NOTES AND CORRESPONDENCE

Nitric Acid–Sea Salt Reactions: Implications for Nitrogen Deposition to Water Surfaces

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ABSTRACT

Many previous studies have indicated the importance of nitric acid (HNO$_3$) reactions on sea salt particles for flux divergence of HNO$_3$ in the marine surface layer. The potential importance of this reaction in determining the spatial and temporal patterns of nitrogen dry deposition to marine ecosystems is investigated using models of sea spray generation and particle- and gas-phase dry deposition. Under horizontally homogeneous conditions with near-neutral stability and for wind speeds between 3.5 and 10 m s$^{-1}$, transfer of HNO$_3$ to the particle phase to form sodium nitrate may decrease the deposition velocity of nitrogen by over 50%, leading to greater horizontal transport prior to deposition to the sea surface. Conversely, for wind speeds above 10 m s$^{-1}$, transfer of nitrogen to the particle phase would increase the deposition rate and hence decrease horizontal transport prior to surface removal.

1. Introduction

a. Nitrogen deposition to aquatic ecosystems

Most oceanic primary production by phytoplankton is limited by nutrient availability. The limiting nutrients commonly are nitrogen (N) and phosphorous (P). Increasing N and P concentrations have profound implications for ecosystem health and productivity. For example, Paerl (1995) suggests “nitrogen-limited estuaries, shallow coastal and continental shelf waters account for nearly half the global oceanic primary production.” Typically, absorption of nitrate (NO$_3^-$), nitrite (NO$_2^-$), and ammonium (NH$_4^+$) from ocean waters supplies N required by organisms. Human activity has increased the concentration of these and other N compounds in coastal waters, leading in some cases to greatly enhanced primary production or eutrophication (Paerl 1995). A number of studies indicate that between 10% and more than 50% of coastal N loading is attributable to atmospheric fluxes (e.g., Paerl 1995; Rendell et al. 1993). Although the contribution of wet and dry deposition and gas- and particle-phase N to this atmospheric flux is uncertain and highly variable spatially, Paerl (1995) summarizes data that suggest dry deposition is a significant contributor to the atmospheric flux to all of the major oceans (i.e., dry deposition is greater than 20% of the total flux), and model calculations for the seas around Denmark indicate that one-third of the total N comes from the atmosphere and approximately three-fifths of the atmospheric deposition (via wet and dry pathways) comes from particulate matter (Asman et al. 1995). It also has been suggested that atmospheric fluxes to midlatitude coastal areas may be largest in the late spring and summer months, when nutrient concentrations are generally at a minimum and hence the effect of this flux may be disproportionately large (Fisher and Oppenheimer 1991; Rendell et al. 1993).

Nitrogen deposition is determined largely by emissions of the following N-containing gases: nitric oxide (NO), nitrogen dioxide (NO$_2$), ammonia (NH$_3$), and nitrous oxide (N$_2$O). Nitric acid (HNO$_3$) is formed principally as a result of NO and NO$_2$ and has been shown to make a significant contribution to total N deposition in a number of diverse terrestrial and marine environments [e.g., in the studies of Sievering et al. (1992), Pryor et al. (1999b), and Asman et al. (1995), HNO$_3$ deposition contributed approximately 10% of the total N flux].

Nitrogen emissions to the atmosphere are currently twice “natural background” levels (Vitousek et al.
b. Dry deposition processes

Because of difficulties in direct measurement of dry deposition fluxes of particles and some gases, dry deposition often is determined by the “concentration method” in which the flux is given by multiplication of the concentration at some level above the surface by a deposition velocity:

\[ F = -u_d(z)[C(z) - C(0)], \]

where \( C(z) \) is concentration at measurement height \( z \); \( C(0) \) is concentration at the surface (which may be zero depending on surface uptake); \( u_d(z) \) is deposition velocity, which may be computed as the inverse of the sum of a number of resistances plus a gravitational settling term for particles:

\[ u_d = \frac{1}{r_a + r_b + r_c + v_s}. \]

In Eq. (2) the following are true.

1) \( r_a \) is aerodynamic resistance. This term represents the resistance to transport by turbulence to the quasi-laminar surface layer.
2) \( r_b \) is quasi-laminar surface layer resistance. Very close to the surface, a laminar boundary layer forms (depth \( \approx 100–1000 \mu m \)), which essentially is free of turbulence. Transport across this layer is largely the result of Brownian diffusion.
3) \( r_c \) is surface resistance. For highly reactive or soluble gases the surface resistance is small. We assume a surface resistance of zero and 100% efficient surface capture for particle deposition to water surfaces.
4) \( v_s \) is gravitational settling velocity. For coarse-mode particles, the downward gravitational force exceeds the drag force from the viscosity of air, and hence \( v_s \) is important. This transport process is negligible for gases and fine particles, however.

Additional processes that may be of importance to particle dry deposition but are not considered here include interception and inertial forces, electrical migration due to surface charge, and thermophoresis caused by temperature gradients (see Zufall and Davidson 1998).

c. The focus of this note

The majority of studies of dry deposition fluxes to surfaces explicitly or implicitly rely upon the constant flux layer assumption (i.e., that the measured or determined flux at a given height above the surface is equal to the flux at the surface). Flux divergence (i.e., violation of this assumption), however, may occur because of advection, storage effects, or chemical reactions between the measurement height and the ground (Kramm and Dlugi 1994). Reaction of HNO\(_3\) on sea salt (NaCl) particles to yield sodium nitrate (NaNO\(_3\)) in the particle phase and volatilize hydrochloric acid vapor (HCl) is a potentially important source of flux divergence of HNO\(_3\) over the sea surface (Geernaert et al. 1998). This chemical reaction and others on and in sea salt aerosols also have been shown to play critical roles in halogen (particularly chlorine and bromine) release in the marine boundary layer (Sander and Crutzen 1996), which has been linked to ozone depletion [e.g., the rapid decrease in ozone concentrations in Arctic air masses during the spring (Barrie et al. 1988)].

In this note, the reaction of HNO\(_3\) on sea salt is considered from a different perspective. The rate constant for the HNO\(_3\)--NaCl reaction is thought to be rapid (Fenter et al. 1994), and the reaction has a large equilibrium constant (Seinfeld and Pandis 1998), so, given sufficient particle surface area (and time), the reaction is expected to reach completion with near total transfer of N to the particle phase. Here a first analysis of the potential role of this reaction in modifying atmosphere–surface fluxes of N is presented. It is demonstrated that this transfer of N from the gas to the particle phase has the potential to modify substantially the spatial and temporal patterns of the flux of N to the sea surface.

2. Modeling particle dry deposition to water surfaces

a. Description of the model

Here the model of particle dry deposition velocity described by Pryor et al. (1999) and based on work by Williams (1982) and Hummelskjø et al. (1992) is used.
A schematic of the model is shown in Fig. 1. The form of the model is

\[
v_d = \frac{(v_h + v_{wy})(v_h + v_{wy})}{v_h + v_g + v_{wy}},
\]

where \(v_d\) is transfer velocity in the layer dominated by turbulent transfer, \(v_{wy}\) and \(v_{wy}\) are gravitational settling transfer velocities (subscripts \(d\) and \(w\) indicate dry and wet particles, respectively, where dry particles are those present in the marine atmosphere above the quasi-laminar surface layer, and wet particles refer to particles that have taken up water as they approach the surface and are subject to higher humidities), and \(v_h\) is transfer velocity across laminar surface layer. These terms are given by the following equations.

1) Transfer velocity due to turbulent processes:

\[
v_h = \frac{1}{\kappa u_y} \ln \left( \frac{z_y}{z_{om}} \right) - \Psi_y \left( \frac{z_y}{L} \right) + \Psi_y \left( \frac{z_{om}}{L} \right),
\]

where \(\kappa\) is the von Kármán constant, \(u_y\) is friction velocity, \(z_y\) is reference height, \(z_{om}\) is momentum roughness length, \(\Psi_y\) is the stability correction, and \(L\) is Monin-Obukhov length.

2) Transfer velocity due to gravitational settling:

\[
v_{wy} = \frac{g}{18\mu} \left( \frac{\rho_p}{\rho_d} \right)^2 \alpha, \quad (5)
\]

where \(g\) is gravity, \(\mu\) is dynamic viscosity, \(\rho_p\) is particle density, \(\rho_d\) is air density, \(d\) is particle diameter \((x = d \text{ or } w)\), and \(C\) is the Cunningham slip correction factor \([C = 1 + (\lambda/d)[2.514 + 0.8 \exp(-0.55d/\lambda)]; \lambda\) is the mean free path of air; \(\text{Seinfeld and Pandis 1998}\). For \(v_{wy}\), \(d\) is adjusted for hygroscopic growth in the quasi-laminar surface layer \([\text{i.e., } x = w, \text{ so } d = d_w]\), where \(d_w\) is dependent on relative humidity \((\leq 98.3\% \text{ over salt water})\) and particle composition using the approximations of Fitzgerald (1975).

3) Transfer velocity across the quasi-laminar surface layer:

\[
v_d = (1 - \alpha_{wb})(c u_y Sc^{-0.5} Re^{-0.5} + u_y \times 10^{-3/6})
\]

\[
+ \alpha_{wb} \frac{u_y}{U_{10}} + \text{Eff}(2\pi r_{drop})(2z_{drop}) \frac{q_{drop}}{\alpha}, \quad (6)
\]

where \(\alpha_{wb}\) is relative area with bursting bubbles, \(c = 1/(c_1 \sqrt{c_2})\), \(c_1\) is \(f\) (thickness of the molecular diffusion layer), \(c_2\) is \(f\) (ratio of the height of roughness elements to the aerodynamic roughness length), \(S_c\) is Schmidt number \([S_c = \nu/D\), where \(\nu\) is the kinematic viscosity of air, diffusivity \(D = kTC/(3\pi\mu d), \ k\) is the Boltzmann constant, and \(T\) is temperature], \(Re\) is Reynolds number \([Re = u_y z_{om}/\nu]\), \(St\) is Stokes number \([St = u_y v_{wy}/(\nu g)]\), \(U_{10}\) is wind speed at 10 m, \(\text{Eff}\) is the effectiveness with which particles are collected by the spray drops, \(z_{drop}\) is the average height that spray drops reach, \(r_{drop}\) is the average radius of spray drops, \(q_{drop}\) is the flux of spray drops from the surface, and \(\alpha\) is the area of sea surface covered by whitecaps:

\[
\alpha = 1.7 \times 10^{-6} \left( \frac{U_{10}}{10} \right)^{0.5}, \quad (7)
\]

from Wu (1988).

Transfer across the quasi-laminar surface layer represents the major limitation on fine particle deposition. The two components of (6) pertain to diffusional transfer through the quasi-laminar surface layer (also referred to as the viscous sublayer) and to the increase in downward movement of particles due to bubble burst activity [see discussion in Pryor and Barthelmie (2000)].

Deposition velocities computed using this model are shown in Fig. 2 for pure NaCl particles and near-neutral atmospheric stratification for four different wind speeds. The characteristic form of the graph with lowest deposition velocity for particles with \(d = 0.1-0.4 \mu m\) reflects higher deposition velocity for larger particles for which gravitational settling is nonnegligible and for smaller particles for which Brownian diffusion is more efficient. This figure also emphasizes the importance of wind speed in determining deposition velocity (e.g., as \(U_{10}\) increases from 5 to 15 m s\(^{-1}\), \(v_d\) for \(d = 0.2 \mu m\) increases more than fourfold). As wind speeds increase, the size dependence of deposition velocity for particles below 1 \(\mu m\) decreases as enhancement of deposition due to bubble burst activity increases, and so the limitation placed on deposition by particle diffusivity is effectively removed.

![Deposition velocity vs. Particle diameter](image-url)
b. Evaluation of the model

Only a few direct measurements of particle dry deposition to water surfaces are available in the literature for evaluation of mathematical models of deposition velocities, and the majority derive from wind-tunnel experiments (Slinn et al. 1978; Larsen et al. 1995; Zufall and Davidson 1998). Table 1 summarizes a comparison of the model performance relative to three wind-tunnel experiments for a range of particle and environmental parameters. As shown, the model performs well relative to the measurements, particularly in light of the experimental error and uncertainties in initializing the model. The model is within a factor of 2 for all comparisons except the experiment reported in Slinn et al. (1978) for a particle diameter of 2.5 μm. For this experiment the model underestimates observations, but this underestimation may be caused by the model assumption that the particles are hydrophobic (the particle composition is not specified in the experimental description). If only 10% of the particles were ammonium nitrate (NH₄NO₃) (or another hydroscopic compound) the model would predict the deposition velocity correctly.

3. The role of particles in modifying gas fluxes: HNO₃–sea salt interactions

To illustrate the potential importance of HNO₃–sea salt reactions on the spatial and temporal patterns of N fluxes to water surfaces, it is useful to compare the deposition velocity for HNO₃ in the absence of reactions with sea spray with the deposition velocity for the particles that might act as the sink for HNO₃ (via formation of NaNO₃). To make this comparison, some simplifying assumptions are made about the uptake of HNO₃ on sea salt and the prevailing atmospheric conditions. With respect to the prevailing meteorological conditions, we assume near-neutral stability and horizontal homogeneity. We also assume that, since reaction of HNO₃ with NaCl particles is a surface reaction (Mamane and Gottlieb 1992; Fenter et al. 1994), the size distribution of the resulting NaNO₃ can be characterized by particle diameters associated with the maximum surface area of NaCl particles.

To calculate the surface-area size distribution for sea spray droplets, the following equations developed by Monahan et al. (1986) to describe spray generation in open ocean conditions are used. The generation of sea salt droplets per unit area of sea surface [by bubble burst (F₀) and spume (F₁)], per increment of droplet radius r per second is given by

\[ \frac{dF₀}{dr} = 2.373U₀₁^{41}r^{-3}(1 + 0.057r^{1.05}) \times 10^{14(G−G′)} \]  

(8)

and spume (r > 10 μm):

\[ \frac{dF₁}{dr} = 8.6 \times 10^{-6}e^{2.08U₁30}r^{-8}, \]

(10)

where \( F₀ \) is the flux due to bubble burst (subscript 0) or spume (subscript 1). Note that (10) is known to overestimate the flux of large droplets, but this overestimation does not affect the analysis because the surface area of sea spray is dominated by r less than 10 μm (Smith et al. 1993).
Figure 3 shows the normalized surface area of NaCl droplets as calculated using (8)–(10) and indicates a defined maximum for diameters between 1.0 and 6.4 µm. For this analysis, we assume that the size distribution generated by the flux equations [(8)–(10)] reasonably represents ambient marine particles in this size range.

If it is assumed that pure NaNO₃ is formed by the reaction of HNO₃ on sea salt particles, a deposition velocity for those particles then can be calculated using (3)–(6) for any wind speed. The deposition velocity for NaNO₃ particles for a wind speed of 7 m s⁻¹ is shown in Fig. 4. This figure indicates that, for diameters between 1.0 and 6.4 µm, the deposition velocity is 0.02–0.8 cm s⁻¹, with a value of 0.2 cm s⁻¹ for the diameter of maximum surface area (d = 3.2 µm).

The deposition velocity for HNO₃ can be calculated using the resistance analogue [(11)–(14)] with the assumption that the surface resistance is zero (i.e., r_s = 0):

\[
  r_a = \frac{1}{\kappa u^*} \left( \ln \frac{z_0}{z_{0c}} \right), \tag{11}
\]

\[
  r_b = \frac{1}{\kappa u^*} \left( \ln \frac{z_0}{z_{0c}} \right), \tag{12}
\]

\[
  \text{Re} < 0.15: \quad z_{0c} = 30 \frac{\nu}{u^*} e^{-13.6 \text{Re}^{0.5}}, \quad \text{and} \quad \tag{13}
\]

\[
  \text{Re} \geq 0.15: \quad z_{0c} = 20z_{0c} e^{-73.6 \text{Re}^{0.5}}, \quad \text{and} \quad \tag{14}
\]

where z₀ₖ is the roughness length for the chemical of interest [from Joffre (1988) and Asman et al. (1994)].

From (11)–(14), the deposition velocity of HNO₃ for near-neutral stability and a wind speed of 7 m s⁻¹ is 0.48 cm s⁻¹.

From these calculations one can observe that, for this scenario (i.e., U = 7 m s⁻¹ and near-neutral stability), transfer of HNO₃ to the particle phase would lead to a reduction in the deposition velocity of N of over 50% (from 0.48 to 0.2 cm s⁻¹) leading to greater horizontal transport of N prior to deposition. In this way a larger geographic area could be affected by influx of anthropogenic N compounds. Alternatively stated, this result implies that, for the stated conditions, the atmospheric contribution to the N flux in the coastal zone would be reduced, but the flux to open waters would be increased by reaction of HNO₃ on sea spray particles.

To investigate whether this result may be generalized for varying conditions, the model described above was used to calculate deposition velocities for HNO₃ and NaNO₃ particles (with d = 1.0–6.4 µm) for a range of wind speed conditions and near-neutral stability. The results, shown in Fig. 5, indicate that at all wind speeds the deposition velocity for HNO₃ is within the envelope defined for particle NaNO₃ deposition. However, at low (U₁₀ < 3.5 m s⁻¹) and high (U₁₀ > 10 m s⁻¹) wind speeds the deposition velocity for HNO₃ is lower than that for an NaNO₃ particle of 3.2-µm diameter, and, for wind speeds between 3.5 and 10 m s⁻¹, transfer of HNO₃ to the surface is more rapid than it is for particle NaNO₃, indicating that transfer of N to the particle phase would decrease the deposition rate and hence increase horizontal transport of N prior to deposition. The source of the wind speed dependence in the ratio of HNO₃:NaNO₃ deposition velocities implied in Fig. 5 is principally that...
the increase of particle deposition with wind speed is greater than that of HNO₃. Particle deposition to water surfaces commonly is limited by the rate of transfer across the quasi-laminar surface layer. Resistance to this transfer is dependent on white cap activity [(6)]. As wind speed increases, white cap activity increases to the 3.75 power [(7)], and hence particle transfer across the quasi-laminar surface layer increases in a nonlinear fashion, leading to larger deposition velocities. This increase in deposition velocity with wind speed continues until the point at which transfer of particles with \( d = 1.0-6.4 \, \mu m \) across the quasi-laminar surface layer ceases to be the major limitation on deposition.

4. Discussion and implications

An examination of the importance of HNO₃–sea salt reactions on the deposition of N to marine ecosystems has been presented. Models of sea spray generation and particle- and gas-phase dry deposition were used to compare deposition velocities for HNO₃ and NaNO₃ formed by reaction on sea spray.

For this study, a number of a simplifying assumptions were made. The reaction of HNO₃ on sea salt was treated in a highly simplified manner. We assume that this reaction dominates HNO₃ chemistry in the marine bound-

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