Development and Evaluation of an Ammonia Bi-Directional Flux Model for Air Quality Models

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Abstract Ammonia is an important contributor to particulate matter in the atmosphere and can significantly impact terrestrial and aquatic ecosystems. Surface exchange between the atmosphere and biosphere is a key part of the ammonia cycle. Agriculture, in particular, is a large source of ammonia emitted to the atmosphere, mostly from animal operations and fertilized crops, while dry and wet deposition are the primary sinks of atmospheric ammonia. Although, current air quality models consider all of these source and sink processes, algorithms for emissions from fertilized crops and dry deposition are too simplistic to provide accurate accounting of the net surface fluxes. New modeling techniques are being developed that replace current ammonia emission from fertilized crops and ammonia dry deposition with a bi-directional surface flux model. Comparisons of the ammonia bi-direction flux algorithm to field experiments involving both lightly fertilized soybeans and heavily fertilized corn are presented and discussed. Initial tests and evaluation of CMAQ modeling results for a full year (2002) at 12 km grid resolution including implementation of a soil nitrification model and the ammonia bi-directional flux algorithm result in improved NH_x wet deposition.

1. Introduction

Ammonia is an important precursor to fine-scale particulate matter ($PM_{2.5}$) which is known to be a serious human health hazard (Pope and Dockery 2006) and is subject to regulation through the National Ambient Air Quality Standards (NAAQS). In addition to the health effects of increased PM due to ammonia emissions there are also significant climate effects by direct scattering of short-wave solar radiation and indirect alteration of cloud albedos and lifetimes through increase cloud condensation nuclei concentrations (Ramanathan et al., 2001). Both of these effects cause negative radiative forcing (cooling). Atmospheric ammonia and ammonium aerosol also contribute a large fraction of reactive nitrogen deposition that is a source of nutrient enrichment and one of the sources of acidification that cause deleterious impacts on terrestrial and aquatic ecosystems such as eutrophication and forest health decline (Dennis, et al., 2007; Driscoll et al., 2001). The importance of reduced forms of nitrogen deposition is expected to increase as NO_x emissions are further controlled and agricultural emissions of ammonia continue to increase (Pinder et al, 2008). Currently, about 85% of the ammonia emissions in the US are from agricultural sources with about 35% of that coming from fertilizer application. Thus, a more accurate and responsive method for modeling ammonia emissions from fertilizer is needed to improve atmospheric modeling of ammonia and ammonium (NH_x) concentrations and deposition.

2. The Bi-Directional Flux Model

When exposed to liquid water ammonia gas ($NH_{3(g)}$) will dissolve and dissociate in solution and establish an equilibrium between ammonia gas, ammonium ion (NH_4^+), and hydroxide ion (OH^-). When combined with the equilibrium dissociation of water, the net equilibrium is between ammonia gas plus hydrogen ion and aqueous ammonium ion:

$$NH_{3(g)} + H^+ \leftrightarrow NH_4^+ \qquad (1)$$

Such equilibria can exist in leaves where $NH_{3(g)}$ in the stomatal cavity is in equilibrium with NH_4^+ and H^+ in the water contained in the apoplast tissue within the leaf and in the soil where $NH_{3(g)}$ in the soil pore air space is in equilibrium with NH_4^+ and H^+ dissolved in soil water . The concentration of $NH_{3(g)}$ in the stomatal cavities (χ_s) and the soil air space (χ_g) can be related to the aqueous concentrations of NH_4^+ and H^+ in the leaves and soil water as (Farquhar et al, 1980):

$$\chi_{s,g} = \frac{A}{T_{s,g}} 10^{-B/T_{s,g}} \Gamma_{s,g} \qquad (2)$$

where $\chi_{s,g}$ is the compensation point-based concentration of NH_3 in the air space inside the leaf stomata and soil pores (μg m^{-3}), A (2.746×10^{15}) and B (4507) are constants derived from the equlibria constants, $T_{s,g}$ is the leaf and soil temperature (K), and $\Gamma_{s,g}$ is the dimensionless NH_3 emission potential from the leaf stomata and soil ($\Gamma = NH_4^+ / H^+$). The direction of ammonia flux to or from the leaf apoplast and soil water depends on the compensation points compared to the air concentration in the canopy, χ_c, such that ammonia will volatilize (emission) when, $\chi_{s,g} > \chi_c$ and deposit when $\chi_{s,g} < \chi_c$.

Like most dry deposition models the bi-directional flux model is based on an electrical resistance analog where flux is analogous to current and concentration difference is analogous to voltage as shown in Figure 1. The total flux between the plant canopy and the overlying atmosphere (F_T) is sum of two bi-directional pathways, to the leaf stomata (F_{st}) and the soil (F_g), and one uni-directional deposition pathway to the leaf cuticle (F_{cut}).

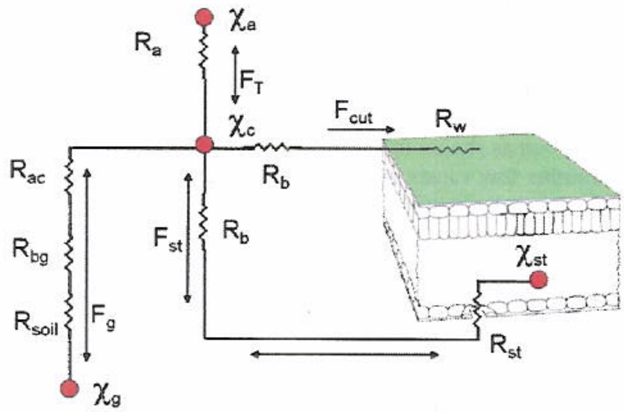

Fig. 1. Schematic of bi-direction flux for soil and leaf.

Some of the resistances are the same as are used for evapotranspiration in meteorology models and dry deposition in air quality models such as R_a, R_b, *and* R_{st} which have been defined in previous papers describing those models (e.g. Pleim 2006, Pleim and Xiu, 2003, and Xiu and Pleim, 2001). The resistances that needed to be developed or refined for this work primarily involve the soil pathway because in fertilized agricultural fields the evasive flux from the ground usually dominates all other flux pathways. For heavily fertilized crops, such as for the field experiment in a North Carolina corn field that is described in Section 3 and a fertilized grassland in Germany described by Personne et al (2009), measured values of Γ_g values are often on the order of 100,000 which, depending on the temperature and pH of the soil, results in soil compensation concentrations of ammonia on the order of 1000 μg m^{-3}. Thus, there must be large resistances in the ground pathway to limit fluxes to realistic levels. The limiting resistance for the ground pathway is the resistance to diffusion through the air within the soil matrix from the soil water to the ground surface (R_{soil}). Since the source of gas-phase NH_3 in the soil is NH_4^+ dissolved in the soil water the soil resistance for NH_3 is analogous to the soil resistance to evaporative flux from moist soil.

3. Comparison to Field Studies

The bi-directional model has been evaluated and improved through comparisons to two field studies. Although both field experiments were performed in agricultural fields their conditions for ammonia fluxes were very different. The first experiment was in a soybean field in Warsaw, NC in the summer of 2002 (Walker et al., 2006) and the second was in a corn field in Lillington, NC during the spring and summer of 2007. In addition to obvious differences in canopy height and leaf structure between soybeans and corn, the most important difference was in the amount of fertilizer that was applied. Soybeans, being nitrogen fixing legumes, require very little fertilization while corn needs large amounts of fertilizer. Thus, for soybeans the ammonia fluxes were truly bi-directional with deposition generally occurring in the morning, peaking at about 830 LT, and evasion from late morning through the mid afternoon as shown in Figure 2. The model was able to replicate this behavior with rather low values of Γ (Γ_s = 1000 and Γ_g = 800) and most of the flux followed the stomatal pathway.

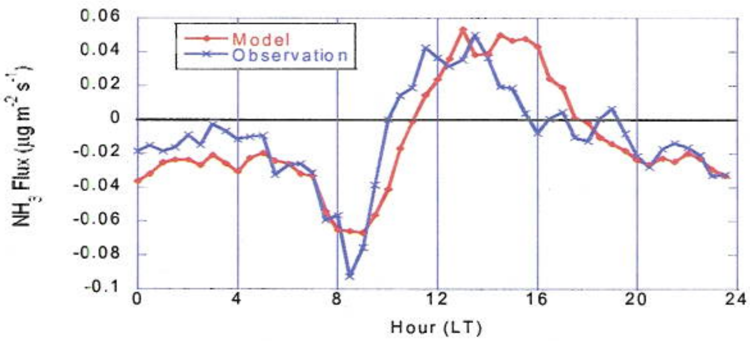

Fig. Fig. 2. Ammonia flux over soybeans in Warsaw, NC averaged over 2 months in summer 2002..

In contrast to the soybean experiment, the ammonia fluxes in the corn field were entirely evasion because of the massive amount of fertilizer that was applied on June 6, just 2 weeks before the measurements shown in Figure 3. Also note that the daily peak fluxes were around 1 $\mu g\ m^{-2}\ s^{-1}$, which is about one order-of-magnitude greater than measured in the soybean field. As shown in the lower panel of Figure 3, the large upward flux was from the soil because the soil Γ ranged from about 100,000 to 200,000. The fluxes for the stomatal and cuticle pathways were always negative indicating that a portion of the ground flux was taken-up by the canopy. Model simulations about a month later (not shown) suggest that about half of the ground flux was intercepted by the canopy, which agrees with an analysis of in-canopy ammonia measurements made by Bash et al., (2010).

4. Conclusions

The two agricultural flux experiments demonstrate that a comprehensive bi-directional flux model must have realistic treatments of the ground, stomatal, and cuticle pathways. Different pathways are dominant in different conditions with complex interactions among them. Critical resistances for the soil and leaf cuticle needed to be developed to create a model capable of reasonable agreement with the measured fluxes for both experiments.

The bi-directional flux model has been applied in the Community Multiscale Air Quality (CMAQ) model along with a fertilizer application tool and a soil nitrification and acidification model to compute soil gamma values (Cooter et al 2010). Preliminary annual model simulations show improved estimates of NH_x wet deposition over the eastern US as a whole (reduction in mean error), with regions of significant reduction in bias and regions of moderate increase in bias.

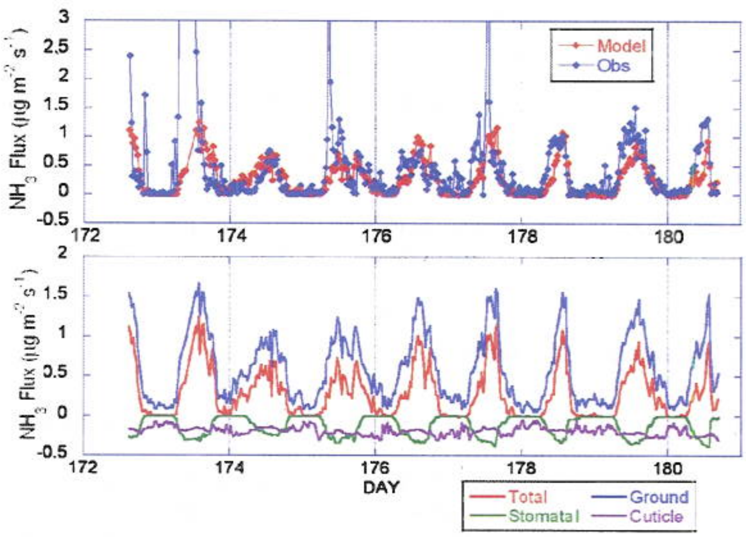

Fig. 3. Ammonia fluxes over a corn field at Lillington, NC, June 21 – 30. Modeled and measured total fluxes (top) and modeled flux components (bottom).

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5. Questions and Answers

Bernard Fisher: Could the large flux spikes of ammonia in the early morning be caused by ammonia dissolved in evaporating dew?

Answer: We wondered about that also, but a quick calculation of the mass of evaporating of water and the aqueous concentrations of ammonia resulting from Henry's law equilibrium show much too little flux. However, we also wonder if ammonia from the soil water somehow mixes into the dew, then this could cause the large measured ammonia fluxes. If this happens then the soil resistance is essentially short-circuited resulting in a big flux spike while the dew evaporates.

Jeff Weil: What is the importance or sensitivity of the modeled flux to the term in the exponential term that is raised to the 5th power? Was that term a physically-derived quantity or was it empirical?

Answer: The equation for soil resistance is based on analogy to an empirical expression for soil moisture evaporation and includes an exponential of the 5th power of one minus relative soil moisture. This resistance is very sensitive to soil moisture especially when very dry. The ammonia flux is also quite sensitive to soil moisture but to a lesser degree because the value of gamma also increases as the soil dries.