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**Accessory publication**

# Coupling between dimethylsulfide emissions and the ocean–atmosphere exchange of ammonia

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## Model description

At each timestep, the model calculates the following fluxes of $NH_X$ between reservoirs:

- $F_{o\text{–}a}$, ocean–atmosphere exchange between $NH_{3(sw)}$ and $NH_{3(g)}$
- $F_{a\text{–}p}$, gas–particle exchange between $NH_{3(g)}$ and $NH_4{}^+{}_{(p)}$

Un-neutralised aerosol sulfate is added to the system at each timestep as a boundary condition ($f\_SO_4{}^{2-}{}_{(p)}$); and a proportion of the aerosol is removed at each timestep ($r_{dep}$), to maintain an approximately constant mass of particulate material in the atmosphere.

## Ocean atmosphere exchange

The ocean–atmosphere exchange of ammonia ($F_{o\text{–}a}$) is calculated according to the 'thin film' model of air–sea trace gas exchange presented by Liss and Slater[57] (Eqn A1).

$$F_{o\text{–}a} = -k_g\{(NH_{3(g)}) - K_H[NH_{3(sw)}]\} \qquad (A1)$$

where $F_{o\text{–}a}$ is the ocean atmosphere flux (in nmol $m^{-2}$ $s^{-1}$), $k_g$ is the gas phase transfer velocity (m $s^{-1}$) and $K_H$ is the dimensionless Henry's Law coefficient for ammonia (i.e. the ratio of gas phase to liquid phase concentration at equilibrium). The concentrations of gas phase and dissolved ammonia must be in the same units (in this case nmol $m^{-3}$). The gas phase transfer velocity is calculated as a function of wind speed according to Duce et al.[58] (Eqn A2).

$$k_g = u[770 + 45 \times (RMM)^{1/3}]^{-1} \qquad (A2)$$

where $u$ is the wind speed (m $s^{-1}$) and RMM is the relative molecular mass of the gas in question (17.03 in the case of ammonia). The concentration of dissolved non-solvated ammonia is given by Eqn A3:

$$[NH_{3(sw)}] = [NH_{X(sw)}] \times K_a(K_a + [H^+])^{-1} \qquad (A3)$$

where $[NH_{X(sw)}]$ is in the units of nmol $m^{-3}$, $[H^+] = 10^{-pH}$ and $K_a = 10^{-pKa}$. $pK_a$ is calculated according to Bell et al.[59] from measured values of the dissociation of ammonium in seawater (Eqn A4):

$$\mathrm{pKa} = 10.0423 - (0.0315536 \times t) + (0.003071 \times \mathrm{S}) \qquad \text{(A4)}$$

where S is the salinity (unitless) and $t$ is the temperature in °C. The Henry's law coefficient, $K_H$, is calculated according to Johnson et al.[24] (Eqn A5):

$$\mathrm{K_H} = \left[\left(17.93 \times \frac{T}{273.15}\right) \times e^{\frac{4092}{T} - 9.70}\right]^{-1} \qquad \text{(A5)}$$

where $T$ is the temperature in Kelvin.

### Gas–particle exchange

The interconversion between $NH_{3(g)}$ and $NH_4{}^+{}_{(p)}$, which occurs on a timescale of between 0.3 and 7 h[22] is represented in the model as an equilibrium (i.e. reversible) process (Eqn A7).

We have compared two approaches to calculate the rate of gas–particle (inter)conversion: a kinetic, unidirectional scheme using the Harrison and Kitto[50] equation (Eqn 1 from main text and Eqn A6); and a simple bidirectional scheme with an exponential decay rate (Eqn A7).

$$\mathrm{K} = 2.3 \times 10^{-4} \left[\frac{\mathrm{H}^+}{\mathrm{NH}_4^+}\right] + 4 \times 10^{-5} \qquad (1)$$

where K is the rate constant (in $s^{-1}$) for the pseudo first order reaction. The flux is then calculated as:

$$F_{a-p} = \mathrm{K} \times (\mathrm{NH}_{3(g)}) \qquad \text{(A6)}$$

Alternatively, as an equilibrium process:

$$F_{a-p} = \tau_{a-p} \left[(\mathrm{pNH}_{3(g)}) - (\mathrm{NH}_{3(g)})\right] \qquad \text{(A7)}$$

where $\tau_{a-p}$ is a time constant (unitless) and $pNH_{3(g)}$ is the partial pressure of ammonia over the aerosol.

The typical equilibration time of the scheme employing the rate constant of Harrison and Kitto[50] is of the order of 1 h, well within the range of 0.3–7 h predicted by Quinn et al.[22] The $NH_4{}^+$ : nss-$SO_4{}^{2-}$ ratio in the model is very insensitive to the rate of equilibration between gas and aerosol phases (Fig. A1) except at very low rates (equilibration times of tens to hundreds of hours), where it approaches the characteristic time of the ocean–atmosphere flux.

We adopt a value of $\tau_{a-p}$ of 0.05, which equates to a 5% decrease in $[(pNH_{3(g)}) - (NH_{3(g)})]$ per 1-min timestep and leads to ~95% equilibration over 1 h of model time.

We use our own parameterisation of $pNH_{3(g)}$, the equilibrium point between gas and aerosol phases, based on output of the Aerosol Inorganics Model (AIM, http://www.aim.env.uea.ac.uk/aim/aim.html, accessed September 2007).[49] As demonstrated by the AIM, $pNH_{3(g)}$ is not dependent on the absolute amount of $NH_4^+{}_{(p)}$ in the aerosol phase but rather the relative amounts of ammonium and sulfate (and other constituents, not considered here), along with the pH of the aerosol, relative humidity and temperature. As our model aerosol only contains ammonium, sulfate and water we can ion-balance the aerosol in the AIM with $H^+$ and calculate $pNH_{3(g)}$ for $NH_4^+$ : nss-$SO_4^{2-}$ ratios between 0 and 2 over a range of temperatures and relative humidities. $pNH_{3(g)}$ is calculated in our model according to Eqn A8, derived from output of the AIM at 75% relative humidity. In order to use our model at different relative humidities, new parameterisations are required.

$$pNH_{3(g)} = 0.00016 \times e^{(0.124T + 4.6R)} \quad \text{(A8)}$$

where $R$ is the $NH_4^+$ : nss-$SO_4^{2-}$ ratio.

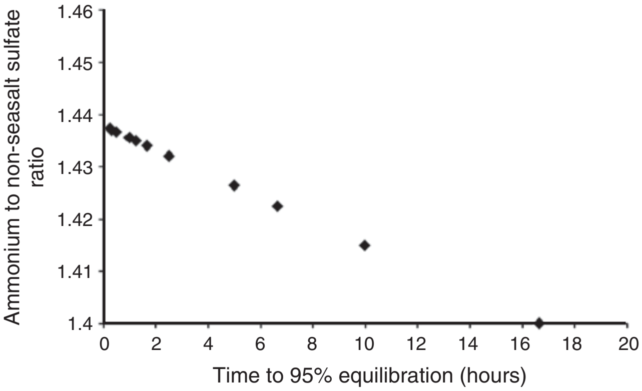

**Fig. A1.** The low sensitivity of $NH_4^+$ : nss-$SO_4^{2-}$ ratio to changing the timescale of gas-particle equilibration in the model. Model run at 75% relative humidity and default parameter values (Tables 1 and 2 in main text). Note the small extent of the $NH_4^+$ : nss-$SO_4^{2-}$ ratio values on the *y*-axis

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