AGRICULTURAL AND FOREST METEOROLOGY 149 (2009) 263–280

available at www.sciencedirect.com

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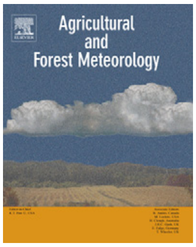

# A new model of bi-directional ammonia exchange between the atmosphere and biosphere: Ammonia stomatal compensation point

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ARTICLE INFO

*Article history:*
Received 30 November 2006
Received in revised form
13 August 2008
Accepted 17 August 2008

*Keywords:*
Ammonia
Deposition
Emission
Compensation point
Modeling
Bi-directional flux
Soybean

## ABSTRACT

A new multi-layer canopy resistance model of bi-directional $NH_3$ exchange is presented. This new model, which is based on the Multi-Layer BioChemical deposition (MLBC) model [Wu, Y., Brashers, B., Finkelstein, P.L., Pleim, J.E., 2003a. A multiplayer biochemical dry deposition model. I. Model formulation. J. Geophys. Res. 108, D1; Wu, Y., Brashers, B., Finkelstein, P.L., Pleim, J.E., 2003b. A multiplayer biochemical dry deposition model. II. Model evaluation. J. Geophys. Res. 108, D1], incorporates a parameterization for the ammonia stomatal compensation point that is theoretically derived to consider the effects of leaf temperature and apoplastic concentrations of $NH_4^+$ and $H^+$. The new ammonia stomatal compensation point scheme accounts for the effects of deposition, emission and leaf temperature on the dynamics of apoplast $[NH_4^+]$ and $[H^+]$. The new model is evaluated against bidirectional $NH_3$ fluxes measured over fertilized soybean. The general patterns of observed deposition and emission are successfully reproduced when the ammonia stomatal compensation point is included. Driven by the effects of deposition, emission and leaf temperature, modeled apoplastic $[NH_4^+]$ and $[H^+]$ display significant diurnal variation when the buffer effect of the underlying metabolic processes generating or consuming $NH_4^+$ were ignored. Model predictive capability is improved slightly by incorporating the feedback into a dynamic stomatal compensation point. A simple implementation of the feedback mechanism in the current model provides opportunities for improvement. While the stomatal flux is shown to be an important process in the regulation of canopy-scale fluxes, it appears that exchange with leaf surface water and soil may also be important.

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0168-1923/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.agrformet.2008.08.012

## 1. Introduction

The exchange of ammonia ($NH_3$) between the atmosphere and biosphere influences atmospheric chemistry (e.g. via emission/deposition) as well as the nitrogen status of terrestrial and aquatic ecosystems (e.g. via deposition). $NH_3$ is a major contributor to secondary aerosol formation in the atmosphere as it reacts rapidly with sulfuric ($H_2SO_4$), nitric ($HNO_3$) and hydrochloric (HCl) acids to form ammonium ($NH_4^+$) aerosol. Vayenas et al. (2005) recently found that for a 50% reduction in $NH_3$ availability, inorganic $PM_{2.5}$ was reduced by 29% in western Pennsylvania. Ammonium aerosol affects Earth's radiative balance, both directly by scattering incoming radiation and indirectly by acting as cloud condensation nuclei (Jennings, 1993; Yu, 2006). Atmospheric deposition of reduced nitrogen (i.e. $NH_3 + NH_4^+$) to terrestrial ecosystems may lead to soil acidification, decreased resistance to climatic stressors, a significant shift in the nutrient economy and shifts in species composition (Nihlgard, 1985; Reuss and Johnson, 1986; Fenn et al., 1998; Schjoerring, 1991; Dentener and Crutzen, 1994; Kramm and Dlugi, 1994; Fangmeier et al., 1994; Asman, 1995). Additionally, nutrient overenrichment of aquatic ecosystems may exacerbate eutrophication (Paerl et al., 2002; Dennis and Mathur, 2001). Atmospheric deposition of nitrogen is the largest single source of human-derived nitrogen in the eastern U.S. coastal waters, and there is now 10–20 times more nitrogen entering coastal rivers in the northeastern U.S. and northern Europe than in pre-industrial times (US Climate Change Science Program/US Global Change Research Program, 1997). In fertilized cropping systems, the plant community may release significant quantities of nitrogen into the atmosphere. Clearly, measuring and modeling the bidirectional exchange of $NH_3$ between the atmosphere and biosphere are important in understanding and evaluating these impacts.

Plants may act as a source or sink for $NH_3$, depending on the difference between the atmospheric concentration and the gaseous concentration in the leaf substomatal cavity. The gaseous concentration in the leaf substomatal cavity is known as the stomatal compensation point (Farquhar et al., 1980). Emission occurs if the mole fraction of $NH_3$ in the atmosphere is lower than the stomatal compensation point, while uptake (deposition) occurs when the mole fraction of $NH_3$ in the atmosphere is higher than the stomatal compensation point. Estimation of the ammonia stomatal compensation point is therefore necessary for the accurate prediction of bidirectional $NH_3$ fluxes over vegetation.

Previous measurements show that the ammonia stomatal compensation point varies by vegetation type, growth stage, and nitrogen status, and can be predicted at the leaf level as a function of temperature and apoplastic $NH_4^+$ and $H^+$ concentrations (Farquhar et al., 1980; Morgan and Parton, 1989; Dabney, 1990; Schjoerring, 1991; Husted and Schjoerring, 1995a,b; Husted et al., 1996; Harper and Sharpe, 1995; Schjoerring et al., 1998). Atkins (1990) proposed an equation to extrapolate the ammonia stomatal compensation point as a function of temperature using a slightly modified form of the Claussius–Clapeyron equation. Nemitz et al. (2000) and Hill et al. (2001) expressed the ammonia stomatal compensation point as a function of leaf temperature and the ratio of $[NH_4^+]/[H^+]$ in the plant apoplast. The ratio of $[NH_4^+]/[H^+]$ is denoted as $\Gamma_s$ (Sutton et al., 1998; Nemitz et al., 2000, 2001; Walker et al., 2006).

Modeling studies of bi-directional $NH_3$ exchange between the atmosphere and biosphere have been extensively conducted in Europe. Sutton and Fowler (1993) proposed the "canopy compensation point" concept, which relates the canopy-scale flux to the net emission potential of the canopy established by competing source/sink processes. Sutton et al. (1998) incorporated the canopy compensation point into a single-layer resistance model to account for stomatal emission and deposition (i.e. stomatal compensation point), deposition to the leaf cuticle, and emission from the soil. Nemitz et al. (2000, 2001) developed a new model to explicitly treat different sources and sinks both within the canopy (e.g. foliage and siliques) and at the ground (e.g. soil and leaf litter). These models, parameterized with constant $\Gamma_s$, have been used successfully to predict bi-directional exchange in fertilized and semi-natural systems (Sutton et al., 1998; Nemitz et al., 2000, 2001). Studies of $\Gamma_s$ and its variability carried out by Mattsson et al. (1997), Schjoerring et al. (1998, 2000), Schjoerring and Mattsson (2001), Hill et al. (2001), Loubet et al. (2002), and Mattsson and Schjoerring (1996a,b, 2002) show that $\Gamma_s$ changes in response to plant growth stage and nitrogen input. However, the potential influence of $\Gamma_s$ variability on canopy-scale fluxes has not yet been examined in detail. Riedo et al. (2002) linked bi-directional $NH_3$ exchange to plant and soil nitrogen status by coupling the resistance model of Nemitz et al. (2001) to a grassland ecosystem model. Apoplastic N was modeled as a function of root N uptake, biological N fixation, symplastic N exchange, and stomatal $NH_3$ exchange with the atmosphere.

In this study, we present a new multi-layer canopy resistance model of bi-directional $NH_3$ exchange in which the dynamics of apoplast chemistry are considered. The model is based on the multi-layer biochemical (MLBC) dry deposition model of Wu et al. (2003a), modified to include bi-directional stomatal $NH_3$ exchange. The apoplastic concentrations of $NH_4^+$ and $H^+$ are linked to the ammonia stomatal compensation point, thereby accounting for potential feedback between the ammonia stomatal compensation point and the apoplastic concentrations of $NH_4^+$ and $H^+$ at the leaf level. In the following sections, we present the MLBC $NH_3$ model and a comparison with flux measurements over a fertilized soybean canopy. The comparison between measured and modeled fluxes addresses the importance of the stomatal $NH_3$ compensation point in predicting net canopy-scale fluxes and the potential for model improvement by accounting for apoplast dynamics.

## 2. Model description

In MLBC, the flux ($F$) of a trace gas between two heights ($z_1$ and $z_2$) can be estimated using the resistance analogy, in which the flux equals the concentration gradient divided by the resistance (Wesely, 1989; Hicks et al., 1991; Meyers et al., 1988; Pleim et al., 1999; Wu et al., 2003a,b): ($F = (C(z_1) - C(z_2))/R$), where $C$ is the concentration and $R$ is the resistance. The soil–plant–atmosphere system can be modeled as a system of