

## Estimation of NH<sub>3</sub> Bi-Directional Flux from Managed Agricultural Soils

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## Abstract

The Community Multi-Scale Air Quality model (CMAQ) is used to assess regional air quality conditions for a wide range of chemical species throughout the United States (U.S.). CMAQ representation of the regional nitrogen budget is limited by its treatment of ammonia ( $\text{NH}_3$ ) soil emission from, and deposition to underlying surfaces as independent rather than tightly coupled processes, and by its reliance on soil emission estimates that do not respond to variable meteorology and ambient chemical conditions. The present study identifies an approach that addresses these limitations, lends itself to regional application, and will better position CMAQ to meet future assessment challenges. These goals were met through the integration of the resistance-based flux model of Nemitz et al. (2001) with elements of the United States Department of Agriculture EPIC (Environmental Policy Integrated Climate) model. Model integration centers on the estimation of ammonium and hydrogen ion concentrations in the soil required to estimate soil  $\text{NH}_3$  flux. The EPIC model was calibrated using data collected during an intensive 2007 field study in Lillington, North Carolina. A simplified process model based on the nitrification portion of EPIC was developed and evaluated. It was then combined with the Nemitz et al. (2001) model and measurements of near-surface  $\text{NH}_3$  concentrations to simulate soil  $\text{NH}_3$  flux at the field site. Finally, the integrated flux (emission) results were scaled upward and compared to recent national ammonia emission inventory estimates. The integrated model results are shown to be more temporally resolved (daily), while maintaining good agreement with established soil emission estimates at longer time-scales (monthly). Although results are presented for a single field study, the process-based nature of this approach and NEI comparison suggest

- 1 that inclusion of this flux model in a regional application should produce useful
- 2 assessment results if nationally consistent sources of driving soil and agricultural
- 3 management information are identified.

## 1. Introduction

Emission of oxidized and reduced atmospheric nitrogen compounds,  $\text{NO}_x$  (including nitrous oxides) and  $\text{NH}_x$  respectively, play an important role in the formation of acidic deposition, tropospheric ozone and particulate matter (Seinfeld and Pandis, 1998). In terrestrial systems, nitrogen deposition can reduce forest productivity (under high loading), increase potential vulnerability to pests and pathogens, alter plant species composition, contribute to soil acidification and cause declines in some sensitive plant populations (Lovett and Tear, 2008). In aquatic ecosystems, nitrogen over-enrichment increases algal growth and contribute to water body acidification (Boyer et al., 2002). Increased algal growth can reduce water clarity and dissolved oxygen concentrations, and degrade nursery habitats in marshes and estuaries (Dennison et al., 1993; Emery et al., 2001; Sarda et al., 1996). Ammonia ( $\text{NH}_3$ ) gas and ammonium ( $\text{NH}_4^+$ ) aerosols comprise  $\text{NH}_x$  in the atmosphere.  $\text{NH}_3$  is the primary atmospheric base and will neutralize atmospheric acids, most notably sulfuric and nitric acid, to form  $\text{NH}_4^+$  aerosols, a major constituent of fine particulate matter ( $\text{PM}_{2.5}$ ) (Nenes et al., 1999).

The majority of U.S.  $\text{NH}_3$  emissions are associated with commercial crop and livestock production. The 2002 EPA National Emissions Inventory (NEI) (<http://www.epa.gov/ttn/chief/2002inventory.htm>) reports that 35% of all agricultural  $\text{NH}_3$  emissions originate from soils receiving commercial nitrogen fertilizer applications. Potter et al. (2006) estimate that, on average, 28% of applied nitrogen (N) is lost from agricultural fields *via* volatilization, surface runoff, leachate, lateral subsurface flow, waterborne sediment and windborne sediment pathways. Of this fraction, 48% (13% of applied N) is lost through volatilization. The Fertilizer Institute reports 2006/2007 U.S.

1 fertilizer sales are 3% higher than those reported in 2000, and this upward trend is  
2 expected to continue, e.g. Erisman, et al. (2008). One potential driver of increased  
3 fertilizer applications and subsequent  $\text{NH}_3$  emission is the Energy Independence and  
4 Security Act (EISA). The 2008 revision to the EISA Renewable Fuel Standard (RFS2)  
5 calls for increasing the Nation's production of ethanol-based fuel from 5.4 billion gallons  
6 by 2022 under the original 2007 Rule, to 9.0 billion gallons per year. Crop varietal and  
7 management shifts to meet the revised EISA bio-fuel demands could result in shifts in  
8 regional  $\text{NH}_3$  patterns of emission, atmospheric transport and deposition.

9       Regional air quality models are useful tools to explore  $\text{NH}_3$  transport and flux  
10 response to policies such as EISA-RFS2. Local, state and federal organizations  
11 frequently address questions regarding the regional transport and fate of pollutants,  
12 including  $\text{NH}_3$ , through the Community Multiscale Air Quality (CMAQ) model (Byun  
13 and Schere, 2006). Treatment of the atmospheric  $\text{NH}_x$  budget in CMAQ v4.7 relies on  
14 independent estimates of  $\text{NH}_3$  emission and a unidirectional dry deposition approach  
15 dating to the mid-1990s. Today, there is renewed recognition of the need to represent  
16 accurately the coupled bi-directional flux behavior of gaseous nitrogen species to reduce  
17 recognized uncertainty in the  $\text{NH}_3$  emission inventory (Dennis et al., 2008; NARSTO,  
18 2005) and to minimize potential inconsistencies in simulated regional N budgets  
19 (Farquhar et al., 1980; Sutton et al., 1993a; Sutton et al., 1993b).

20       A resistance-based bi-directional flux model for agricultural soils amended with  
21 commercial fertilizer is proposed that addresses these limitations while positioning  
22 CMAQ to more fully address complex emerging issues such as EISA. First, we describe a  
23 process-based equilibrium parameterization that is expanded to explicitly address  $\text{NH}_3$

1 flux from agricultural soils. The parameterization requires knowledge of hydrogen ( $H^+$ )  
2 and  $NH_4^+$  soil concentrations that depend on local environmental and agricultural  
3 management practices. The ability to obtain such information from a widely used  
4 process-based agricultural management model is demonstrated through calibration to  
5 results of a recent field study. Relevant portions of the management model are extracted  
6 into a simplified nitrification process model, which is then validated against the full  
7 management model. Results of the simplified process model are then combined with  
8 additional field data and a refined resistance-based  $NH_3$  model to estimate soil  $NH_3$  flux.

9

10

## 11 **2. Methodology**

### 12 *2.1 The CMAQ v4.7 surface exchange model*

13 The CMAQ v4.7  $NH_3$  surface exchange model provides a methodological  
14 framework for the bi-directional model development that follows. CMAQ employs a 3-  
15 dimensional Eulerian modeling approach to address air quality issues such as  
16 tropospheric ozone, fine particles, acid deposition and visibility degradation (Byun and  
17 Schere, 2006). The system comprises a meteorological modeling system for the  
18 description of atmospheric conditions, emission models for anthropogenic and natural  
19 emissions that are injected into the atmosphere, and a chemical-transport modeling  
20 system (CTM) to simulate chemical transformations, and atmospheric fate and transport.

21 The National Emission Inventory (NEI) provides estimates of  $NH_3$  emissions  
22 from croplands receiving commercial fertilizer applications. The most recently available  
23 inventory is NEI 2002af (USEPA, 2006). The NEI begins with annual state-level

1 emission estimates produced by the Carnegie Mellon University (CMU) ammonia  
2 emission inventory model version 3.6 (Goebes et al., 2003). The CMU estimates are  
3 based on fixed fertilizer emission factors (Battye et al., 1994; European Environment  
4 Agency, 2001) and Association of American Plant Food Control Officials (AAPFCO)  
5 Commercial Fertilizer sales (AAPFCO, 2002). The NEI process allocates the annual  
6 CMU estimates spatially using the sum of land area for the 1992 National Land Cover  
7 Database (NLCD) imagery classes for pasture/hay, grains, row crops, fallow land and  
8 orchards/vineyards  
9 ([http://www.epa.gov/ttn/chief/emch/spatial/new/surrogate\\_development\\_process\\_03115.](http://www.epa.gov/ttn/chief/emch/spatial/new/surrogate_development_process_03115.pdf)  
10 pdf). Temporal allocation is performed using state-specific monthly profiles provided by  
11 CMU (<http://www.epa.gov/air/interstateairquality/pdfs/finaltech01.pdf>). A mean daily  
12 emission is estimated by dividing the monthly total by the average number of days in a  
13 calendar month and a standard diurnal profile is applied to derive the estimated hourly  
14 emissions that are required input to CMAQ.

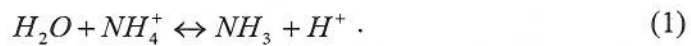
15 The CTM combines these emissions with chemical boundary conditions from the  
16 surface upward to ~ 100 hPa to simulate chemical transformations, atmospheric transport  
17 and fate. The mass of a chemical contaminant deposited to an underlying surface is  
18 computed for each model time step within the CTM. Dry deposition processes in CMAQ  
19 affect chemical concentrations at each model time step (often 5 min) and include the  
20 removal of chemical species from the atmosphere as they adsorb to, absorb into or react  
21 with surfaces such as soil, water, vegetation or hardened structures. Equilibrium  
22 interactions between  $\text{NH}_3$  and other inorganic sulfur and nitrogen species are included  
23 (Nenes et al., 1999). A full photochemistry simulation accounts for multi-pollutant

interactions among the oxidized nitrogen species. The mass of chemical dry deposited during a model time step is computed as the product of atmospheric concentration ( $C_a$ ) and deposition velocity ( $V_d$ ).  $V_d$  is dependent on the aerodynamic resistance ( $R_a$ ), the laminar sub-layer resistance ( $R_b$ ), in-canopy aerodynamic resistance ( $R_{ac}$ ), boundary layer resistance at the soil surface ( $R_{bg}$ ), stomatal resistance ( $R_{st}$ ), mesophyll resistance ( $R_m$ ) and cuticular resistance ( $R_w$ ) (Figure 1a) (Pleim et al., 2001).

## 2.2 The bi-directional flux model

Sutton et al. (1998) and Nemitz et al. (2001) propose a resistance-based bi-directional flux model based on the comparison of equilibrium concentrations of  $NH_4^+$  and  $NH_3$  in leaf apoplast to ambient canopy air concentrations. Figure 1b illustrates the integration of this interaction across vegetation and soil surfaces, while Figure 1c illustrates a more explicit treatment of near-soil resistances.

For a vegetation canopy, Nemitz et al. (2001) begin by assuming that the cuticle is a sink for atmospheric  $NH_3$  and that  $NH_3$  gas in the sub-stomatal cavity exists in equilibrium with  $NH_4^+$  such that,



The concentration of  $NH_3$  at the air-leaf interface can then be related to the concentration of  $NH_4^+$  in the leaf mesophyll by the Henry's Law and dissociation equilibria (Nemitz et al., 2001),

$$X_m = \frac{A}{T_L} \exp^{-B/T_L} \Gamma_m , \quad (2)$$

1 where  $X_m$  is the equilibrium concentration of  $\text{NH}_3$  at the air-leaf interface ( $\text{mol m}^{-3}$ ),  $A$   
2 (161500) and  $B$  (10380) are constants associated with the temperature adjusted Henry's  
3 Law coefficient,  $T_L$  is the leaf temperature (K), and  $\Gamma_m$  is the dimensionless  $\text{NH}_3$   
4 emission potential ,

$$\Gamma_m = \frac{[\text{NH}_4^+]}{[\text{H}^+]} \quad , \quad (3)$$

6  
7 where  $[\text{H}^+]$  is the concentration of hydrogen ion and  $[\text{NH}_4^+]$  is the concentration of  $\text{NH}_4^+$   
8 ion in  $\text{mol L}^{-1}$  of leaf water. If the ambient air concentration in the vegetation canopy is  
9 less than  $X_m$ ,  $\text{NH}_3$  will volatilize (emission). If the ambient air concentration is greater  
10 than  $X_m$ ,  $\text{NH}_3$  will deposit. Further development of this canopy model is discussed in  
11 Bash et al. (2010).

12 Nemitz et al. (2001) imply the extension of their model to managed agricultural  
13 soils through their analysis of  $\text{NH}_3$  flux over wheat stubble. In that case, a resistance-  
14 based framework is used to represent conditions at the soil surface (no soil resistance).  
15 Intensively managed U.S. agricultural systems often inject or incorporate commercial  
16 fertilizer into the plow layer. Even when surface-applied, commercial N can be  
17 transported short distances into the upper soil layer. The present study formally develops  
18 and evaluates refinements to the Nemitz et al. (2001) model for  $\text{NH}_3$  flux over a managed  
19 agricultural soils that includes a soil resistance term. We begin by assuming that  $\text{NH}_4^+$   
20 and  $\text{NH}_3$  exist in equilibrium in the soil (Saffingna and Freney, 2006). N in agricultural  
21 soils derives from mineralization of organic material, rainfall, manure, biological  
22 nitrogen fixation (BNF) and the application of commercial fertilizer. The focus here is  
23 on the availability of soil N from commercial sources which is a function of the form of

1 N applied, amount applied and mode of application. Since commercial agriculture is the  
2 largest producer of  $\text{NH}_3$  emissions, we turn to a widely used United States Department of  
3 Agriculture (USDA) nutrient management model for a well-vetted approach to the  
4 simulation of these transformation processes.

5

6

### 7 *2.3 The Environmental Policy Integrated Climate (EPIC) Model*

8 The EPIC model was developed in the early 1980's to assess the effect of erosion  
9 on agricultural productivity (Williams et al., 1984). More recently, the model has been  
10 expanded and refined to allow simulation of many processes important in agricultural  
11 management (Sharpley and Williams, 1990; Williams et al., 1985). EPIC operates on a  
12 daily time-step but can simulate time periods extending 100 years or more. The drainage  
13 area considered is generally up to about 100 ha ( $\sim 1 \text{ km}^2$ ). Most recently EPIC was  
14 applied across the continental U.S. to assess soil loss, nutrient loss and change in soil  
15 organic carbon associated with crop production (Potter et al., 2006). Regional and  
16 national analyses based on EPIC simulations are widely used by national policy analysts  
17 and local decision makers for current and future environmental management assessments.

18 EPIC utilizes user-defined farm management configurations and field operations  
19 including tillage and fertilization of a wide range of commercial field crops. The timing  
20 and amount of nitrogen applied to the field system can be user specified or estimated by  
21 the model itself as a function of environmental and crop growth parameters. EPIC  
22 assumes that all fertilizer N derives from anhydrous  $\text{NH}_3$ , urea, ammonium nitrate, or  
23 mixtures of these forms. Our initial hypothesis is that characterization of the nitrification

1 process alone will adequately simulate the concentration of  $\text{NH}_4^+$  and  $\text{H}^+$  in the soil for  
2 regional air quality applications.

3 EPIC simulates nitrification, which is the microbial transformation of  $\text{NH}_4^+$  to  
4  $\text{NO}_3^-$ , through a combination of the first-order kinetic rate equation of Reddy et al. (1979)  
5 and methods described in Godwin et al. (1984). A maximum rate of N transformation is  
6 computed, which is then reduced *via* a series of environmental indices reflecting ambient  
7 pH, temperature, and soil moisture conditions on nitrification and subsequent  
8 volatilization rates. The EPIC method requires knowledge or model estimates of physical  
9 properties of the ambient soil profile, weather, and crop management actions such as  
10 tillage and, if available, fertilizer application timing and amount. The present application  
11 draws upon conditions during an intensive field study conducted at Lillington, North  
12 Carolina, for this information.

13

14

#### 15 2.4 The field study

16 During the summer of 2007, a field experiment was conducted near Lillington,  
17 NC, to examine  $\text{NH}_3$  exchange processes in a fertilized corn field. The site is a 200 ha  
18 field in Harnett County, NC (35° 22' 35.7" Lat. -78° 46' 45.1" Long. 45 m Elev.). The  
19 field was planted in corn (*Zea mays*, Pioneer varieties 31G66 and 31P41 ) on April 18,  
20 2007 at a density of approximately 70,000 plants  $\text{ha}^{-1}$ . Anhydrous  $\text{NH}_3$  (ammonium  
21 polyphosphate, 18.5 kg  $\text{ha}^{-1}$  N) was injected to a depth of 5.0 cm between April 18 and  
22 April 23. A second application of urea-ammonium nitrate solution (94.1 kg  $\text{ha}^{-1}$  N) with  
23 Agrotain nitrogen stabilizer was dribble-band applied between May 25 and May 29,

2007. Harvesting took place on August 15, 2007. Details of the field study sampling and analytical methods are provided in the Supplemental material.

### 3. Results

Three aspects of model development are presented here. First, successful calibration of the EPIC biogeochemical budget to 2007 Lillington, NC, field observations is confirmed and the relevant transformation processes from EPIC are transferred to a simplified model to support simulation of soil  $\text{NH}_3$  emission potential ( $I_g$ ) and equilibrium concentration ( $X_g$ ). The  $X_g$  estimate is then combined with additional field data and environmental parameterizations to simulate  $\text{NH}_3$  soil flux at the field site. Although this study focuses on results from a single field site, the process-driven nature of the approach, combined with the history of successful regional to national application of the farm management model suggests it should adapt well to regional-scale applications.

#### 3.1 Model field-scale calibration, simplification, validation and integration

Little EPIC model calibration is needed to obtain model/observation agreement because of its process-based design. Observed daily maximum and minimum temperature, wind speed, solar radiation, and rainfall observed at the site April 15 - August 10 were combined with EPIC-simulated weather (based on 2007 monthly statistics from a near-by cooperative site) between January 1 - April 14 and August 11 -

1 December 31. EPIC crop growth parameters were adjusted to simulate observed LAI  
2 (observed median LAI = 1.38; RMSE = 0.24) and crop height data (observed median  
3 crop height = 142 cm; RMSE = 8.50). Observed field-scale variability on each of the 12  
4 sample collection days was characterized by collecting and compositing three soil  
5 samples, 5 cm in depth, at each of 12 field locations for later chemical analysis (see  
6 Supplemental material). Soil physical properties were sampled on only one occasion at a  
7 location that was nearby, but not co-located with any chemistry sample locations. The  
8 EPIC model calibration goal for this application is to simulate analyzed soil and chemical  
9 conditions that fall within the range of observed conditions on each sampled day. Figures  
10 2a-c show EPIC field-scale calibration results for soil moisture (g-H<sub>2</sub>O/g-fresh soil),  
11 [NH<sub>4</sub><sup>+</sup>] (mol L<sup>-1</sup>), and [H<sup>+</sup>] (mol L<sup>-1</sup>) in the composite 5 cm soil layer sample. Field-scale  
12 soil moisture calibration is achieved by modifying initial soil property estimates based on  
13 the four property samples provided to the EPIC model. No additional parameter  
14 calibration was performed to achieve the Figure 2a-c results. These figures illustrate that  
15 the majority of calibrated model values lie within the observed inner quartile range (IQR)  
16 and that, with only three soil moisture and one [NH<sub>4</sub><sup>+</sup>] exceptions, the simulated values  
17 lie within the observed sample ranges.

18 Having demonstrated that the EPIC model adequately simulates [NH<sub>4</sub><sup>+</sup>] and [H<sup>+</sup>]  
19 for this field site, relevant EPIC process algorithms are extracted into a simplified  
20 nitrification process model. The simplified version is tested against the full EPIC model  
21 to confirm proper code extraction and implementation. Simplified model assumptions  
22 include that 1) there is no significant N loss in runoff, leaching or sub-surface flow from  
23 the field site, 2) a 2-layer soil characterization, i.e. a 1 cm surface layer and a 1 m

1 underlying layer with a clay pan located at 0.3 m, is sufficient to represent local edaphic  
2 conditions, 3) the first fertilizer application is injected into the underlying layer, 4) that  
3 the second fertilizer application remains primarily in the surface (1 cm) layer, and 5)  
4 there is no significant litter build-up on the soil surface. The absence of horizontal and  
5 vertical loss is acceptable here because the field has a slope near zero, there is an  
6 impervious clay pan at 0.3 m, and 2007 was a climatologically dry year. The assumption  
7 of only two model soil layers recognizes that CMAQ itself contains only two soil layers.  
8 This configuration allows us to determine if such a minimal configuration is sufficient to  
9 capture critical signals in the field data. The assumption of no surface litter is reasonable  
10 for the Lillington site and for standard intensive agricultural production systems in the  
11 U.S. This is not the case for minimum- or no-till management systems. Comparison of  
12 the full to simplified models yields agreement (median bias) within 1.5% of median  
13  $[\text{NH}_4^+]$  values and within 2% of median  $[\text{H}^+]$ . This bias likely reflects the error  
14 introduced by the omission of horizontal and vertical N losses in the simplified model.

15 As a final step, the results of the validated simplified process model are provided  
16 to Eqs 3 and 4. Figure 3 compares median  $I_g$  and  $X_g$  for  $\text{NH}_3$  within the upper 5 cm soil  
17 layer using observed  $[\text{NH}_4^+]$ ,  $[\text{H}^+]$  and soil temperatures, to simulated  $X_g$  values using  
18 simplified model  $[\text{NH}_4^+]$ ,  $[\text{H}^+]$  and observed soil temperatures. All simulated values lie  
19 within the observed data range, confirming the ability of the integrated parameterization  
20 to simulate  $I_g$  and  $X_g$  values that are representative of the Lillington field from  
21 observation-based input parameters.

22

### 23 3.2 The integrated $\text{NH}_3$ soil flux model

1           Figure 3 confirms the simplified model's ability to support simulation of  
 2   observed soil  $[\text{NH}_4^+]$ ,  $[\text{H}^+]$  and  $X_g$ . The air-soil  $\text{NH}_3$  exchange is evaluated by comparing  
 3   resistance-based flux estimates that incorporate the integrated simplified process model to  
 4   observation-based soil  $\text{NH}_3$  fluxes. The full CMAQ bi-directional implementation  
 5   illustrated in Figure 1b represents the soil and canopy along with the appropriate  
 6   resistances as an integrated in-canopy concentration,  $X_{z0}$ . The focus of the present  
 7   analysis is the validation of the air-soil exchange portion of this schematic only, which  
 8   requires the more explicit treatment of near-soil resistances and concentrations (Figure  
 9   1c). In this case, flux ( $\text{ng m}^{-2} \text{s}^{-1}$ ) between the soil and air at some distance,  $z$ , above the  
 10   soil is simulated as,

$$F_z = \frac{(X_g - C_z)}{R_{ac,z} + R_{bg} + R_{soil}} \quad , \quad (4)$$

14   Here,  $z = 0.1 \text{ m}$ ,  $C_z$  ( $\text{ng m}^{-3}$ ) is the measured  $\text{NH}_3$  concentration at height  $z$ ,  $X_g$  is  $[\text{NH}_3]$  in  
 15   the soil layer ( $\text{ng m}^{-3}$ ),  $R_{ac,z}$  is the aerodynamic canopy resistance ( $\text{s m}^{-1}$ ) at height  $z$ ,  $R_{bg}$   
 16   is the air-side boundary layer (laminar) resistance at the soil surface ( $\text{s m}^{-1}$ ) and  $R_{soil}$  is the  
 17   soil resistance ( $\text{s m}^{-1}$ ). Stomatal and cuticular resistances were assumed to be negligible  
 18   here as there was no measureable leaf area between the soil surface and  $0.1 \text{ m}$   
 19   measurement height. Estimation of  $X_g$  has been discussed previously. CMAQ 4.7  
 20   computes  $R_{ac}$  as a function of the canopy height and the friction velocity at the top of the  
 21   canopy (Erisman et al., 1994). Development of a new parameterization for under-canopy  
 22   near-surface conditions  $R_{ac,z}$  such as those considered here is beyond the scope of the

present study. It is assumed that when  $X_g > C_{0.1}$  (emission) and  $z = 0.1$  m,  $R_{ac,z}$  is negligible relative to  $R_{bg}$ .  $R_{bg}$  is estimated as (Schuepp, 1977),

$$R_{bg} = \frac{Sc - \ln(\frac{d_0}{z_l})}{ku_{gstar}} \quad , \quad (5)$$

where  $Sc$  is the Schmidt number for  $NH_3$ ,  $d_0$  (m) the laminar layer thickness,  $z_l$  (here, 0.1 m) is the distance across which exchange from the ground takes place,  $k$  (0.41) is the dimensionless von Karman constant and  $u_{gstar}$  ( $m\ s^{-1}$ ) is the friction velocity at the soil surface. Bash et al. (2010) propose a parameterization for  $u_{gstar}$  derived from first order closure principles. Assuming the canopy drag coefficient of Massman (1997), the analytical parameterization of the in-canopy friction velocity at the soil surface becomes,

$$u_{gstar} = u_*(z_r) \exp[-\phi_m LAI] \quad , \quad (6)$$

where  $u_*(z_r)$  is the friction velocity at the top of the canopy, i.e.,  $z_r$  = the canopy height,  $\phi_m$  is the dimensionless wind shear and  $LAI$  is the total (living and senesced) leaf area.

For  $NH_3$  emission, the gas must diffuse to the surface through soil air- and water-filled pore space. Most previous research regarding the estimation of this diffusion rate,  $D_p$ , is based on the behavior of relatively insoluble gases e.g., Thorbjørn et al. (2008). However,  $NH_3$  is highly soluble and so here we assume it behaves in a fashion similar to water vapor, with the source of evasion and deposition at the soil air-water interface. Sakaguchi and Zeng (2009) estimate the diffusion coefficient for water vapor,  $D_p(H_2O)$  for undisturbed soil from an early model proposed by Moldrup et al. (1999),

$$D_p(H_2O) = D_0 \theta_{sat}^2 \left(1 - \frac{\theta_r}{\theta_{sat}}\right)^{2+3/b}$$

1 (7)

2

3 Where  $\theta_{sat}$  is the volumetric water content at saturation,  $b$  is the fitting parameter for the  
4 soil water characteristic curve and depends on soil texture (Clapp and Hornberger, 1978),  
5 and  $\theta_r$  is the residual water content approximated by the soil wilting point. Sakaguchi  
6 and Zeng (2009) define soil resistance as,

7

$$8 \quad R_{soil} = \frac{L}{D_p(H_2O)} \quad (8)$$

9 where  $L$  is the dry layer thickness defined as,

$$10 \quad L = d_l \frac{\exp[(1 - \theta_l / \theta_{sat})^w] - 1}{e - 1} \quad (9)$$

11

12 where,  $d_l$  is the soil diffusion layer thickness (here, 0.01 m),  $e$  is the constant (2.718), and  
13  $w$  is a parameter that controls the concavity of the curve. Sakaguchi and Zeng (2009)  
14 recommend a value of  $w = 5$ . Our study site soil is classified as sandy loam for which a  
15 value of  $b = 4.9$  is most appropriate (Clapp and Hornberger, 1978).

16 Figure 4a and Table 1 compare modeled fluxes ( $F_{z=0.1m}$ ) and observed  $NH_3$  flux  
17 measurements made during the intensive field study conducted at the Lillington site from  
18 July 6<sup>th</sup> - August 1<sup>st</sup>. The observed flux range was computed as described in the  
19 Supplemental material. Table 1 indicates modeled values are biased low (median daily  
20 bias =  $-119 \text{ ng m}^{-2} \text{ s}^{-1}$ ) which most likely results from an implicit assumption that  
21 commercial N is evenly mixed throughout the 5 cm soil sample. We know this is not the  
22 case, and that the majority of the volatilizing commercial N measured during the  
23 intensive study most likely derives from the second fertilizer application and lies very

1 near the soil surface. Figure 4b and Table 1 show that if we assume the N-source is  
2 focused in the upper 1cm of our modeled soil, the computed flux is biased high relative to  
3 observations (median daily bias = +105 ng m<sup>-2</sup> s<sup>-1</sup>). Similar results, i.e., flux over-  
4 prediction, are noted in Nemitz et al. (2001) in which  $\Gamma_g$  is reduced by 85% to achieve  
5 modeled and observation flux agreement over wheat stubble. The authors suggest that  
6 sources of this model bias could include omission of a soil resistance term, which we  
7 have now included, or derives from the NH<sub>4</sub><sup>+</sup> extraction technique, which may remove  
8 more NH<sub>4</sub><sup>+</sup> than is naturally available for evaporation in the soil pore water. We have begun  
9 to explore this latter bias and preliminary results appear to confirm a likely extraction  
10 bias of 35 - 45% (see Supplemental material). Figure 4c illustrates model to observation  
11 agreement when this bias adjustment ( $\Gamma_g$  reduced by 45%) is applied to our integrated  
12 process-based flux model. One source of remaining model uncertainty is illustrated by  
13 the first sample day (Figure 4c). In this case, unlike the other sample periods during  
14 which the in-canopy NH<sub>3</sub> concentration decreases exponentially with height above the  
15 soil surface, the profile decreases in a nearly linear fashion (Bash et al., 2010) resulting in  
16 a substantial model over-prediction (observed = 13.5 ng m<sup>-2</sup> s<sup>-1</sup>; model = 128 ng m<sup>-2</sup> s<sup>-1</sup> ).  
17 A second source of model uncertainty derives from the assumptions associated with our  
18 resistance estimates:  $R_{ac} \gg R_{bg}$  at  $z = 0.1$  m; diffusion through managed agricultural  
19 soils  $\approx$  diffusion through undisturbed soils; and  $D_p(NH_3) \approx D_p(H_2O)$ . These issues are  
20 being considered further as part of a program of continuing model development and  
21 evaluation studies.

22

#### 23 4. Discussion

1    4.1 *Comparison to established emission regional inventory estimates*

2           It has been demonstrated that a simplified nitrification model, when combined  
3 with site-specific information and appropriate media resistances, can reproduce observed  
4 median daily soil NH<sub>3</sub> flux and variability. This approach represents a departure from the  
5 current methods of NEI estimation used in policy assessments for most of the last decade.  
6 The research reported here represents a refinement of the estimates at the daily and  
7 hourly scales that should reduce emission estimate uncertainty associated with the use of  
8 emission factors that do not respond to variable environmental conditions or ambient  
9 concentrations. However, previous evaluation of the NEI soil emission estimates  
10 aggregated over the longer temporal (monthly) and larger spatial (county) scales should  
11 be in general agreement. This question is explored by temporally and spatially  
12 aggregating the observed and modeled flux for the summer intensive study to the most  
13 recently available NEI estimate, i.e., NEI 2002af. First, daily NEI emissions for Harnett  
14 County, North Carolina for urea, Source Classification Code (SCC) 2801700004 and  
15 ammonium nitrate, SCC 2801700005 commercial fertilizer applications are extracted  
16 from the NEI 2002af database. Only these SCC classes are considered since, as  
17 established previously, they represent the N-form of the second application and should be  
18 the principle emission classes at our site during the intensive study. Next, comparable  
19 county-scale soil emissions based on our intensive field study observations are estimated  
20 by computing an average daily flux for each observation day (n = 9) and then scaling  
21 these by USDA survey-based information regarding the fraction of county corn cropland  
22 receiving commercial fertilizer (Potter and Pitts, n.d.) and all reported cropland in the  
23 county during 2002. This approach assumes that all county cropland is planted to corn

1 and is fertilized in the same manner as our study site. Corn is one of the most highly  
2 fertilized crops in the U.S. and so this approach should produce a daily county estimate  
3 that is biased somewhat high relative to reality. Figure 5 and Table 2 show the results of  
4 this comparison. All three flux totals spanning the month of July are in relative  
5 agreement. The integrated model does indeed slightly overestimate observed total flux,  
6 but median modeled flux agrees more closely with observed values than does the NEI  
7 estimate, the normalized mean error for the model is 7% smaller than the NEI, and  
8 modeled values are significantly correlated with observations ( $p < 0.05$ ). These findings  
9 confirm we have developed a process-based ammonia flux model that is capable of  
10 responding to more highly temporally resolved meteorology and ambient chemical  
11 conditions while maintaining general agreement with established estimates at larger  
12 spatial scales and longer averaging periods.

13

#### 14 *4.2 Regional implementation*

15 Previous regional-to-national application of the EPIC model suggests regional  
16 integration of the soil flux model into CMAQ is feasible. A soil nitrogen biogeochemical  
17 model coupled in CMAQ would provide a powerful tool to assess the impact of local-  
18 scale agricultural management practices and land use changes on regional scale air  
19 quality and nitrogen deposition. Estimates of the the air-side resistance components used  
20 in Eq. 4 are routinely produced as part of CMAQ N deposition assessments, e.g., Sullivan  
21 et al. (2003), but implementation of the full bi-directional flux model would impose  
22 substantial new input requirements. For instance, the CMAQ domain (typically with 12  
23 km horizontal grids) covers the continental United States. Agricultural soil management

1 and fertilizer input information is needed for each grid cell. Management information  
2 must include date, form, mode of application and quantity of fertilizer applied. This  
3 information is needed for multiple crops within each grid cell and must then be  
4 aggregated into larger land cover classes such as those of the 2001 NLCD (Homer et al.,  
5 2007) for input to the regional air quality model. Two sources of this information are  
6 under consideration; the National Nutrient Loss & Soil Carbon Database (Potter and  
7 Pitts, n.d.) and the heat-unit and crop-demand based management and fertilizer options in  
8 EPIC. Regional implementation will also require the review of many site-specific  
9 assumptions made in the present evaluation. For instance, our assumption of little or no  
10 fertilizer loss in surface runoff was acceptable for this particular field site, but Potter et al.  
11 (2006) estimate an annual average applied N loss in surface runoff of ~5 -10% .  
12 Parameterization of this loss will be highly dependent on dominant slope and soil  
13 conditions within each grid cell as well as inter- and intra-annual meteorological  
14 variability. The use of additional information produced by the EPIC model, in  
15 combination with nationally consistent sources of U.S. agri-business information, are  
16 being explored to meet these needs as part of a pilot regional application of the full  
17 integrated bi-directional flux model. Results of the pilot will be compared to a previous  
18 CMAQ simulation to assess the impact of the bi-directional flux model on regional multi-  
19 pollutant chemical budgets.

## 21 **5. Summary**

22 The goal of this research has been to develop a process-based approach to the  
23 simulation of bi-directional fertilizer-derived  $\text{NH}_3$  flux from agricultural soils that can

1 successfully verify against individual field studies, utilizes widely available input data,  
2 and produces area flux estimates that are consistent with established emission estimates  
3 for larger spatial and longer temporal scales. A previously published model has been  
4 refined to estimate field-level soil NH<sub>3</sub> flux. Comparison of model results to recent NEI  
5 estimates suggests that over a monthly time period and across a county, modeled  
6 estimates agree with NEI, but inclusion of more accurate day-to-day variability is  
7 expected to reduce errors in current regional chemical budget estimates.

8       This study focuses on evaluation against a single field study, but the process-  
9 based approach should make the method generally applicable to a variety of crop and  
10 environmental conditions. To confirm this proposition, ongoing field studies are  
11 underway that will support model evaluation in other crop/environmental, forest and  
12 minimally or un-managed terrestrial ecosystems. A pilot CMAQ application is underway  
13 that combines soil and canopy flux estimates to confirm the benefits suggested here, and  
14 to facilitate further regional-scale model evaluation. In addition to reducing current  
15 sources of known model uncertainty, the linkage of agricultural pollutant flux to the  
16 atmosphere to a well-vetted agricultural management model could free air quality  
17 assessments from their current reliance on historical fertilizer sales, landuse and  
18 management practices. Thus positioning CMAQ to more thoroughly address emerging  
19 policy and multi-media environmental management questions.

20

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11 *publication, it may not necessarily reflect official Agency policy.*  
12  
13

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## Supplemental Material

### Field Study Description and Laboratory Analysis Methods

The  $\text{NH}_3$  soil flux and in-canopy sources and sinks were estimated using first order closure principles applied to measured profiles of turbulence and  $\text{NH}_3$  concentrations (Bash et al., 2010). Wind observations, measured at 4 heights (from 0.5 to 10 m) and temperature profiles collected at 5 heights (from 0.1 to 2.25 m) were measured by 3-D sonic anemometry and fast-response copper-constantan thermocouples, respectively. Ammonia concentrations were measured at 5 heights (from 0.1 to 2.25 m) by sampling through phosphorous-acid coated glass denuders. Each denuder sampling period encompasses several turbulent averaging periods, and so an observed flux range (uncertainty) can be determined as the variability in the ensemble averages of the meteorological and turbulent exchange parameters. This range is conservative as there are other sources of measurement uncertainty that have not been included (Bash et al. 2010).

Soil  $\Gamma_g$  values were calculated from measurements of extractable  $\text{NH}_4^+$  and  $\text{H}^+$ . Samples were collected approximately weekly at 12 locations within 100 m of the  $\text{NH}_3$  flux measurement tower; 6 locations in the fields to the north and south of the tower, respectively. At each location, 3 soil samples (0 to 5 cm) were taken at the mid-point and sides of the planting row. To ensure no loss of  $\text{NH}_3$  or conversion of  $\text{NH}_4^+$ , soil samples were extracted in the field with 1M KCL within 1 hour of collection and extracts were frozen until analysis. The gravimetric  $\text{H}_2\text{O}$  subsample was weighted and immediately placed in the oven at the time of the KCL extraction. Immediate processing of the samples ensured no loss of  $\text{H}_2\text{O}$  or  $\text{NH}_3/\text{NH}_4^+$  from the samples. Samples were placed in clean air-tight plastic bags for transport from the point of collection to the field laboratory in which the extractions were performed. Samples were composited and

subsamples were analyzed for chemistry and moisture. A 5 g subsample of field moist soil was extracted within 1 hour of collection in 25 mL of 1M KCl. Extracts were analyzed for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  by colorimetry (Lachat QuickChem Model 8000 Flow-Injection Autoanalyzer). The detection limit for  $\text{NH}_4^+$  is equivalent to 0.25 mg  $\text{NH}_4^+$  kg<sup>-1</sup> dry soil or less. All samples collected exceeded this threshold.

Data analysis and reports from previous findings suggest that the standard KCl extraction method may not be the most appropriate method for deriving  $\Gamma_g$  since KCl may yield more  $\text{NH}_4^+$  than is naturally available in the pore water, potentially overestimating what is available for loss to the atmosphere. To investigate this hypothesis, we recently compared (using soil from the Lillington field site) 1M KCl extractable  $\text{NH}_4^+$  to extractions with 0.01  $\text{CaCl}_2$  (ionic strength of 0.03 M) and Type I deionized water. We did this with field moist soil with a mass wetness of 0.25g- $\text{H}_2\text{O}$ /g-soil (very wet) and after drying the soil to 0.01 g-  $\text{H}_2\text{O}$ /g-soil. The lower ionic strength extractions yielded less  $\text{NH}_4^+$ . For wet and dry soil respectively, 0.01M $\text{CaCl}_2$  extracted 64 and 55% of the amount extracted with KCl (49 and 46%, respectively with the deionized water). While the indication is that we should use a lower gamma than what the KCl extracts give us, we do not yet know the optimum ionic strength of extract to use. These results should not be generalized, but should be consistent for soils with similar cation exchange capacity.

Soil pH was measured within 1 hour of sample collection in a 1:5 soil:deionized water mixture using a standard glass electrode with an accuracy of roughly 0.01 pH units. Gravimetric soil moisture was determined by weight loss after heating 10 g of soil for 48 hours at 60 °C with a detection limit on the order of 0.01 g  $\text{H}_2\text{O}$  g<sup>-1</sup> fresh soil. Drought conditions prevailed during the intensive July sampling period, but all samples exceeded this threshold. Water retention was determined using a combination of low pressure (0, 2.5, 5.0, 10.0 and 33.3 kPa) and high

pressure (100, 500, and 1500 kPa) systems as described by Klute (1986). Field capacity and permanent wilting point were assumed as the water contents corresponding to 33.3 and 1500 kPa water retention measurements, respectively. Particle size distribution was determined by the hydrometer method (Day, 1965). Bulk density was determined by the core method (Blake and Hartge, 1986). Single-sided leaf area index was measured approximately bi-weekly by destructive and optical methods (LAI-2000) along with plant height.

## Figure Captions

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1 Figure 1. Resistance model schematic for a) Uni-directional exchange in CMAQ version  
2 4.7, b) Bi-directional  $\text{NH}_3$  flux and c) Bi-directional flux with highlighted soil exchange.

3

4 Figure 2. Epic calibration results for 2007 corn at Lillington, North Carolina for a) soil  
5 moisture, b)  $\text{NH}_4^+$  concentration and c)  $\text{H}^+$  concentration. Diamond symbols represent  
6 field sample medians and vertical bars represent the inner quartile range (IQR), i.e., 25<sup>th</sup>  
7 through 75<sup>th</sup> quartiles. Dashed lines indicate daily sample (n=12) maxima and minima,  
8 i.e., range. Open Markers represent EPIC simulated values.

9

10 Figure 3. Lillington study site upper 5 cm soil layer a)  $\Gamma_g$  calculated from observed and  
11 modeled  $[\text{NH}_4^+]$  and  $[\text{H}^+]$ , and b)  $X_g$  calculated using observed soil temperatures and the  
12 range of observation-based  $\Gamma_g$  (n=12 per sampled day) compared to  $X_g$  calculated using  
13 observed soil temperature and modeled  $\Gamma_g$ .

14

15 Figure 4. Comparison of observed  $\text{NH}_3$  soil flux to a) modeled flux from upper 5 cm of  
16 soil, b) modeled flux from upper 1 cm of soil, and c) modeled flux from upper 1 cm of  
17 soil with emission potential reduced by 55%.

18

19 Figure 5. Comparison of daily Harnett County, North Carolina modeled  $\text{NH}_3$  flux from  
20 the upper 1 cm soil layer to NEI 2002af seasonally adjusted Harnett County emissions.

21

22

23

Figure 1  
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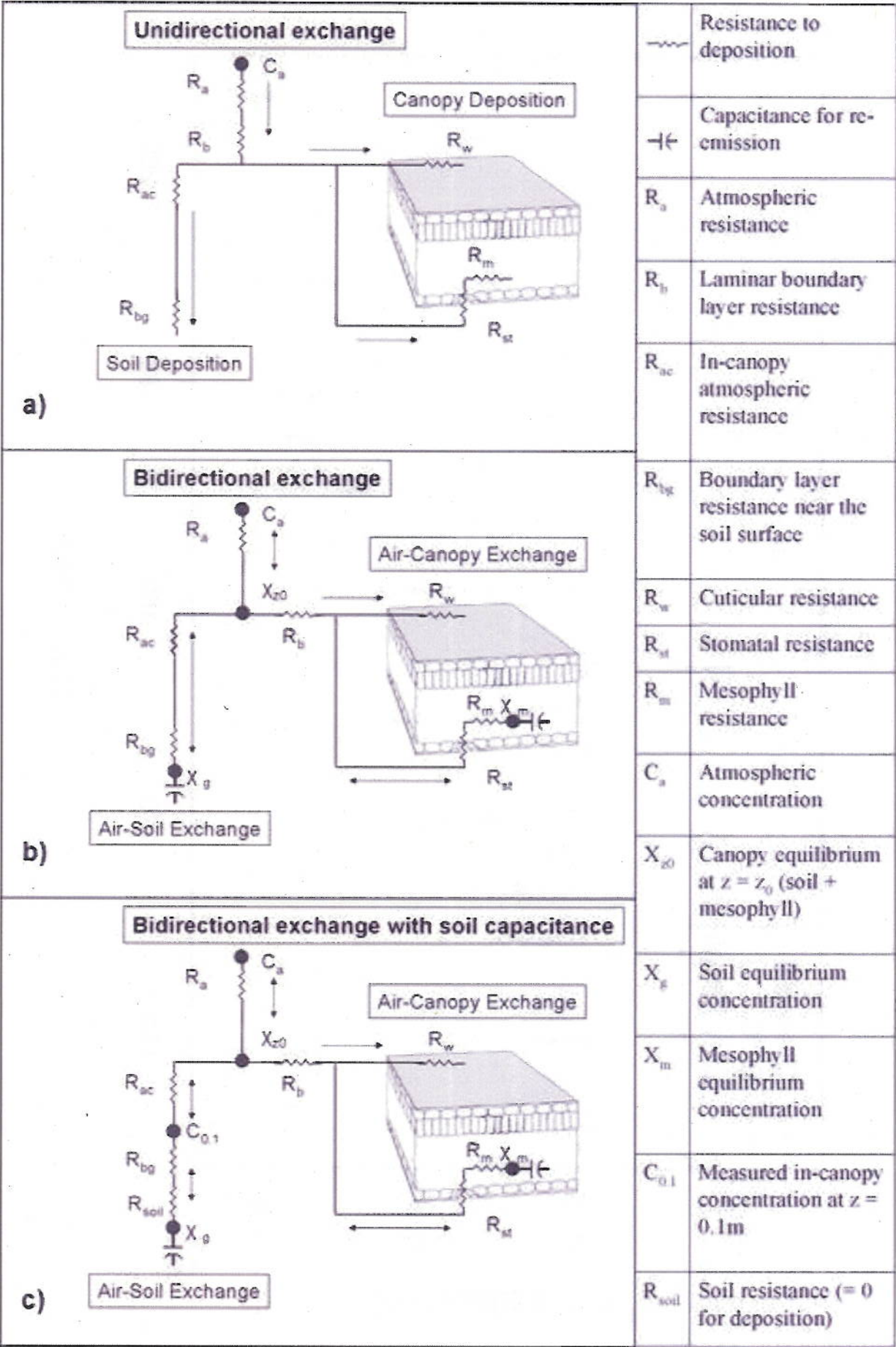


Figure 2a  
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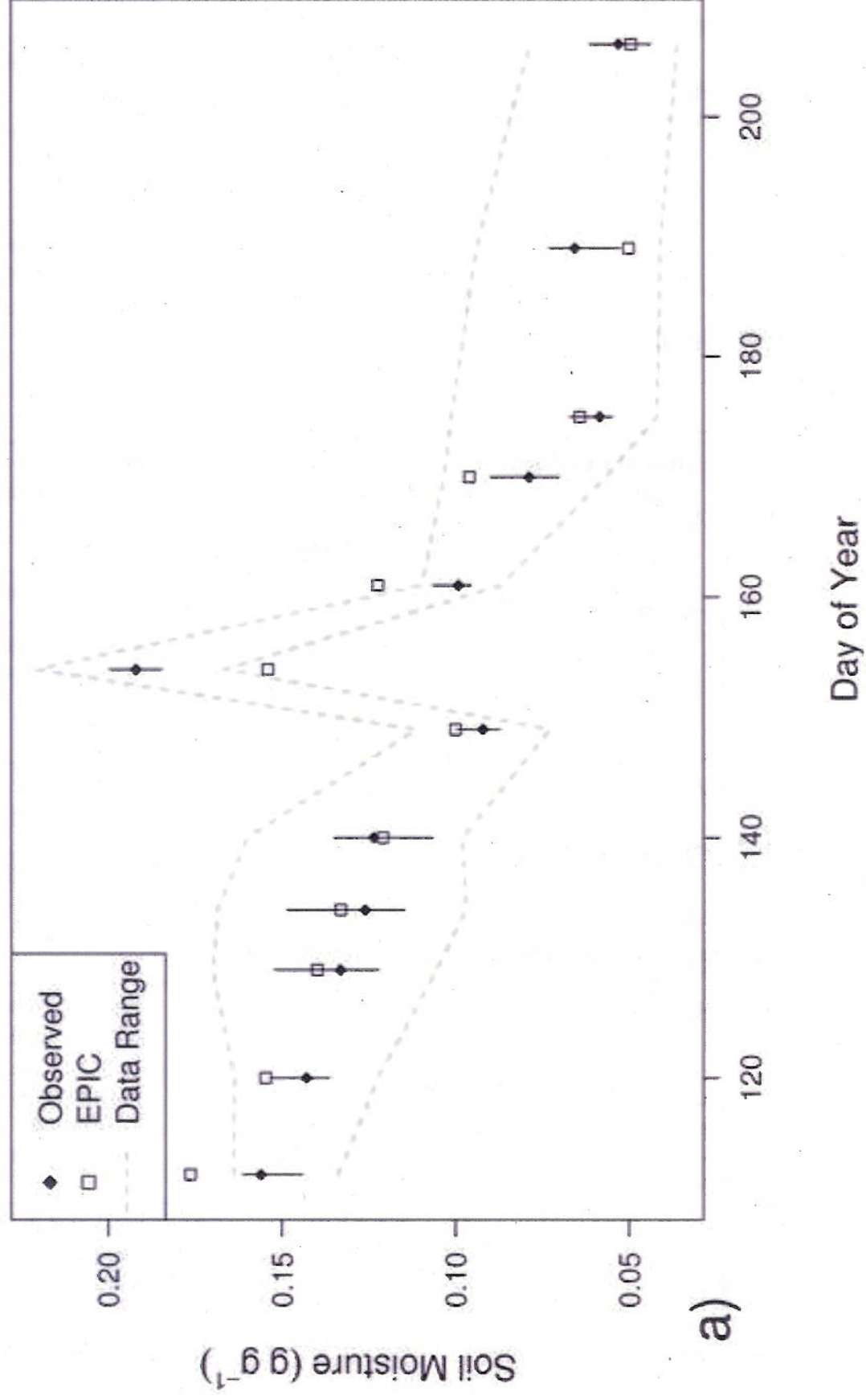


Figure 2b

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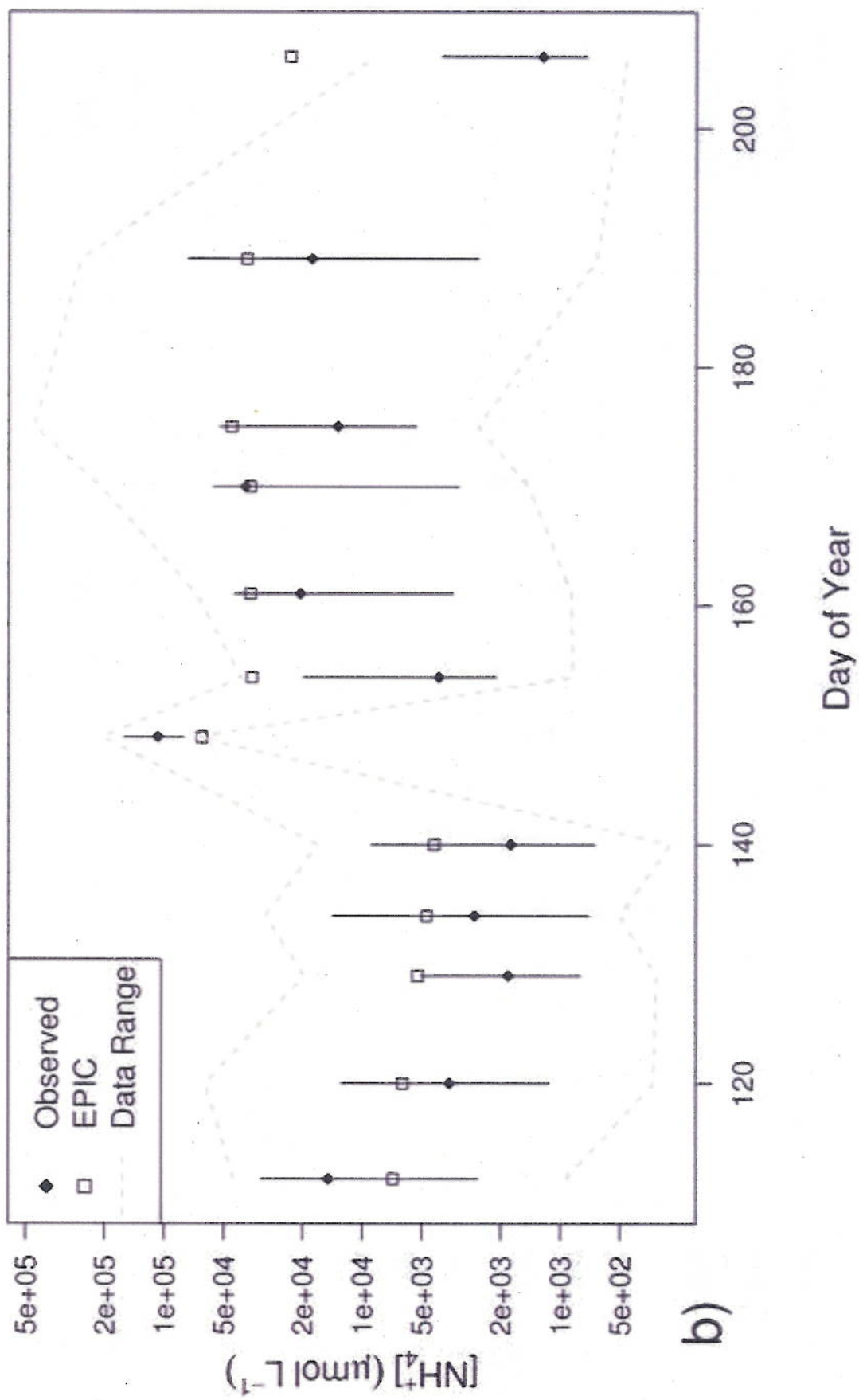


Figure 2c  
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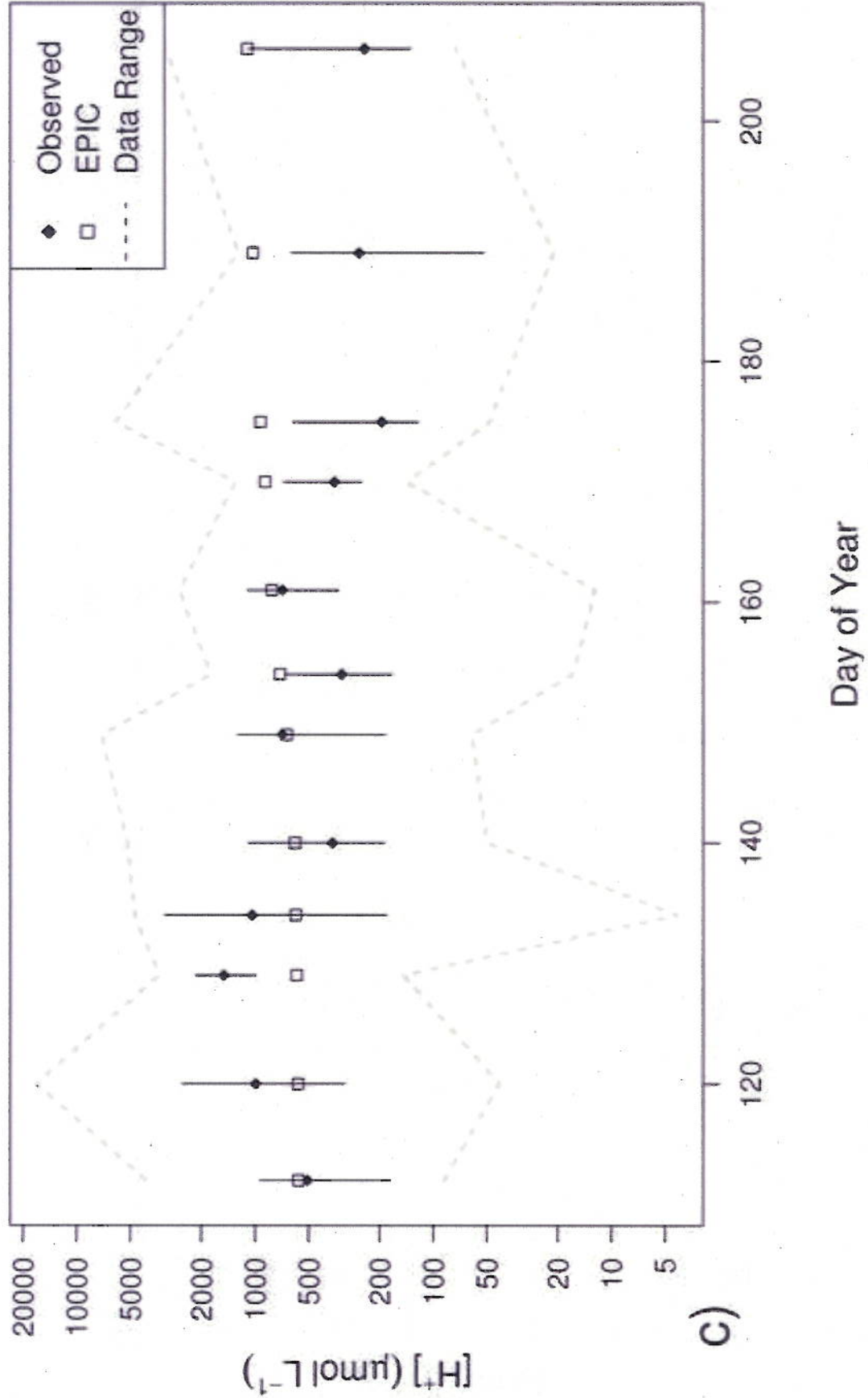


Figure 3a

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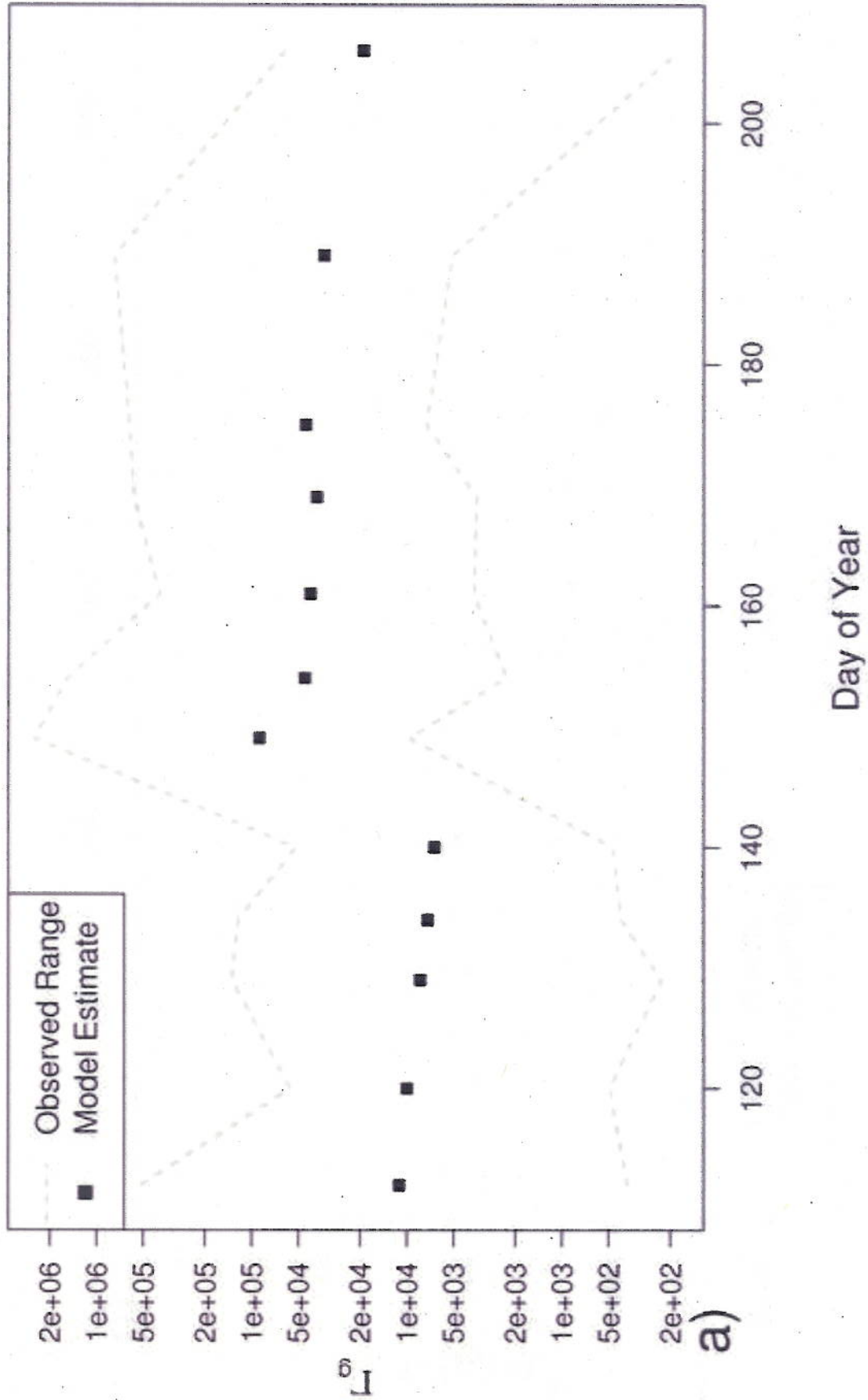


Figure 3b  
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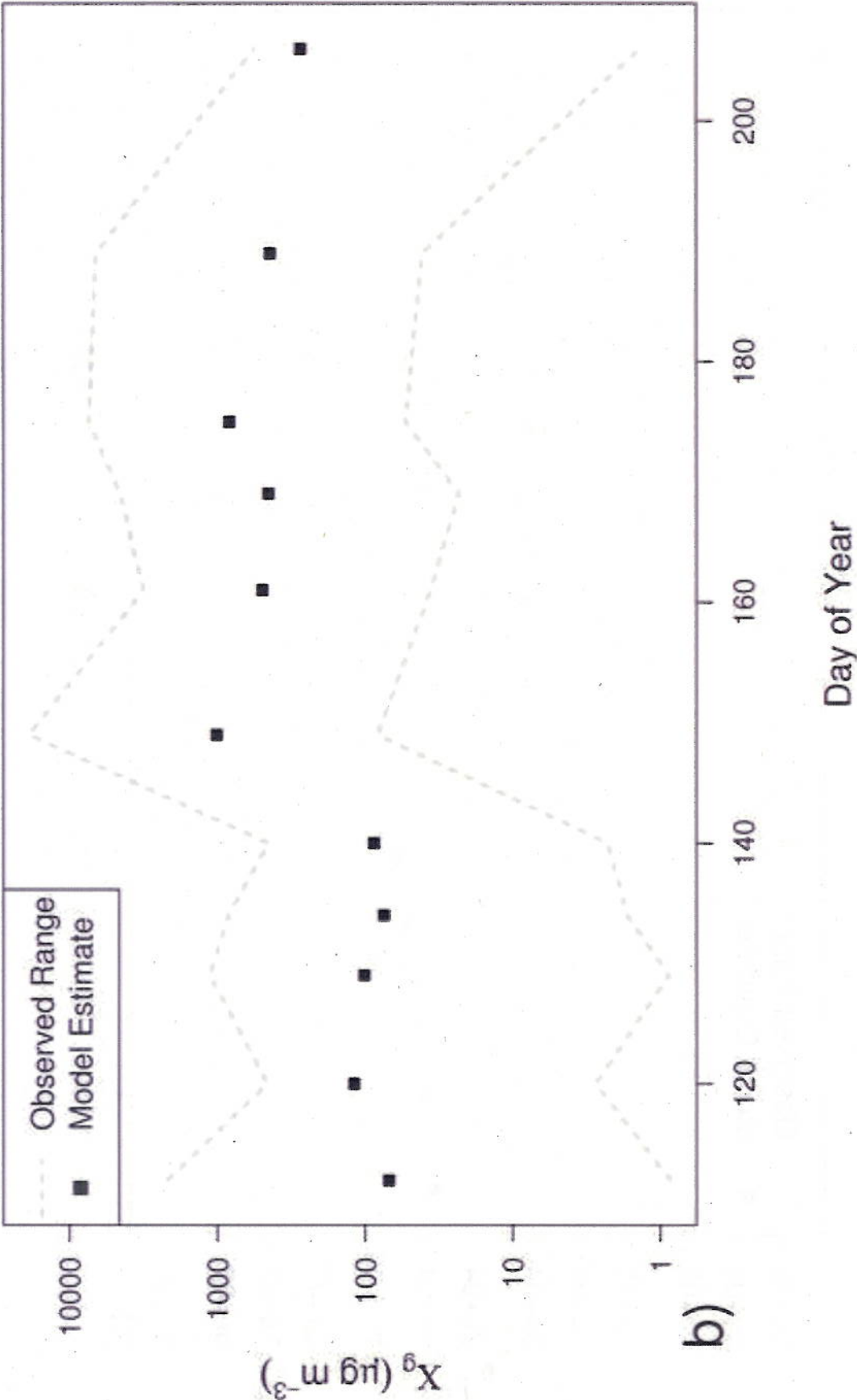


Figure 4a  
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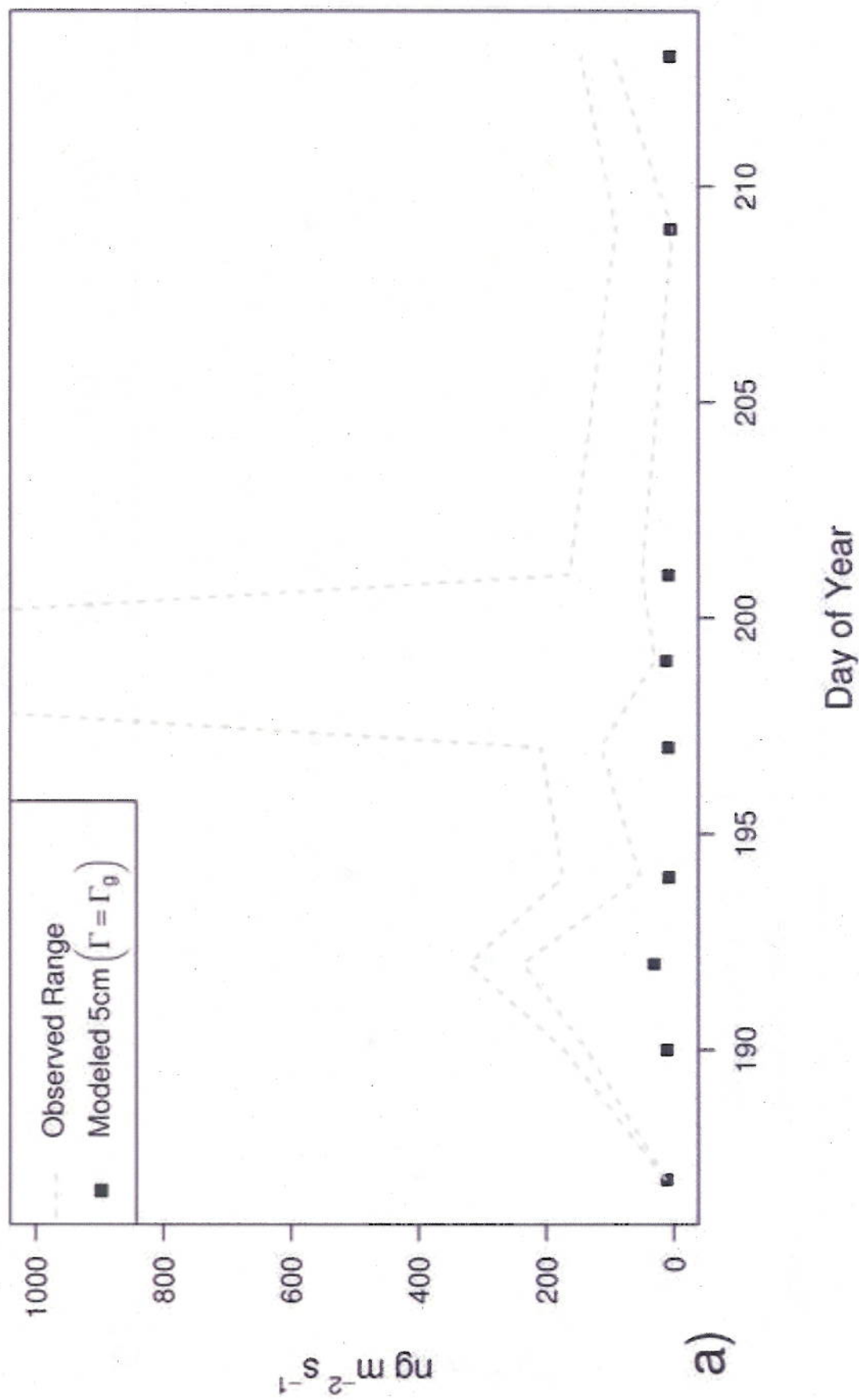


Figure 4b

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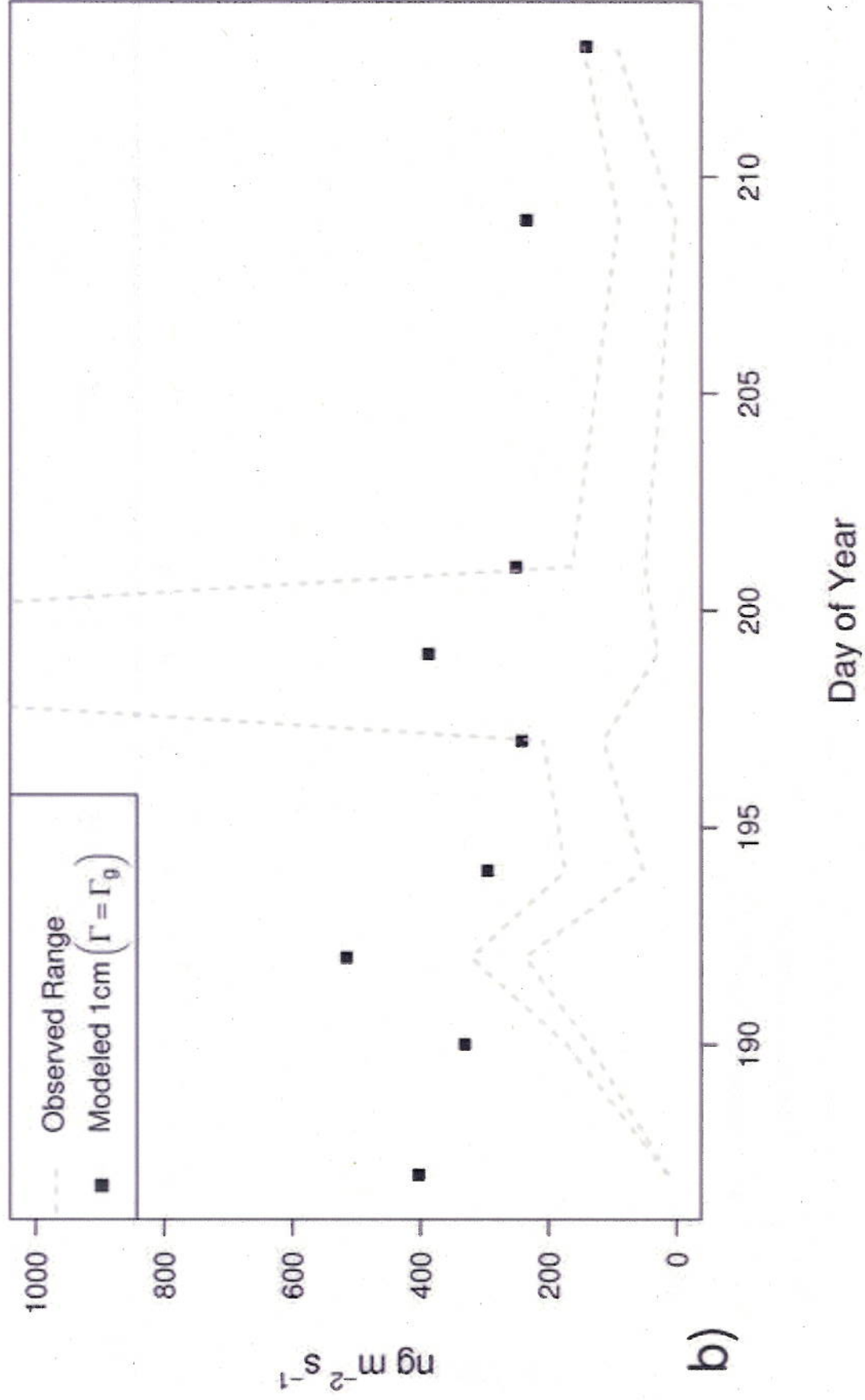


Figure 4c  
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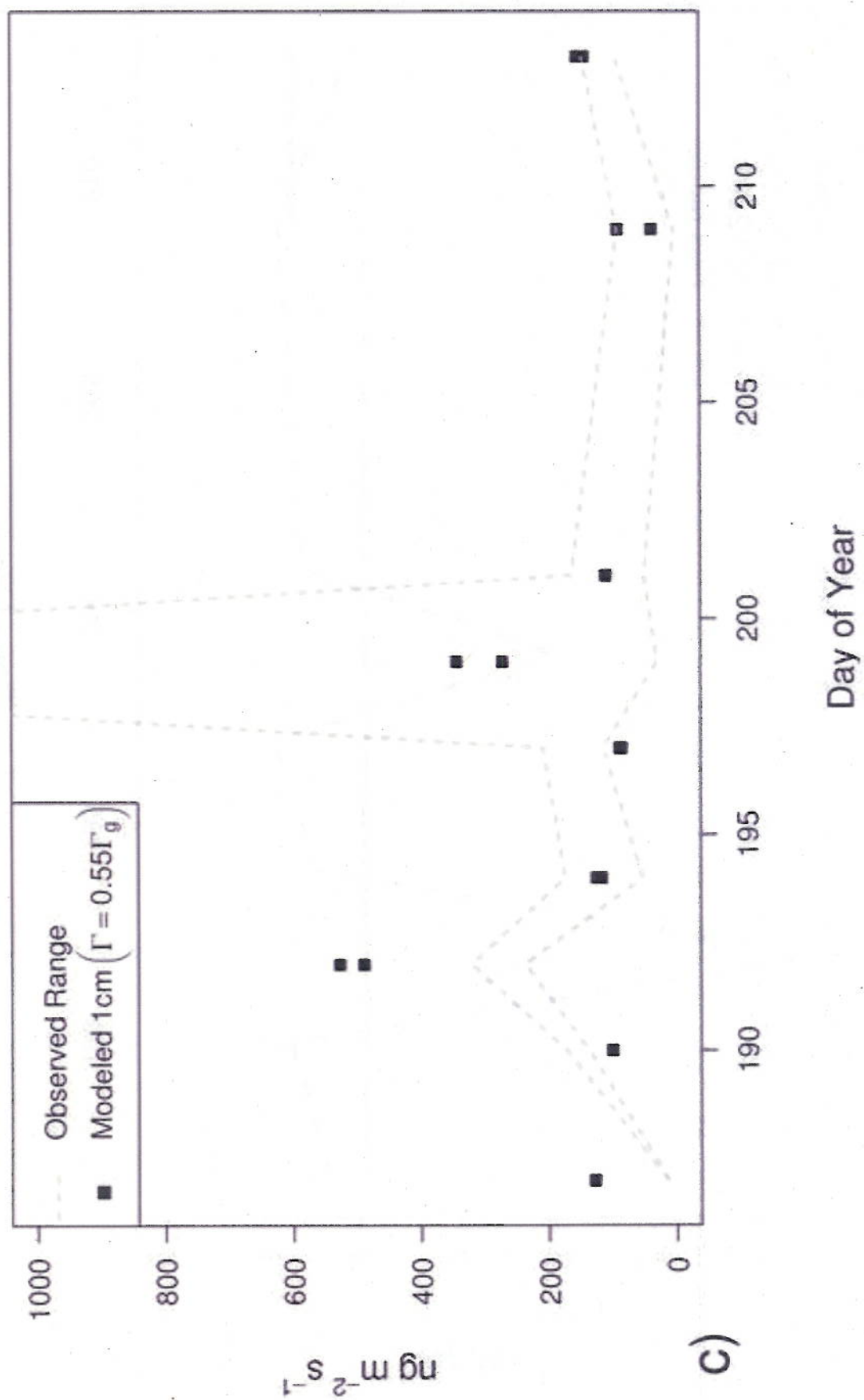


Figure 5  
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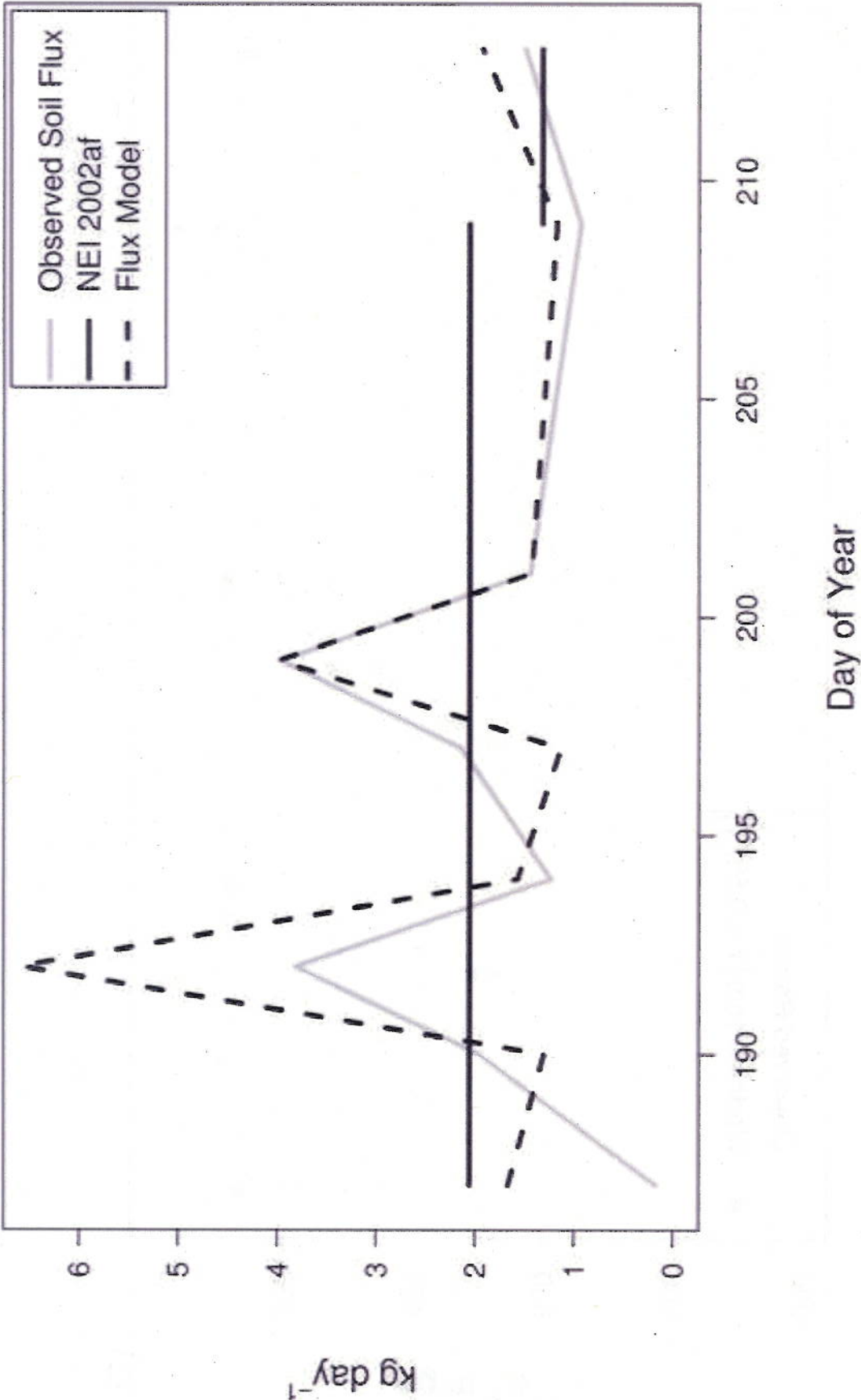


Table 1. Comparison statistics for field-scale model estimates of NH<sub>3</sub> soil flux and observation-based flux estimates. All fluxes reported in ng m<sup>-2</sup> s<sup>-1</sup>.

	median	median daily bias	Normalized mean error	RMSE
Observation-based flux	127	-	-	-
Model flux from upper 5 cm soil	9	-119	92%	194
Model flux from upper 1 cm soil	234	+105	129%	287
Model flux from upper 1cm soil ( $\Gamma = \Gamma*0.55$ )	125	+19	58%	121

Table 2. Comparison the integrated agriculture and air quality model NH<sub>3</sub> flux to recent National Emission Inventory NH<sub>3</sub> soil emission estimates.

	Total (n=9) NH <sub>3</sub> flux (kg)	Median daily (n=9) flux (kg day <sup>-1</sup> )	median daily bias (kg day <sup>-1</sup> )	Normaliz ed mean error	Root Mean Square Error	Pearson r
County (scaled) Observation- based soil flux	17.10	1.49				
County (scaled) simplified soil flux model	18.80	1.50	+0.13	42%	1.91	0.79 (p < 0.05)
NEI 2002af County soil flux	17.70	2.05	+0.09	49%	1.18	0.01 (p > 0.05)