

1 **Highlights**

- 2 • Estimates of transference ratios and related modeled parameters for oxidized sulfur and
3 oxidized nitrogen were made using five years (2002-2006) of 12-km grid cell-specific
4 annual output from EPA's Community Air Quality Model (CMAQ) for five selected sub-
5 regions in the eastern US.
- 6 • Model estimated annual transference ratios have both spatial variability (grid cell-to-grid
7 cell) and temporal variability (across the five modeled years).
- 8 • Assuming proportionality rather than equality between cell-specific and regional
9 deposition appears to reduce the impact of modeled spatial variability of transference
10 ratios on estimates of regional total deposition by a substantial margin.
- 11 • Examination of five years of annual model predictions (along with an assumed annual
12 CV of 10% for the monitored airborne concentration) suggests that in the sub-regions that
13 were considered, estimates of modeled regional total deposition have maximum 95% CIs
14 of $\pm 26\%$ for oxidized sulfur and $\pm 25\%$ for NO_Y .

“Transference Ratios” to Predict Total Oxidized Sulfur and Nitrogen Deposition – Part II, Modeling Results

Joseph E. Sickles, II^{a*}, Douglas S. Shadwick^b, J. Vasu Kilaru^a, K. Wyatt Appel^a

^a US EPA, ORD, NERL, Research Triangle Park, NC 27711, U.S.A;

^b Computer Sciences Corporation, Durham, NC 27713, U.S.A;.

* Corresponding author; e-mail: sickles.joseph@epa.gov

Abstract.

The current study examines predictions of transference ratios and related modeled parameters for oxidized sulfur and oxidized nitrogen using five years (2002-2006) of 12-km grid cell-specific annual estimates from EPA’s Community Air Quality Model (CMAQ) for five selected sub-regions in the eastern US. Modeled total deposition and modeled airborne concentrations are moderately to poorly correlated in the selected sub-regions of the eastern US. The monitored oxidized nitrogen species (OxN) considered in the current study include airborne gaseous nitric acid (HNO₃) and particulate nitrate (NO₃⁻), and nitrate ion (NO₃⁻) in precipitation. Modeled airborne OxN accounts for approximately 20% of the modeled airborne concentration of the total reactive oxidized oxidized nitrogen (NO_y) but is responsible for approximately 80% of the modeled total deposition of NO_y. Airborne OxN concentration may be a better predictor of total deposition of NO_y in some locations; whereas, airborne NO_y concentration may be better in others. Modeled airborne concentration and total deposition for both oxidized sulfur and OxN tend to be higher than corresponding monitoring-based results, suggesting a need for both model refinement and more comprehensive comparisons with monitoring results. Model estimated annual transference ratios have both spatial variability (grid cell-to-grid cell) and temporal variability (across the five modeled years). Two approaches are explored to investigate the impacts of modeled spatial variability of transference ratios on estimates of regional total deposition. Assuming proportionality rather than equality between cell-specific and regional

deposition appears to reduce the impact of modeled spatial variability of transference ratios on estimates of regional total deposition by a substantial margin, to perhaps $\pm 20\%$ for oxidized sulfur and $\pm 10\%$ for oxidized nitrogen. Overall estimates of the variability of estimated regional total deposition were made, considering modeled cell-to-cell spatial variability and modeled year-to-year temporal variability along with the variability of monitored airborne concentration. The variability of monitored airborne concentration was found to influence strongly the resulting variability in regional total deposition estimated with input from CMAQ. Examination of five years of annual model predictions (along with an assumed annual CV of 10% for the monitored airborne concentration) suggests that in the sub-regions that were considered, estimates of modeled regional total deposition have maximum 95% CIs of $\pm 26\%$ for oxidized sulfur and $\pm 25\%$ for NO_Y . These findings should be considered with caution because they are based almost entirely on modeled annual results (i.e., modeled spatial and modeled temporal variability along with variability of monitored airborne concentrations), and they fail to consider several sources of uncertainty, including discrepancies between model predictions and monitoring results as well as important deposition processes.

Keywords: Model estimates; CMAQ; transference ratio; oxidized sulfur; oxidized nitrogen; total deposition

1. Introduction

The US Environmental Protection Agency (EPA) is considering the use of “transference ratios” in the formulation of Secondary National Ambient Air Quality Standards (NAAQS) for oxides of nitrogen and oxides of sulfur as a means to estimate their total atmospheric deposition (US EPA, 2011). The concept of a “transference ratio,” introduced in US EPA (2011), was defined as the ratio of total (i.e., dry plus wet) deposition to the airborne concentration of the species of interest. This expresses the notion that the amount of an acidifying species deposited to the earth’s surface within a given area over a given period of time is proportional to the average airborne concentration of the acidifying species over the same area during the same time period, where the proportionality constant is called a transference ratio.

In the development of the Secondary NAAQS, combinations of maximum one-year acceptable (i.e., critical) total acidic deposition loads will be determined for geographical areas of interest (US EPA, 2011). Transference ratios of acidic species of interest will be predicted using air quality models (e.g., EPA's Community Air Quality Model (CMAQ (Byun and Schere (2006))). These model-estimated transference ratios will be used with monitored atmospheric concentrations to estimate total acidic deposition loads that can be compared with one-year critical total acidic deposition loads to determine compliance of the monitored ambient acidic airborne concentrations.

A brief examination of transference ratios for oxidized sulfur and monitored oxidized nitrogen has been performed using monitoring data from the Clean Air Status and Trends Network (CASTNET for dry deposition) and the National Acid Deposition Program (NADP for wet deposition) (Sickles and Shadwick, 2012). That study focused on the major oxidized sulfur species (i.e., airborne gaseous sulfur dioxide (SO_2), airborne particulate sulfate (SO_4^{2-}), and sulfate ion (SO_4^{2-}) in precipitation). Total reactive atmospheric oxidized nitrogen includes nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), peroxyacetyl nitrate (PAN), nitrous acid (HONO), other organic nitrates, and airborne particulate nitrate (NO_3^-). Since monitoring data for the total of all major oxidized nitrogen species (commonly known as NO_Y) are not currently available, a parallel analysis of NO_Y could not be performed. Nevertheless, using the available monitoring data, analogous analyses of airborne concentration and total deposition were performed for the monitored oxidized nitrogen species, OxN (i.e., airborne gaseous HNO_3 , airborne particulate NO_3^- , and NO_3^- in precipitation). Site-specific transference ratios were examined at weekly, seasonal, and annual temporal scales. That study found that at specific sites in the eastern US, annual estimates of total deposition to within ± 25 to $\pm 35\%$ might be expected using species- and site-specific transference ratios along with annual average monitored airborne concentrations. However, considerable uncertainty remained because the concept failed to account explicitly for highly variable wet deposition processes.

The goal of the current study is to examine predictions of transference ratio and related parameters for oxidized sulfur (T_S), the monitored oxidized nitrogen species, noted above (T_{OxN}),

and the total of all major oxidized nitrogen species, noted above (T_{NO_y}) using five years of model estimates from CMAQ, Version 4.7. The following related issues are explored: typical variability of model-predicted annual transference ratio across time (2002-2006) and across space (the eastern US and five selected sub-regions within the east); the variability across time and space associated with model-predicted airborne concentration and total deposition of oxidized sulfur and oxidized nitrogen; and selected implications of modeled variability across time and space on estimated total deposition that may be relevant in the formulation of a standard.

2. Approach

Air quality simulations for the eastern US have been produced using EPA's CMAQ, Version 4.7 (Foley et al., 2010), with 5-minute time steps and a 12-km grid size. Although predictions are available for 24 layers between the earth's surface and the tropopause, the current study employed only values associated with the lowest layer (≈ 36 m thick). Modeled hourly values have been aggregated and stored and may subsequently be aggregated to the temporal resolution of interest. Annual aggregates for the years 2002-2006 are used in the current study. Details of model inputs and configuration (e.g., emissions, meteorological driver, and deposition schemes) have been described by Foley et al. (2010), Appel et al. (2011), and Pleim et al. (2001). In addition, an operational performance evaluation of these 2002-2006 CMAQ model simulations has been reported by Appel et al. (2011). Model output includes many parameters (e.g., airborne concentrations of many chemical species, as well as their dry and wet deposition). Transference ratio is taken to be the species-specific ratio of annual total deposition to annual airborne concentration. Consistent terminology is employed to permit comparison between the modeled results in the current document and the monitored results of Sickles and Shadwick (2012). Oxidized sulfur species is designated by "S;" monitored oxidized nitrogen species by "OxN;" and the total of all major oxidized nitrogen species by " NO_y " in the text and in various figures and tabulations.

The geographical area considered is illustrated in Fig. 1 and includes the eastern US (starting one state west of the Mississippi River and moving east to the Atlantic Ocean). In

addition, five selected sub-regions are considered: the Adirondack (ADR) in northern New York; the Potomac (POT) from northern Virginia to south central Pennsylvania; the Coastal Carolinas (CC) in southeastern Virginia and northeastern North Carolina; the Neuse (NEU) an area contained within the CC; and the high elevation (HEL) area, above 600m, of western North Carolina and Virginia and eastern Tennessee and Kentucky. These sub-regions were chosen to represent a range of conditions and are similar to selected eastern US case study regions in US EPA (2011). The number of 12-km model grid cells within each region is given as follows: ADR, 162; CC, 500; HEL, 276; NEU, 101, POT, 251; and East, 21106. It should be noted that although cloud deposition may be a sizable and important contributor to total acidic deposition to vulnerable ecosystems located at high elevations (Sickles and Grimm, 2003), the contribution of cloud deposition to the total is not considered in the current study because it is neither modeled nor monitored extensively on a routine basis.

3. Results and Discussion

3.1. Site-Specific Comparisons: Same Years of CASTNET and CMAQ Results

Two earlier studies of dry, wet, and total deposition in the eastern US over the 15-years between 1990 and 2004 have been published using measurements from CASTNET and NADP monitoring sites (Sickles and Shadwick, 2007a&b). Sites, land use, terrain features, elevation, latitude, longitude, and mapped location are shown in Sickles and Shadwick (2007b). Analogous CASTNET and NADP data with four complete seasons of monitoring data for specific years between 2002 and 2004 have been compiled for comparison with corresponding CMAQ annual estimates. Quantitative comparisons between monitored and corresponding model estimates of airborne concentration, total deposition, and transference ratio are shown in Table 1. Here, relative differences (RDs) between model- and monitor-based results are displayed for 17 site-years of oxidized sulfur data and 13 site-years of OxN data. The chemical species comprising airborne oxidized sulfur include gaseous sulfur dioxide (SO_2), airborne particulate sulfate (SO_4^{2-}), and sulfate ion (SO_4^{2-}) in precipitation. Although a parallel analysis of monitored NO_Y species could not be performed, analogous analyses of airborne concentration and total deposition were

performed for the available OxN species. As noted earlier, the OxN species include airborne gaseous nitric acid (HNO_3), airborne particulate nitrate (NO_3^-), and nitrate ion (NO_3^-) in precipitation.

As indicated in Table 1, model estimates of airborne concentration and total deposition for both oxidized sulfur and OxN tend to be higher than the corresponding monitoring-based results. Median RDs between model- and monitor-based results for airborne oxidized sulfur concentration (C_{Sg}) and total deposition (D_{Stotal}) are 12% and 37%, respectively. Corresponding median RDs for airborne OxN concentration (C_{OxNg}) and OxN total deposition (D_{OxNtotal}) are 42% and 39%. Relative differences between model- and monitor-based results for transference ratios of oxidized sulfur (T_{S}) range between -14 and 134%, with mean and median values of 38% and 24%. Relative differences between model- and monitor-based results for transference ratios of OxN (T_{OxN}) range between -37 and 64%, with mean and median values of 2% and -5%. While these comparisons are promising, they also suggest the need for both model refinement and more comprehensive comparisons with monitoring results.

3.2. Correlation of CMAQ Grid Cell Estimates in Various Eastern Regions

Annual values of selected variables have been retrieved from five years (2002-2006) of CMAQ runs and averaged by cell. Pearson correlation values are given in Table 2 for various pairings of the modeled 5-year average concentration of selected species and modeled 5-year average total deposition values in each geographical area. In addition, mean ratios of modeled airborne concentrations of OxN and NO_Y (i.e., $C_{\text{OxNg}} / C_{\text{NOyg}}$), as well as mean ratios of their total deposition values (i.e., $D_{\text{OxNtotal}} / D_{\text{NOYtotal}}$) are illustrated in Table 2.

Modeled total deposition of oxidized sulfur (D_{Stotal}) and modeled airborne concentrations of oxidized sulfur (C_{Sg} , expressed as S) are moderately correlated in each of the sub-regions of the eastern US, with correlation values ranging from 0.46 to 0.80.

Modeled airborne concentrations of NO_Y (C_{NOyg}) and modeled airborne concentrations of OxN (C_{OxNg} , expressed as N) are moderately correlated in each of the eastern sub-regions, with

correlation values ranging from 0.69 to 0.84. The modeled airborne concentration of OxN accounts for between 18% and 24% of the modeled airborne concentration of NO_Y (see ratio, C_{OxNg} / C_{NOyg}). Modeled total deposition of OxN (D_{OxNtotal}) and modeled total deposition of NO_Y (D_{NOytotal}) are highly correlated in each of the various regions of the eastern US, with correlation values ranging from 0.94 to 1.00 (0.998). However, in contrast to the relatively small (i.e., 20%) contribution of modeled airborne OxN concentration to that of modeled NO_Y, the modeled total deposition of OxN accounts for 75% to 85% of the modeled total deposition of NO_Y.

Correlation coefficients between modeled total deposition values of OxN and NO_Y with their corresponding modeled airborne concentrations are also shown in Table 2. Modeled total deposition of NO_Y (D_{NOytotal}) and modeled airborne concentration of NO_Y (C_{NOyg}) are moderately to poorly correlated in the eastern sub-regions ($0.76 > r > 0.08$). Corresponding correlations for OxN ($0.48 > r > 0.20$) are higher for ADR and HEL, but lower for CC, NEU, and POT. Their relative magnitudes reflect to a large extent differences in chemical composition imposed by complex and heterogeneous source-sink relationships and differences in deposition velocities of individual oxidized nitrogen species present in air masses arriving at various receptor sub-regions. For example, the two relatively high elevation sub-regions (ADR and HEL) show much higher correlations between both modeled total deposition of OxN (D_{OxNtotal}) and modeled total deposition of NO_Y species (D_{NOytotal}), with the modeled airborne concentration of OxN (C_{OxNg}) than with the modeled airborne concentration of NO_Y (C_{NOyg}). This may be due to OxN at high elevations being composed largely of HNO₃, a highly soluble species with a very high deposition velocity. Although detailed interpretation of the tabulated correlation values is beyond the scope of the current effort, these results do suggest that the airborne OxN concentration (C_{OxNg}) may be a better predictor of total deposition of NO_Y in some locations; whereas, the airborne NO_Y concentration (C_{NOyg}) may be better in others.

3.3. CMAQ Regional Estimates: Deposition, Concentration, Transference Ratio and Variability

Regional means across cells of 5-year average cell values of modeled total deposition, modeled airborne concentration, and transference ratio are illustrated in Table 3. Modeled airborne regional oxidized sulfur concentrations range between 1.9 (ADR) and 6.4 (POT)

$\mu\text{gS}/\text{m}^3$, and modeled regional total deposition of oxidized sulfur ranges between 9.5 (ADR) and 15.8 (POT) $\text{kgS}/\text{ha}\cdot\text{y}$. Spatial CVs of these two indices (designated as CV(s) in Table 3) range between 12% and 28% for the sub-regions, but are near 60% for the very large eastern US (not shown). In addition, the spatial CVs of modeled regional total deposition and modeled airborne concentration are remarkably similar year-to-year for each of the five years as well as for the 5-year means (not shown).

Modeled regional airborne NO_Y concentrations range between 1.8 (ADR) and 5.6 (POT) $\mu\text{gN}/\text{m}^3$, and modeled regional total deposition of NO_Y ranges between 6.0 (ADR) and 7.9 (POT) $\text{kgN}/\text{ha}\cdot\text{y}$. Spatial CVs are substantial for modeled regional airborne NO_Y concentration, ranging between 20 and 55% in the sub-regions, but only range between 13 and 21% for total deposition of NO_Y .

Transference ratio for a grid cell may be illustrated by the slope (through zero) of a plot of modeled cell-specific airborne concentration versus modeled total deposition within that cell. The ensemble of such points for all the cells in the sub-region under consideration illustrates the spatial variability of transference ratios for that sub-region. The spatial variability of cell-specific modeled 5-year average transference ratios is shown by the range of slopes associated with cells across each of the five sub-regions for oxidized sulfur in Fig. 2 and for NO_Y in Fig. 3. Note the constant slope (transference ratio) reference lines for the five regional ensembles of cells illustrated in these two figures.

As shown in Table 3, the magnitude of the mean modeled 5-year mean regional transference ratio for oxidized sulfur is about 50% larger than that for NO_Y , ranging between 2.5 (POT) and 4.9 (ADR) $[(\text{kgS}/\text{ha}\cdot\text{y})(\text{m}^3/\mu\text{gS})]$ for oxidized sulfur and between 1.6 (NEU) and 3.4 (ADR) $[(\text{kgN}/\text{ha}\cdot\text{y})(\text{m}^3/\mu\text{gN})]$ for NO_Y . Cell-by-cell maps of these modeled 5-year mean transference ratios, illustrating their spatial distribution across the eastern US, are shown in Fig. 4 for oxidized sulfur and Fig. 5 for NO_Y . Quartiles of the distribution of transference ratios in the eastern US are identified by color in these figures (note that the median T_S is 2.78 and the median T_{NO_Y} is 1.71).

Variability of modeled total deposition, modeled airborne concentration, and modeled transference ratio is illustrated both spatially (i.e., CV(s), using 5-year average cell values across the cells contained within each region) and temporally (i.e., CV(t), across five years of annual CMAQ model estimates). Modeled 5-year average transference ratios for both oxidized sulfur and oxidized nitrogen show considerable spatial variability across cells (i.e., CV(s) > 12% for all regions (i.e., 13 to 36%); also see Fig. 2 and 3). In contrast to the magnitudes of the modeled transference ratios themselves, the spatial variability of modeled NO_y transference ratios is about 50% larger than those for oxidized sulfur.

Regional distributions of temporal variability of modeled transference ratios are illustrated by mean, minimum, and maximum CV(t) values in Table 3. Mean CV(t) values for oxidized sulfur are ≤ 10% and are lower still (≤ 6%) for oxidized nitrogen, while the ranges are fairly narrow for both species at between approximately 5 and 13%. Maps of CV(t) for the eastern US are shown in Fig. 6 for oxidized sulfur and Fig. 7 for NO_y. Although there is some evidence for trends in the modeled 5-year behavior of airborne NO_y concentration and total deposition, there is no trend evidence for airborne oxidized sulfur concentration or total deposition and none for the transference ratios for either oxidized sulfur or oxidized nitrogen (not shown). The lack of trend in the model-based transference ratios of oxidized sulfur and oxidized nitrogen suggests that their temporal variability may represent their natural variability. Since 95% CI for 4 degrees of freedom are defined by 2.776 x CV, temporal 95% CI of ±25% corresponds to CV(t) ≤ 9% (i.e., 25/2.776=9.0). Using the results shown in Fig. 6 and 7, it may be inferred that large areas in the East have temporal 95% CI for transference ratios of oxidized sulfur that exceed ±25%; while in contrast, very few areas have corresponding temporal 95% CI for transference ratios of oxidized nitrogen that exceed ±25%.

The spatial variability (CV(s)) of modeled transference ratios of both oxidized sulfur and oxidized nitrogen shown in Table 3 exceed their corresponding 5-year temporal variability (CV(t)). The CV(s) of the modeled transference ratio of oxidized sulfur exceeds CV(t) by a factor of approximately two; while this factor is approximately six for the modeled transference ratio of oxidized nitrogen. The rather large spatial variability of modeled transference ratios underscores the importance of selecting regionally representative monitoring sites if location-

specific monitored concentrations and grid cell-specific modeled transference ratios are to be used to estimate regional total deposition.

3.4. Considerations in the Development of an Atmospheric Standard

A regression approach for predicting site-specific total oxidized sulfur deposition from airborne oxidized sulfur concentration has been examined using monitoring data by Sickles and Shadwick (2012). This approach assumes that the airborne concentration is measured without error. EPA has proposed an approach using a model-estimated transference ratio that has the same form as the regression estimator examined previously (Sickles and Shadwick, 2012). This approach assumes that model-estimated transference ratios for species “i” (T_i^{model}) will be used with monitored airborne concentrations (C_i^{mon}) to estimate total acidic deposition loads (D_i^{est}) that may be compared with critical total acidic deposition loads to determine compliance of monitored ambient acidic precursor airborne concentrations (see Equation (1) below).

$$D_i^{\text{est}} = C_i^{\text{mon}} T_i^{\text{model}} \quad (1)$$

It is uncertain how well airborne concentration monitored at a point in space is represented by a modeled three-dimensional average (i.e., across a 12-km grid cell within the lowest model layer). Results, shown earlier in Table 1, provide some insight, but more comprehensive study is needed to permit quantification. Uncertainty also exists with both the model-estimated transference ratios and monitored airborne concentrations. In addition, it is unclear how an approach incorporating the transference ratio concept will be implemented in practice. As a result, it is unclear how uncertainties in both the model-estimated transference ratios and monitored airborne concentrations will impact estimates of total deposition. Two cases are examined in this section to explore the implications of spatial variability and assumptions regarding spatial representativeness. Finally, an attempt is made to incorporate spatial variability, temporal variability, and variability associated with monitored airborne concentration into overall estimates of the variability of estimated regional total deposition.

3.4.1. Case 1: Assume Estimated Cell-Specific Deposition Represents the Whole Sub-Region

All the previously developed discussion surrounding modeled transference ratios (for chemical species “i”) is grid cell-specific and may be expressed in Equation (2).

$$T_{iC} = D_{iC} / C_{iC} \quad (2)$$

In this equation T_{iC} , D_{iC} , and C_{iC} represent the modeled (the superscript “model” as shown in Equation (1) has been omitted in this and subsequent equations) cell-specific transference ratio, modeled cell-specific total deposition, and modeled cell-specific airborne concentration of chemical species “i” within a sub-region where air monitoring occurs. One approach toward using this concept in the development of a standard is to assume that the modeled grid cell behavior is representative of the region under consideration. This means that the modeled grid cell-specific transference ratio, modeled grid cell-specific total deposition, and modeled grid cell-specific airborne concentration of species “i” represent the region under consideration. This is expressed in Equation (3), where T_{iR} , D_{iR} , and C_{iR} represent the modeled regional transference ratio, modeled regional total deposition, and modeled regional airborne concentration.

$$T_{iC} = D_{iC} / C_{iC} \approx T_{iR} = D_{iR} / C_{iR} \quad (3)$$

Under the assumption that the airborne concentration of species “i” monitored within a grid cell within the region (C_{iC}^{mon}) represents the regional average airborne concentration, the cell-specific total deposition may be estimated (D_{iC}^{est}) and the regional total deposition may be estimated (D_{iR}^{est}) according to Equation (4).

$$C_{iC}^{mon} T_{iC} = D_{iC}^{est} \approx D_{iR}^{est} \quad (4)$$

Modeled grid cell-specific transference ratios exhibit sizable spatial variability, as shown by examining the regional mean and regional CV(s) of cell-specific five-year average ratios in Table 3 (i.e., regional CV(s) of $\leq 22\%$ for oxidized sulfur and $\leq 36\%$ for NO_Y) and Fig. 2 to 5. This raises concern about how well any value from one three-dimensional grid cell represents the value across multiple grid cells defining a sub-region of interest. To address this representativeness issue resulting from spatial heterogeneity, assessments have been performed

using CMAQ model output. Three-year means of annual 2002-2004 grid cell-specific transference ratios (i.e., T_{iC} in Equation (4)) were determined for both oxidized sulfur and for NO_Y . Two individual years of model output (2005 and 2006) were used to provide grid cell-specific concentration values for both oxidized sulfur and for NO_Y to simulate monitored concentration (i.e., C_{iC}^{mon} in Equation (4)). Modeled 2005 and 2006 regional total deposition for both oxidized sulfur and for NO_Y were determined to simulate regional total deposition for these two years. These simulated regional total deposition values were then compared on a cell-by-cell basis in the Case 1 assessment with estimates of regional total deposition (i.e., D_{iR}^{est}) determined using Equation (4). This assessment may be illustrated as regional distributions of cell-specific relative differences (RD), and results are summarized in Table 4. Relative differences depend on the specific cell chosen to designate as the simulated monitoring location and, depending on region, range between -48% and 170% for oxidized sulfur and between -64% and 62% for NO_Y over the two years considered. The inner quartile ranges of RD values are similar across both chemical species and years at approximately 30%.

3.4.2. Case 2: Assume Estimated Cell-Specific Deposition Can Be Scaled to the Sub-Region

The sizable spatial variability of modeled grid cell-specific transference ratios evident in estimates of regional total deposition derived from Equation (4) is demonstrated in distributions of RD values for Case 1 shown in Table 4. This apparently stems from the impact of spatial variability introduced by assuming that modeled grid cell-specific behavior is representative of the region under consideration. One potential approach to reducing the impact of spatial variability is to assume that grid cell-specific total deposition is not equal to, but is proportional to total deposition in the region under consideration on an annual basis and to scale the modeled cell-specific total deposition (D_{iC}) according to the ratio of modeled regional to modeled grid cell total deposition (D_{iR} / D_{iC}) to estimate regional total deposition of species “i” (D_{iR}^{est}). Assessment of this approach for species “i” requires obtaining the modeled total deposition for both the region of interest (D_{iR}) and for the grid cell containing the monitoring site (D_{iC}), the modeled transference ratio for the grid cell containing the monitoring site (T_{iC}), the monitored airborne concentration (C_{iC}^{mon}), and using Equation (5) below to estimate regional total deposition (D_{iR}^{est}). This approach assumes that the monitored air quality represents the grid cell containing the monitoring site and that the modeled total deposition within each grid cell (D_{iC}) is

directly and uniquely proportional to the modeled value for the larger sub-region under consideration (D_{iR}) annually. This approach captures regional cell-to-cell (spatial) variability predicted by the model within the region under consideration that is missed in the Case 1 approach.

$$C_{iC}^{mon} T_{iC} (D_{iR} / D_{iC}) = D_{iR}^{est} \quad (5)$$

Equation (5) can then be simplified by substitution of the expression for T_{iC} from Equation (2) and algebraic cancelation of D_{iC} , resulting in an alternate expression, Equation (5a). The ratio, D_{iR} / C_{iC} in this expression is of the same form as earlier expressions of transference ratios, except that it relates modeled concentration in a specific grid cell to the modeled regional (rather than cell-specific) total deposition. This modeled cell-to-region transference ratio is designated as $T_{iR/C}$ in Equation (5a).

$$D_{iR}^{est} = C_{iC}^{mon} (D_{iR} / C_{iC}) = C_{iC}^{mon} T_{iR/C} \quad (5a)$$

The Case 2 assessment was conducted using Equation (5a) and CMAQ model output in an analogous manner to that performed above in Case 1. Three-year means of modeled annual cell-to-region transference ratio ($T_{iR/C}$) were determined from modeled annual 2002-2004 regional total deposition and modeled grid cell-specific airborne concentration (i.e., D_{iR} and C_{iC} in Equation (5a)) for both oxidized sulfur and for NO_Y . Two individual years of model output (2005 and 2006) were used to provide grid cell-specific airborne concentration values for both oxidized sulfur and for NO_Y to simulate monitored concentration (i.e., C_{iC}^{mon} in Equation (5a)). Modeled 2005 and 2006 regional total deposition for both oxidized sulfur and for NO_Y were determined to simulate regional total deposition for these two years. These simulated regional total deposition values were then compared on a cell-by-cell basis with estimates of regional total deposition (i.e., D_{iR}^{est}) determined using Equation (5a). This Case 2 assessment may be illustrated as regional distributions of cell-specific RDs, and results are summarized in Table 4. Relative differences depend on the specific cell chosen to designate as the simulated monitoring location and, depending on region, range from -28% to 35% for oxidized sulfur and -25% to 16% for NO_Y . In most cases, empirical 95% CI of RD values fall roughly between -10% and 20% for

oxidized sulfur and $\pm 10\%$ for NO_Y . The inner quartile ranges of RD values are similar across both chemical species and years at approximately 5%, a factor of six less than the corresponding value for Case 1. The Case 2 approach appears to reduce the impact of spatial variability of transference ratios apparent in the Case 1 approach by a substantial margin.

3.4.3. Overall Estimates of the Variability of Estimated Regional Total Deposition

An overall estimate of the variability of estimated regional total deposition was made, considering modeled cell-to-cell spatial variability and modeled year-to-year temporal variability along with the variability associated with monitored airborne concentration. The lack of evidence of trend in the modeled transference ratios of oxidized sulfur and NO_Y , noted earlier in Section 3.3, suggests that their temporal variability may represent their natural variability. Estimates of the variability of transference ratio may be derived as follows. Output from the CMAQ model may be thought of as representing a five-year time series of annual values. If the transference ratios in the time series are considered to be independent and identically distributed, then the mean of the cell-specific transference ratios in the time series may be used as an estimate of the transference ratio for that location. The variance of the estimate is the variance of the transference ratios in the time series divided by the number of years in the time series (the CV is estimated by the square root of the variance of the mean transference ratio divided by the mean transference ratio).

To explore overall estimates of the variability (CV) of D_{iR}^{est} , two modeled time series from CMAQ are considered, along with the variability of the hypothetical monitored airborne concentration, a random variable. One time series is represented by modeled airborne concentrations and the other time series by modeled regional total deposition. The cell-to-region transference ratio ($T_{iR/C}$) is formed from the two modeled time series. This approach uses the product ($C_{iC}^{\text{mon}} T_{iR/C}$) as shown in Equation (5a) to estimate the regional total deposition for a specific area. The variance of ($C_{iC}^{\text{mon}} T_{iR/C}$) is defined below in Equation (6), where $E\{.}$ denotes the expected value of $\{.\}$, and C_{iC}^{mon} and $T_{iR/C}$ are independent (see Stewart and Ord (2009) for the variance of a product of random variables).

$$\text{Var}\{D_{iR}^{\text{est}}\} = \text{Var}\{C_{iC}^{\text{mon}} T_{iR/C}\} =$$

$$E^2\{C_{iC}^{mon}\} * Var\{T_{iR/C}\} + E^2\{T_{iR/C}\} * Var\{C_{iC}^{mon}\} + Var\{T_{iR/C}\} * Var\{C_{iC}^{mon}\} \quad (6)$$

The coefficient of variation for estimated regional total deposition can be derived from Equation (6). Independence and algebraic manipulation of Equation (6) (divide both sides by $E^2\{C_{iC}^{mon} T_{iR/C}\}$ and note $E\{C_{iC}^{mon} T_{iR/C}\} = E\{C_{iC}^{mon}\} * E\{T_{iR/C}\}$ by independence) yields Equation (7), a formula for the CV of the product.

$$CV\{C_{iC}^{mon} T_{iR/C}\} = [CV^2\{C_{iC}^{mon}\} + CV^2\{T_{iR/C}\} + CV^2\{C_{iC}^{mon}\} * CV^2\{T_{iR/C}\}]^{1/2} \quad (7)$$

Spatial distributions of variability estimates of the estimated regional total deposition (D_{iR}^{est}) using modeled regional total deposition (D_{iR}), modeled airborne concentration for the hypothetical grid cell containing the monitoring site (C_{iC}), and their variability, as well as assumed variability of hypothetically monitored cell-specific airborne concentrations (C_{iC}^{mon}) are summarized in Table 5 for the ensembles of cells within each of the selected sub-regions. In the current example, five-year variabilities for modeled annual (2002-2006) D_{iR} and C_{iC} (i.e., $T_{iR/C}$) were used. As indicated in Table 5, the variability in the hypothetically monitored airborne concentration to a large extent drives the resulting variability in estimated regional total deposition. Annual precision (i.e., CV) estimates of monitored airborne concentrations of 5% to 8% for SO_2 , 3% to 12% for SO_4^{2-} , 5% to 12% for HNO_3 , and 6% to 17% for NO_3^- have been reported at selected collocated CASTNET sites (Sickles and Shadwick, 2002; Clarke et al., 1997). Assuming a conservative annual CV of 10% for the hypothetical monitored airborne concentration, five years of monitoring are estimated to yield mean monitored airborne concentrations with CVs of 4.47% (i.e., $10/\sqrt{5}$). Using this CV for the five-year mean hypothetical monitored airborne concentration in Table 5 for the CC sub-region, yields maximum CVs of 9.4% for regional total deposition of oxidized sulfur and 8.9% for NO_Y . Thus, based almost entirely on modeled annual total deposition and modeled annual concentration fields, 95% CIs for estimates of regional deposition from airborne concentrations monitored in grid cells with median variability are $\pm 16\%$ (i.e., 95% CI for 4 degrees of freedom are defined by $2.776 \times CV$) for oxidized sulfur and $\pm 13\%$ for NO_Y . Corresponding 95% CIs for estimates of regional deposition from airborne concentrations monitored in grid cells with maximum variability are $\pm 26\%$ for oxidized sulfur and $\pm 25\%$ for NO_Y .

4. Conclusions

The goal of the current study is to examine predictions of transference ratios and related modeled parameters for oxidized sulfur and oxidized nitrogen using five years of 12-km grid cell-specific annual estimates from EPA's Community Air Quality Model (CMAQ) for five selected sub-regions in the eastern US. The variability of model output across time and space is explored, and resulting implications on estimated total deposition that may be relevant in the formulation of a standard are discussed.

Modeled total deposition and modeled airborne concentrations are moderately to poorly correlated in the sub-regions of the eastern US for oxidized sulfur ($0.80 > r > 0.46$) and for NO_Y ($0.76 > r > 0.08$). Modeled total deposition of OxN and modeled total deposition of NO_Y are highly correlated ($r > 0.94$). Modeled airborne OxN concentration accounts for approximately 20% of the modeled airborne NO_Y concentration but is responsible for approximately 80% of the modeled total deposition of NO_Y . Comparisons of modeled total deposition for OxN and for NO_Y with modeled airborne concentration have inconsistent correlation coefficients that vary by region. This suggests that airborne OxN concentration may be a better predictor of total deposition of NO_Y in some locations; whereas, airborne NO_Y concentration may be better in others.

Modeled airborne concentration and total deposition for both oxidized sulfur and OxN tend to be higher than the corresponding monitoring-based results. Relative differences between model- and monitor-based results for transference ratios of oxidized sulfur range between -14 and 134% and between -37 and 64% for OxN. These comparisons suggest the need for both model refinement and more comprehensive comparisons with monitoring results.

Model estimates have both spatial variability (grid cell-to-grid cell) and temporal variability (across the five modeled years). In the estimation of regional total deposition one possible approach that may be relevant in the formulation of a standard could assume that any

cell-specific value is regionally representative. An alternate approach could assume that any cell-specific total deposition value is uniquely proportional to the regional value. Assessments using the same model output with these two approaches suggest that the second approach reduces the impact of spatial variability apparent in the first approach by a substantial margin. Assuming proportionality, rather than equality, between cell-specific and regional deposition appears to reduce the impact of modeled spatial variability of transference ratios on estimates of regional total deposition by a substantial margin, to perhaps $\pm 20\%$ for oxidized sulfur and $\pm 10\%$ for oxidized nitrogen.

Overall estimates of the variability of estimated regional total deposition were made, considering modeled cell-to-cell spatial variability and modeled year-to-year temporal variability along with the variability of monitored airborne concentration. The variability of monitored airborne concentration was found to influence strongly the resulting variability in regional total deposition estimated with input from CMAQ. Examination of five years of annual model predictions (along with an assumed annual CV of 10% for the monitored airborne concentration) suggests that in the sub-regions that were considered, estimates of modeled regional total deposition have maximum 95% CIs of $\pm 26\%$ for oxidized sulfur and $\pm 25\%$ for NO_y .

Although impacts of several sources of variability of regional total deposition in the possible formulation of a standard have been explored in the current document, other sources of uncertainty remain to be examined. These neglected uncertainty sources include: fidelity (i.e., accuracy and precision) of modeled output; fidelity of the monitoring results; representativeness of modeled values averaged across three dimensions at corresponding points in space (i.e., monitoring sites); and important deposition processes (e.g., deposition from clouds and fogs at high elevations and in coastal regions).

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List of Figures

Fig. 1. Geographical area under consideration: East, 21106 12-km grid cells; Adirondack, ADR (grey), 162 cells; Potomac, POT (orange), 251 cells; Neuse, NEU (blue), 101 cells; Coastal Carolinas, CC (green + blue), 500 cells; and High Elevation, HEL (red), 276 cells.

Fig. 2. Modeled 5-year average concentration of oxidized sulfur (C_{Sg} , $\mu\text{gS}/\text{m}^3$) versus 5-year average total oxidized sulfur deposition (D_{Stotal} , $\text{kgS}/\text{hA}\cdot\text{y}$) at each grid cell within each of the eastern sub-regions: ADR (black); POT (orange); NEU (blue); CC (green); and HEL (red). Reference lines represent lines of constant slope (i.e., transference ratio) between 1.5 and 8.0.

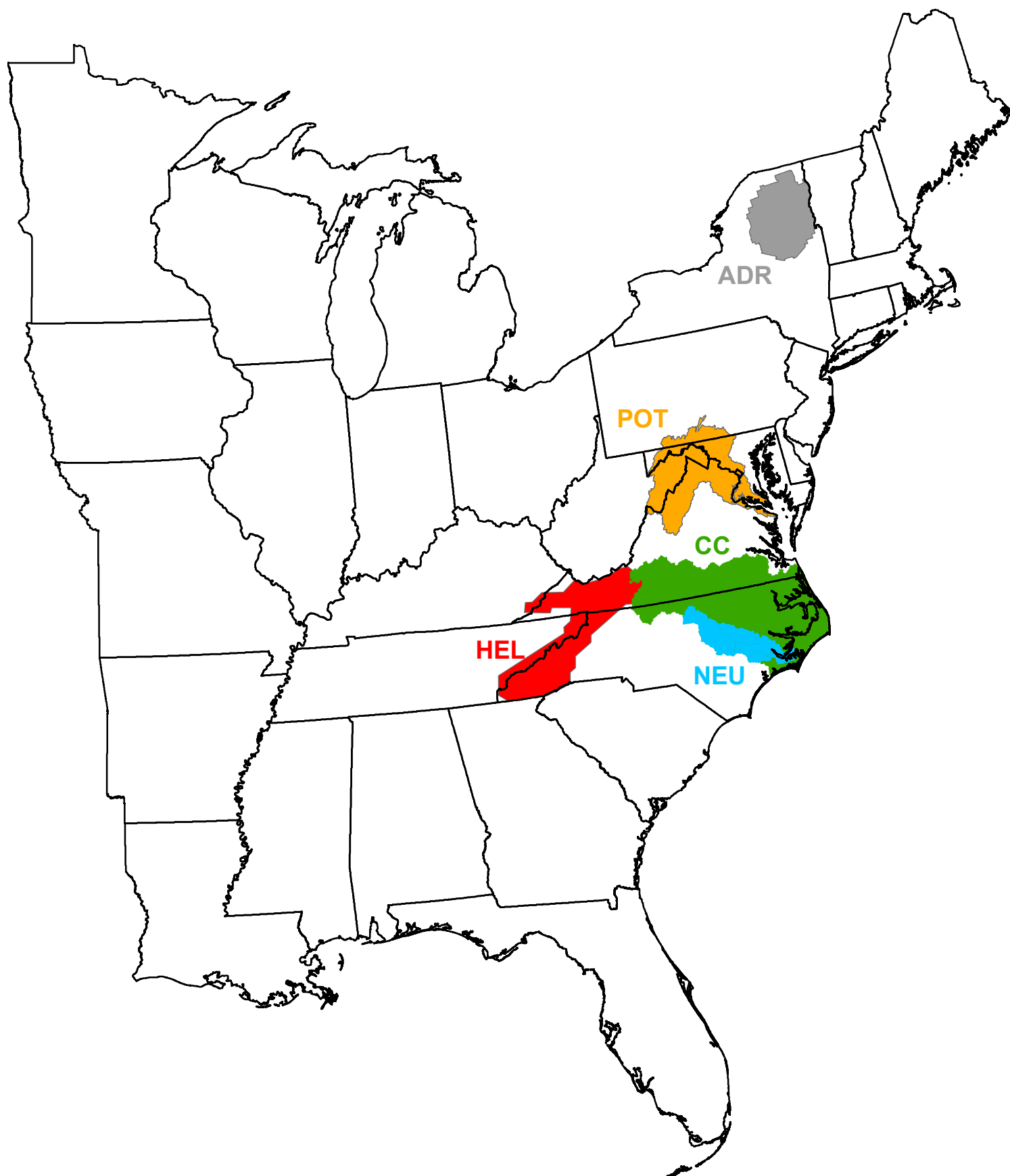
Fig. 3. Modeled 5-year average concentration of oxidized nitrogen ($C_{\text{NOy}g}$, $\mu\text{gN}/\text{m}^3$) versus 5-year average total oxidized nitrogen deposition (D_{NOytotal} , $\text{kgN}/\text{hA}\cdot\text{y}$) at each grid cell within each of the eastern sub-regions: ADR (black); POT (orange); NEU (blue); CC (green); and HEL (red). Reference lines represent lines of constant slope (i.e., transference ratio) between 0.5 and 6.0.

Fig. 4. Map of cell-specific modeled 5-year average transference ratio in quartiles for oxidized sulfur (T_S) in the eastern US (note the median T_S is $2.78 (\text{kgS}/\text{hA}\cdot\text{y})(\text{m}^3/\mu\text{gS})$).

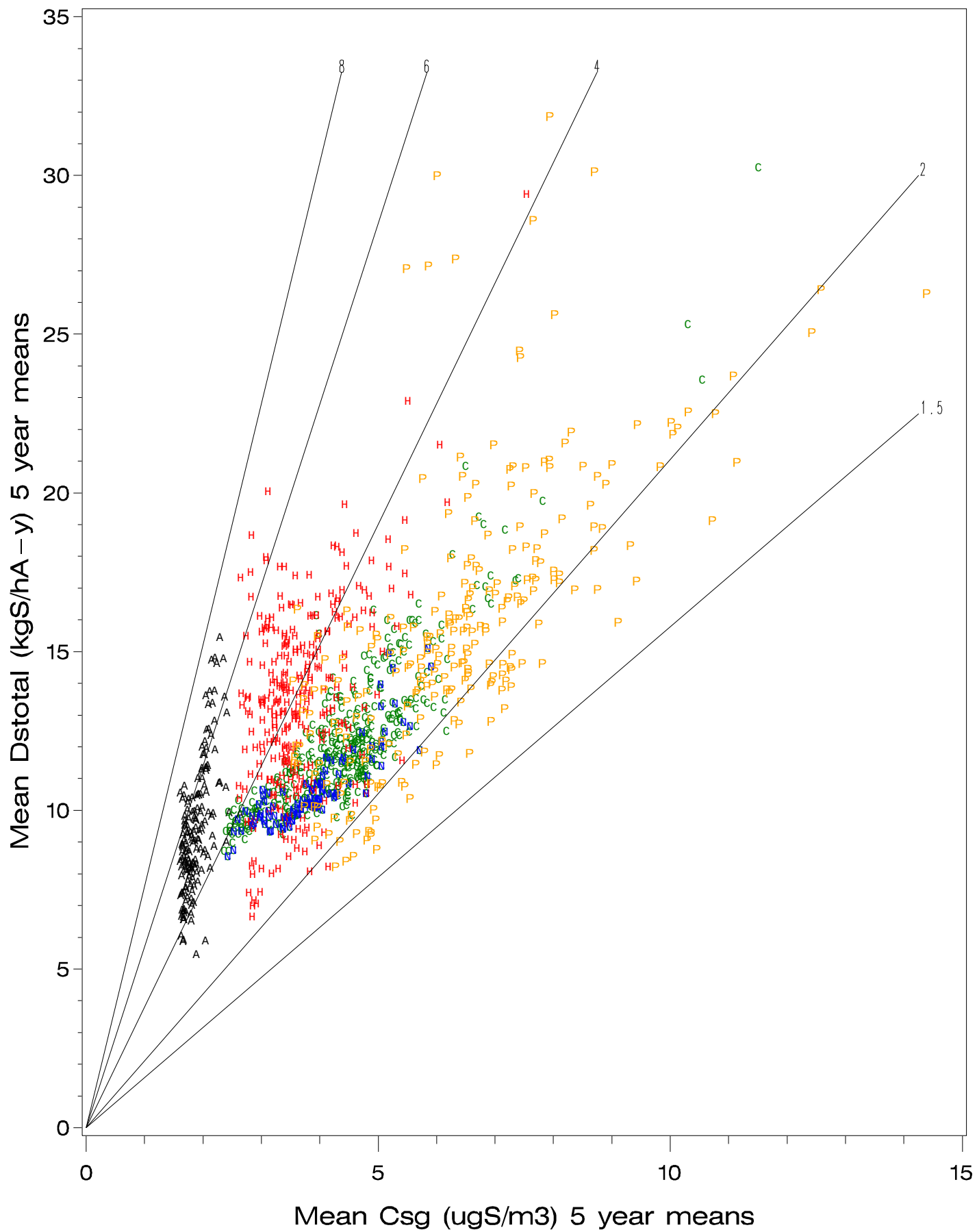
Fig. 5. Map of cell-specific modeled 5-year average transference ratio in quartiles for oxidized nitrogen (T_{NOy}) in the eastern US (note the median T_{NOy} is $1.71 (\text{kgN}/\text{hA}\cdot\text{y})(\text{m}^3/\mu\text{gN})$).

Fig. 6. Map of modeled temporal variability of T_S in the eastern US, expressed as coefficients of variation (%) for each cell-specific 5-year mean ($\text{CV}(t)$).

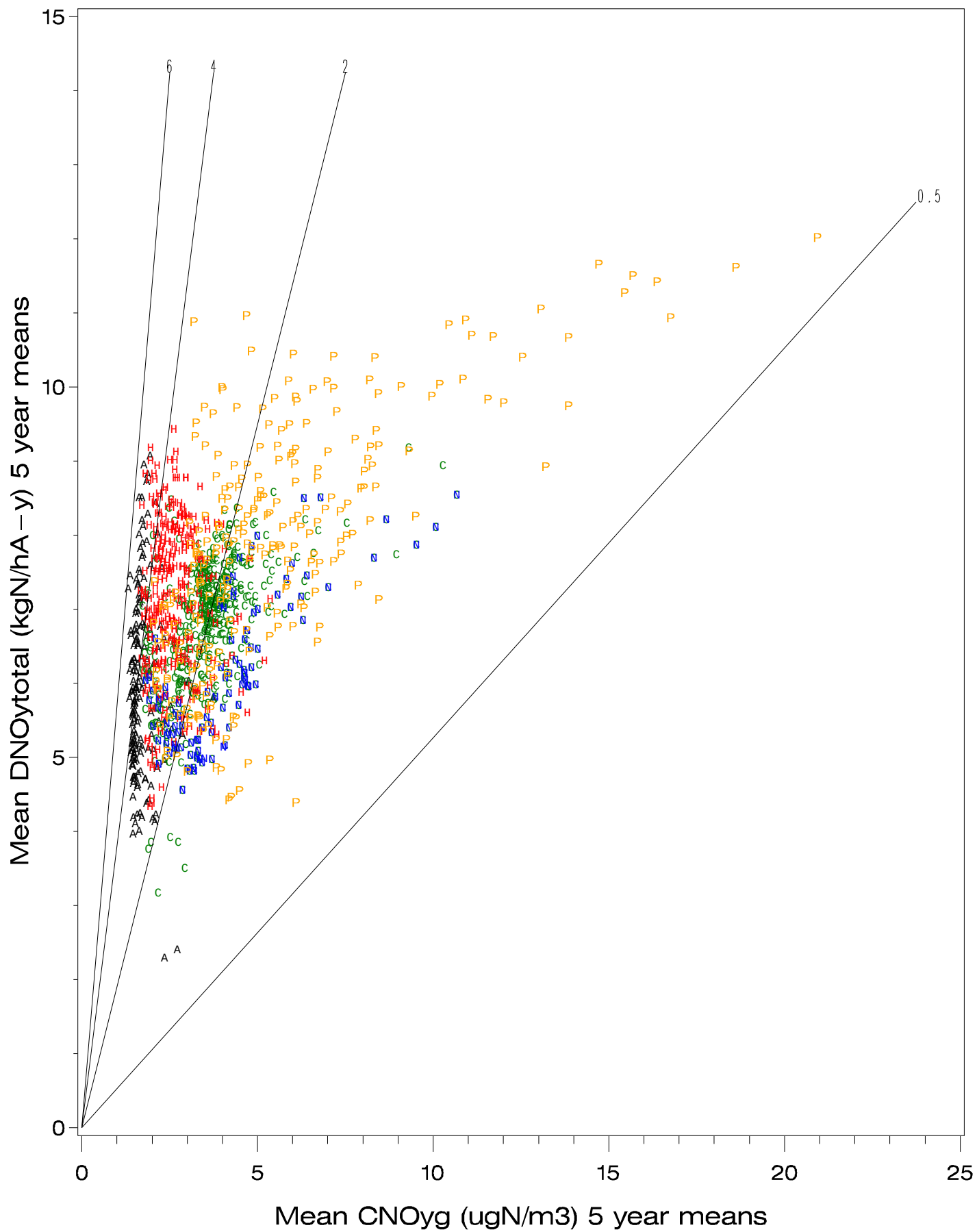
Fig. 7. Map of modeled temporal variability of T_{NOy} in the eastern US, expressed as coefficients of variation (%) for each cell-specific 5-year mean ($\text{CV}(t)$).

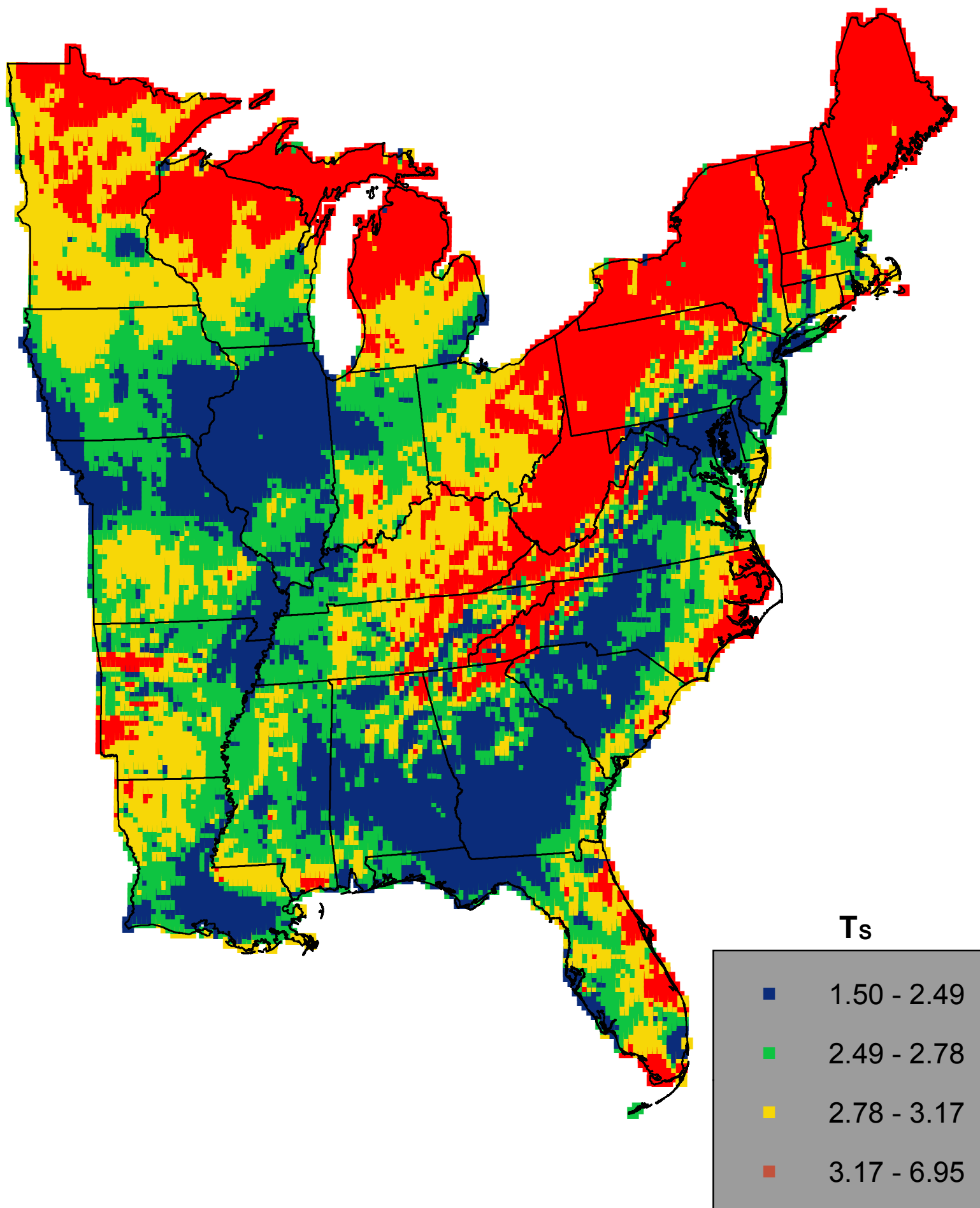


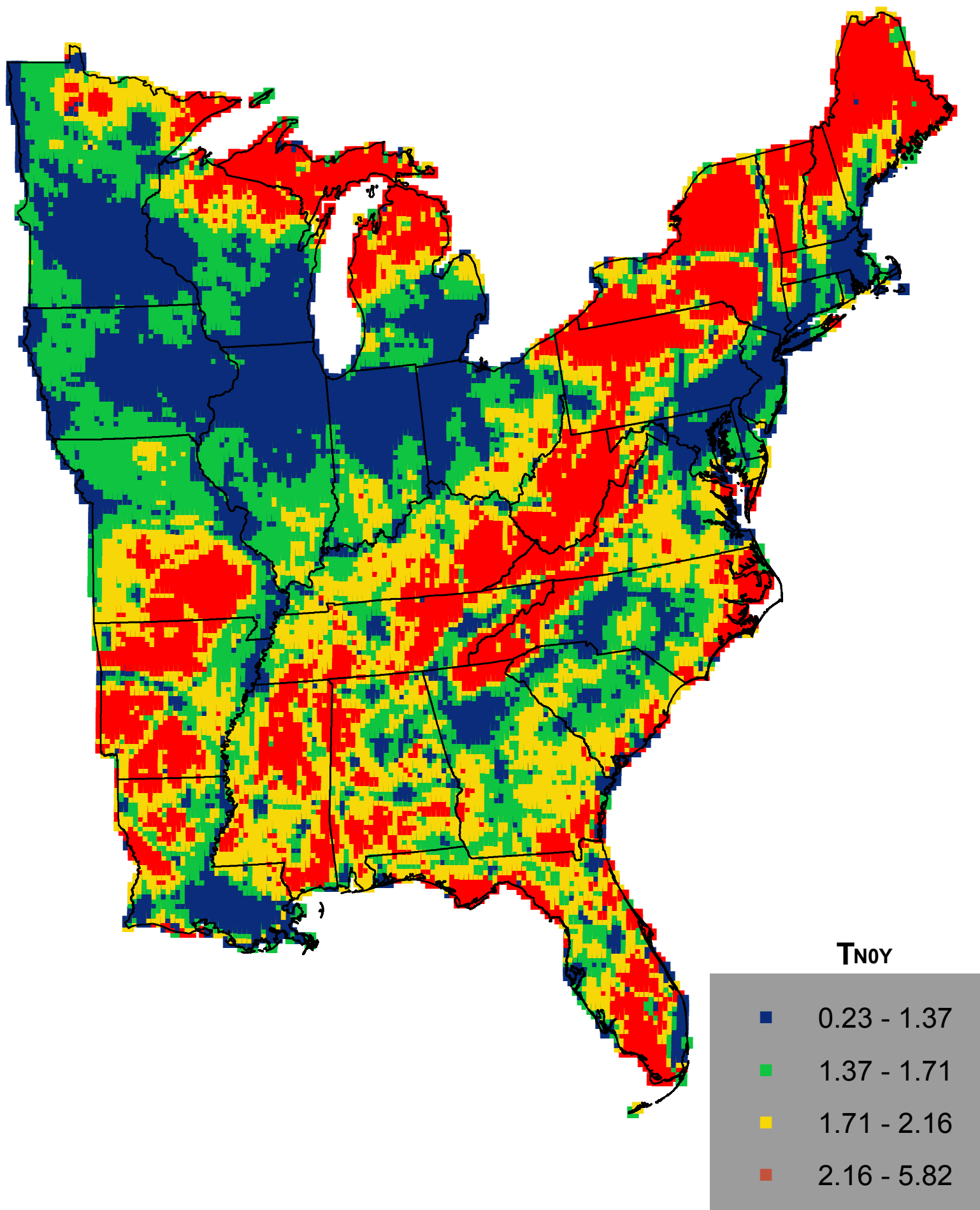
CMAQ (mean) Dstotal vs Csg
5 year means

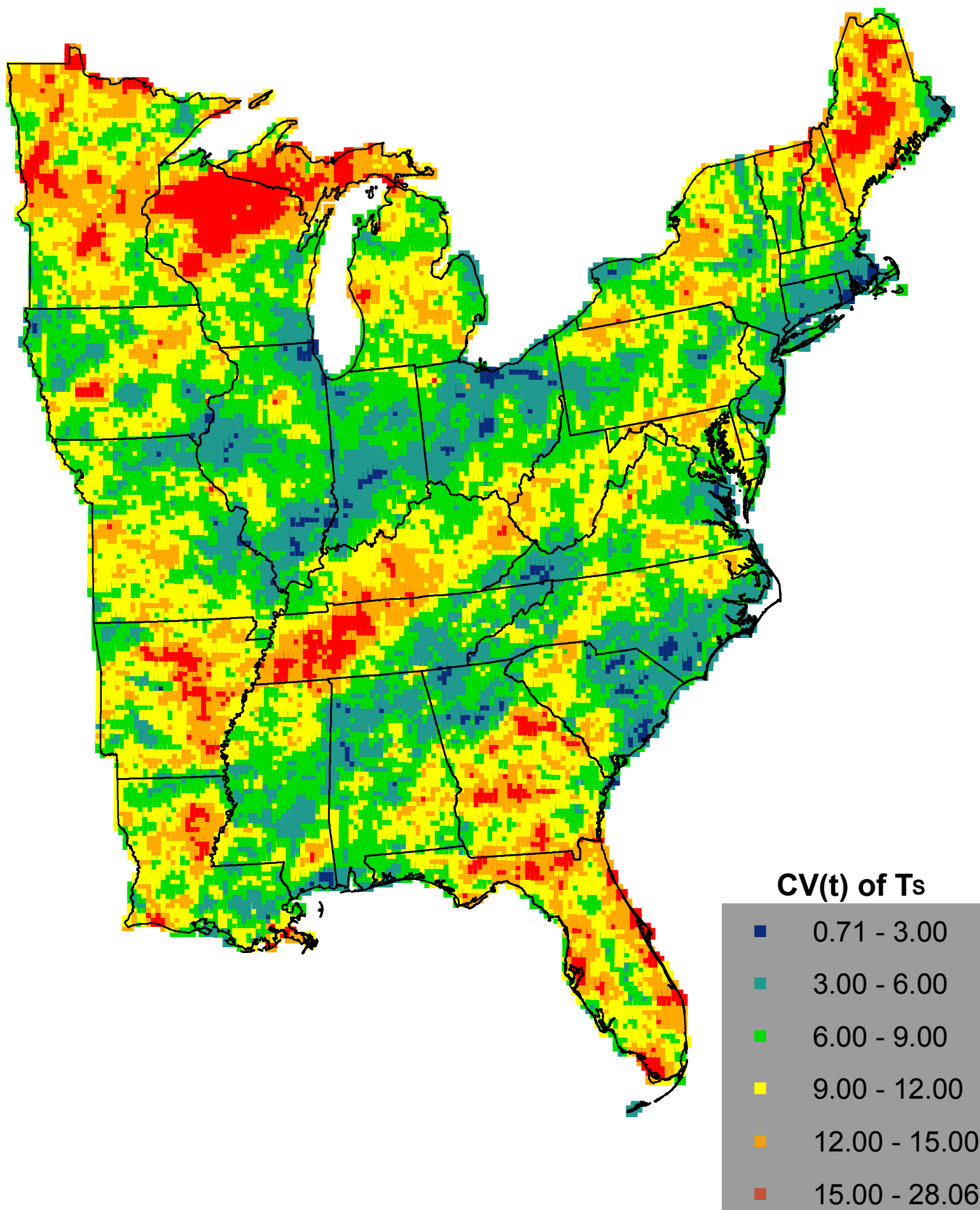


CMAQ (mean) DNOytotal vs CNOyg
5 year means









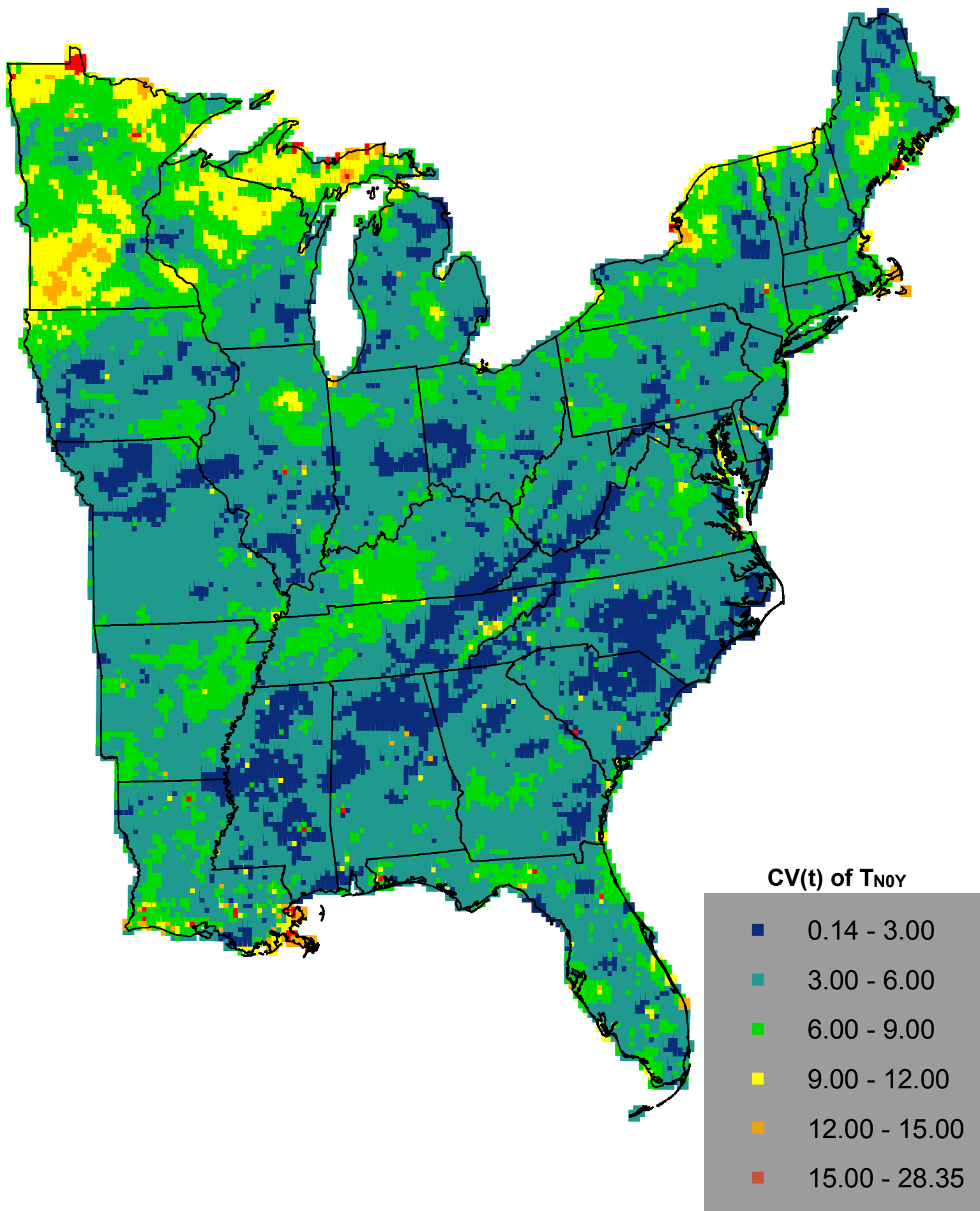


Table 1. Model and monitored concentration, total deposition, transference ratios, and relative differences at CASTNET site locations for specific years

Site	Year	Concentration RD, %			Deposition RD, %			Transference Ratio RD, %		
		CMAQ	CASTNET		CMAQ	CASTNET		CMAQ	CASTNET	
Oxidized Sulfur		C _{Sg} (µgS/m3)			D _{Stotal} (kgS/hA-y)			T _s (kgS/hA-y)(m3/µgS)		
BVL130	2002	5.36	4.38	22	10.73	8.93	20	2.00	2.04	-2
BVL130	2003	5.54	4.54	22	12.28	8.95	37	2.22	1.97	12
COW137	2002	2.82	2.06	37	8.22	5.64	46	2.92	2.74	6
COW137	2004	2.77	1.88	47	8.07	6.37	27	2.91	3.39	-14
CTH110	2002	4.44	5.03	-12	17.77	10.52	69	4.00	2.09	91
ESP127	2004	3.99	3.69	8	12.60	10.71	18	3.16	2.91	9
OXF122	2002	8.16	6.93	18	22.50	13.74	64	2.76	1.98	39
OXF122	2003	8.19	7.66	7	23.73	17.72	34	2.90	2.31	25
OXF122	2004	8.33	8.07	3	22.84	15.15	51	2.74	1.88	46
PAR107	2002	4.70	4.67	1	29.11	12.39	135	6.20	2.65	134
PSU106	2002	6.28	7.04	-11	18.28	17.85	2	2.91	2.53	15
PSU106	2004	6.25	7.35	-15	18.25	19.35	-6	2.92	2.63	11
SAL133	2002	5.61	4.74	18	13.16	8.96	47	2.35	1.89	24
SHN418	2004	4.71	4.79	-2	14.29	10.65	34	3.03	2.22	37
VPI120	2002	6.48	5.77	12	23.23	9.06	156	3.58	1.57	128
VPI120	2003	6.45	5.70	13	22.20	11.24	98	3.44	1.97	74
WSP144	2002	6.97	6.22	12	17.04	13.28	28	2.45	2.14	15
Monitored Oxidized Nitrogen (OxN)		C _{OxNg} (µgN/m3)			D _{OxNtotal} (kgN/hA-y)			T _{OxN} (kgN/hA-y)(m3/µgN)		
COW137	2002	0.48	0.23	107	4.93	2.90	70	10.26	12.50	-18
COW137	2004	0.43	0.20	120	4.15	2.97	39	9.61	15.13	-37
CTH110	2002	0.69	0.63	10	7.16	5.43	32	10.30	8.58	20
ESP127	2004	0.67	0.47	42	6.01	4.10	47	9.01	8.70	4
OXF122	2002	1.48	0.94	57	8.02	5.71	40	5.42	6.07	-11
OXF122	2003	1.39	0.95	47	7.74	6.40	21	5.55	6.75	-18
OXF122	2004	1.26	0.84	49	7.05	4.74	49	5.61	5.63	0
PAR107	2002	0.62	0.42	50	11.86	4.88	143	19.01	11.76	62
PSU106	2002	0.88	0.75	18	7.04	6.72	5	7.99	8.96	-11
PSU106	2004	0.83	0.73	14	6.46	5.70	13	7.78	7.84	-1
SHN418	2004	0.72	0.56	29	4.99	4.74	5	6.88	8.44	-18
VPI120	2002	0.61	0.60	1	7.06	4.24	66	11.63	7.09	64
WSP144	2002	1.18	0.83	42	8.46	6.27	35	7.17	7.52	-5

Relative Difference (RD) = 100 (CMAQ-CASTNET) / CASTNET

To convert the units of transference ratio to cm/s, divide by 3.1536.

Table 2. Regional correlation and mean ratios of selected CMAQ variables using 5-year (2002-2006) cell mean values

Region	Variable	Pearson Correlation				Mean Ratio	
		Concentration		Deposition		Concentration	Deposition
		C_{Sg}	C_{OxNg}	C_{NOyg}	$D_{NOytotal}$	C_{OxNg} / C_{NOyg}	$D_{OxNtotal} / D_{NOytotal}$
EAST	D_{Stotal}	0.90					
ADR	D_{Stotal}	0.54					
CC	D_{Stotal}	0.80					
HEL	D_{Stotal}	0.46					
NEU	D_{Stotal}	0.79					
POT	D_{Stotal}	0.66					
EAST	C_{NOyg}		0.64			0.21	0.78
ADR	C_{NOyg}		0.84			0.24	0.85
CC	C_{NOyg}		0.69			0.20	0.78
HEL	C_{NOyg}		0.72			0.20	0.79
NEU	C_{NOyg}		0.75			0.20	0.75
POT	C_{NOyg}		0.79			0.18	0.77
EAST	$D_{OxNtotal}$		0.55	0.49	0.98		
ADR	$D_{OxNtotal}$		0.41	0.07	1.00		
CC	$D_{OxNtotal}$		0.20	0.25	0.95		
HEL	$D_{OxNtotal}$		0.30	-0.06	0.99		
NEU	$D_{OxNtotal}$		0.22	0.51	0.94		
POT	$D_{OxNtotal}$		0.48	0.47	0.97		
EAST	$D_{NOytotal}$		0.58	0.62			
ADR	$D_{NOytotal}$		0.43	0.10			
CC	$D_{NOytotal}$		0.39	0.53			
HEL	$D_{NOytotal}$		0.38	0.08			
NEU	$D_{NOytotal}$		0.47	0.76			
POT	$D_{NOytotal}$		0.62	0.66			

See Table 1 for units on concentration (C) and deposition (D).

Table 3. CMAQ-estimated deposition, concentration, and transference ratios for 2002-2006: Regional means (across cells) of 5-year average cell values, spatial variability (CV(s)) and temporal variability (CV(t))

Oxidized Sulfur		D _{Stotal}					C _{Sg}					T _s				
Sub-Region	n	Mean	CV(s)	CV(t)			Mean	CV(s)	CV(t)			Mean	CV(s)	CV(t)		
				Mean	Min	Max			Mean	Min	Max			Mean	Min	Max
ADR	162	9.47	21	8	1	15	1.93	12	7	5	8	4.90	16	10	3	15
CC	500	11.90	19	7	1	17	4.35	25	4	1	22	2.80	14	8	3	14
HEL	276	13.51	22	5	2	24	3.71	19	5	0	16	3.70	22	6	2	13
NEU	101	10.75	12	6	3	10	3.93	20	4	2	12	2.80	13	6	3	11
POT	251	15.79	27	10	3	22	6.38	28	4	2	19	2.54	22	10	2	15
NO _y		D _{NOytotal}					C _{NOyg}					T _{NOy}				
ADR	162	6.01	21	10	5	16	1.79	20	7	5	13	3.44	24	6	1	11
CC	500	6.75	13	7	1	16	3.76	32	6	2	24	1.92	26	4	1	10
HEL	276	7.17	15	6	2	11	2.70	23	6	1	15	2.78	24	4	1	12
NEU	101	6.12	16	6	2	9	4.15	42	6	2	14	1.63	30	3	1	6
POT	251	7.89	21	8	5	12	5.55	55	7	3	19	1.67	36	4	1	10

See Table 1 for units on deposition (D), concentration (C), and transference ratio (T)

CV(s) is a measure of spatial variability; it is the CV of 5-year means across cells within a sub-region (a specific value)

CV(t) is a measure of temporal variability from the regional distribution of cell-specific 5-year CV values

Table 4. Assessments using two sets of assumptions of modeled cell behavior representing modeled regional behavior

Case 1: Assume modeled cell-specific values are regionally representative																	
Year		RD = Relative Difference (%) = 100 (Estimated-Simulated) / Simulated															
Sub-Region		RD for Oxidized Sulfur Total Deposition								RD for NO_y Total Deposition Predictions							
		Min	2.5%-tile	25%-tile	Median	75%-tile	97.5%-tile	Max	Mean	Min	2.5%-tile	25%-tile	Median	75%-tile	97.5%-tile	Max	Mean
2005	ADR	-35	-25	-2	14	31	82	91	16	-60	-28	-11	5	24	53	62	7
2005	CC	-32	-25	-15	-4	6	43	155	-1	-51	-31	-12	-2	5	21	42	-4
2005	HEL	-48	-36	-11	6	22	45	121	7	-41	-33	-13	-1	8	23	29	3
2005	NEU	-24	-19	-10	-4	3	39	45	6	-28	-24	-16	-7	8	32	40	-2
2005	POT	-39	-34	-5	8	27	86	130	-1	-44	-37	-13	1	20	44	53	-4
2006	ADR	-48	-40	-22	-10	5	46	53	-7	-64	-34	-15	-1	17	49	58	1
2006	CC	-28	-21	-10	3	14	56	170	5	-50	-26	-9	2	9	22	37	0
2006	HEL	-47	-38	-9	8	23	50	140	6	-39	-31	-12	0	10	24	31	1
2006	NEU	-23	-18	-10	-3	5	42	45	7	-26	-22	-15	-5	13	42	49	-2
2006	POT	-36	-28	-1	12	26	112	149	0	-43	-37	-15	0	16	45	55	0
Case 2: Assume modeled cell-specific values can be scaled to become regionally representative																	
2005	ADR	9	13	16	17	18	19	21	17	-4	0	4	7	10	14	16	7
2005	CC	-25	-7	-2	-1	1	3	6	-1	-25	-12	-6	-3	0	3	13	-3
2005	HEL	-11	-2	4	6	8	13	17	6	-11	-8	-4	-2	-1	2	7	-2
2005	NEU	-20	-6	-2	-1	0	2	3	-1	-17	-9	-5	-4	-2	2	2	-4
2005	POT	-7	5	12	14	16	19	20	14	-14	-4	0	4	5	8	11	3
2006	ADR	-11	-9	-8	-7	-7	-5	-4	-7	-6	-4	0	2	3	4	5	1
2006	CC	-20	0	4	5	7	10	16	5	-16	-6	-2	0	1	5	15	0
2006	HEL	-28	-5	6	8	10	13	15	7	-12	-8	-4	-2	0	5	9	-2
2006	NEU	-12	-4	-1	0	1	3	4	0	-10	-4	-1	-1	1	5	6	0
2006	POT	-16	2	12	17	24	32	35	18	-13	-5	-1	1	3	7	9	1

Table 5. Variability estimates for regional deposition associated with uncertainties in hypothetical monitored airborne concentration and temporal variability in 5-y averages of annual CMAQ-estimated cell-specific airborne concentration and regional deposition

Sub-Region	Hypothetical Concentration CV (%)	Regional Deposition CV (%)									
		Oxidized Sulfur					NO _y				
		Min	2.5%-tile	Median	97.5%-tile	Max	Min	2.5%-tile	Median	97.5%-tile	Max
ADR	3	4.3	4.6	4.8	5.1	5.2	3.2	3.3	3.6	4.3	4.4
ADR	4.47	5.5	5.7	5.9	6.1	6.2	4.6	4.6	4.9	5.4	5.5
ADR	5.77	6.6	6.8	6.9	7.1	7.2	5.9	5.9	6.1	6.5	6.6
ADR	10	10.5	10.6	10.7	10.8	10.9	10.1	10.1	10.2	10.5	10.5
ADR	15	15.3	15.4	15.5	15.6	15.6	15.0	15.1	15.1	15.3	15.4
CC	3	3.4	3.7	4.5	5.4	8.8	3.1	3.2	3.5	4.2	8.2
CC	4.47	4.8	4.9	5.6	6.3	9.4	4.6	4.6	4.8	5.4	8.9
CC	5.77	6.0	6.1	6.7	7.3	10.1	5.8	5.9	6.1	6.5	9.6
CC	10	10.1	10.2	10.6	11.0	13.0	10.0	10.1	10.2	10.4	12.6
CC	15	15.1	15.2	15.4	15.7	17.2	15.0	15.0	15.1	15.3	16.9
HEL	3	3.2	3.3	3.8	4.7	8.1	3.0	3.0	3.1	3.8	5.0
HEL	4.47	4.6	4.7	5.0	5.7	8.7	4.5	4.5	4.6	5.0	6.0
HEL	5.77	5.9	6.0	6.2	6.8	9.5	5.8	5.8	5.8	6.2	7.0
HEL	10	10.1	10.1	10.3	10.6	12.5	10.0	10.0	10.0	10.3	10.8
HEL	15	15.0	15.1	15.2	15.4	16.8	15.0	15.0	15.0	15.2	15.5
NEU	3	3.4	3.4	3.5	4.1	6.7	3.1	3.1	3.2	3.7	5.1
NEU	4.47	4.7	4.7	4.8	5.3	7.5	4.5	4.5	4.6	5.0	6.1
NEU	5.77	6.0	6.0	6.1	6.4	8.3	5.8	5.8	5.9	6.2	7.1
NEU	10	10.1	10.1	10.2	10.4	11.7	10.0	10.0	10.1	10.2	10.8
NEU	15	15.1	15.1	15.1	15.3	16.2	15.0	15.0	15.0	15.2	15.6
POT	3	3.4	4.0	5.2	6.8	7.6	3.0	3.1	3.4	4.7	6.2
POT	4.47	4.7	5.2	6.2	7.6	8.3	4.5	4.6	4.8	5.7	7.1
POT	5.77	6.0	6.4	7.2	8.4	9.0	5.8	5.8	6.0	6.8	8.0
POT	10	10.1	10.4	10.9	11.8	12.2	10.0	10.0	10.1	10.6	11.4
POT	15	15.1	15.2	15.6	16.2	16.6	15.0	15.0	15.1	15.4	16.0

Assuming a hypothetical annual CV of 10% for monitored concentration, five years of monitoring would yield mean monitored concentrations with 5-y CVs of 4.47% (i.e., $10/\sqrt{5} = 4.47$), and three years of monitoring would yield mean monitored concentrations with CVs of 5.77%