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

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Reactive nitrogen ($N_x$) 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 $N_x$ 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 ($N_x$) over the past century and a half [1], the input and removal of atmospheric $N_x$ has increased substantially [2] leading to deleterious impacts on ecosystem health and associated human health [3–5]. $N_x$ gases and particles in the atmosphere are removed by surface fluxes (air–surface exchange) and wet deposition. Chemical transformation of the form of $N_x$ can impact the rate of deposition by effectively changing the reactivity of $N_x$ species with land surface receptors. The rate at which different forms of $N_x$ 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 $N_x$ 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
fluxes in the planetary boundary layer [6]. The turbulent air–
surface exchange is typically described as analogous to an elec-
trical 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 reci-
procal of the sum of the atmospheric ($R_a$), quasi-laminar
boundary layer ($R_b$) and surface resistances ($R_s$). $R_s$ is the resis-
tance 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 dif-
fusion of the pollutant transported. $R_a$ is the resistance to the
uptake of the pollutant by the surface receptor, typically
vegetation or soil. The surface resistance can collectively com-
prise stomatal uptake ($R_a$), 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 complica-
ted when accounting for bi-directional surface fluxes. The complica-
tion arises from having to account for non-zero con-
centrations 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 predomi-
nately 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
Nr 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 Nr species, total oxidized and reduced Nr, and
total Nr 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 mod-
delling, SMOKE uses the Biogenic Emission Inventory System, v.
3.14 (BEIS3). The WRF model [11] is a mesoscale numerical pre-
diction 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 capa-
bility 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 uni-
directional 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 uni-
directional 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 depo-
sition 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,
$R_a$ 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 rela-
tive 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 resist-
ance 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 parametriza-
tion for Nr 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 frame-
work 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 sur-
face application and injection of fertilizer. To compute the soil
emissions potential, CMAQ uses the United States Depart-
ment of Agriculture’s Environmental Policy Integrated
Climate (EPIC) model [18] to simulate crop-specific agri-
cultural management practices for each model grid cell
following Cooter et al. [19]. A crop-specific soil emission
potential \( I_{v} = \text{NH}_4^+ / \text{H}^+ \) 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\(_4^+\) and NH\(_3\) 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\(_3\) 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 \( I_{v} \) values are merged into a general NLCD agricultural category to estimate the NH\(_3\) fluxes to agricultural ecosystems [15,19]. Vegetation \( (I_{v}) \) and non-agricultural soil \( (I_{v}) \) 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 & Shanker [22] and Feng [23]. The modal-integrated \( V_d \) is a function of modal mass mean diameter \( D_{v} \). 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.

### 3. Approach

In this study, we examined US continental oxidized, reduced and total N\(_2\) 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 (uni-directional) \( V_d \). 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...
The 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 km² grid size. We compared the CMAQ Nr 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>
<thead>
<tr>
<th>species</th>
<th>deposition (10^6 kg N)</th>
<th>relative portion</th>
<th>deposition (10^6 kg N)</th>
<th>relative portion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox-N total</td>
<td>3927</td>
<td>100.0%</td>
<td>63.01%</td>
<td>360</td>
</tr>
<tr>
<td>wet Ox-N</td>
<td>1667</td>
<td>42.44%</td>
<td>26.74%</td>
<td>165</td>
</tr>
<tr>
<td>dry Ox-N</td>
<td>2261</td>
<td>57.56%</td>
<td>36.27%</td>
<td>195</td>
</tr>
<tr>
<td>NOₓ</td>
<td>216</td>
<td>9.57%</td>
<td>3.47%</td>
<td>19</td>
</tr>
<tr>
<td>HNO₃</td>
<td>1440</td>
<td>63.69%</td>
<td>23.10%</td>
<td>152</td>
</tr>
<tr>
<td>NO₃</td>
<td>125</td>
<td>5.54%</td>
<td>2.01%</td>
<td>8</td>
</tr>
<tr>
<td>PANs</td>
<td>218</td>
<td>9.66%</td>
<td>3.50%</td>
<td>8</td>
</tr>
<tr>
<td>organic-N</td>
<td>176</td>
<td>7.79%</td>
<td>2.82%</td>
<td>5</td>
</tr>
<tr>
<td>other</td>
<td>85</td>
<td>3.76%</td>
<td>1.36%</td>
<td>3</td>
</tr>
<tr>
<td>Red-N total</td>
<td>2306</td>
<td>100.0%</td>
<td>36.99%</td>
<td>281</td>
</tr>
<tr>
<td>wet Red-N</td>
<td>1195</td>
<td>51.83%</td>
<td>19.17%</td>
<td>148</td>
</tr>
<tr>
<td>dry Red-N</td>
<td>1110</td>
<td>48.17%</td>
<td>17.82%</td>
<td>133</td>
</tr>
<tr>
<td>NH₃</td>
<td>1001</td>
<td>90.17%</td>
<td>16.07%</td>
<td>124</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>109</td>
<td>9.83%</td>
<td>1.75%</td>
<td>9</td>
</tr>
<tr>
<td>total</td>
<td>6233</td>
<td>100.0%</td>
<td>641</td>
<td>100.0%</td>
</tr>
</tbody>
</table>

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
associated with \( \text{HNO}_3 + \text{NO}_3 \) (\( = \text{TN0}_3 \) 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. \( \text{TN0}_3 \) 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 \( \text{NO}_x \) is third, at 9.4 per cent. The ‘other’ category includes \( \text{N}_2\text{O}_5 \) and \( \text{HONO} \). 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 \( \text{NH}_3 \) 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; \( = \text{ammonia + ammonium} \)), 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 1c), 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.

### 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.

<table>
<thead>
<tr>
<th>year</th>
<th>model version</th>
<th>exported (%)</th>
<th>deposited (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>CMAQ v. 4.7 at 36 km without lightning</td>
<td>42</td>
<td>58</td>
</tr>
<tr>
<td>2002</td>
<td>CMAQ v. 4.7.1 at 12 km without lightning</td>
<td>38</td>
<td>62</td>
</tr>
<tr>
<td>2002</td>
<td>CMAQ v. 4.7.1_research at 12 km with lightning</td>
<td>33</td>
<td>67</td>
</tr>
<tr>
<td>2006</td>
<td>CMAQ v. 5.0_beta at 12 km with lightning</td>
<td>36</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>Kasibhatla et al. [26]</td>
<td>25 – 30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liang et al. [27]</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dentener et al. [28] and median 23 global models</td>
<td>37</td>
<td>63</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>sensitivity species</th>
<th>species</th>
<th>absolute change (10^6 kg-N)</th>
<th>relative change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dry total nitrate</td>
<td>13.28</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>other dry Ox-N</td>
<td>2.01</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>dry Red-N</td>
<td>13.98</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>dry total change</td>
<td>29.27</td>
<td>8.9</td>
</tr>
<tr>
<td>competing species</td>
<td>wet total nitrate</td>
<td>-9.49</td>
<td>-5.9</td>
</tr>
<tr>
<td></td>
<td>other wet Ox-N</td>
<td>-0.015</td>
<td>-0.4</td>
</tr>
<tr>
<td></td>
<td>wet Red-N</td>
<td>-8.07</td>
<td>-5.5</td>
</tr>
<tr>
<td></td>
<td>wet total change</td>
<td>17.57</td>
<td>-5.6</td>
</tr>
<tr>
<td>resultant</td>
<td>total N deposition change</td>
<td>11.70</td>
<td>1.8</td>
</tr>
</tbody>
</table>
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 NH3 in transported air masses.

**Continental budgets**

For the 2002 annual CMAQ simulations, 67 per cent of the US NOx (as N) emissions are deposited back onto the US, whereas 78 per cent and 71 per cent of the US NH3 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 NOx, the CMAQ estimate of the fraction of NOx 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 NOx and 22 per cent of the NH3 emissions are exported off the continent (table 2). For NOx, 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 NOx; thus, recent CMAQ and median global model budgets have converged. However, for the global models, 80–90% of the Ox-N is associated with HNO3, 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 TNO3 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.

**Gaseous oxidized nitrogen air–surface exchange uncertainties**

Removal of oxidized nitrogen from the atmosphere is primarily due to deposition of the gaseous species of NOy, particularly nitric acid (HNO3), PAN and associated ORGN, and nitrogen dioxide (NO2). The Vd 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 Vd parametrization indicated that the main sources of uncertainty in VdPAN and VdORGN are the cuticular and soil resistances. VdHNO3 is most sensitive to the aerodynamic resistance (Rd). VdNO2 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.

**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 Vd as a surrogate, so changing the reactivity scaling factor for PAN also changes the Vd for ORGN. Continentally, increasing cuticular and soil resistances for PANs and ORGN by 50 per cent decreases their dry deposition by 18 per cent.
Importantly, because PAN decomposes to release NO2 for later HNO3 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.

(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 NO2 and NO deposition in opposite directions, but the change is dominated by NO2, which increases by 37 per cent (table 4) because NO is rapidly converted to NO2 and because $v_{\text{NO}} < v_{\text{NO2}}$. However, for the continental domain the increase in NO2 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 NO2 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 $6.3 \times 10^6$ ([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

### Table 4. Sensitivity of the continental nitrogen deposition to a 90% decrease in mesophyll resistance of NO2 (Vd cut in half).

<table>
<thead>
<tr>
<th>sensitivity to NO2 mesophyll resistance decrease June 2006</th>
<th>continental domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>species</td>
<td>absolute change ($10^6$ kg N)</td>
</tr>
<tr>
<td>sensitivity species</td>
<td>dry NO2 N</td>
</tr>
<tr>
<td>competing oxidized species</td>
<td>dry total nitrate</td>
</tr>
<tr>
<td></td>
<td>wet total nitrate</td>
</tr>
<tr>
<td></td>
<td>dry NO nitrogen</td>
</tr>
<tr>
<td>resultant Ox-N</td>
<td>total oxidized nitrogen</td>
</tr>
<tr>
<td></td>
<td>total reduced nitrogen</td>
</tr>
<tr>
<td>total deposition change</td>
<td></td>
</tr>
</tbody>
</table>
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 and 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 $\Gamma_s$ (1–4%), and unidirectional $\Gamma_g$ (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 cent. The majority of values of apoplastic gamma for forest and semi-natural vegetation summarized in CMAQ v. 5.0 beta. The majority of values of apoplastic gamma for forest and semi-natural vegetation summarized in 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].
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.

We gratefully acknowledge Rohit Mathur and two anonymous reviewers for their suggestions. The United States Environmental Protection Agency through its Office of Research and Development funded and managed the research described here. It has been subjected to the Agency’s administrative review and approved for publication.

### 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 appoplast gamma as a function of the annual nitrogen deposition and fertilizer application following Massad et al. [34].

<table>
<thead>
<tr>
<th>Sensitivity of the bi-directional ammonia system June 2006 continental domain</th>
<th>50% increase in soil gamma</th>
<th>50% increase in crop fertilization</th>
<th>Massad et al. [34] appoplast gamma</th>
</tr>
</thead>
<tbody>
<tr>
<td>relative change (%)</td>
<td>relative change (%)</td>
<td>relative change (%)</td>
<td></td>
</tr>
<tr>
<td>fertilizer emissions</td>
<td>42.3</td>
<td>31.0</td>
<td>17.5</td>
</tr>
<tr>
<td>total NH₃ emissions</td>
<td>11.8</td>
<td>8.6</td>
<td>4.9</td>
</tr>
<tr>
<td>NH₃ air concentration</td>
<td>6.8</td>
<td>6.8</td>
<td>3.2</td>
</tr>
<tr>
<td>NH₄⁺ air concentration</td>
<td>0.7</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Red-N dry deposition</td>
<td>11.4</td>
<td>8.5</td>
<td>4.1</td>
</tr>
<tr>
<td>Red-N wet deposition</td>
<td>7.7</td>
<td>5.2</td>
<td>3.5</td>
</tr>
<tr>
<td>Red-N total deposition</td>
<td>8.9</td>
<td>6.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Total N deposition</td>
<td>3.8</td>
<td>2.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>

### References

29. Turnipseed AA et al. 2006 Eddy covariance fluxes of peroxyacetyl nitrates (PANs) and NOy to a coniferous forest. Atmos. Chem. Phys. 6, 10 359 – 10 386. (doi:10.5194/acp-6-10359-2006)