

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

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Environmental context. Dimethylsulfide (DMS) is recognised as a potentially significant climate-forcing gas, owing to its role in particle and cloud formation in the marine atmosphere, where it is the dominant source of acidity. Ammonia, the dominant naturally occurring base in the atmosphere, plays an important role in neutralising particles formed from DMS oxidation products and may even enhance the formation rate of new particles. A biogeochemical coupling has previously been proposed between DMS and ammonia fluxes from the ocean to the atmosphere, in the form of coproduction of the two gases in seawater. We revise this suggestion by introducing the concept of ‘co-emission’ of the gases, where DMS emission controls the rate of emission of ammonia from the ocean by acidifying the atmosphere.

Abstract. A strong correlation between aerosol ammonium and non-sea salt sulfate is commonly observed in the remote marine boundary layer. It has been suggested that this relationship implies a biogeochemical linkage between the nitrogen (N) and sulfur (S) cycles at the cellular biochemical level in phytoplankton in the ocean, or a linkage in the atmosphere (see P. S. Liss and J. N. Galloway, *Interactions of C, N, P and S biogeochemical cycles and global change* (Springer, 1993), and P. K. Quinn et al. in *J. Geophys. Res. – Atmos.* **1990**, 95). We argue that an oceanic linkage is unlikely and draw on mechanistic and observational evidence to make the argument that the atmospheric connection is based on simple physical chemistry. Drawing on an established analogous concept in terrestrial trace gas biogeochemistry, we propose that any emission of dimethylsulfide (DMS) from the ocean will indirectly influence the flux of NH₃ from the ocean, through the neutralisation of acidic DMS oxidation products and consequent lowering of the partial pressure of NH₃ in the atmosphere. We present a simple numerical model to investigate this hypothesised phenomenon, using a parameterisation of the rate and thermodynamics of gas-to-particle conversion of NH_x and explicitly modelled ocean–atmosphere NH₃ exchange. The model indicates that emission of acidic sulfur to the atmosphere (e.g. as a product of DMS oxidation) may enhance the marine emission of NH₃. It also suggests that the ratio of ammonium to non-sea salt sulfate in the aerosol phase is strongly dependent on seawater pH, temperature and wind speed – factors that control the ocean–atmosphere ammonia flux. Therefore, it is not necessary to invoke a stoichiometric link between production rates of DMS and ammonia in the ocean to explain a given ammonium to non-sea salt sulfate ratio in the aerosol. We speculate that this mechanism, which can provide a continuous resupply of ammonia to the atmosphere, may be involved in a series of biogeochemical-climate feedbacks.



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Introduction

Dimethylsulfide (DMS)

DMS is a biogenic trace gas whose flux is consistently from ocean to atmosphere. Its emission is of particular interest owing to the potential climate-forcing effect of its oxidation products, particularly H_2SO_4 , the dominant source of strong acidity in the atmosphere and key species in new particle formation and growth. This is the basis of the ‘CLAW’ hypothesis,^[1] which suggests a biological climate control (i.e. negative feedback) mechanism, although this is still open to debate (see ref. [2] and ‘opinion’ articles immediately following in the same issue). What is known with certainty is that there is a marine source of DMS^[3–6] and that a substantial proportion of fine-mode aerosol in the marine boundary layer (MBL) is composed of non-sea salt sulfate (nss-SO_4^{2-}), which in remote regions is derived from the oxidation of DMS and is the predominant source of aerosol acidity.^[7]

The ocean–atmosphere flux of DMS is unidirectional because (i) DMS is a relatively insoluble gas (Henry’s law constant, $K_H \approx 0.5 \text{ M atm}^{-1}$ ^[8]), and (ii) it is relatively short-lived in the atmosphere (lifetime $\approx 1 \text{ day}$ ^[9]) with relatively rapid removal via oxidation by various pathways.^[10,11] These factors combine to maintain a strong concentration gradient (and thus flux) across the ocean–atmosphere interface.

Once in the atmosphere, DMS will oxidise on a timescale of hours by reaction with NO_3 radical (at night) and BrO radical,^[11] or days with oxidation by OH radical.^[10] The end points of these oxidation reactions are MSA (methanesulfonic acid, HOSO_2CH_3) and sulfuric acid (H_2SO_4), the partitioning between these species being dependent on temperature and the relative concentrations of available oxidants.^[11] These processes are effectively irreversible in Earth’s oxidising atmosphere.

A proportion of the H_2SO_4 will be taken up by coarse mode sea salt aerosol,^[12] this proportion being strongly dependent on wind speed and the enrichment of CaCO_3 alkalinity in the coarse mode aerosol.^[13] The remaining H_2SO_4 can condense spontaneously to form sulfate particles (classically considered to occur via binary nucleation with water molecules) and will also condense onto or dissolve into existing fine mode particles in the atmosphere.^[14,15] Whereas the propensity for H_2SO_4 to enter the particulate phase is governed by equilibrium thermodynamics (higher temperatures favouring the gas phase), it is generally thought that it will not re-enter the gas phase under normal atmospheric conditions owing to its extremely high solubility (in aqueous solutions) and ‘stickiness’ to dry surfaces.^[16] Thus the gas-to-particle conversion of sulfuric acid can also be considered as an effectively irreversible process.

Ammonia (NH_3)

NH_3 and its protonated equivalent (ammonium, NH_4^+), together referred to henceforth as NH_x , are ubiquitous in the ocean and in the atmosphere. In the latter, NH_3 is the dominant gaseous base and neutraliser of strong acidity. NH_3 is emitted to the atmosphere in large quantities by anthropogenic activities, both industrial and agricultural,^[17,18] as well as by natural biogenic production in the terrestrial and marine environments. Anthropogenic emissions have led to perturbations in the global NH_x cycle many times greater than the pre-industrial fluxes.^[19,20] However, NH_x is relatively short-lived in the atmosphere (of the order of days), so the majority of NH_x from strong terrestrial sources tends to be deposited from the atmosphere before reaching remote marine environments.^[17,21,22]

In contrast to DMS, all of the processes linking dissolved ammonium in the marine surface layer ($\text{NH}_4^+_{(\text{sw})}$) with particulate ammonium in the atmosphere ($\text{NH}_4^+_{(\text{p})}$) are completely reversible. $\text{NH}_4^+_{(\text{sw})}$ exists in thermodynamic equilibrium with $\text{NH}_3_{(\text{sw})}$ (dissolved, non-solvated NH_3), the protonation reaction occurring near-instantaneously to maintain equilibrium.^[22] Under typical seawater conditions, $\sim 1\text{--}10\%$ of the total $\text{NH}_{x(\text{sw})}$ exists as $\text{NH}_3_{(\text{sw})}$.^[23]

Ammonia is considerably more soluble than DMS ($K_H \approx 60 \text{ M atm}^{-1}$ ^[8]). Its solubility means that for typical surface seawater and MBL concentrations, the ocean and atmosphere are generally close to equilibrium with respect to NH_3 ^[21,24–27] and thus its ocean–atmosphere exchange can be considered a bidirectional process that is highly sensitive to temperature, pH and concentrations of NH_3 in both surface ocean and MBL.^[24]

Once in the atmosphere, $\text{NH}_3_{(\text{g})}$ will react readily with acidic gases and particles to enter the particulate phase as $\text{NH}_4^+_{(\text{p})}$. The direction of $\text{NH}_3_{(\text{g})}$ flux between the gas and aerosol phases is determined by the difference in concentration between $\text{NH}_3_{(\text{g})}$ and $\text{pNH}_3_{(\text{g})}$ (the partial pressure of NH_3 over the aerosol phase). In aqueous aerosol, this process is reversible,^[22] as it is with dry ammonium salts of nitrate and chloride.^[21,28] The lower partial pressure of NH_3 over the much less volatile ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and ammonium bisulfate (NH_4HSO_4) means that any $\text{NH}_4^+_{(\text{p})}$ in dry salts formed with nss-SO_4^{2-} are likely to be irreversibly reacted. However, these salts are highly deliquescent (i.e. water-attracting), so are unlikely to remain in the solid phase in the relatively humid MBL.^[21]

Quinn et al.^[22] considered all components of the ‘multiphase’ ammonia system ($\text{NH}_4^+_{(\text{sw})} \rightleftharpoons \text{NH}_3_{(\text{sw})} \rightleftharpoons \text{NH}_3_{(\text{g})} \rightleftharpoons \text{NH}_4^+_{(\text{p})}$) in the remote marine environment. They found that the characteristic time for equilibration between the surface ocean and $\text{NH}_3_{(\text{g})}$ in the atmosphere is of the order of a few days to a week (dependent on wind speed), whereas the equilibration between gas and aerosol (or cloud) waters occurs on a timescale of hours. Oxidation of $\text{NH}_3_{(\text{g})}$ by OH radical is rather slow, and considered insignificant relative to other removal processes (wet and dry deposition, mostly from the particulate phase).^[17,22] There is generally a disequilibrium observed between the atmosphere and ocean with respect to ammonia,^[22,24,27,29,30] supporting the suggestion that air–sea equilibration is a relatively slow process in the system. Therefore, the major control on the concentration of $\text{NH}_3_{(\text{g})}$ in the remote MBL (neglecting advection from other sources) must be the equilibrium between gas and particle phases; i.e. on timescales of hours, $\text{NH}_3_{(\text{g})}$ will tend to reach equilibrium with $\text{pNH}_3_{(\text{g})}$.

Proposed biogeochemical couplings

Quinn et al.^[29] observed average $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ molar ratios of 1.5 ± 0.44 in air of remote marine source (and substantially different and more variable ratios in air of terrestrial and volcanic sources). In addition, relatively consistent $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ molar ratios (typically between 1 and 2) have been observed in marine-source aerosols sampled in the remote MBL of the Atlantic (T. G. Bell, A. R. Baker and T. D. Jickells, unpubl. data). An exception to this trend in clean marine air is the data of Savoie et al.,^[31] who observed substantially lower ratios (annual minimum of 0.6) at Mawson, Antarctica. In addition, their data suggest strong coupling of the seasonal trends in nss-SO_4^{2-} and $\text{NH}_{x(\text{p})}$ concentrations over a 5-year period at several Antarctic and Southern Ocean sites.

Quinn et al.^[29] propose that the relative constancy of the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio in clean marine air may indicate a biogeochemical linkage between the processes that produce DMS and NH_4^+ in the surface ocean, although they do not observe any relationship between the concentrations of these two species in seawater. Links at the biochemical level have been proposed, for example the possible coproduction of the osmolytes DMSP (dimethylsulfoniopropionate, the precursor to DMS) and glycine betaine (or 2-trimethylammonioacetate, the nitrogenous analogue to DMSP) (see ref. [32], after ref. [33]).

Liss and Galloway^[32] propose that the linkage is more likely to be in the atmosphere and driven by the scavenging of NH_3 by acidic sulfate particles, and that the resulting $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio would be dependent on the relative amounts of NH_3 and H_2SO_4 available from various sources (marine emissions, transport from continental regions, etc.). There is substantial evidence for an atmospheric coupling through the titration of aerosol acid sulfate with ammonia.^A

Following the hypothesis of Quinn et al.,^[29] Liss and Galloway^[32] invoke ‘coproduction’; i.e. they assert that a given $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio in the remote marine environment (away from continental sources) must represent the ratio of the production of ammonia and DMS in the surface ocean. We argue that this is unlikely, because the source regions of the NH_4^+ and nss-SO_4^{2-} found in a given aerosol particle will be spatially separated owing to the timescale of DMS oxidation. Thus the likelihood of uniform coupling between the N and S cycles in the marine environment over such scales of space and time is unlikely. Second, only a tiny proportion of the NH_4^+ produced by biological activity in the ocean will be emitted to the atmosphere; relatively constant surface seawater concentrations are a result of the tight coupling between rapid uptake and regeneration by the mixed plankton community.^[34–36] In other words, sea-to-air flux is not the dominant loss of NH_x from seawater and the same appears to be true for DMS.^[37] Finally, only a proportion of the DMS emitted from the ocean will be oxidised to nss-SO_4^{2-} .^[10]

However, in a system where all of the atmospheric N and S is derived from the surface ocean, it must be the case that a given $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ molar ratio in the aerosol will have resulted from emission of a stoichiometrically equivalent ratio of ammonia and DMS-derived sulfate. Therefore, there must be a process by which there is atmospheric control on the rate of emission of one or both of the gases in question and we invoke the concept of ‘co-emission’, a recognised process in the terrestrial environment, to explain this.

Coupling of DMS emission and NH_3 flux

We hypothesise that away from significant terrestrial influence, any un-neutralised sulfate acidity in the atmosphere will

scavenge NH_3 towards a ‘titration end-point’. This depletion of gas-phase NH_3 will favour the ocean-to-atmosphere flux of NH_3 , which, in the case of the remote marine atmosphere where nss-SO_4^{2-} is predominantly derived from DMS emissions, can be considered a DMS-driven ‘co-emission’ of ammonia.^B Ammonia, however, cannot have the same driving effect on DMS emission owing to the irreversible nature of the processes transforming $\text{DMS}_{(\text{sw})}$ to nss-SO_4^{2-} .

This hypothesised neutralisation mechanism for atmospheric acidity is consistent with the observed constancy in $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratios in the marine environment. Whenever atmospheric acidity increases, $\text{pNH}_{3(\text{g})}$ over the aerosol decreases, leading to enhanced uptake of $\text{NH}_{3(\text{g})}$ onto the aerosol and consequent increased flux of NH_3 from the ocean to compensate the change.

As ocean–atmosphere exchange is the slowest process in the multiphase ammonia system in the marine environment, we predict that factors affecting the flux of ammonia from the ocean will be key controls on the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio. We have identified in Johnson et al.^[24] that temperature is a fundamental constraint on the magnitude and direction of ocean–atmosphere ammonia exchange such that, at a global scale, it outweighs the effects of biological activity. We predict that temperature is therefore likely to be a key control on the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio. However, on a regional scale, where temperature is relatively invariable, biological activity and associated concentration and pH changes are likely to be important determinants of the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio.

Analogous processes in the terrestrial environment

An analogous process is well established in studies of terrestrial trace gas biogeochemistry – that of ‘co-deposition’ of NH_3 and SO_2 to wet and dry surfaces.^[38,39] The concept was first suggested by Brimblecombe,^[40] where NH_3 was invoked as a neutralising agent facilitating the dissolution of SO_2 onto the ‘dew’ on the surface of leaves. Subsequent laboratory studies observed enhanced efficiency of deposition of both NH_3 and SO_2 in the presence of both gases,^[38] particularly under high relative humidities. The mechanism invoked to explain this co-deposition is the ‘suppression of the pH limitation to solubility for either gas in the presence of the other’.

In data presented by Sutton et al.,^[38] we see a process more directly analogous to that which we propose for the marine environment (Fig. 1). The process, which they term ‘co-emission’, is driven by SO_2 release due to drying on the leaf surfaces in a wheat field. Prior to drying, the atmosphere and wet leaf surfaces were close to equilibrium. Following drying and subsequent emission of SO_2 , NH_3 was depleted by gas-to-particle conversion to below a ‘compensation point’ i.e. $\text{pNH}_{3(\text{g})}$ over the

^AHarrison and Kitto^[50] found kinetic control of aerosol sulfate neutralisation by NH_3 during a ‘connected flow’ study over S.E. England. They observed that the pseudo-first order rate constant (with respect to NH_3) for the reaction decreases with increasing neutralisation (Eqn 1).

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

where K has units of s^{-1} . Although these observations were made under a very different biogeochemical regime to that of the remote marine atmosphere, they strongly indicate a decrease in reaction rate towards aerosol neutralisation.

Quinn et al.^[22] predict exponentially increasing $\text{pNH}_{3(\text{g})}$ over aerosol tending towards neutralisation in their thermo-dynamic model of the atmospheric NH_x system. The authors do not present the details of their model, but we have closely reproduced their findings using the Aerosol Inorganics Model (AIM) described in Clegg et al.^[49] and in a related model, PIZ93, which is more reliable at near-neutral pH (S. Clegg, pers. comm.). Furthermore, the strong pH dependence of $\text{pNH}_{3(\text{g})}$ over ammonium sulfate aerosols has been observed in laboratory studies.^[55]

^BIn regions where seawater temperatures are low and ambient ammonia fluxes are likely to be from atmosphere to ocean (owing to advection from source regions), the coupling of the fluxes may in fact be via an inhibition of NH_3 flux into the ocean, rather than enhanced emission of NH_3 from the sea surface.

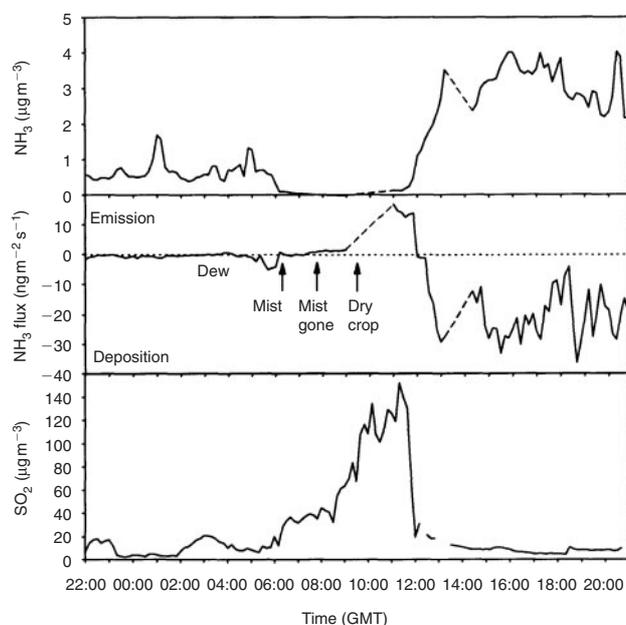


Fig. 1. Evidence for co-emission of SO_2 and NH_3 from a wheat field, presented by Sutton et al.^[38] Reproduced with permission. See text for details.

substomatal cavities of leaf surfaces.^[41] This led to an emission of NH_3 from the surface as a direct result of the sulfur emissions. This is a process that occurs on a small timescale relative to our hypothesised process, but evidence for longer-term connections between atmospheric ammonium and sulfur in the terrestrial realm are demonstrated by Fowler et al.,^[42] who find strong relationships between deposited ammonium and SO_2 surface equilibrium concentrations over a 2-year period.

Applicability to less remote regions

We focus in the present manuscript on the remote marine environment, where the system of interest is relatively close to equilibrium and thus our hypothesised process should be most easy to identify. However, the implications of the proposed mechanism also apply to more complex (e.g. terrestrially influenced) systems. For instance, wherever there is a net flux of sulfuric acidity from the land surface over the ocean (the norm in many regions of the world^[17,43]), gas-phase ammonia concentrations are likely to rapidly fall under control of the aerosol phase (i.e. tend towards $\text{pNH}_{3(\text{g})}$) as the air moves away from terrestrial source regions, owing to the relative slowness of air-sea exchange and oxidation by OH. Low aerosol pH will result in low $\text{pNH}_{3(\text{g})}$ and thus enhance the flux of NH_3 from the ocean, or inhibit influx, depending on ambient conditions and concentrations. Zhuang and Huebert^[44] present data from a Lagrangian experiment, which show an increasing $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio as sulfate-rich air is advected over the ocean, with evidence of rapid conversion of ocean-emitted NH_3 to the particulate phase, providing strong circumstantial evidence of sulfate-driven ammonia emission in continental air masses.

Observed coupling in Antarctic data

The data of Savoie et al.^[31] show strong evidence of a coupling between the emissions of NH_3 and DMS, with strong synchronicity between nss-SO_4^{2-} and NH_4^+ (Fig. 2a). This

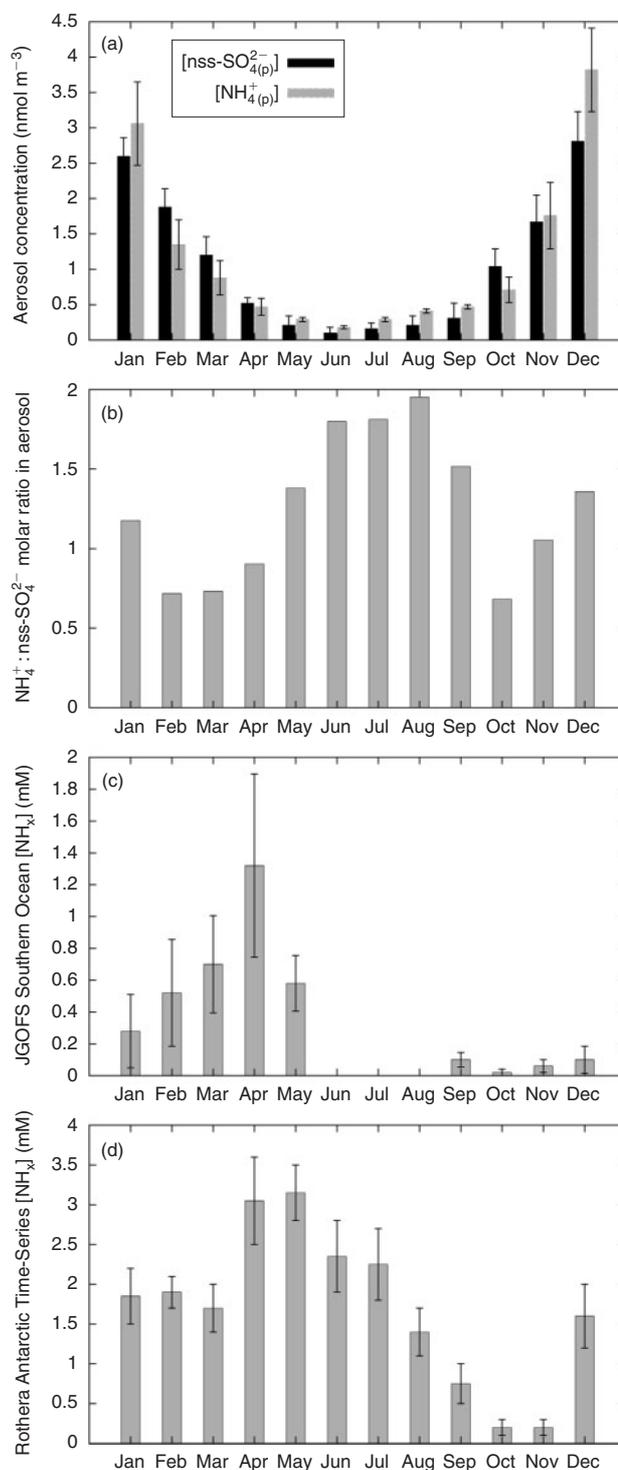


Fig. 2. Antarctic data: (a) Monthly averaged aerosol ammonium and non-sea salt sulfate (nss-SO_4^{2-}) digitised by these authors from 5 years of measured data presented by Savoie et al.^[31] at Mawson, Antarctica; (b) $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ molar ratio calculated from the data in (a); (c) monthly averaged surface seawater NH_x concentrations from the Joint Global Ocean Flux Study (JGOFS) Southern Ocean dataset (<http://usjgofs.whoi.edu/jg/dir/jgofs/southern/>, accessed April 2008), and (d) from the Rothera Atlantic Time-Series.^[42]

synchronicity cannot be explained by the seasonal cycles of $\text{NH}_{x(\text{sw})}$ observed in the Southern Ocean, or the Antarctic coastal seas (Fig. 2c, d). The Joint Global Ocean Flux Study (JGOFS) Southern Ocean dataset (<http://usjgofs.whoi.edu/>

Table 1. Input parameters, boundary conditions, variables and processes in the box model of the $\text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_4^+(\text{p})$ system

Aqueous phase (seawater) concentrations in this table are in brackets, atmospheric concentrations (i.e. per m^3 of air) are in parentheses

Symbol	Default or initial value	Description
Input parameters (constant over model run)		
t	15°C	Temperature (uniform across system)
pH	8.1	pH of surface seawater
h_{MBL}	500 m	Marine boundary layer height
Boundary conditions (prescribed or constant over model run)		
$[\text{NH}_x(\text{sw})]$	150 nM	Seawater ammonium concentration
$f_{\text{SO}_4(\text{p})}^{2-}$	$0.5 \text{ nmol m}^{-2} \text{ min}^{-1}$	Sulfate input to aerosol (i.e. acidity flux)
r_{dep}	0.0003%	Percentage aerosol loss per minute
Variables, all in units of nmol m^{-3}		
$(\text{NH}_3(\text{g}, \text{eq}))$	–	Henry's law equilibrium concentration (partial pressure) of NH_3 over seawater
$(\text{NH}_3(\text{g}))$	1	Gas phase NH_3 concentration
$(\text{pNH}_3(\text{g}))$	–	Partial pressure of NH_3 over aerosol
$(\text{NH}_4^+(\text{p}))$	2	Particulate phase ammonium concentration
$(\text{SO}_4^{2-}(\text{p}))$	3	Particulate phase sulfate concentration
Processes modelled, all in units of $\text{nmol m}^{-3} \text{ min}^{-1}$		
$F_{\text{o-a}}$	–	Ocean–atmosphere NH_3 flux, depends on t , pH, $(\text{NH}_3(\text{g}, \text{eq}))$, and $(\text{NH}_3(\text{g}))$
$F_{\text{a-p}}$	–	Gas–particle flux, depends on $(\text{NH}_3(\text{g}))$, $(\text{pNH}_3(\text{g}))$ and $\text{NH}_4^+(\text{p}) : \text{SO}_4^{2-}(\text{p})$

kg/dir/jgofs/southern/, accessed April 2008) and the Rothera Antarctic Time Series data^[45] show $\text{NH}_x(\text{sw})$ at its most depleted during the months where the data of Savoie et al.^[31] demonstrates the greatest aerosol ammonium (December, January). This is consistent with our current understanding of the seasonal cycle of $\text{NH}_x(\text{sw})$ in temperate and high-latitude oceans where the nutrient-limited months of high summer tend to efficiently re-use remineralised N, keeping concentrations low.^[21,34] The peaks in $\text{NH}_4^+(\text{p})$ also occur out of phase with surface temperatures, which reach their annual maximum in March.

We therefore argue that the only likely explanation for the synchronicity between $\text{NH}_4^+(\text{p})$ and $\text{nss-SO}_4^{2-}(\text{p})$ in Antarctic air is our hypothesised process of coupled DMS and NH_3 fluxes from the ocean. In doing so we make some assumptions: (i) windspeed and ocean pH are relatively small controls over the ocean–atmosphere NH_3 flux over commonly observed ranges^[21,22] and therefore the seasonal changes of these parameters in the Antarctic are unlikely to be responsible for the observed changes in $\text{NH}_4^+(\text{p})$; and (ii) the data of Savoie et al.^[31] are (as indicated by the authors) under strong influence of seawater emissions, i.e. not dominated by advection or local point sources such as penguin colonies, which are substantial sources of ammonia^[46] and can affect local $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratios substantially.^[47]

A simple model of the system

Below we present the details of a simple zero-dimensional finite difference box model of the ocean–atmosphere NH_x – SO_4^{2-} system, which is intended to test the hypotheses: (i) that stoichiometric production of DMS and NH_4^+ is not required in seawater to give a constant $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio in aerosol; and (ii) that acidic DMS oxidation products added to the atmosphere can drive NH_3 emission from the ocean by depletion of $\text{NH}_3(\text{g})$. Only the nitrogen side of the system is explicitly modelled, i.e. we do not attempt to investigate the effects of the relative timescales of DMS and NH_3 release and subsequent

incorporation into aerosol, as this is not practicably possible in a model with no horizontal extent. In brief, the model is driven by input of SO_4^{2-} directly into the aerosol phase, and the response of the NH_x system and the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio are investigated.

Model description

Input parameters, variables and boundary conditions are listed in Table 1 and full details of the model can be found in the Accessory publication. Ocean–atmosphere exchange of NH_3 is calculated using the thin film model (concentration difference) approach^[48] using a scheme identical to that presented by Johnson et al.^[24] Equilibration time across the air–sea interface according to this scheme is on the order of 100 h under typical conditions.^[21]

This is much slower than the characteristic time of the other modelled process, the interconversion between $\text{NH}_3(\text{g})$ and NH_4^+ , which occurs on a timescale of between 0.3 and 7 h.^[22] We employ an equilibrium scheme where the rate of flux between gas and particle phases is proportional to the difference between the concentration of $\text{NH}_3(\text{g})$ and $\text{pNH}_3(\text{g})$ (Eqn A6, Accessory publication). We use our own parameterisation of $\text{pNH}_3(\text{g})$, based on output of the Aerosol Inorganics Model (AIM, <http://www.aim.env.uea.ac.uk/aim/aim.html>, accessed September 2007)^[49] (Eqn A7 and associated text, Accessory publication).

The $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio in the model is found to be very insensitive to the rate of equilibration between gas and aerosol phases 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 time constant for this process that results in 95% equilibration over ~ 1 h, in keeping with the observations and models of Harrison and Kitto^[50] and Quinn et al.^[22]

Initial conditions and default parameter values are selected to represent typical ‘average’ conditions in the global remote

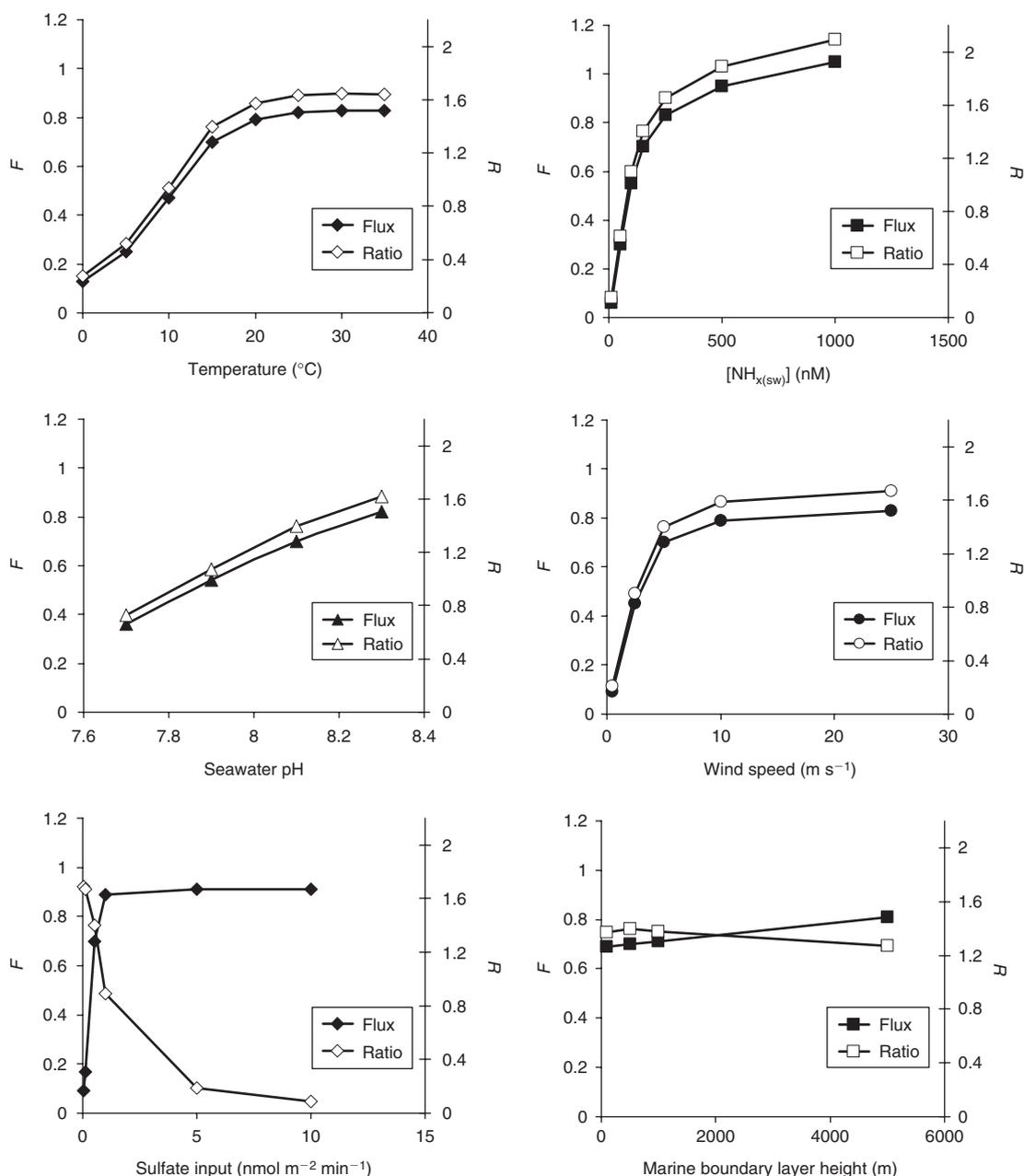


Fig. 3. Model output showing the effect of various parameters on the NH_4^+ : non-sea salt sulfate (nss-SO_4^{2-}) molar ratio (R) and the sea-air NH_3 flux (F , in $\text{nmol m}^{-2} \text{min}^{-1}$). Note that points of F and R at each x -axis parameter value represent the dynamic steady-state solution to a discrete model run.

ocean and MBL, particularly the Southern Ocean. The seawater ammonium concentration is taken as a high-latitude average concentration of 150 nM after Johnson^[21]; the sulfate input is considered as a per-unit area flux and is taken as the mean value of the Southern Ocean DMS flux observed by Shon et al.^[51] ($1.3 \mu\text{mol m}^{-2} \text{day}^{-1}$), multiplied by their mean observed SO_2 conversion factor of 0.6, giving a sulfate input of $0.5 \text{ nmol m}^{-2} \text{min}^{-1}$. The aerosol loss term is selected to maintain a constant sulfate loading, although the NH_4^+ : nss-SO_4^{2-} ratio is entirely insensitive to this term as ammonium and sulfate are removed from the model atmosphere in the same ratio as they exist in the aerosol. The model is found to be very insensitive to initial values of $\text{NH}_3(\text{g})$, $\text{NH}_4^+(\text{p})$ and $\text{nss-SO}_4^{2-}(\text{p})$ concentrations

over a wide range of values, so arbitrary values of 1, 2 and 3 nmol m^{-3} respectively are adopted as defaults, based on previous observations.^[19,22,28] Sensitivity of the model to other factors is considered below.

Model results

The model is run from starting conditions (concentrations of $\text{NH}_3(\text{g})$, $\text{NH}_4^+(\text{p})$, and $\text{SO}_4^{2-}(\text{p})$) until a dynamic steady-state (constant values of all fluxes and concentrations) is reached. Generally, such a state is reached within 48 h of model time, and in all cases within 7 days. The results of the model over a range of values of input variables and boundary conditions are

presented in Fig. 3. Note that the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio rarely exceeds a value of just over 2. This is due to the rapid increase in $\text{pNH}_{3(\text{g})}$ when the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio approaches or surpasses neutralisation, inhibiting further gas-to-particle flux.

Changes in $[\text{NH}_{\text{x}(\text{sw})}]$, temperature (t), wind speed and pH all lead to a directly proportional response in $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio and sea-air NH_3 flux. This is because all of these parameters directly affect the rate of sea-air NH_3 flux and thus the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio, in agreement with our hypothesised effect, sea-air flux being the rate-limiting step in the system.

The effect of sulfate input rate on the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio and sea-air NH_3 flux is different. As would be expected, increasing the sulfate input to the system causes the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio to decrease, as the rate-limiting sea-air NH_3 flux struggles to compensate. However, the sea-air NH_3 flux increases (up to a maximum value), because the increase in aerosol acidity is leading to uptake of $\text{NH}_{3(\text{g})}$ and consequent enhancement of sea-air NH_3 flux, demonstrating our hypothesised DMS-driven co-emission.

To further investigate this interaction between sulfate input and sea-air NH_3 flux in the model, we compare the effect of sulfate input and temperature (as a proxy for all of the parameters that enhance sea-air ammonia flux) on the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio (Fig. 4). The maximum value of air-sea flux is reached in each case when the sulfate loading is sufficient to consume effectively all of the available $\text{NH}_{3(\text{g})}$ at each timestep. This demonstrates that although DMS-driven co-emission of DMS and ammonia may occur over the range of conditions encountered in the remote marine environment, low sulfate emission rate and/or a combination of factors favouring enhanced sea-air NH_3 flux are required to ensure substantial neutralisation of the aerosol through emission of ammonia.

Discussion

Our results indicate that in the remote marine environment, any DMS-derived sulfate can enhance the rate of sea-air NH_3 flux, as hypothesised. Furthermore, it appears that the physical factors controlling ocean-atmosphere ammonia exchange are of fundamental importance to the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ molar ratio in the marine atmosphere, i.e. biological production alone cannot account for high ratios in the marine environment. Although DMS emission is clearly a significant control on the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio in remote marine environments through increasing the concentration of nss-SO_4^{2-} , this is somewhat moderated, particularly at higher temperatures and wind speeds, by the enhanced flux of NH_3 from the ocean. Thus, physical and chemical forcings (temperature, wind speed and pH) have a greater than expected control on the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio and consequently any climate-biogeochemical feedbacks in the Earth-system involving the reduced N and S cycles. For instance, the continuous resupply of NH_3 to the remote MBL through co-emission may be important in enhancing new particle formation through ternary nucleation^[52,53] or other mechanisms.^[15,54] This is not currently considered in models of particle formation over the ocean.^C In this role, our proposed mechanism provides a possible positive reinforcement of the CLAW hypothesis. Thus

^CRecent modelling studies have suggested that new particle formation is rare or non-existent in the MBL, owing to high temperatures inhibiting particle formation.^[56] These modelling studies consider only binary homogeneous nucleation between sulfuric acid and water (probably not the only process in new particle formation in the marine atmosphere^[15]) and thus may not be entirely correct. Either way, it has no bearing on our hypothesised process: the co-emitted DMS and ammonia are already spatially and temporally separated owing to the oxidation time for DMS and an extension to this separation while new particles sink back into the MBL is of little consequence at large scales of space and time.

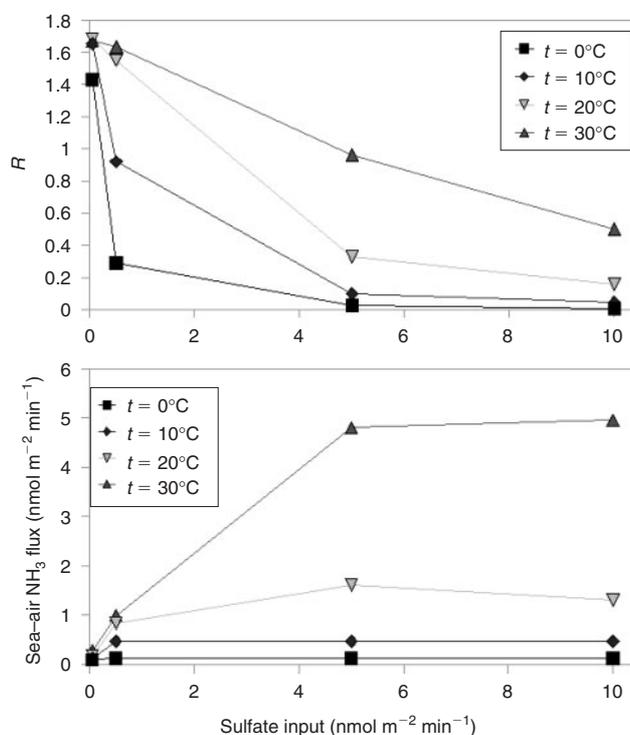


Fig. 4. Model output showing the effect of sulfate input on (a) $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ molar ratio (R) and (b) sea-air NH_3 flux, over a range of temperatures. This highlights that sulfate input drives sea-air NH_3 flux up to a maximum value that is strongly dependent on temperature (and other factors influencing the strength of ammonia emission from the ocean, not shown).

long-term changes in ocean pH, temperature or wind fields may have significant effects on the radiative budget in Earth's past or future climate.

These same factors (t , pH and wind) and consequent changes in atmospheric acidity through changing neutralisation by NH_3 may have important effects on aerosol iron processing and consequent availability of Fe to plankton in iron-limited regions of the World's oceans. Whether these potential feedbacks are positive or negative at a given point in Earth's history (or future) in part depends on the relative changes in magnitude of t and pH with changing atmospheric CO_2 (pCO_2) as they tend to act against each other in their effect on NH_3 flux (i.e. an increase in pCO_2 will tend to decrease ocean pH, thus inhibiting marine NH_3 emission, while increased temperature will favour NH_3 emission).

Conclusions

We have proposed a mechanism by which observed $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratios can be explained without the need to invoke the stoichiometric coproduction of the precursor gases NH_3 and DMS in seawater. Our simple model has demonstrated that in the remote MBL, where the predominant sources of $\text{NH}_4^+_{(\text{p})}$ and $\text{nss-SO}_4^{2-}_{(\text{p})}$ are marine and where the system is relatively close to

equilibrium with respect to NH_x , the hypothesised mechanism appears to exert a significant control on the $\text{NH}_4^+ : \text{nss-SO}_4^{2-}$ ratio. However, the model only solves for a dynamic steady-state and therefore accounts for neither fine-scale variation in marine emissions nor the advection of air masses enriched in either NH_x or SO_4^{2-} from the terrestrial realm. For large tracts of the contemporary ocean, these are likely to alter the signal that might be expected from our proposed process.

However, in pre-industrial times, when anthropogenic and natural terrestrial emissions were minor contributors to the reduced N and S global biogeochemical cycles, our hypothesised coupling mechanism is more likely to be applicable over most of the open ocean. Therefore, we argue that the suggestion to assume that marine NH_3 emissions scale with DMS emissions globally^[17] is probably reasonable for pre-industrial times but is not likely to be applicable in the modern era owing to large anthropogenic perturbations of the S and reduced N cycles.

To further test the real-world significance of co-emission of DMS and ammonia from the ocean, observational evidence must be combined with analysis using detailed box models of DMS oxidation and the next generation of ocean-coupled atmospheric chemical transport models, which will explicitly model ammonia and DMS fluxes and their interactions.

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