A dynamic chemical model of bi-directional ammonia exchange between semi-natural vegetation and the atmosphere

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Summary

A mechanistic, dynamic compensation point model to simulate the vegetation/atmosphere exchange of ammonia (NH3) is described. The model is applied to long-term micrometeorological measurements of NH3 exchange obtained over moorland in southern Scotland (1995–96). The model describes the gaseous bi-directional exchange between the atmosphere, leaf surface water films, plant stomata and apoplast. A simple chemistry module is included to simulate the exchange of water-soluble atmospheric pollutants at the air–water interface on wet plant surfaces. Initialization of the chemistry module is achieved during rain events using measured rain chemical composition. The exchange of NH3 with stomata is based on the concept of a stomatal compensation point parameterized by means of the apoplastic ammonium/hydronium (H+) ratio. The trans-cutticular transfer of ammonium may also constitute a sink for dissolved ammonia on plant cuticular water films, and is parametrized using a trans-cutticular resistance and the concentration difference between leaf surface water and the apoplast. The leaching of base cations from the inside of the plant to foliar surfaces is simulated in a similar fashion to ammonium transfer, and the heterogeneous oxidation of sulphur dioxide (SO2) in thin water films is also treated. Numerical iterative procedures at each time-step allow the calculation of pH and dissolved ion concentrations.

Modelled NH3 fluxes were compared with 3259 half-hourly micrometeorological measurements over moorland, and with two existing modelling approaches, the static canopy compensation point model and the canopy resistance model. The dynamic and static canopy compensation point models both gave long-term estimates of the NH3 dry deposition flux to moorland within 10% of actual measurements, while the canopy resistance approach overestimated deposition by about 30%. The dynamic model performed best during wet conditions for which it was designed, and performed reasonably well during dry conditions using a more empirical resistance approach.

The model was also capable of simulating SO2 dry deposition fluxes to within 20% of measured fluxes. The model provides a tool that may also be used to simulate scenarios, whereby NH3/SO2 concentration ratios in the atmosphere vary, and examine ‘co-deposition’ interactions of these two species.

Keywords: Ammonia Compensation point Dry deposition Resistance modelling Surface exchange

1. Introduction

Atmospheric inputs of nitrogen (N) to ecosystems throughout Europe currently constitute approximately half of the acidifying input, and in areas of large N deposition lead to species composition changes in ground flora (RGAR 1997). Thus the emphasis in control measures is now on nitrogen compounds, among which reduced nitrogen, i.e. ammonia (NH3) and ammonium (NH4+), contribute more than half of the total N input (RGAR 1997). In developing control strategies for N deposition, a critical loads approach has been adopted by the United Nations Economic Commission for Europe (UNECE). For such an approach, the ability to quantify N inputs to Europe with high spatial resolution is a primary requisite.

Recent long-term micrometeorological measurements of the dry exchange of NH3 over three sites across Europe (Fir forest, the Netherlands; moorland, Scotland; grassland, eastern Germany) have shown that the annual net dry deposition of NH3 contributes between 30% (moorland site) and 40% (forest and grassland sites) of the total dry and wet, reduced and oxidized nitrogen deposition flux at these sites (Erisman et al. 1996). As monitoring strategies for the exchange of NH3 have so far been hampered by the costs and complexity of equipment and maintenance associated with long-term flux measurements, there are currently no networks to provide continuous measurements.

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of the surface/atmosphere exchange of NH$_3$ at the ecosystem scale. The estimation of annual dry fluxes of NH$_3$ to European ecosystems therefore currently relies on (1) model computations of the atmospheric transport and diffusion of NH$_3$ from terrestrial emissions for which inventories are constantly updated (e.g. Sutton et al. 1995a; Dragosits et al. 1996; Asman and Van Jaarsveld 1992; Singles et al. 1998), and (2) the use of surface/atmosphere exchange inferential models to derive fluxes from monitored or modelled air concentrations, and atmospheric and surface resistances (Hicks et al. 1987; Erisman et al. 1994; Sutton et al. 1998; Sorteberg and Hov 1996).

Canopy resistance ($R_c$) deposition models (e.g. Erisman et al. 1994) assume zero concentration at the surface and therefore treat plant surfaces exclusively as sinks for atmospheric NH$_3$. By contrast, canopy compensation point ($\chi_c$) models (e.g. Sutton et al. 1995b) allow for the bi-directional nature of NH$_3$ fluxes often reported over plant communities by considering non-zero NH$_3$ concentrations within or at the surface of the canopy. The stomatal compensation point ($\chi_s$), a component term of $\chi_c$ models, is of particular relevance for arable crops with a high nitrogen status which have been shown to be net sources of NH$_3$ during the growing season as well as during senescence (Farquhar et al. 1980; Sutton et al. 1995b; Nemitz et al. 1998). Over nitrogen-limited semi-natural vegetation, much smaller $\chi_s$ generally occur with the result that deposition to the surface prevails (Sutton et al. 1993a; Duyzer 1994). However, the sink strength of semi-natural vegetation has been shown to be highly variable and dependent on canopy wetness, temperature and ambient NH$_3$ concentrations, with occasional upward fluxes during drying of surface water layers on plant cuticles (Sutton et al. 1995d; Flechard and Fowler 1998). Although leaf surface water chemistry constitutes a driving force behind epicuticular fluxes of water-soluble pollutants such as NH$_3$ and SO$_2$ (Cape 1996), chemical processes in thin water films on plant surfaces generally have not been included in exchange models to date, in which more empirical approaches have been applied.

In this paper, the canopy/atmosphere exchange of NH$_3$ over semi-natural vegetation is described using a new dynamic canopy compensation point model based on the approach of Sutton et al. (1995c). The new model includes the physiological control of NH$_3$ exchange through the use of a stomatal compensation point ($\chi_s$) and cuticular absorption/desorption, but adds a dynamic leaf surface water chemistry module to simulate epicuticular fluxes. The long-term measurements of NH$_3$ fluxes obtained during a 13-month flux monitoring period at a moorland site in Scotland as part of the LIFE programme (Flechard and Fowler 1998) is used to derive model parametrizations. Soil/ground fluxes and emission fluxes of NH$_3$ from decaying plant material are not treated explicitly in this model and are assumed to be negligible given the wet and acidic nature of the peat soil at the moorland site under consideration.

Leaf surface solution chemistry is simulated using the Henry and dissociation equilibria for the trace gases NH$_3$, SO$_2$, CO$_2$, HNO$_2$, HNO$_3$, HCl; SO$_2$ oxidation and cation exchange between the leaf surface and plant interior are also accounted for. Activity coefficients are included in the numerical calculations of the equilibrium pH and solute concentrations for solutions with ionic strengths up to 0.3 M. For more concentrated solutions such as those present as deliquescent salts on plant surfaces in dry conditions (relative humidity (r.h.) $< \sim 70\%$), bulk ‘ideal’ chemistry and Henry’s law are not applicable; in these conditions, simple transfer resistances are used to obviate the need for a more complex treatment of salt-ion chemistry. This simplified approach is justified in the present model as the bulk of the exchange of NH$_3$ and other water-soluble gases between plant cuticles and the atmosphere is likely to occur during periods when the surface is effectively wet; the fraction of dry-deposited NH$_3$ under
very dry conditions (r.h. < 70%) is believed to be small relative to the total deposition flux (Duyzer 1994; Flechard and Fowler 1998).

The modelling objectives addressed here include an accurate prediction of long-term fluxes, the relative quantification of both stomatal and epicuticular fluxes of NH₃ and their variations in response to changes in ambient NH₃ and other pollutant concentrations, air temperature, leaf wetness and atmospheric humidity, time of day and season. The model should also simulate the bi-directional nature of the surface/atmosphere exchange of NH₃ which has been observed in field measurements in warm summer conditions. Comparisons are provided between the model presented here and other existing modelling approaches. The model also provides a framework for the investigation of potential interactions between NH₃ and acidic compounds such as SO₃ on leaf surfaces in the light of previous studies (e.g. Van Breemen et al. 1982; Erisman and Wyers 1993) suggesting that 'co-deposition' processes may be important.

2. THEORY OF RESISTANCE MODELLING

Trace gas fluxes between the atmosphere and terrestrial surfaces have long been viewed as analogous to electrical currents flowing through resistance networks following Ohm's law (e.g. Monteith 1973; Fowler and Unsworth 1979), where a vertical concentration gradient drives a trace gas flux \( F_i (\text{g m}^{-2} \text{ s}^{-1}) \) across a physical resistance \( R (\text{s m}^{-1}) \):

\[
F_i = \frac{\chi(z_1) - \chi(z_2)}{R_{z_1z_2}} \tag{1}
\]

where \( i \) denotes trace gas, and \( \chi(z) (\text{g m}^{-3}) \) is trace gas concentration at height \( z \) above the surface.

The aerodynamic atmospheric resistance to turbulent transfer \( R_a \) is generally calculated between a reference height \( z - d \) and the notional height \( d + z_0 \), where \( d \) is the displacement height associated with aerodynamically rough plant canopies and \( z_0 \) is the roughness length of the surface. A second atmospheric resistance, \( R_b \), accounts for the trace gas transfer between \( z_0 \) and \( z'_0 \), the notional height of the surface for entrained property exchange, mainly by molecular diffusion across a viscous laminar sublayer immediately above the plant's surface. \( R_a \) and \( R_b \) were in this study calculated according to Garland (1977) and Chamberlain (1966). The canopy (or surface) resistance \( R_c \) was originally seen as an 'excess' resistance across the residual concentration difference above an absorbing surface in the case of dry deposition (Fowler and Unsworth 1979).

(a) Existing resistance models for NH₃ exchange

Resistance models applied to the plant/atmosphere exchange of NH₃ have recently been reviewed by Sutton et al. (1998) and Nemitz et al. (1998); only a brief overview is therefore presented here. These models fall readily into two categories: (1) canopy resistance models (Fig. 1(a)) assuming zero surface concentrations, largely applied to dry deposition of NH₃ over semi-natural ecosystems (Erisman and Wyers 1993; Sutton et al. 1993a; Duyzer 1994); (2) stomatal and canopy compensation point models (Figs. 1(b) and 1(c)) allowing bi-directional fluxes (Sutton et al. 1995b).

Canopy resistance models of dry deposition (Hicks et al. 1987) treat \( R_c \) itself as equivalent to a network of parallel resistances e.g. stomatal, cuticular and soil resistances to gaseous uptake. Such models break down when, as is the case for NH₃, surface concentrations differ from zero and gases can be emitted by plant canopies
through physiological and/or physico-chemical processes. In such situations, the use of canopy compensation points represents a viable alternative to $R_c$ models, whereby dry deposition occurs if $\chi_c$ is lower than the ambient concentration $\chi(z-d)$ of the trace gas, and emission is triggered whenever $\chi_c > \chi(z-d)$ (e.g. Sutton et al. 1995b, 1998).

A distinction is made between the stomatal compensation point $\chi_s$ (Farquhar et al. 1980), and the canopy compensation point $\chi_c$, with the latter including epicuticular physico-chemical processes as well as physiological aspects. The stomatal compensation point model (Fig. 1(b)), used mainly in laboratory-based physiological studies, deals solely with the exchange of NH$_3$ between the atmosphere and the intercellular fluid of leaf mesophyll, the apoplast, containing dissolved NH$_3$ and NH$_4^+$ in thermodynamic equilibrium with the air within sub-stomatal cavities (see also Fig. 2).

The epicuticular exchange of NH$_3$ between the atmosphere and thin water films or moist cuticular waxes, ignored in $R_c$ models and $\chi_s$ models, is explicitly treated in the $\chi_c$ model (Fig. 1(c)) through the use of an additional resistance for deposition to wet surfaces, $R_w$ (Sutton et al. 1995b), although this approach fails to simulate desorption fluxes from plant cuticles. Alternative modelling techniques need to identify physico-chemical processes that regulate the sink- and/or source-strength of leaf surface water films as these may be regarded as chemical reactors for dissolved atmospheric gases and ions.

(b) Dynamic modelling of ammonia exchange

Treating leaf surfaces as potentially infinite sinks for atmospheric NH$_3$ as has often been done for semi-natural vegetation (e.g. Erisman et al. 1994) will result in an overestimation of annual deposition fluxes, as the sink strength of leaf surfaces is highly
Figure 2. Schematic representation of the dynamic canopy compensation point model incorporating a leaf surface chemistry module, showing the exchange between the atmospheric gaseous phase, the aqueous phase of water droplets on leaf cuticles, and plant apoplast. Note that $\chi_d$ is a notional atmospheric concentration that would be in Henry equilibrium with the concentration of the dissolved species $X_{aq}$. Also note that the site of exchange between the atmosphere and the liquid film is at the notional height $z_0'$ and that $R_d$ is effectively a resistance to transfer across the air/water interface.
variable with time of day and month of year and largely dependent on surface humidity and temperature (Sutton et al. 1995b). Thin water films on plant surfaces may indeed behave as perfect sinks for NH₃ for limited periods of time in wet conditions after rain or during dewfall, in which circumstances atmospheric transport constitutes the main limitation to the deposition flux. However, the dry deposition of NH₃ onto a wet surface is not an irreversible process since the NH₃ molecule is not immediately "destroyed" or removed from solution. The sorption process at the water/atmosphere interface is followed by solution, then dissociation of the hydrated molecule into NH₄⁺ and OH⁻, raising the pH of the solution. As NH₃ is less soluble at high pH values, an equilibrium would develop between the atmosphere and the water film, limiting the dry deposition process (van Hove and Adema 1996). This, however, is not true in the presence of atmospheric CO₂ concentrations where the pH of water in equilibrium with CO₂ would not show a large response to NH₃ uptake at typical ambient NH₃ concentrations (a few ppb). Wet canopies generally do not reach the saturation level and provide efficient sinks for NH₃ for as long as the size of the water pool remains large enough to buffer the alkalinizing effect of NH₃. As a dew layer or intercepted rain water evaporates from the leaf surface, the buffering capacity decreases, potentially resulting in a NH₃-saturated film (Cape 1996). Measurements and modelling of cloud chemistry at Great Dun Fell (northern England) have shown that NH₃ could also be released from evaporating cloud droplets (Wells et al. 1997). As relative humidity decreases and temperature increases, NH₃ is emitted by the solution until most of the free water on the leaf surface has evaporated. Ammonia is then largely present on leaf surfaces as NH₄⁺ in ammonium sulphate and ammonium nitrate salts.

Since NH₃ dry deposition to leaf surfaces is reversible and dependent on previous fluxes, hysteresis effects can only be accounted for in dynamic compensation point models. Ammonia fluxes are affected to some extent by all previous pollutant fluxes including both wet and dry deposition. It is therefore also important to consider fluxes of other water-soluble gases such as SO₂, HNO₂, HNO₃, HCl, CO₂, which influence the pH of water droplets on leaves, when measurements of atmospheric concentrations of these species are available. Trans-epidermal fluxes of NH₄⁺, H⁺ and base cation leaching (Mg²⁺, Ca²⁺, K⁺ and Na⁺) may also be important, especially for canopies subjected to acidic rainfall or dew (e.g. Adams and Hutchinson 1987). Initial boundary conditions may be provided for a wet canopy during a rain event from measured rain chemistry data.

3. Model Description

(a) Formulation of the dynamic canopy compensation point model

The framework for the calculation of the canopy compensation point χₑ and hence the surface/atmosphere fluxes of water-soluble gases (see Fig. 2), was provided by Sutton et al. (1998) as:

\[
\begin{align*}
\chi_e &= \frac{\chi(z - d)/(R_a(z - d) + R_b) + \chi_s/R_s + \chi_d/R_d}{(R_a(z - d) + R_b)^{-1} + R_s^{-1} + R_d^{-1}} \\
F_{i,t} &= \frac{\chi_e - \chi(z - d)}{R_a(z - d) + R_b} = F_{i,s} + F_{i,d} \\
F_{i,s} &= \frac{\chi_s - \chi_e}{R_s}
\end{align*}
\]
where $i$ denotes trace gas, $F_{i,d}$ is the total flux, $F_{i,s}$ the stomatal flux and $F_{i,d}$ the epicuticular flux. $\chi_d$ is a notional gaseous concentration in Henry’s law equilibrium with the aqueous form of the molecule $X_{aq}$, such that:

$$\chi_d = \frac{[X_{aq}]c}{K_h}$$

where $K_h$ is the Henry’s law coefficient for species $X$ (M atm$^{-1}$). Throughout this paper, the notation $[X]$ denotes bulk solution concentrations in mol l$^{-1}$ (molarities); $[X]_c$ are molarities in water films on cuticles, while $[X]_a$ represent apoplast concentrations.

The cuticular absorption resistance $R_d$ can be interpreted as the constraint maintaining dis-equilibrium of the solution/atmosphere system. When transport within the aqueous phase is fast relative to $F_{i,d}$, $z'_0$ for the leaf surface is the same as for stomata; $R_d$ accounts for any difference in $z'_0$ and transport, plus an allowance for mixing terms in solution. In a situation of equilibrium, $\chi_d$ equals $\chi_c$, and $F_{i,d}$ is negligible; on the other hand, a larger $R_d$ allows a substantial departure of the canopy compensation point $\chi_c$ from the equilibrium value $\chi_d$ (Fig. 2). This framework was initially developed using an empirical parametrization of leaf surface water as a capacitor with a charge $Q_d$ and capacitance $C_d$, charging and discharging with the resistance $R_d$ (Sutton et al. 1998).

However, in the absence of a mixed chemical treatment of leaf surface wetness, $C_d$ had to be parametrized with arbitrary values of cuticular pH. In the present model, the need to impose cuticular pH is avoided as it is numerically calculated using modelled aqueous chemistry, including $SO_2$ oxidation and other ion transfers, thus driving surface/atmosphere fluxes in a less empirical fashion.

Wet deposition is also included in the model using actual precipitation chemistry data when available. Particle deposition was not simulated in the present study as it was believed to have a minimal influence on leaf surface chemistry at the site where measurements reported in this paper were made, owing to small aerosol fluxes (Erisman et al. 1996).

Trace gas fluxes between surface water films or water droplets and the atmosphere are integrated over time in the model using time-steps of mostly $10^{-1}-10^2$ seconds. The duration of each time-step is calculated at each new time-step in such a way that the maximum rate of change in $\chi_d$ for all the gases considered does not exceed a set value e.g. 5%. This allows the model to run faster when trace gas fluxes do not significantly affect the composition of the surface solution over longer periods of time (a few minutes), such as in night-time dewy conditions or over a rain-wetted canopy. Shorter time-steps allow the model to remain stable in dryer daytime conditions. At the end of each time-step, the new pH and chemical composition of the surface solution are determined numerically from group concentrations (e.g. $NH_3$, $S^{IV}$, $S^{VI}$) using Newton–Raphson’s method (Press et al. 1989) to solve the electroneutrality equation:

$$[H^+]_c + [NH_4^+]_c + [Na^+]_c + [K^+]_c + 2[Mg^{2+}]_c + 2[Ca^{2+}]_c = [OH^-]_c + [HCO_3^-]_c + 2[CO_3^{2-}]_c + [HSO_4^-]_c + 2[SO_3^{2-}]_c$$

$$+ [HSO_4^-]_c + 2[SO_4^{2-}]_c + [NO_2^-]_c + [NO_3^-]_c + [Cl^-]_c$$

Subsequent to integration over a time-step and calculation of the new equilibrium pH, new values of $\chi_d$ for the different reactive gases are provided using Henry’s law
TABLE 1. HENRY’S LAW AND DISSOCIATION THERMODYNAMIC CONSTANTS USED IN THE CHEMISTRY MODULE. THE TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANTS IS GIVEN BY VAN’T HOFF’S EQUATION, $\frac{d \ln K}{dT} = \frac{\Delta H_0}{RT^2}$

<table>
<thead>
<tr>
<th>Equilibria</th>
<th>Constants</th>
<th>$K_{298.15K}$</th>
<th>log($K_{298.15K}$)</th>
<th>$\Delta H_{298-298.15K}$ kcal mol$^{-1}$</th>
<th>Source/Adapted from</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$($g$) $\leftrightarrow$ NH$_3$(aq)</td>
<td>$K_{ha}$ (M atm$^{-1}$)</td>
<td>56.04</td>
<td>1.75</td>
<td>$-8.17$</td>
<td>Dasgupta and Dong (1986)</td>
</tr>
<tr>
<td>CO$_2$($g$) $\leftrightarrow$ CO$_2$(aq)</td>
<td>$K_{hc}$ (M atm$^{-1}$)</td>
<td>$3.26 \times 10^{-2}$</td>
<td>$-1.49$</td>
<td>$-4.85$</td>
<td>Chameides (1984)</td>
</tr>
<tr>
<td>SO$_2$($g$) $\leftrightarrow$ CO$_2$(aq)</td>
<td>$K_{ha}$ (M atm$^{-1}$)</td>
<td>1.24</td>
<td>0.09</td>
<td>$-6.25$</td>
<td>Maiba (1982)</td>
</tr>
<tr>
<td>HNO$_2$($g$) $\leftrightarrow$ HNO$_2$(aq)</td>
<td>$K_{hs}(n_0)$ (M atm$^{-1}$)</td>
<td>48.98</td>
<td>1.69</td>
<td>$-9.5$</td>
<td>Jacob and Hoffmann (1983)</td>
</tr>
<tr>
<td>H$_2$O $\leftrightarrow$ H$^+$ + OH$^-$</td>
<td>$K_w$ (M)</td>
<td>$1.01 \times 10^{-14}$</td>
<td>$-14.00$</td>
<td>$13.35$</td>
<td>Seinfeld (1986)</td>
</tr>
<tr>
<td>NH$_4^+$ $\leftrightarrow$ NH$_3$(aq) + H$^+$</td>
<td>$K_a$ (M)</td>
<td>$5.67 \times 10^{-10}$</td>
<td>$-9.25$</td>
<td>$12.47$</td>
<td>Bates and Pinching (1950)</td>
</tr>
<tr>
<td>CO$_2$aq $\leftrightarrow$ HCO$_3^-$ + H$^+$</td>
<td>$K_{cl}$ (M)</td>
<td>$4.28 \times 10^{-7}$</td>
<td>$-6.37$</td>
<td>$1.825$</td>
<td>Seinfeld (1986)</td>
</tr>
<tr>
<td>HCO$_3^-$ $\leftrightarrow$ CO$_3^{2-}$ + H$^+$</td>
<td>$K_{c2}$ (M)</td>
<td>$4.69 \times 10^{-11}$</td>
<td>$-10.33$</td>
<td>$3.55$</td>
<td>Seinfeld (1986)</td>
</tr>
<tr>
<td>SO$_2$aq $\leftrightarrow$ HS$O_3^-$ + H$^+$</td>
<td>$K_{s1}$ (M)</td>
<td>$1.32 \times 10^{-11}$</td>
<td>$-1.88$</td>
<td>$-4.16$</td>
<td>Maiba (1982)</td>
</tr>
<tr>
<td>HS$O_3^-$ $\leftrightarrow$ SO$_3^{2-}$ + H$^+$</td>
<td>$K_{s2}$ (M)</td>
<td>$6.42 \times 10^{-11}$</td>
<td>$-7.19$</td>
<td>$-2.23$</td>
<td>Maiba (1982)</td>
</tr>
<tr>
<td>HSO$_3^-$ $\leftrightarrow$ H$^+$ + SO$_3^{2-}$</td>
<td>$K_{s3}$ (M)</td>
<td>$1.20 \times 10^{-2}$</td>
<td>$-1.92$</td>
<td>$-5.23$</td>
<td>Sturmin and Morgan (1981)</td>
</tr>
<tr>
<td>HNO$_2$aq $\leftrightarrow$ NO$_2^-$ + H$^+$</td>
<td>$K_{n1}$ (M)</td>
<td>$5.13 \times 10^{-4}$</td>
<td>$-2.59$</td>
<td>$-2.5$</td>
<td>Schwartz and White (1983)</td>
</tr>
<tr>
<td>HNO$_3$($aq$) $\leftrightarrow$ NO$_3^-$ + H$^+$</td>
<td>$K_{n2}$ (M$^2$ atm$^{-1}$)</td>
<td>$3.24 \times 10^6$</td>
<td>$6.51$</td>
<td>$-17.3$</td>
<td>Jacob and Hoffmann (1983)</td>
</tr>
<tr>
<td>HCl($g$) $\leftrightarrow$ Cl$^-$ + H$^+$</td>
<td>$K_{cl1}$ (M$^2$ atm$^{-1}$)</td>
<td>$2.00 \times 10^8$</td>
<td>$6.30$</td>
<td>$-17.89$</td>
<td>Liljestrand (1985)</td>
</tr>
</tbody>
</table>

The canopy compensation point $X_{c}$ at the beginning of the next time-step is calculated following Eq. (2) and using the new $\chi_d$ value for each trace gas. Having determined $X_{c}$, the stomatal and epicuticular fluxes are computed from Eq. (4) and Eq. (5), respectively, and they are assumed to remain constant for the duration of the following time-step over which fluxes are integrated. Stomatal compensation points ($X_{s}$) are taken to be zero for all pollutant gases considered in the model except for CO$_2$ and NH$_3$; possible values for $X_{s}$(NH$_3$) are discussed in the parametrization section.

Corrections for activity effects are provided in the model for highly concentrated solutions in dry conditions when very little free water remains on leaf cuticles and the relative humidity at the surface approaches that of the deliquescence point of e.g. ammonium salts. At lower relative humidities, ideal solution thermodynamics are no longer appropriate, as the ‘solution’ essentially consists of a very thin water film (<50 nm) bridging gaps between individual clusters to hydrated ammonium and base cation salts (Burkhardt and Eiden 1994). To account for non-ideal solutions with ionic strengths (I) up to 0.5, aqueous ionic concentrations were routinely substituted in the model by activities using activity coefficients $\gamma_i$ calculated from the Davies equation (Seinfeld 1986):

$$ \log \gamma_i = -0.5085z_i^2 \left( \frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right) $$

where $z_i$ is the charge of the ion and I the ionic strength of the solution is a function of all individual ionic charges $z_i$ and molalities $m_i$;

$$ I = 0.5 \sum_i z_i^2 m_i. $$
For neutral species in solution such as NH$_3$$_{aq}$ or SO$_2$$_{aq}$, activity coefficients were calculated such that (Wells 1996; Wells et al. 1997):

$$\log \gamma_1 = 0.1I.$$  \hspace{1cm} (12)

At higher ionic strengths such as those encountered in highly concentrated particles in warm, dry (r.h. < 60%) conditions, the above treatment of non-ideal solution thermodynamics is no longer justifiable. More complex developments of the theory would then be needed as Henry’s law for dissolved gaseous species breaks down, and gas/particle thermodynamic equilibria should be considered in a similar way to general equilibrium models for multicomponent atmospheric aerosols (Seinfeld 1986; Pilinis and Seinfeld 1987). However, such complex treatment of the surface chemistry in dry conditions lies beyond the scope of this paper; the focus of the present study is the simulation of the aqueous chemistry of leaf surfaces whenever activity-corrected Henry’s law applies with reasonable accuracy, i.e. for solution ionic strengths below a critical value e.g. 0.3 M.

(b) Parametrizations

Model parametrizations were, when possible, derived from the micrometeorological measurements obtained at the moorland site of the LIFE programme, Auchencorth Moss (S. Scotland), during a 13-month pollutant monitoring period in 1995–96 (Erisman et al. 1996). Available data include NH$_3$, SO$_2$, CO$_2$, O$_3$ and NO$_x$ atmospheric concentrations and fluxes on a half-hourly basis as well as HNO$_3$, HNO$_2$ and HCl concentrations on a weekly basis. Meteorological data were collected half-hourly and include wind speed, temperature, friction velocity, sensible and latent heat fluxes, total solar and net radiation, soil heat flux, relative humidity and precipitation amounts from a tipping bucket precipitation collector. Weekly rain samples were analyzed for all major ions including NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, Cl$^-$, K$^+$, Ca$^{2+}$, Mg$^{2+}$. The model was first parametrized using a small data subset (a few days) from Auchencorth Moss, and then applied to a much larger dataset containing a wider variety of meteorological and environmental conditions, thus providing an independent model validation.

Cuticular adsorption resistance ($R_d$). $R_d$ is parametrized as an exponential function of the ionic strength $I$ of the solution (Eq. 13), being negligible ($R_d \sim 1$ s m$^{-1}$) for $I$ in the range $10^{-4}$–$10^{-2}$ and very large ($R_d > 1000$ s m$^{-1}$) for $I > 10^{-1}$:

$$R_d = \exp^{(100I)}.$$ \hspace{1cm} (13)

It is believed that for highly concentrated solutions, electric forces between ionic species counteract the rapid establishment of a local Henry’s law equilibrium. This parametrization of $R_d$, however, is only applied up to a critical value of $I$ of 0.3. For more concentrated solutions, the uncertainty associated with calculating values of $\chi_d$ from Henry’s law and solution molarities is such that an empirical approach is preferred. Continuity between ‘wet’ periods is provided in the model by applying and integrating over time small downward fluxes of all gaseous species onto cuticles during dry conditions, assuming zero values for all $\chi_d$ concentrations and using an $R_d$ value of 100 s m$^{-1}$. This approach to simulate cuticular fluxes ($F_d$) in dry conditions is effectively the static approach described in Fig. 1(c) (Sutton et al. 1995b). The value 100 s m$^{-1}$ was derived from field micrometeorological measurements throughout 1995 at Auchencorth Moss, where surface fluxes for water-soluble species such as NH$_3$ and SO$_2$ were generally downward and small in dry conditions. The simulation of the solution/atmosphere chemistry resumes with increasing humidity, dewfall or rainfall as
the bulk canopy surface solution volume increases and the ionic strength decreases, justifying the renewed use of Henry’s law. The discrepancy between very large \( R_d \) values (>1000 s m\(^{-1}\)) associated with evaporating water films and \( I > 0.3 \) on the one hand, and an \( R_d \) of 100 s m\(^{-1}\) during dry conditions on the other hand, may appear counter-intuitive to continuity between ‘wet’ and ‘dry’ phases. However, the \( R_d \) term takes very different meanings in these contrasting conditions, as two different modelling approaches are effectively adopted, with a non-zero \( \chi_d \) in the former case, and a zero \( \chi_d \) in the latter. This results in arbitrarily turning small bi-directional fluxes into small dry deposition fluxes to the leaf cuticle as \( I \) increases past the threshold value of 0.3.

Leaf surface water storage (\( V_S \)). The moorland canopy is considered in this model to hold a highly variable amount of liquid water on its leaf surfaces, ranging from about \( 10^{-4} \) mm \((\approx 100 \text{ mm} \approx 10^{-4} \text{ m}^2)\) to a maximum value \( V_{S,max} \), the water-saturated canopy holding capacity, of up to \( \approx 1-2 \) mm. \( V_{S,max} \) is treated as the product of the leaf area index (LAI) and the storage capacity \( H_{S,max} \) expressed as equivalent thickness of water per unit leaf area. \( H_{S,max} \) is characteristic of individual species and is particularly dependent on the wettability of individual leaf surface waxy cuticles; \( H_{S,max} \) has been shown to range from values of less than 0.1 mm for species such as \textit{Vicia faba} (Huber 1988) up to 0.8 mm for \textit{Triticum aestivum} (Butler 1983). The value used in the model was \( H_{S,max} = 0.1 \) mm.

The efficiency of rainfall interception by a canopy is inversely related to rainfall intensity, being as high as 75% for a wheat canopy for precipitation rates <1 mm h\(^{-1}\) and of the order of 20% for rates >1.8 mm h\(^{-1}\) (Butler 1996). The interception efficiency decreases when large raindrops colliding onto leaf surfaces with large kinetic energies break up into smaller drops being redistributed, also potentially shaking off previously intercepted droplets. Large wind speeds also reduce the rainfall interception efficiency by inducing mechanical shaking of leaves within the canopy (Butler 1983). In the present study, the rainfall interception efficiency was assumed to be 75% for rainfall intensities <0.5 mm h\(^{-1}\), 50% for rainfall intensities between 0.5 and 1 mm h\(^{-1}\) and 25% for rainfall intensities >1 mm h\(^{-1}\). Dew formation and evaporation are simulated in the present model from latent heat fluxes measured by Bowen ratio techniques at Auchencorth Moss; water vapour fluxes are integrated over successive time steps to provide a canopy estimate of \( V_S \).

In dry daytime conditions, however, subsequent to evaporation of dew or rain from the vegetation, stomatal transpiration dominates the H\(_2\)O flux and the above approach becomes inadequate. In these conditions, the estimation of \( V_S \) is based on the assumption that deliquescent ammonium sulphate salts make up the bulk of the solutes present on leaf cuticles. \( V_S \) is estimated using the salt-ion effect describing the lowering of the water vapour partial pressure over a concentrated solution (Pruppacher and Klett 1978). Relative humidities at \( z_0' \), estimated from micrometeorological measurements, are used to derive the mass \( a_{AS} \) (g) of \((\text{NH}_4)\text{2SO}_4\) per 100 g of H\(_2\)O as described in Fig. 3. Assuming that droplet radii exceed 0.1 \( \mu \)m, the effects of interface curvature and surface tension (Kelvin effect) can be neglected (Pruppacher and Klett 1978). Thus, \( a_{AS} \), combined with the modelled canopy dry mass \( M_{AS} \) (g m\(^{-2}\)) of \((\text{NH}_4)\text{2SO}_4\) salts present on plant cuticles and with the solution density \( \rho_S \) (g cm\(^{-3}\)) calculated as a function of the percentage of ammonium sulphate in solution (Garland 1969), provides an estimate of \( V_S \) (mm) as:

\[
V_S = \frac{M_{AS}}{a_{AS}\rho_S},
\]  

(14)
Figure 3. Lowering of atmospheric relative humidity immediately above a concentrated pure (NH₄)₂SO₄ solution. The empirical sigmoidal fit was obtained using values from the International Critical Tables (Vol. 3, p363). $a_{AS}$ can be obtained from measured relative humidity at $z_0$ using the inverse relationship such that $a_{AS} = 150.57((1 - 0.38)/(r.h. - 0.38) - 1)^{1/1.22}$. Assuming that the bulk of solutes present on the leaf surface in dry conditions is made up of deliquescent (NH₄)₂SO₄ salts, $a_{AS}$ together with the canopy mass of cuticular ammonium sulphate $M_{AS}$ and the solution density $\rho_{AS}$ provide an estimate of the volume of water present on leaf surfaces.

For surface relative humidities below the deliquescence point of ammonium sulphate (~81%), $a_{AS}$ [r.h.] is assumed to be identical to $a_{AS}$ [81%].

SO₂ heterogeneous oxidation. Numerous studies have been published on heterogeneous SO₂-oxidation in rain/cloud/fog water, identifying H₂O₂ and O₃ as the primary oxidants, the heavy metal-catalyzed oxidation by O₂ in the aqueous phase, and the role of NH₃ as a catalyst (Beilke and Gravenhorst 1978; Schwartz and FreiBer 1981; Benner et al. 1992). Recent evidence suggests that the oxidation of SO₂ during dry deposition on wet terrestrial surfaces takes place at the air/water interface and is mainly attributable to the oxidation of an activated HSO₃⁻ or HS₂O₅⁻ surface complex by O₃ and O₂, even without heavy metals as catalysts (Adema and Heeres 1995). Surface oxidation rates suggested by these authors were used in the model here such that:

$$\frac{d[S^{IV}]_c}{dt} = k_{OX}[HSO_3]_c^{2/3}[Ox]_g^{2/3}$$

(15)

where concentrations, both gaseous ($Ox_g^{2/3}$) and aqueous ([S^{IV}]_c, [HSO₃]_c), are given in mol m⁻³, and Ox is oxidant i.e. O₂ or O₃. The oxidation rates $k_{OX}$ provided between 5 and 20 °C decrease exponentially with increasing absolute temperature (K):

$$k_{O_2} = 3.3 \times 10^{-21} \exp^{6820/T}$$

(16)

and

$$k_{O_3} = 1.7 \times 10^{-7} \exp^{1750/T}.$$  

(17)

For an HSO₃⁻ concentration of 10⁻⁶ mol l⁻¹ and at a temperature of 20 °C with an O₃ concentration of 20 ppbv, the combined SO₂ oxidation rate is about 1.8% min⁻¹.
Direct oxidation of $S^{IV}$ by $H_2O_2$ was not treated as no data were available for this site. However, at a typical atmospheric $H_2O_2$ concentration of 0.1 ppbv with a solution pH of 5, and assuming the rate of oxidation by $H_2O_2$ to be satisfactorily described by a third order rate equation as obtained from cloud studies (RGAR, 1997; Cape et al. 1998), $H_2O_2$ may be expected to be responsible for $HSO_3^-$ oxidation at a rate of 5–10% min$^{-1}$. In acidic solutions, $H_2O_2$ thought to be the major oxidant for $S^{IV}$, whereas the role of $O_3$ becomes more important above pH 6 (Cape et al. 1998). Despite these uncertainties, it is clear that $SO_2$ oxidation on wet leaf surfaces happens with characteristic times of a few minutes, and that $SO_2$ oxidation is almost certainly limited by $(R_a + R_b)$ and the availability of $H_2O_2$ since the leaf surface is generally acidic.

**Stomatal compensation point ($\chi_s$).** The $NH_3$ concentration of intercellular air spaces in thermodynamic equilibrium with dissolved $NH_3/NH_4^+$ in plant cell walls (apoplast) is commonly referred to as the stomatal compensation point (Sutton et al. 1995b). Direct measurements of $\chi_s$ have been made for a variety of plant species by extracting apoplastic solutions and analysing for NH$^+_4$, and it has been shown to depend on several factors including N fertilization and plant development stage (Husted and Schjørring 1995). Since the partitioning between $NH_3_{aq}$ and $NH_4^+$ in solution is pH-sensitive, it is appropriate to deal with the ammonium/hydronium molar ratio ($\Gamma$) to establish the temperature dependence of $\chi_s$. It can be shown combining the temperature dependences of both the Henry coefficient $K_{ha}$ (Dasgupta and Dong 1986) and the dissociation constant $K_a$ for $NH_3$ (Bates and Pinching 1950) that the partial pressure $p_{NH_3}$ (atm) in equilibrium with an $NH_4^+$-containing solution is such that (Flechard and Fowler 1998):

$$p_{NH_3} = 10^{4.1218-4507.05/T \Gamma}$$

(18)

with

$$\Gamma = \frac{[NH_4^+]_a}{[H^+]_a}$$

(19)

and $T$ the absolute temperature (K).

Published values of $\Gamma$ for growing arable crops are mostly in the range 250–4000, but estimates for moorland vegetation appear to be substantially lower (80–3000), due to smaller quantities of available N in semi-natural plant communities. In the absence of measurements of $\Gamma$ at Auchencorth Moss by apoplast $NH_4^+$ extraction, micrometeorological $NH_3$ flux measurements made at this site in the summer 1995 under dry (r.h. <7%) conditions were used to provide an estimate of $\Gamma$. The data selection was based on the assumption that under these dry conditions, the leaf cuticle/atmosphere flux of $NH_3$ is negligible, and thus the bulk of the exchange is between stomata and the atmosphere. A further selection was performed to retain only the half-hourly measurement runs during which the $NH_3$ flux changed sign, i.e. the exchange switched from deposition to emission or vice-versa, implying equality between the measured air concentration and the stomatal compensation point. Ammonia concentrations for these runs were then plotted versus measured surface temperatures $T(z_0)$ (Fig. 4) to examine the temperature dependence of the estimated stomatal compensation point and derive a best fit estimate for $\Gamma$ using Eq. (18) for modelling purposes. Figure 4 indicates a value of $\Gamma = 180$, which yields $\chi_s$ of 0.15 ppb (0.11 $\mu$g m$^{-3}$) at 5 °C and 1.85 ppb (1.29 $\mu$g m$^{-3}$) at 25 °C. It represents a mean value of $\Gamma$ for the growing, ‘green’ season of the moorland vegetation (May to September), and seasonal variations might be expected (Husted and Schjørring 1995).
Stomatal resistance \( (R_s) \). Measurements of stomatal resistance by Bowen ratio techniques over the moorland site provided diurnal and seasonal cycles in evapotranspiration patterns. Water vapour fluxes measured in conditions of large relative humidity (>70%) were rejected for the calculation of bulk stomatal resistances from measurements as part of the flux may originate from wet or moist plant cuticles. The parameters \( R_s' \) and \( b' \) in Eq. (20) (after Hicks et al. 1987) were fitted to the measured data using least square methods, so that the bulk stomatal resistance to water vapour transfer \( R_{seb} \) (s m\(^{-1}\)) of the moorland canopy may be predicted from the total incoming solar radiation \( S_t \) (W m\(^{-2}\)) and the physiological stress factors \( f_c \) (vapour pressure deficit), \( f_T \) (temperature) and \( f_w \) (water potential):

\[
R_{seb} = \frac{R_s'(1 + \frac{b'}{S_t})}{f_c f_T f_w}.
\]  

(20)

This approach slightly differs from that described by Hicks et al. (1987) who parametrized the stomatal resistance as a function of the Photosynthetically Active Radiation (PAR); the parameter \( b' \) therefore has a marginally different meaning in the present study. A comparison is presented in Fig. 5 between measured and parametrized stomatal resistances for water vapour transfer for July and August 1995.

Trans-cuticular fluxes of base cations, ammonium and other ions. An important feature of the exchange model presented in this paper is the transfer of ions across plant cuticles (Fig. 2), which has been shown to influence the chemical composition and pH of leaf surface water films, and thus the rates of gaseous exchange between wet leaf surfaces and the atmosphere. In particular, the trans-cuticular transfer of base cations and ammonium ions may potentially represent important pathways into or out of plants.
Field throughfall measurements (Lovett et al. 1985) and laboratory-based experiments (Adams and Hutchinson 1987) have long suggested that plant leaves have the ability to neutralize, to some extent, the acidity of rain or dew present on cuticles, thus limiting foliar injury. Base cations, particularly Mg$^{2+}$, Ca$^{2+}$ and K$^+$, are released from (or through) the cuticle, displacing H$^+$ from surface water onto dipolar binding sites of $-\text{OH}$ and $-\text{COOH}$ groups of cellulose, hemicellulose and phospholipids composing the cuticle. Under *Picea sitchensis* subjected to simulated precipitation acidified with sulphuric and nitric acid, Skiba et al. (1986) found that the sum of the cations in throughfall (Mg$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, K$^{2+}$ and Na$^+$) was linearly related to the extent of H$^+$ uptake. Similarly, ammonium ions have been shown to be taken up by leaves through cuticles in exchange for leaching base cations. Bobbink et al. (1992) found that the concentrations of Mg$^{2+}$, Ca$^{2+}$ and K$^+$ in throughfall increased significantly after passage through *Calluna vulgaris* compared with bulk precipitation, and that the amount of base cation leaching roughly balanced the uptake of NH$_4^+$ by the canopy.

The comparative magnitude of plant apoplastic concentration [NH$_4^+$]$_a$ and the surface solution concentration [NH$_4^+$]$_c$ (Fig. 2) are expected to determine a cross-cuticle gradient in NH$_4^+$ concentration. The exchange flux of NH$_4^+$ ions between the leaf interior and the epicuticular solution may be assumed to result from this concentration difference across a cuticular resistance $R_{cut}$ (Sutton et al. 1995d). Using an approach similar to that of Sutton et al. (1995d), an $R_{cut}$ of 1.9 $\times$ 10$^8$ s m$^{-1}$ for NH$_4^+$ was calculated for wet cuticles from the work of Wilson and Tiley (1998) on $^{15}$NH$_4^+$ uptake by Norway spruce needles. In the case of base cation leaching, a parametrization based on $R_{cut}$ and a concentration difference between the leaf surface and the apoplast was also applied, assuming leaf apoplast concentrations of 1 mM for K$^+$, Ca$^{2+}$ and Mg$^{2+}$.
TABLE 2. SUMMARY OF INPUT AND OUTPUT MODEL VARIABLES

<table>
<thead>
<tr>
<th>INPUT</th>
<th>OUTPUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trace gas concentrations</td>
<td></td>
</tr>
<tr>
<td>at reference height, $x (z - d)$</td>
<td>Canopy compensation points $\xi$ and exchange fluxes $F_x$</td>
</tr>
<tr>
<td>(e.g. $z - d = 1$ m)</td>
<td>$\text{NH}_3$, $\text{SO}_2$</td>
</tr>
<tr>
<td>(CO$_2 = 355$ ppm)</td>
<td>$\text{HNO}_2$, $\text{HCl}$, $\text{HNO}_3$</td>
</tr>
<tr>
<td>Micrometeorological variables</td>
<td>Transfer resistances $R_{\text{air}} (z - d)$, $R_0$, $R_v$, $R_d$</td>
</tr>
<tr>
<td>$u$, $u_a$</td>
<td>$\text{Stomatal compensation point}, Z_s$</td>
</tr>
<tr>
<td>$\mathbf{H}$, $\mathbf{G}$, $\mathbf{E}$, $S_i$, $R_n$</td>
<td>$\text{Stomatal fluxes}, F_s$</td>
</tr>
<tr>
<td>$T_i$, $i$.h.</td>
<td>$\text{Epicuticular fluxes}, F_d$</td>
</tr>
<tr>
<td>$R_{\text{sub}}^+$</td>
<td>$\text{Leaf surface water storage}, V_S$ (mm)</td>
</tr>
<tr>
<td>Precipitation rate, $V_p$ (mm)</td>
<td>$\text{Leaf surface chemistry}, [X_{aq}]$</td>
</tr>
<tr>
<td>Rainfall chemistry, $[X_{aq}]$</td>
<td>pH</td>
</tr>
<tr>
<td>$\text{pH}$</td>
<td>$\text{NH}_4^+$</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Cl}^-$</td>
<td>$\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$</td>
</tr>
<tr>
<td>$\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$</td>
<td>Ionic strength</td>
</tr>
<tr>
<td>Site/season specific data</td>
<td>$\text{Trans-cuticular fluxes, } F_{\text{cut}}$</td>
</tr>
<tr>
<td>$I$, $M$, $d$, $R_{\xi}$, $\beta$</td>
<td>$\text{NH}_4^+$, $\text{NO}_3^-$, $\text{SO}_4^{2-}$</td>
</tr>
<tr>
<td>$\Gamma = [\text{NH}_4^+] / [\text{H}^+]^{\beta}$</td>
<td>$\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$</td>
</tr>
</tbody>
</table>

*: measured concentration if available; †: measured latent heat flux if available, otherwise computed as the difference between $R_{\text{air}}$ and $(\mathbf{H} + \mathbf{G})$ where $\mathbf{H}$ is sensible heat flux and $\mathbf{G}$ is soil heat flux; ‡: measured bulk stomatal resistance if available, otherwise computed from Eq. (20); §: plant apoplastastic ammonium/hydronium ratio, derived from Fig. (4); †: dissolved CO$_2$, HCO$_3^-$ and CO$_3^{2-}$; ‡: dissolved HNO$_2$ and NO$_2$—

(Scherbatskoy and Tyree 1990). Published values of apparent permeability coefficients for these cations at pH 5.4 (Scherbatskoy and Tyree 1990) provided estimates of $R_{\text{cut}}$ of $1.9 \times 10^9$, $3.0 \times 10^9$ and $5.8 \times 10^{10}$ s m$^{-1}$ for K$^+$, Ca$^{2+}$ and Mg$^{2+}$, respectively. Despite certain limitations associated with parametrizations based on cuticular transfer resistances and concentration gradients (Cape 1996; Scherbatskoy and Tyree 1990), and in the absence of a comprehensive knowledge and quantification of cuticular exchange processes, a simple $R_{\text{cut}}$ parametrization seemed the most viable option for the purposes of this model.

(c) Summary of model input and output variables

Measured input meteorological variables or gas concentrations may be supplied on an hourly or half-hourly time basis; at each time-step, the model interpolates input variables and outputs pH, liquid film ionic or dissolved gas concentrations, stomatal and epicuticular fluxes, cross-cuticular fluxes. Time-weighted average fluxes are provided on the same time basis as the input data and measured fluxes. Table 2 gives an overview of required input data and of the main output variables.

4. Results

(a) Simulation of long-term ammonia fluxes and comparison with other exchange models

The dynamic chemical compensation point model was applied to measured data collected in 1995–96 at Auchencorth Moss. The model could not be applied to the whole dataset, consisting of $\sim 10^8$ half-hourly flux measurements (Flechard and Fowler 1998), as some critical input variables were frequently missing. To increase the duration of individual modelling runs, small gaps in the NH$_3$ or SO$_2$ concentration data were bridged whenever possible, except when interpolation over a few hours became too speculative. The absence of rainfall during long periods prevented the initialization of the model and further reduced the available dataset of modelling purposes. Although
the model might also be initialized without measured rain chemistry and come to equilibrium after a number of hours, this approach was not used in this study.

The measured and modelled data presented here consist of 3259 half-hourly runs (equivalent to about 68 days), spanning 16 time intervals of 1 to 11 days for different seasons and growing stages of the moorland vegetation (Tables 3, 4). For each of the 16 runs, model input parameters are provided, such as the leaf area index (LAI), the apoplast ammonium/hydronium ion ratio (Γ'), the stomatal resistance parameters $R_{s}'$ and $b'$, as well as the weekly measured rainfall composition used in the initialization of the chemical module (Table 3). Results of the dynamic model are shown in Tables 4–5, alongside measured data and the results of two other modelling approaches described in section 2(a) namely the canopy resistance ($R_c$) approach (Hicks et al. 1987; Erisman et al. 1994), and the static canopy compensation point model of Sutton et al. (1995b, 1998). For all three models, identical values or parametrizations for $R_a$, $R_b$ and $R_s$ were used in the simulations reported here, so that only the surface terms differed, allowing a more realistic comparison of modelling approaches. Parametrizations for $R_c$[NH$_3$] in the canopy resistance model were those of the DEPAC/EDACS models (Erisman et al. 1994; Jan Willem Erisman, personal communication). The $R_w$ term of the static canopy compensation point model (Fig. 1(c)) was fitted to data measured at Auchencorth Moss from April to September 1995, so that:

$$R_w = 20 + 100(1 - \exp^{-2vpd})$$

where $vpd$ is water vapour deficit in units of kPa, and $R_w$ in units of s m$^{-1}$.

Half-hourly runs for which $T < 0$ °C were removed from the original datasets for model comparisons in Tables 4–5, as the chemistry and thermodynamics used in the chemistry module are not appropriate for freezing conditions. This is illustrated in Fig. 6 where NH$_3$ flux measurements are plotted alongside modelled fluxes, measured concentrations, temperature and relative humidity (r.h.) for a period of ~9 days in March 1995. In the early stages, from 18/06/95 1800 to 21/03/95 2100, substantial departures of all modelled fluxes from measured values are observed while surface temperatures $T[z']$ are frequently in the range [-5; 0] °C. In the latter stages, however, the accuracy of prediction increases for the dynamic model as well as for the other approaches, as surface temperature largely remains in the range [1; 10 °C].

All models performed generally well in winter or autumn, wet/moist, mild conditions, as shown in Fig. 7. In this case study, NH$_3$ was deposited to the moorland surface at rates close to the maximum deposition velocity permitted by turbulence $V_{max}[z-d] = 1/(R_a[z-d] + R_b)$. The dynamic, chemical model provided for this run the best 11-day flux estimate of the three models (within 2% of the measured value; Tables 4–5), although differences between models were small. However, none of the models could simulate two emission/desorption peaks observed during the second and the last day of the 11-day run. By contrast to Fig. 7, Fig. 8 presents the variations in measured and modelled fluxes over a period of 4 days in summer, warm and relatively dry conditions. The canopy resistance approach then fails to simulate the reduction in flux that occurs in dry daytime conditions, while a compensation point approach seems better suited to the situation. The dynamic and static compensation point models generally provide similar estimates, although leaf surface exchange is treated entirely differently in these models in wet conditions.

Table 4 provides an overview of NH$_3$ flux measurements and model estimates for the 16 runs considered. As NH$_3$ fluxes are not normally distributed to this site (Flechard and Fowler, 1998), median values are provided for comparisons as well as mean values,
<table>
<thead>
<tr>
<th>Modelled Runs</th>
<th>Model input parameters</th>
<th>Rainfall Chemistry*</th>
<th>Ion bal.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LAI†</td>
<td>Γ‡</td>
<td>Rst §</td>
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<tr>
<td>Start date</td>
<td>End date</td>
<td>m² m⁻²</td>
<td>MM⁻¹</td>
</tr>
<tr>
<td>11/03/95</td>
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<td>3</td>
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<tr>
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<td>26/03/95</td>
<td>3</td>
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<td>50</td>
</tr>
<tr>
<td>16/02/96</td>
<td>23/02/96</td>
<td>3</td>
<td>20</td>
</tr>
</tbody>
</table>

*: weekly measured values; †: measured or estimated values; §: fitted (Fig. 4) or estimated; §: fitted parameters (Fig. 5).
<table>
<thead>
<tr>
<th>Modelled Runs</th>
<th>Rainfall (mm)</th>
<th>% time wet</th>
<th>Mean Fluxes</th>
<th>Median Fluxes</th>
<th>Relative Error in Modelled Fluxes</th>
<th>Measured Fluxes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start date</td>
<td>End date</td>
<td>N*</td>
<td>Meas. flux</td>
<td>Dyn.†</td>
<td>Stat.**</td>
<td>R_c ††</td>
</tr>
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<td>11/03/95</td>
<td>16/03/95</td>
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<tr>
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<td>15/05/95</td>
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<tr>
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<td>-61.3</td>
<td>-6.3</td>
<td>-5.3</td>
<td>-7.7</td>
</tr>
</tbody>
</table>

*: half-hourly fluxes; †: negative fluxes denote deposition; ‡: calculated as r.e. (%) = -100(F_{mod} - F_{meas})/F_{meas}; §: not including precipitation used in initialization of dynamic model; ††: fraction of the time during which the moorland surface was wet or moist (wetness sensor) or r.h. >95%; †: dynamic canopy compensation point model (this paper); **: static canopy compensation point model (Sutton et al. 1995b); ††: canopy resistance (R_c) model (Erisman et al. 1994).
for measurements and all model estimates. The whole modelled dataset was also subdivided in classes of measured NH$_3$ flux ($< -20$, $[-20; -5]$, $[-5; 0]$, $> 0$ ng m$^{-2}$ s$^{-1}$), as it appeared that the accuracy of model predictions depended on the magnitude of the measured flux (see also Fig. 9 and Table 5). Table 5 presents a summary of the results of linear regressions of individual half-hourly model estimates versus measured values, for all three models, with the key parameters slope ($a$), intercept ($b$) and coefficient of determination ($r^2$). These results are summarized in Fig. 9 where the regression equations of individual half-hourly modelled values versus measured fluxes are displayed, while for clarity only block-averaged fluxes are plotted.

As a first approach (Table 4), it appears that the dynamic model provided the best long-term estimate of the three models of the dry deposition flux of NH$_3$ to moorland, yielding an average downward flux of $-6.3$ ng NH$_3$ m$^{-2}$ s$^{-1}$ (equivalent to $\sim 300$ g NH$_3$-N ha$^{-1}$ over a period of 68 days, or, using a linear extrapolation, $\sim 1.6$ kg NH$_3$-N ha$^{-1}$ a$^{-1}$). This figure was within 3% of the measured flux ($-6.1$ ng m$^{-2}$ s$^{-1}$) while the static compensation point model underestimated the deposition flux by 12% and the canopy resistance approach overestimated deposition by 27%. The median dynamic model flux estimate ($-4.0$ ng m$^{-2}$ s$^{-1}$) was also the closest estimate of the median measured flux ($-3.9$ ng m$^{-2}$ s$^{-1}$), although the median relative error in the dynamic model flux estimate ($-10\%$) was in absolute terms larger than the median relative error in the static model flux estimate ($4\%$). All models underestimated deposition for measured fluxes in the class $< -20$ ng m$^{-2}$ s$^{-1}$; on the other hand, they all generally failed to simulate positive, upward fluxes observed in the class of measured fluxes $> 0$ ng m$^{-2}$ s$^{-1}$. This resulted in simple linear regressions of modelled vs. measured fluxes having substantially negative intercepts, and slopes being smaller than 1 (Table 5).

The effect of large deposition fluxes on regression statistics may be established clearly on Fig. 9; for deposition fluxes between $-20$ and 0 ng m$^{-2}$ s$^{-1}$, the regression

<table>
<thead>
<tr>
<th>Measured flux range</th>
<th>$&lt; -20$ ng m$^{-2}$ s$^{-1}$</th>
<th>$-20$ to $-5$</th>
<th>$-5$ to 0</th>
<th>$&gt; 0$</th>
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<tbody>
<tr>
<td>$N$</td>
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<td>1136</td>
<td>12</td>
<td>128</td>
<td>3259</td>
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<td>$F_{\text{dynamic}}$ vs. $F_{\text{measured}}$</td>
<td>$a$</td>
<td>$b$</td>
<td>$r^2$</td>
<td>$a$</td>
<td>$b$</td>
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<tr>
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<tr>
<td>$F_{\text{static}}$ vs. $F_{\text{measured}}$</td>
<td>$a$</td>
<td>$b$</td>
<td>$r^2$</td>
<td>$a$</td>
<td>$b$</td>
</tr>
<tr>
<td>0.64</td>
<td>-2.26</td>
<td>0.50</td>
<td>0.57</td>
<td>-1.88</td>
<td>0.65</td>
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</tbody>
</table>

*: dynamic canopy compensation point model (this paper); †: static canopy compensation point model (Sutton et al. 1998); ‡: canopy resistance ($R_c$) model (Erisman et al. 1994).
Figure 6. Time course of NH$_3$ exchange in winter conditions, and comparison of micrometeorological flux measurements with exchange models. All three modelling approaches overestimate the deposition flux of NH$_3$ in frozen conditions during the first three days of the period, whereas they all provide reliable estimates and capture most of the variability of the NH$_3$ flux in milder, humid conditions.

of $F_{dyn}$ vs. $F_{meas.}$ would provide an intercept close to 0 with a slope close to 1, while $F_{stat.}$ would show an intercept of $\sim$0 but with a slope $<$1, and the canopy resistance
Figure 7. Time course of NH$_3$ exchange in autumn, wet conditions, and comparison of micrometeorological flux measurements with exchange models.

The approach would have a slope of $\sim$1 but with a significant intercept. The fact that long-term model estimates were within 10% of the measured flux, in the case of the dynamic and static $\chi_c$ models, indicated that the seldom-observed, underestimated
large fluxes (< - 20 ng m\(^{-2}\) s\(^{-1}\)) were on average balanced by the more frequent, overestimated small deposition fluxes (> - 5 ng m\(^{-2}\) s\(^{-1}\)). All NH\(_3\) exchange models could be considered to have captured at least 50% of the variability in measured fluxes,
Figure 9. Scatter plot of modelled versus measured NH$_3$ fluxes at Auchencorth Moss for 16 time periods ranging from 1 to 11 days following a rain event. For graphic clarity, fluxes were block-averaged ($N = 25$) from the original 3259 half-hourly measurements for which simple linear regressions are given (see also Tables 3-5).
as reflected by the overall coefficients of determination in Table 5. However, $r^2$ proved an unreliable statistical tool to describe the accuracy of model prediction, giving too much statistical weight to large flux values and thus not adequately taking into account the pseudo-lognormal nature of the NH$_3$ flux distribution. The relative error in modelled fluxes (Table 4) is considered preferable to describe the departure of modelled estimates from measured values.

(b) Relative magnitudes of stomatal ($F_s$) and cuticular ($F_d$) ammonia fluxes

Although the moorland vegetation at Auchencorth Moss was a net sink for NH$_3$, with deposition fluxes observed more than 93% of the time (Flechard and Fowler 1998), NH$_3$ emission does occasionally occur from stomata as a consequence of apoplastic NH$_3$. This results in the dynamic model predicting stomatal emission of NH$_3$ during the warm afternoons of the summer months (Fig. 10), although a large fraction of this emission flux, if not all of it, was predicted to be immediately recaptured by plant cuticles, yielding a net deposition flux from the atmosphere to the surface. Figure 10 shows that the dynamic $\chi_e$ model predicts that the bulk of the surface/atmosphere exchange of NH$_3$ at this site occurs on wet or moist cuticles, and that the fraction exchanged between stomata and the atmosphere is small in comparison. The importance of stomatal exchange is expected to be much larger in drier climates, and over arable crops owing to larger apoplastic $\Gamma$ ratio, or indeed over semi-natural ecosystems in more polluted areas such as in the Netherlands (Sutton et al. 1995b). This may also apply immediately downwind from agricultural sources where the stomatal compensation point of vegetation is raised following large nitrogen inputs, leading to smaller dry deposition fluxes as a feedback process.
5. Discussion

The model of surface/atmosphere exchange presented in this paper has so far been described in terms of its comparative ability to simulate long-term fluxes of ammonia at a moorland site in S. Scotland. The dynamic $\chi_e$ model showed a predictive ability comparable to that of the static $\chi_e$ approach of Sutton et al. (1995b), and the canopy resistance approach (Erisman et al. 1994) overestimated NH$_3$ deposition by about 30% at Auchencorth Moss. Both compensation point models simulated NH$_3$ exchange more accurately over wet surfaces than over dry or frozen surfaces. The reasons for the dynamic approach failing to provide a satisfactory estimate of the flux in dry or cold conditions stem from the inadequacy of ideal solution chemistry and Henry's law in these conditions. It was shown that stomatal exchange of NH$_3$ at wet sites with a low nitrogen status is likely to be negligible compared with cuticular uptake. Apart from its use in modelling the exchange of NH$_3$ per se, this model has also scope for the simulation of other water-soluble trace gases such as SO$_2$ and the investigation of chemical processes that occur on wet surfaces. These points shall be discussed further in the following sections.

(a) Effects of leaf surface wetness on exchange rates of ammonia

The dominating influence of leaf wetness on deposition rates of water-soluble trace gases such as NH$_3$ and SO$_2$ onto terrestrial surfaces has been well documented (Fowler and Unsworth 1979; Sutton et al. 1993a; Duyzer 1994), with generally larger deposition velocities measured over wet canopies. As a result, parametrizations have been developed for canopy resistance ($R_c$) deposition models assuming zero surface concentrations, particularly in the case of semi-natural ecosystems with a small stomatal compensation point (Erisman et al. 1994).

While surface wetness clearly provides an additional sink for NH$_3$, the efficiency of NH$_3$ uptake is expected to decrease as the dissolved NH$_3$ concentration and hence the gaseous NH$_3$ concentration in equilibrium with the solution ($\chi_d$) increases. The uptake of NH$_3$ by surface water films is expected to decline during evaporation of rainwater or a dew layer in the morning, especially at high temperatures (Eq. 18). This is illustrated in a case study in Fig. 11 in which the evaporation of leaf surface water following rainfall is simulated and compared with field assessment of leaf wetness (Fig. 11(a),(b)). The measured NH$_3$ concentration at a reference height (model input) is given alongside the profile-extrapolated and modelled NH$_3$ concentrations at $z_0'$, modelled bulk dissolved NH$_3$ concentration in surface solution is also plotted (Fig. 11(c)). Measured and modelled surface/atmosphere fluxes of NH$_3$ are compared in Fig. 11(d).

Field assessment of leaf wetness was made possible by the use of sensors developed by Burkhardt and Gerchau (1994). These sensors are miniature ‘alligator’ metal devices clipped onto individual leaves and were originally designed for pine needles (Burkhardt and Eiden, 1994). The electrical conductance along the surface of the leaf is measured by applying an AC voltage. Although absolute, repeatable conductance values cannot be obtained, the relative fluctuations of the signal have been shown to constitute reliable estimates of cuticular wetness and/or ionic strength of the surface solution (Burkhardt and Gerchau, 1994).

In the present case study, the measured electrical conductance was generally larger for a wet surface (Fig. 11(a)), although the signal increased slightly when evaporation of rainwater started (0800 to 0900 GMT on 14/08/95) before falling rapidly as evaporation continued. This short-lived rise in solution conductance occurred as relative humidity approached ~81% which is near the deliquescence point of ammonium sulphate; as
Figure 11. Diurnal course of NH$_3$ concentrations of fluxes and relevant environmental variables at Auchencorth Moss. (a) Modelled leaf surface canopy-equivalent water storage ($V_S$), and leaf surface electrical conductance of Eriophorum vaginatum measured using special leaf wetness sensors kindly supplied by J. Burkhardt (Burkhardt and Cernichau, 1994). (b) Surface relative humidity r.h. ($z_0'$) and air temperature $T(z_0)$ extrapolated from micrometeorological profile measurements. (c) Ammonia concentration at 1 m above the surface $\chi$NH$_3[1m]$; measured and modelled NH$_3$ canopy compensation points $\chi$NH$_3(z_0')$; dissolved ammonia concentration $[\text{NH}_3\text{,aq}]_c$. (d) Measured and modelled surface/atmosphere NH$_3$ fluxes. Vertical arrows indicate rainfall events.
relative humidity further decreased, the electrical conductance also decreased, indicating lower ion mobility across the leaf surface. A maximum in dissolved NH$_3$ concentration was predicted by the model shortly after the rise in surface electrical conductance, and this value decreased subsequently as the leaf surface became very dry and acidic, turning dissolved NH$_3$ into NH$_4^+$. The model also predicted NH$_3$ desorption from cuticular water between 0700 and 0800 GMT, although this was not observed in field micrometeorological measurements (Fig. 11(d)). The modelled outgassing of NH$_3$ at this time may be the result of ammonium sulphate formation not being simulated as the surface dries out, while a possible underestimation of trans-cuticular NH$_4^+$ absorption in the hours preceding the evaporation may have led to the NH$_4^+$ concentration in solution at 0700 GMT being over-estimated.

The dynamic chemical model presented in this paper fails to reproduce the exact behaviour of thin water films drying out during dew evaporation or following rain events (Figs. 7 and 11). However, it does provide a valuable method of examining chemical processes on wet leaf surfaces. This is particularly relevant at the site studied in this paper where the moorland canopy could be considered wet more than two thirds of the time, but is also appropriate across many sites throughout north-western Europe where winters are generally mild and wet. Given more severe climatic conditions such as those of eastern Europe (cold in winter) or southern Europe (hot and/or dry), the model loses some of its usefulness as the fraction of the time when surfaces are wet decreases. Despite the simplifications adopted in the numerical treatment of leaf surface chemistry (sections 3(a), 3(b)) in order to make the model usable routinely, the chemistry module provides a reasonably good picture of chemical processes during wet periods. As suggested earlier, a more detailed treatment of leaf surface wet chemistry than the empirical capacitance based, dynamic model of Sutton et al. (1998) has provided more reliable estimates of surface pH and ion concentrations.

(b) Potential interactions between ammonia and sulphur dioxide on leaf surfaces

The total modelled deposition flux of SO$_2$ at the same site, for the same 68-day period as the NH$_3$ modelling exercise described above, using the same dynamic model, was $-210$ g SO$_2$-S ha$^{-1}$, i.e. a 20% underestimation of the measured flux ($-260$ g SO$_2$-S ha$^{-1}$). This is roughly equivalent to an average deposition velocity of 5 or 6 mm s$^{-1}$ with an average SO$_2$ concentration of 0.6 ppbv over the whole period. It is also equivalent to a total of about 8 moles of SO$_2$ deposited to one hectare of moorland for the same time period, while the flux of NH$_3$ was $-300$ g NH$_3$-N, or about 21 moles NH$_3$ ha$^{-1}$ (Table 4). Deposition of NH$_3$ was therefore well in excess of SO$_2$ at this site with respect to ammonium sulphate formation on leaf surfaces, considering the molar ratio of the deposition of the two species $21/8 = 2.6$. The concept of co-deposition of NH$_3$ and SO$_2$ onto wet vegetation (Brimblecombe 1978) has been supported by Van Breemen et al. (1982) who measured equivalent amounts of NH$_4^+$ and SO$_4^{2-}$ under a forest canopy. It was hypothesized that the acidity produced by SO$_2$ on leaf surfaces was buffered by NH$_3$ dry deposition and that both gases enhanced each other’s deposition by preventing saturation that would otherwise occur. This has been demonstrated in controlled environment laboratory studies (Van Hove et al. 1989), but field micrometeorological measurements in support of these data have so far been elusive (Erisman and Wyers 1993) and occasionally in conflict (Sutton et al. 1993b).

Such questions may be addressed using long-term continuous and simultaneous NH$_3$ and SO$_2$ flux measurements such as those obtained at Auchencorth Moss and at the
other LIFE sites in eastern Germany (grassland) and the Netherlands (coniferous forest). These three sites have contrasting pollution climates (Erisman et al. 1996), Auchencorth Moss being by far the 'cleanest', the coniferous forest being the most exposed to NH₃, while the grassland site experiences the largest SO₂ exposure. Co-deposition effects may not be important at certain drier sites where wet surface chemistry does not dominate the exchange, while other wetter or more polluted sites may show direct effects (Erisman and Wyers 1993). A potential use of the dynamic model presented here may be to simulate varying scenarios, looking at e.g. the change in NH₃ flux if the SO₂ concentration in air increases or decreases by a given percentage, or vice-versa. This may prove valuable policy support for abatement strategies for N and S compounds to achieve the most cost-effective reduction in critical load exceedance. A more detailed analysis of NH₃/SO₂ interactions on leaf surfaces is the focus of a subsequent paper (Flechard et al. 1999).

(c) Areas of future research and recommendations

The dynamic canopy compensation point approach presented here to model the exchange of water-soluble trace gases between vegetation and the atmosphere constitutes a step forward from the more empirical capacitance based, dynamic model of Sutton et al. (1998) and a substantial advance on simple surface resistance treatments of the processes (Erisman et al. 1994; Sutton et al. 1993a). The model is capable of simulating long-term fluxes with about the same accuracy as a static kᵣ model, but it requires considerably more input variables such as rain chemistry and net radiation which may not be routinely available. The reduction in empiricism inherent in a more mechanistic model also implies that, quite apart from the variables mentioned above, there is much uncertainty in model parameters or parametrizations such as Γ, the rates of ammonium and base cation transfer across plant cuticles, sulphur dioxide oxidation rates.

While a detailed sensitivity analysis for model parameters would help quantify the uncertainty, it can be inferred from model results at Auchencorth Moss that stomatal exchange over moorland in wet climates is likely to be small compared with leaf surface uptake, but the choice of Γ over N-rich ecosystems would influence greatly modelled net exchange fluxes. Over arable crops in particular, the importance of Γ cannot be over-emphasized, and substantial research efforts are currently being carried out to characterize the variability in apoplastic ammonium content (Husted and Schjørring 1995). Over taller canopies such as maize or oilseed rape, the vertical distribution of sources and sinks within the canopy and the presence of decaying material on the ground (Nemitz et al. 1998), as well as soil processes, would probably question the validity and applicability of the ‘big leaf’, single layer dynamic model presented in this paper. Nevertheless, the fundamental principles of this model may still apply, while allowances for more sinks and sources within the canopy would have to be made.

The sensitivity of modelled NH₃ fluxes to the rates of SIV oxidation used in the chemistry module is likely to be small, as NH₃ is very soluble in water for pH values up to 7 and NH₃ deposition is only weakly dependent on NH₄⁺ and pH. The large cuticular resistances used for base cation transfer also imply that surface pH values generally remained at levels well below 5 (the median leaf surface pH of all 3259 modelled half-hourly runs was 3.57, the 90th percentile was 4.78 and the 99th percentile was 6.64). On the other hand, the use of faster SO₂ oxidation rates of H₂O₂ than those currently based on O₃/O₂ (Eqs. (15)–(17); Adema and Heeres 1995), as discussed in the parametrizations section, may increase rates of SO₂ uptake by wet leaf surfaces.
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