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Sensitivity of continental United States atmospheric budgets of oxidized and reduced nitrogen to dry deposition parametrizations

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Reactive nitrogen (N_r) is removed by surface fluxes (air–surface exchange) and wet deposition. The chemistry and physics of the atmosphere result in a complicated system in which competing chemical sources and sinks exist and impact that removal. Therefore, uncertainties are best examined with complete regional chemical transport models that simulate these feedbacks. We analysed several uncertainties in regional air quality model resistance analogue representations of air–surface exchange for unidirectional and bi-directional fluxes and their effect on the continental N_r budget. Model sensitivity tests of key parameters in dry deposition formulations showed that uncertainty estimates of continental total nitrogen deposition are surprisingly small, 5 per cent or less, owing to feedbacks in the chemistry and rebalancing among removal pathways. The largest uncertainties (5%) occur with the change from a unidirectional to a bi-directional NH_3 formulation followed by uncertainties in bi-directional compensation points (1–4%) and unidirectional aerodynamic resistance (2%). Uncertainties have a greater effect at the local scale. Between unidirectional and bi-directional formulations, single grid cell changes can be up to 50 per cent, whereas 84 per cent of the cells have changes less than 30 per cent. For uncertainties within either formulation, single grid cell change can be up to 20 per cent, but for 90 per cent of the cells changes are less than 10 per cent.

1. Introduction

Owing to the increase in the anthropogenic input of reactive nitrogen (N_r) over the past century and a half [1], the input and removal of atmospheric N_r has increased substantially [2] leading to deleterious impacts on ecosystem health and associated human health [3–5]. N_r gases and particles in the atmosphere are removed by surface fluxes (air–surface exchange) and wet deposition. Chemical transformation of the form of N_r can impact the rate of deposition by effectively changing the reactivity of N_r species with land surface receptors. The rate at which different forms of N_r are emitted and deposited affects their relative contribution to ecosystem and human health impacts.

The chemistry and physics of the atmosphere result in a complicated system in which competing chemical and physical sources and sinks coexist. Regional- and global-scale air quality models are an important tool capable of exploring the effects of these system dynamics on the N_r budget. These models, through representation of atmospheric chemical transformations, physical partitioning between gases and particles, wet deposition and air–surface exchange, can help to understand the impact that the anthropogenic alteration of the nitrogen cycle has on air quality and atmospheric removal.

Of particular interest to ecosystem studies are the aspects of the models that control atmospheric exchange, especially dry deposition. Dry deposition models are developed from parametrizations of air–surface exchange processes based on limited field studies. Our understanding of turbulent trace gas exchange is largely drawn from similarity with meteorological heat, moisture and momentum

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fluxes in the planetary boundary layer [6]. The turbulent air–surface exchange is typically described as analogous to an electrical circuit in terms of resistances that operate in series and in parallel, which are used to define a transfer velocity [7]. The transfer velocity is calculated following Ohm's law as the reciprocal of the sum of the atmospheric (R_a), quasi-laminar boundary layer (R_b) and surface resistances (R_s). R_a is the resistance to transport through the atmosphere above the surface receptors. R_b is the resistance to transport across the thin layer of air that is in contact with the surface and varies with the diffusion of the pollutant transported. R_s is the resistance to the uptake of the pollutant by the surface receptor, typically vegetation or soil. The surface resistance can collectively comprise stomatal uptake (R_{st}), deposition to leaf cuticles (R_w) and deposition to ground surfaces (R_g). Surface exchange is further influenced by canopy structure, and resistance to absorption into the apoplastic solution and reactivity with the mesophyll tissue inside the stomatal cavity (R_m).

The resistance representation becomes more complicated when accounting for bi-directional surface fluxes. The complication arises from having to account for non-zero concentrations in surface reservoirs. An electrical analogue can again be drawn where the emission potential from a receptor can be modelled as a capacitance. Ammonia is the key nitrogen species that exhibits bi-directional exchange with primarily evasive fluxes (emissions) for fertilized crops and predominately deposition for unfertilized semi-natural vegetation. Compensation points, the ambient concentrations at which the net flux is zero, are usually different for the soil, stomata and cuticle (i.e. leaf surface water). The ammonia flux depends on the relation of the soil or canopy compensation points to the ambient concentration of ammonia. Two-layer models based on the work of Nemitz *et al.* [8] and Sutton *et al.* [9] that account for soil and canopy compensation points have been able to describe this bi-directional exchange.

While turbulent flux through the atmospheric surface layer is similar to gases, for aerosol dry deposition there are several key processes that are unique relative to trace gases, including gravitational settling, Brownian diffusion, surface impaction, surface interception and rebound, which depend on the size of the aerosol. Unlike gas deposition, the quasi-laminar boundary layer resistance R_b is usually the limiting resistance for aerosols, because Brownian diffusion is much slower for particles than molecular diffusion is for gases.

In this study, we examined the effects of uncertainties in the parametrization of the air–surface exchange on the N_r budget, with a focus on aggregating to continental United States budgets. Using the Community Multi-scale Air Quality (CMAQ) modelling system, we used sensitivity tests to vary key resistances in the air–surface exchange algorithms for gases and analysed the resulting changes in individual N_r species, total oxidized and reduced N_r and total N_r budgets. Using CMAQ can uncover the dynamic interactions of the system that would not be apparent in simpler models.

2. Overview of the Community Multi-scale Air Quality model system

The CMAQ modelling system incorporates output fields from emissions (Sparse Matrix Operator Kernel Emissions; SMOKE) and meteorological (Weather Research and Forecasting; WRF) systems and several other data sources into the CMAQ chemical transport model (CCTM). The SMOKE system [10] is an emissions processing system designed to create gridded, speciated, hourly emissions for input into CMAQ. SMOKE provides area, biogenic, mobile (both onroad and non-road) and point source emissions of gases and fine and coarse particles. For biogenic emissions modelling, SMOKE uses the Biogenic Emission Inventory System, v. 3.14 (BEIS3). The WRF model [11] is a mesoscale numerical prediction system designed to serve both operational forecasting and atmospheric research needs. It features a three-dimensional variational and a four-dimensional [12] data assimilation system for developing three-dimensional meteorological fields. CMAQ [13] is intended to provide a 'one-atmosphere' modelling capability based mainly on 'first principles' descriptions of the atmospheric system. CMAQ simulates atmospheric processes affecting the transport, transformation and deposition of such pollutants as ozone, particulate matter, airborne toxics, and acidic and nutrient pollutant species. Evaluation results for unidirectional and bi-directional CMAQ are given in Foley *et al.* [14] and Bash *et al.* [15], respectively.

Approaches in CMAQ for modelling dry deposition have evolved as our understanding of the surface exchange processes has improved. CMAQ v. 4.7 only considered unidirectional surface exchange, but introduction of a state-of-the art bi-directional surface exchange parametrization for chemicals such as ammonia and mercury was begun in a research version of CMAQ v. 4.7.1 and released to the public in CMAQ v. 5.0. The unidirectional dry deposition flux of each chemical species is calculated by multiplying the concentration in the lowest model layer by the dry deposition velocity (V_d). The flux is accumulated at each computational time step and output for each hour. The V_d is computed by the resistance analogy, using the suite of resistances described earlier. The aerodynamic and stomatal resistances are calculated in WRF in the Pleim-Xiu land surface model [16] and passed to CMAQ so that they are consistent with the momentum and moisture fluxes. In WRF, subgrid land-use-specific parameters such as surface roughness and leaf area index are averaged to produce values for each grid which are then used in the resistance calculations. In CMAQ, R_{st} is scaled by the diffusivity of the chemical relative to water vapour to create species-specific values. For the dry cuticular and ground resistances, CMAQ assumes that the relative propensity to deposit to these different surfaces is similar, so a common scaling factor is used to scale these resistances relative to O_3. For wet surfaces (cuticle and ground), the resistance is a function of the Henry's law constant for the specific chemical. A detailed description of the CMAQ V_d model for unidirectional exchange can be found in Pleim & Ran [17].

The focus of the bi-directional air–surface parametrization for N_r to date has been on NH_3. The CMAQ bi-directional approach estimates NH_3 fluxes by integrating a two-layer resistance model, based on the resistance framework of Nemitz *et al.* [8], with an agro-ecosystem model. The details of this model can be found in Bash *et al.* [15]. Two soil layers were added to CMAQ to parametrize the surface application and injection of fertilizer. To compute the soil emissions potential, CMAQ uses the United States Department of Agriculture's Environmental Policy Integrated Climate (EPIC) model [18] to simulate crop-specific agricultural management practices for each model grid cell following Cooter *et al.* [19]. A crop-specific soil emission potential ($\Gamma_g = NH_4^+/H^+$) is estimated daily from the agricultural soil ammonium concentration modelled in CMAQ and the crop-specific fertilization rate, application depth and pH from EPIC. The soil and atmospheric NH_3 and NH_4^+ budgets are maintained in CMAQ by accounting for soil evasion, deposition and soil nitrification (incorporated from EPIC) at each model time step, fully coupling the soil NH_4^+ biogeochemistry with the air–surface exchange.

Both WRF and CMAQ simulations use fractional land cover information for each grid cell from the National Land Cover Database (NLCD; [20]) to estimate the micrometeorological variables, canopy height, leaf area index, canopy resistances and bi-directional NH_3 fluxes for each land cover category. Individual crop-type soil Γ_g values are merged into a general NLCD agricultural category to estimate the NH_3 fluxes to agricultural ecosystems [15,19]. Vegetation (Γ_s) and non-agricultural soil (Γ_g) emission potentials are modelled as function of land cover type similar to Zhang *et al.* [21]. We included additional diagnostic calculations to separate the net flux into emissions and deposition for use in the budget analyses.

To calculate the V_d for aerosols, CMAQ considers aerosol size distributions by three log-normal modes and computes aerosol V_d as a function of particle diameter and meteorological conditions for each mode for mass, surface area and number. An integrated V_d is computed for each mode by integrating these equations over each log-normal size distribution as described by Binkowski & Shankar [22] and Feng [23]. The modal-integrated V_d is a function of modal mass mean diameter D_g. Aerosol treatment in CMAQ v. 5.0 includes a dynamically interactive coarse mode for NO_3, hygroscopic growth of particles and advanced treatment of secondary organic aerosols. Recent reviews of air–surface exchange [24] indicate the need to account for the canopy structure and its effects on particle V_d. Characterizing the fine scale morphology in a regional air quality model remains a challenge and will be a future focus area for CMAQ model development.

In CMAQ, pollutant scavenging is calculated by two methods, depending on whether the pollutant participates in the cloud water chemistry [13]. For those pollutants that participate in the cloud chemistry, the amount of scavenging depends on Henry's law constants, dissociation constants and cloud water pH. For pollutants that do not participate in aqueous chemistry, CMAQ uses the Henry's law equilibrium equation to calculate cloud water concentrations based on the liquid water content of the cloud. The wet deposition of a chemical species depends on the precipitation rate and the cloud water concentration.

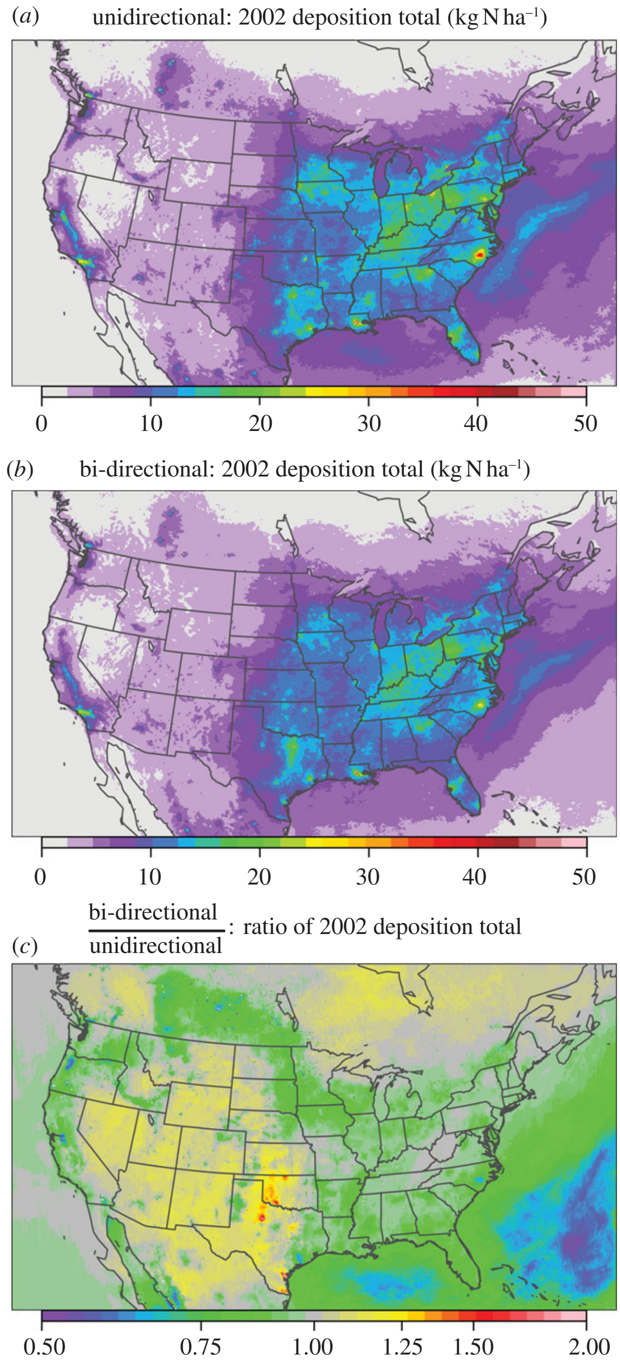

Figure 1. Maps of 2002 annual total nitrogen deposition (kg per hactare) for (*a*) unidirectional CMAQ and (*b*) bi-directional CMAQ; (*c*) total N deposition ratio.

3. Approach

In this study, we examined US continental oxidized, reduced and total N_r budgets and assessed the sensitivity of CMAQ estimates of the budgets to uncertainties in the parametrizations of the V_d. The calculation of the stomatal resistance (R_{st}) is an integral part of the evapotranspiration budget in the Pleim-Xu land surface model used in this study. The Pleim-Xu model constrains the surface energy balance, including transpiration and soil moisture, using four-dimensional data assimilation of 2 m temperature and moisture analyses [25]. This approach, therefore also constrains R_{st}, so it was not included in the sensitivity analysis. For ammonia, the R_{st} is more naturally examined as part of the study of the bi-directional vegetation emission potential. Instead, we focused on the parametrizations that are not constrained in the meteorological model and for which measurements are scarce or unavailable, resulting in higher uncertainty. We first used the CMAQ V_d algorithm as a box model to identify uncertainties that caused the greatest change in (unidirectional) V_d. Sensitivity ranges were selected based on the range of observed values in the literature and expected or documented uncertainty in specific variables. To complete the analysis, we used the sensitivity tests with the full CMAQ model to examine the effect of parameter variations on nitrogen flux budgets.

Two modelling periods were used in this study. Full annual simulations were carried out using unidirectional and bi-directional CMAQ v. 4.7.1_research for the year 2002 to establish annual budgets and compare the results from the

Table 1. Continental scale nitrogen budgets for 2002 annual and June 2006 simulations for unidirectional and bi-directional CMAQ versions.

species	deposition (10^6 kg N)	relative portion			deposition (10^6 kg N)	relative portion		
	unidirectional CMAQ annual 2002 deposition, continental United States				unidirectional CMAQ June 2006 deposition, continental United States			
Ox-N total	3927		100.0%	63.01%	360		100.0%	56.19%
wet Ox-N	1667		42.44%	26.74%	165		45.94%	25.81%
dry Ox-N	2261	100.0%	57.56%	36.27%	195	100.0%	54.06%	30.38%
NO_x	216	9.57%		3.47%	19	9.67%		2.94%
HNO_3	1440	63.69%		23.10%	152	78.08%		23.72%
NO_3	125	5.54%		2.01%	8	4.14%		1.26%
PANs	218	9.66%		3.50%	8	3.95%		1.20%
organic-N	176	7.79%		2.82%	5	2.39%		0.73%
other	85	3.76%		1.36%	3	1.76%		0.54%
Red-N total	2306		100.0%	36.99%	281		100.0%	43.81%
wet Red-N	1195		51.83%	19.17%	148		52.67%	23.07%
dry Red-N	1110	100.0%	48.17%	17.82%	133	100.0%	47.33%	20.73%
NH_3	1001	90.17%		16.07%	124	93.34%		19.35%
NH_4^+	109	9.83%		1.75%	9	6.66%		1.38%
total	6233			100.0%	641			100.0%
	bi-directional CMAQ annual 2002 deposition, continental United States				bi-directional CMAQ June 2006 deposition, continental United States			
Ox-N total	3917		100.0%	66.09%	360		100.0%	59.70%
wet Ox-N	1581		40.36%	26.67%	165		45.79%	27.34%
dry Ox-N	2336	100.0%	59.64%	39.42%	195	100.0%	54.21%	32.36%
NO_x	216	9.25%		3.65%	22	11.49%		3.72%
HNO_3	1513	64.78%		25.53%	149	76.08%		24.62%
NO_3	119	5.09%		2.01%	8	4.06%		1.32%
PANs	223	9.56%		3.77%	7	3.77%		1.22%
organic-N	178	7.63%		3.01%	5	2.33%		0.75%
other	86	3.69%		1.45%	4	2.26%		0.73%
Red-N total	2010		100.0%	33.91%	243		100.0%	40.30%
wet Red-N	1358		67.55%	22.91%	159		65.43%	26.37%
dry Red-N	652	100.0%	32.45%	11.00%	84	100.0%	34.57%	13.93%
NH_3	548	83.96%		9.24%	75	89.18%		12.42%
NH_4^+	105	16.04%		1.77%	9	10.82%		1.51%
total	5927			100.0%	604			100.0%

bi-directional exchange algorithm with those from the unidirectional approach. Further sensitivity studies were conducted using meteorological and emissions data for June 2006 as it was impractical to perform the needed number of model runs for an annual simulation. CMAQ v. 5.0_beta was used for these sensitivity studies owing to the availability of input data. All model runs used a 12 × 12 km^2 grid size. We compared the CMAQ N_r budgets from the 2002 annual runs with those from the June 2006 run to establish comparability. Because conclusions on model sensitivity are based on comparisons of runs from the same model version, differences in model version used for the 2002 and 2006 data are unimportant.

4. Results

(a) Unidirectional versus bi-directional air–surface exchange

Total annual nitrogen deposition for 2002 using the unidirectional and bi-directional versions of CMAQ v. 4.7.1 is shown in figure 1. CMAQ deposition outputs are summarized in table 1 for the continental United States domain for the annual simulations and the June 2006 sensitivity base case. For the 2002 annual simulation, CMAQ suggests that at the continental scale roughly half of the total nitrogen deposition is

Table 2. Mass balance estimates for the continental United States for oxidized and reduced nitrogen for successive versions of CMAQ compared with successive global model estimates.

mass balance estimates for the continental United States			
year	model version	exported (%)	deposited (%)
Ox-N			
2002	CMAQ v. 4.7 at 36 km without lightning	42	58
2002	CMAQ v. 4.7.1 at 12 km without lightning	38	62
2002 (this study)	CMAQ v. 4.7.1_research at 12 km with lightning	33	67
2006	CMAQ v. 5.0_beta at 12 km with lightning	36	64
	Kasibhatla *et al.* [26]	25–30	
	Liang *et al.* [27]	30	
	Dentener *et al.* [28] and median 23 global models	37	63
Red-N			
2002 (this study)	CMAQ v. 4.7.1 at 12 km, unidirectional NH_3	22	78
2002 (this study)	CMAQ v. 4.7.1_research at 12 km, bi-directional NH_3	29	71
2006	CMAQ v. 5.0_beta at 12 km, unidirectional NH_3	20	80
	Dentener *et al.* [28] and median 23 global models	22	78

Table 3. Sensitivity of the continental nitrogen deposition to a 40% decrease in aerodynamic resistance across all nitrogen species.

sensitivity to 40% decrease in aerodynamic resistance June 2006			
		continental domain	
	species	absolute change (10^6 kg-N)	relative change (%)
sensitivity species	dry total nitrate	13.28	8.3
	other dry Ox-N	2.01	5.8
	dry Red-N	13.98	10.5
	dry total change	29.27	8.9
competing species	wet total nitrate	−9.49	−5.9
	other wet Ox-N	−0.015	−0.4
	wet Red-N	−8.07	−5.5
	wet total change	−17.57	−5.6
resultant	total N deposition change	11.70	1.8

associated with $HNO_3 + NO_3^-$ (= TNO_3 or total nitrate) wet and dry deposition. Oxidized nitrogen (Ox-N) dominates with 63 per cent and 66 per cent of the total N deposition for unidirectional and bi-directional cases, respectively. TNO_3 is the dominant form of Ox-N deposition, at approximately 70 per cent, peroxyacetyl nitrate (PAN) + oxidized organic nitrogen (ORGN) is next, at 17 per cent, and NO_x is third, at 9.4 per cent. The 'other' category includes N_2O_5 and HONO. Continental dry deposition of Ox-N is 36 per cent and 48 per cent greater than wet deposition of Ox-N for unidirectional and bi-directional cases, respectively. Annual NH_3 emissions estimated for the two runs were fairly comparable, because confined animal feeding operation (CAFO) emissions were unchanged, even though the bi-directional run used EPIC fertilizer application rates and the internal CMAQ conversion to emissions. Dry deposition of reduced nitrogen (Red-N; = ammonia + ammonium), is 93 per cent and 48 per cent of the Red-N wet deposition for the unidirectional and bi-directional cases, respectively. Interestingly, except for Red-N dry deposition, the relative fractions of the total N budget are fairly similar between unidirectional and bi-directional models. The mean continental change in annual total N deposition is 5 per cent; however, local changes can be higher. Comparing the bi-directional with the unidirectional case (figure 1*c*), there are decreases in total N deposition of up to 20 per cent in roughly 60 per cent of the cells, and decreases of 20–50 per cent or more in 11 per cent of the cells. Decreases are principally in cells with significant agricultural emissions with the largest decreases in cells dominated by large CAFO emissions. There are increases of up to 20 per cent in 29 per cent of the cells with just a few cells having increases of 20–50%. Increases are principally in low emission areas in western US with semi-natural land cover, owing to introduction of an emission potential where none existed, thus, creating an emission source lacking in standard inventories. Semi-natural areas in eastern US isolated from agricultural emissions have less than a 1 per cent change owing to abundant NH_3 in transported air masses.

(b) Continental budgets

For the 2002 annual CMAQ simulations, 67 per cent of the US NO_x (as N) emissions are deposited back onto the US, whereas 78 per cent and 71 per cent of the US NH_3 emissions (as N) are deposited back onto the US for the unidirectional and bi-directional cases, respectively (table 2). As shown in table 2, with CMAQ improvements and the inclusion of lightning NO_x, the CMAQ estimate of the fraction of NO_x emissions exported has decreased. At the global scale, Dentener *et al.* [28] summarized year 2000 deposition budgets for the continental US for 23 models. The median global model estimates are that 37 per cent of the NO_x and 22 per cent of the NH_3 emissions are exported off the continent (table 2). For NO_x, the 2000 global model export estimates are larger than earlier ones of Kasibhatla *et al.* [26] and Liang *et al.* [27]. The global models include lightning NO_x; thus, recent CMAQ and median global model budgets have converged. However, for the global models, 80–90% of the Ox-N is associated with HNO_3 and particulate nitrate deposition, a significantly larger role for nitric acid deposition than in the regional CMAQ model results, perhaps owing to differences in grid size, photochemistry and aerosol physics.

A comparison of the 2002 annual and 2006 June simulations indicates a fair degree of similarity of the nitrogen deposition budgets. Wet plus dry deposition of TNO_3 still contributes about half of the total nitrogen budget in both simulations. As expected, the fraction of PAN + ORGN is smaller in the summer, owing to higher temperatures, and the fraction of Red-N deposition is larger, owing to higher fertilizer application in June compared with the annual average. Previous testing with CMAQ [14] suggests that insights gained from sensitivity studies with June 2006 regarding system responses can be generalized to annual values.

(c) Gaseous oxidized nitrogen air–surface exchange uncertainties

Removal of oxidized nitrogen from the atmosphere is primarily due to deposition of the gaseous species of NO_y, particularly nitric acid (HNO_3), PAN and associated ORGN, and nitrogen dioxide (NO_2). The V_d of nitric oxide (NO) is low and it is rapidly transformed to other oxidized forms through atmospheric chemistry, so its contribution to the budget is very small. Initial box model sensitivity testing of the CMAQ unidirectional V_d parametrization indicated that the main sources of uncertainty in V_{dPAN} and V_{dORGN} are the cuticular and soil resistances. V_{dHNO_3} is most sensitive to the aerodynamic resistance (R_a). V_{dNO_2} is more affected by changes in the mesophyll resistance than by changes in the cuticular and soil resistances. Thus, three sets of sensitivities with CMAQ were conducted for the month of June 2006 to explore the impact of the uncertainties for these three sets of chemicals on the overall oxidized nitrogen removal budget.

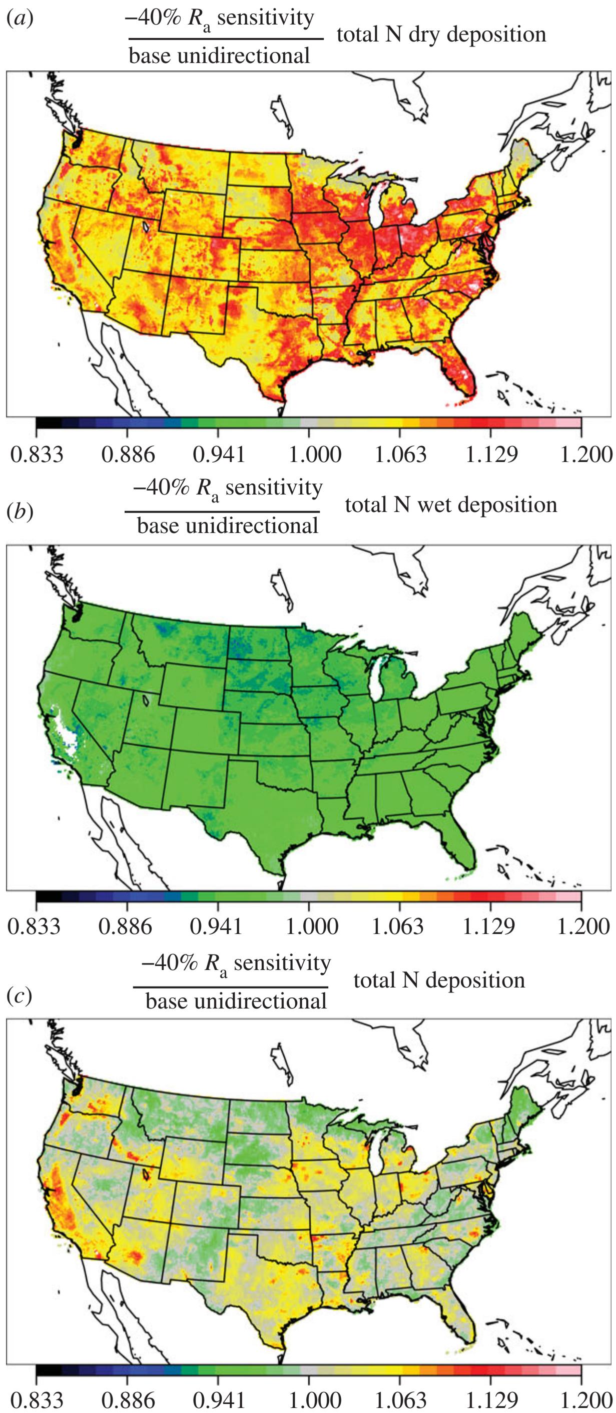

Figure 2. Ratio of sensitivity case to base case for aerodynamic resistance sensitivity (40% decrease): (*a*) increased dry Ox-N + Red-N deposition; (*b*) decreased wet Ox-N + Red-N deposition; (*c*) total N deposition ratio.

(i) Cuticular and ground resistance sensitivity involving peroxyacetyl nitrate and oxidized organic nitrates

The exchange of PAN and other acyl peroxy nitrates with ground and cuticular surfaces remains poorly characterized [29,30]. In the absence of measurements to define the uncertainty in the ground and cuticular resistances, a range of ±50% was applied to both ground and cuticular resistances by varying the reactivity scaling factor for PAN. Dry deposition of ORGN is modelled in CMAQ using the PAN V_d as a surrogate, so changing the reactivity scaling factor for PAN also changes the V_d for ORGN. Continentally, increasing cuticular and soil resistances for PANs and ORGN by 50 per cent decreases their dry deposition by 18 per cent.

Table 4. Sensitivity of the continental nitrogen deposition to a 90% decrease in mesophyll resistance of NO_2 (V_d cut in half).

sensitivity to NO_2 mesophyll resistance decrease June 2006			
		continental domain	
	species	absolute change (10^6 kg N)	relative change (%)
sensitivity species	dry NO_2 N	7.70	37.0
competing oxidized species	dry total nitrate	−2.56	−1.6
	wet total nitrate	−1.96	−1.2
	dry NO nitrogen	−0.62	−38.1
resultant Ox-N	total oxidized nitrogen	2.44	0.68
	total reduced nitrogen	0.06	0.02
total deposition change		2.49	0.39

Importantly, because PAN decomposes to release NO_2 for later HNO_3 production in the dynamic atmosphere, the total nitrate dry and wet deposition is increased by a modest amount sufficient to offset 57 per cent of the decrease in PAN and ORGN deposition. There is also a negligible increase in reduced nitrogen deposition. Because PAN and ORGN are small fractions of the overall oxidized nitrogen budget, the change in the overall nitrogen budget related to this change in the cuticular resistance is small, with a mean continental change of only 0.2 per cent and no cell has a relative change greater than 1 per cent.

(ii) Sensitivity to R_a

The aerodynamic resistance was modified by applying an adjustment factor of ± 40 per cent within the CCTM. While estimates derived from measurements are well constrained to 10 per cent or less [31,32], we considered the additional error introduced by meteorological model error. Modifying the aerodynamic resistance changes the dry deposition of all oxidized and reduced nitrogen species, as shown in table 3 and illustrated in figure 2. For the continental domain, a reduction in the aerodynamic resistance by 40 per cent leads to an increase in nitric acid dry deposition of 9 per cent, which leads to a decrease in the concentration of HNO_3 and a decrease in its availability for particulate nitrate formation. This leads to a decrease in the particulate nitrate deposition of 9 per cent, giving an overall total nitrate dry deposition increase of 8 per cent. The increase in reduced nitrogen dry deposition is approximately 11 per cent, leading to an overall increase in dry deposition of total nitrogen of 9 per cent. The resulting decrease in concentration results in lower wet deposition. Over half (62%) of the oxidized nitrogen dry deposition increase is offset by the reduction in wet deposition, and 58 per cent of the reduced nitrogen dry deposition increase is offset by the reduction in wet deposition. For total nitrogen, 60 per cent of the increase in dry deposition is counterbalanced by a reduction in wet deposition of nitrogen. So, the mean continental change in total N deposition is 1.8 per cent. In the majority of the cells (94%) changes were less than 5 per cent, mostly associated with semi-natural areas with some agriculture. The cells with changes larger than 10 per cent are principally associated with water. This sensitivity demonstrates the strong oppositional interplay between dry and wet deposition, buffering the overall atmospheric removal of nitrogen from changes in the rate of air–surface exchange.

(iii) Mesophyll resistance sensitivity involving nitrogen dioxide

As a result of box model testing, the parametrization in CMAQ for calculating the mesophyll resistance was changed from a lookup table to an empirical function based on solubility and reactivity with mesophyll or stomatal guard cell surfaces following Wesely [33]. The change in the mesophyll resistance affects NO_2 and NO deposition in opposite directions, but the change is dominated by NO_2, which increases by 37 per cent (table 4) because NO is rapidly converted to NO_2 and because $V_{dNO} \ll V_{dNO_2}$. However, for the continental domain the increase in NO_2 deposition is significantly offset by decreases in wet and dry total nitrate deposition and therefore the oxidized nitrogen budget increases by only 0.68 per cent. The mean continental reduction in total N deposition is 0.4 per cent. Total N deposition changes in a grid cell ranged from 0 per cent to a maximum of 14 per cent. However, 89 per cent of the cells have a change of less than 1 per cent in predominantly semi-natural and agricultural areas. Changes greater than 5 per cent (only 0.7% of cells) are associated with urban cells and adjacent semi-natural areas. In summary, the NO_2 change is largely offset by the change in total nitrate owing to compensations by the dynamic photochemical system. The change is further diminished by the lack of change in the reduced nitrogen species, leading to minimal change on a continental scale.

(d) Bi-directional air–surface exchange uncertainties

The parametrization of soil gammas with respect to fertilizer applications remains uncertain [34]. Measured values of soil gammas for arable land and grassland receiving fertilizer range from 360 to 6.3×10^6 ([34] and references therein, [35]). This range of values represents differences in fertilizer type and amount, soil type and time since fertilization. In CMAQ v. 5.0_beta, for arable land, the soil gamma is predicted using crop-specific fertilizer information and soil pH. For the apoplast gamma, a value of 100 is applied to forest and grassland and a value of 160 applied to fertilized crops

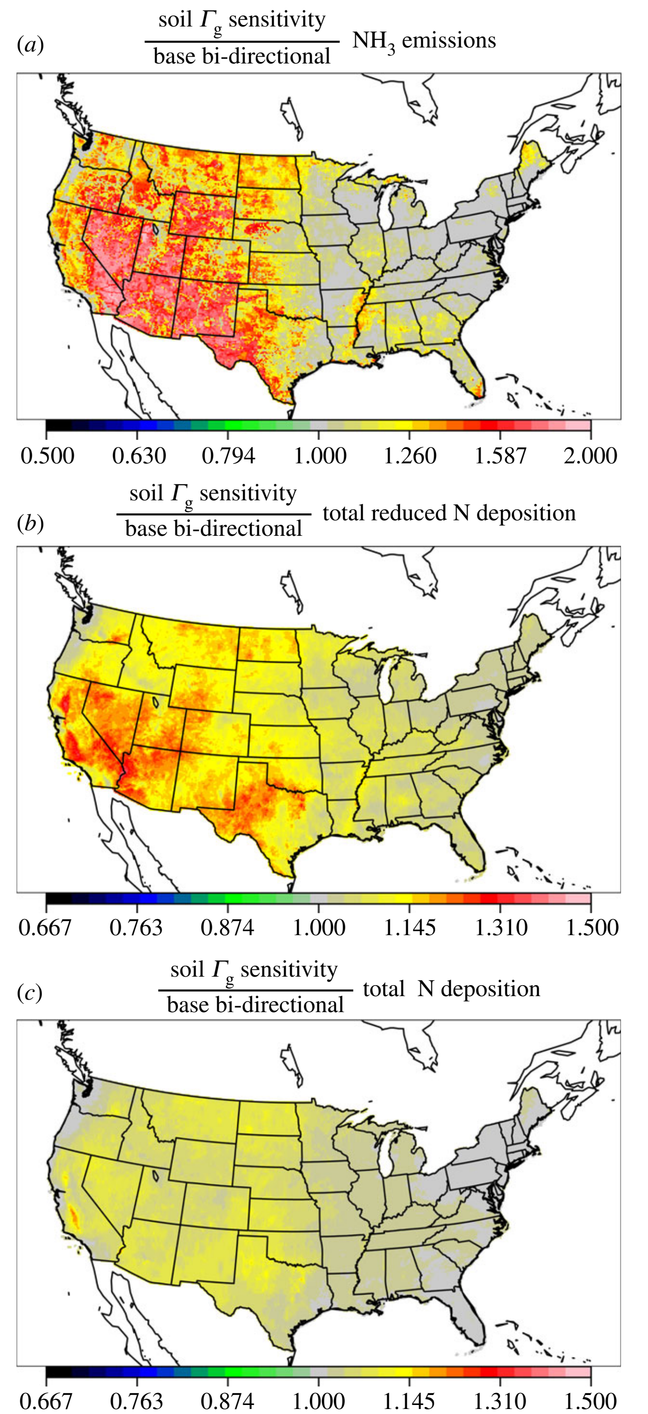

Figure 3. Ratio of sensitivity case to base case for soil gamma sensitivity (50% increase): (*a*) increased NH_3 emissions; (*b*) increased wet + dry Red-N deposition; (*c*) total N deposition ratio.

in CMAQ v. 5.0_beta. The majority of values of apoplast gamma for forest and semi-natural vegetation summarized by Massad *et al.* [34] range from 250 to 500; higher values correspond to sites with higher atmospheric N deposition rates. Values for fertilized systems fall within a similar range though the average peak value is higher (approx. 900) than that for unfertilized vegetation. This sensitivity simulation covers the range of values of vegetation emission potentials estimated from *in situ* measurements and from bioassay techniques, the former generally yielding higher estimates [34,36].

The effect of these uncertainties in the bi-directional exchange of NH_3 on the atmospheric N deposition budget was explored by adjusting soil gamma and crop fertilization rate by ± 50 per cent and evaluating the change in the N budget owing to the incorporation of a dynamic leaf apoplast gamma following Massad *et al.* [34]. It is noteworthy that, in the bi-directional approach, changing the gammas will simultaneously affect the emissions as well as the deposition.

The soil gamma sensitivity is dominated by the influence of the agricultural component that is associated with fertilizer application. For the continental domain, as shown in figure 3 and summarized in table 5, increasing the soil gamma by 50 per cent increases the fertilizer emissions of ammonia by 42.3 per cent while an increase in the fertilization rate by 50 per cent increased the emissions by 31.0 per cent. The 50 per cent increase in soil gamma resulted in the Red-N deposition being increased by 8.9 per cent and the total N deposition being increased by 3.8 per cent. Only 1.7 per cent of the cells have a change greater than 10 per cent and 0.15 per cent of the cells had a change greater than 15 per cent, principally in agricultural areas with adjacent semi-natural land use. The 50 per cent increase in the fertilization rate resulted in the Red-N deposition being increased by 6.3 per cent and the total N deposition being increased by 2.6 per cent. Total N deposition changes less than 5 per cent and 10 per cent in 84 per cent and 99 per cent of the cells, respectively, predominantly in mixed agricultural semi-natural areas. The dynamic apoplastic compensation point following Massad *et al.* [34] resulted in an increase in the apoplastic gamma of approximately 3 times to more than 10 times in areas that were recently fertilized. This resulted in an increase in the NH_3 emissions from agricultural areas of 17.5 per cent and an increase in the total NH_3 emissions of 4.9 per cent and increased the reduced and total N deposition on the continental domain by 3.7 per cent and 1.6 per cent, respectively. No cell has a change in total N deposition greater than 5 per cent and 15 per cent of the cells have a change less than 1 per cent. The change in ammonia deposition does not match the change in emissions, because the compensation point has also been changed, feeding back to the flux of ammonia to the surface. Semi-natural land cover was the most sensitive to the change in apoplastic gamma, and these areas are also sensitive to changes in the soil gamma owing to the transport of ambient NH_3 from agricultural areas.

5. Conclusions

Based on this study's results, changing from a unidirectional to a bi-directional NH_3 formulation produces the largest change in total nitrogen deposition. However, within each of these two approaches to air–surface exchange, the dry deposition parametrizations are not a major source of uncertainty regarding the continental nitrogen removal budgets, owing to the feedbacks in the chemistry and removal pathways of the atmospheric nitrogen system. The uncertainty estimates of total nitrogen deposition at the continental scale are surprisingly small (5% or less): unidirectional versus bi-directional NH_3 (5%), bi-directional Γ_s (1–4%) and unidirectional R_a (2%). At the local scale, differences in a single 12 km grid cell between unidirectional and bi-directional simulations can be up to 50 per cent or more, but 28 per cent of the cells have changes within 10–30% and 66 per cent of the cells have changes less than 10 per cent. Uncertainties within either the bi-directional or the unidirectional formulation can lead to changes per grid cell of up to 20 per

Table 5. Sensitivity of emissions, concentration and deposition in the bi-directional ammonia system to a 50 per cent increase in the soil gamma, a 50 per cent increase in the fertilization rate and parametrizing the apoplast gamma as a function of the annual nitrogen deposition and fertilizer application following Massad *et al.* [34].

sensitivity of the bi-directional ammonia system June 2006 continental domain			
	50% increase in soil gamma	50% increase in crop fertilization	Massad *et al.* [34] appoplast gamma
	relative change (%)	relative change (%)	relative change (%)
fertilizer emissions	42.3	31.0	17.5
total NH_3 emissions	11.8	8.6	4.9
NH_3 air concentration	9.3	6.8	3.2
NH_4^+ air concentration	0.7	0.4	0.9
Red-N dry deposition	11.4	8.5	4.1
Red-N wet deposition	7.7	5.2	3.5
Red-N total deposition	8.9	6.3	3.7
Total N deposition	3.8	2.6	1.6

cent; but for 90 per cent of the cells changes are less than 10 per cent and for 80 per cent of the cells less than 5 per cent.

It is crucial to use advanced regional and global models with advanced representations of transport, gas-phase chemistry, particle physics, clouds and wet removal to represent the interactions and feedbacks between species and pathways in the system. Simpler models would inadequately represent the feedbacks and compensations. Obtaining good emissions estimates for these models would appear still to be at the heart of the uncertainties.

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