistance from Hans E. Jørgensen, Risø National Laboratory, Denmark, in working out the solution to the equation presented here. We also acknowledge Dr. Sylvain Joffre for providing useful comments, which helped to improve this paper. This work is part of a Ph.D. study supported by the Danish Research Academy. The work was furthermore funded by The Danish Environmental Protection Agency within the Danish Sea Research Programme 90, The Nordic Council of Ministers, The Danish Environmental Research Programme and US., Office of Naval Research.

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