3.2 MODELLING LONG-TERM SULPHUR AND NITROGEN DEPOSITION USING LAGRANGIAN CHEMICAL TRANSPORT MODELS

Michael D. Moran* and Qiong Zheng
Meteorological Service of Canada, 4905 Dufferin Street, Toronto, Ontario, M3H 5T4, Canada

1. INTRODUCTION

A crucial link in understanding and managing acid deposition is the ability to relate *quantitatively* the magnitudes and geographic distributions of acidifying emissions to the resulting air-concentration and deposition patterns of acidifying species. Lagrangian chemical transport models (LCTMs) are prognostic, emissions-based numerical models that have been used extensively to predict present and future-year seasonal and annual acid deposition. Because LCTMs are simpler in their formulations and less demanding in their computational and input requirements than Eulerian models (e.g., Pasquill and Smith, 1983), LCTMs have been the preferred means to perform the data-intensive and computationally-demanding generation of reduced-form representations of long-term atmospheric dispersion, chemistry, and removal known as source-receptor matrices (SRMs). Such reduced-form representations are needed by integrated assessment models, dynamic surface-water-chemistry models, life-cycle analysis models, and other multi-disciplinary modelling systems to link changes in emissions with changes in atmospheric concentrations and deposition and subsequent aquatic and terrestrial environmental effects (e.g., Lam et al., 1998; Clair et al., 2004; Norris, 2003).

This paper explores the adaptation of two regional LCTMs to simulate long-term sulphur and nitrogen ambient concentrations and deposition in North America. The first LCTM, the AES[†] Lagrangian Sulphur Model or ALSM, is a simple and venerable sulphur-cycle LCTM that has been extended to generate three types of sulphur-specie SRMs for the 1990 meteorological year for 40 SO_2 emission regions and 200 receptors spanning most of North America. Before creating the SRMs, annual and quarterly results for the ALSM using full 1990 emissions showed good agreement with 1990 observed air- and precipitation-chemistry station data. 1990-based SRM predictions have also been evaluated against 2001-2003 observations and against the observed *changes* between 1990 and 2001-2003. As well, it is demonstrated with the use of examples that visualization of the rows and columns of the new 1990-based unit-emission SRMs and percent-contribution SRMs can provide useful insights into potential and actual source and receptor “footprints” for different regions of the continent.

The second LCTM is a new and more complex model called LIAM (Lagrangian Inorganic Aerosol Model) that is being developed at the Meteorological Service of Canada (MSC) to predict sulphur, oxidized nitrogen, and reduced nitrogen concentrations and deposition with the objective of generating SRMs for both sulphur and nitrogen species. LIAM includes 28 transported gas-phase species plus particulate sulphate, nitrate, and ammonium, a detailed gas-phase chemistry mechanism, simple SO_2 aqueous-phase chemistry and NH_4NO_3 heterogeneous chemistry, and dry and wet removal processes for both gases and particles.

The ALSM is described in Section 2 along with results from an evaluation of its predictions of North American sulphur-species air concentrations and wet deposition for 1990. Section 3 presents results from the application of the ALSM (a) to calculate 1990 sulphur-species SRMs and (b) to predict sulphur-species air-concentration and wet-deposition fields for 2002 using the 1990 SRMs. LIAM is described in Section 4, followed by a summary and conclusions in Section 5.

2. AES LAGRANGIAN SULPHUR MODEL

2.1 ALSM Model Description

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* *Corresponding author address:* Michael D. Moran, Air Quality Research Branch, Meteorological Service of Canada, Toronto, Ontario, M3H 5T4, Canada; e-mail: mike.moran@ec.gc.ca

[†] The Atmospheric Environment Service (AES) is the former name of the Meteorological Service of Canada (MSC).

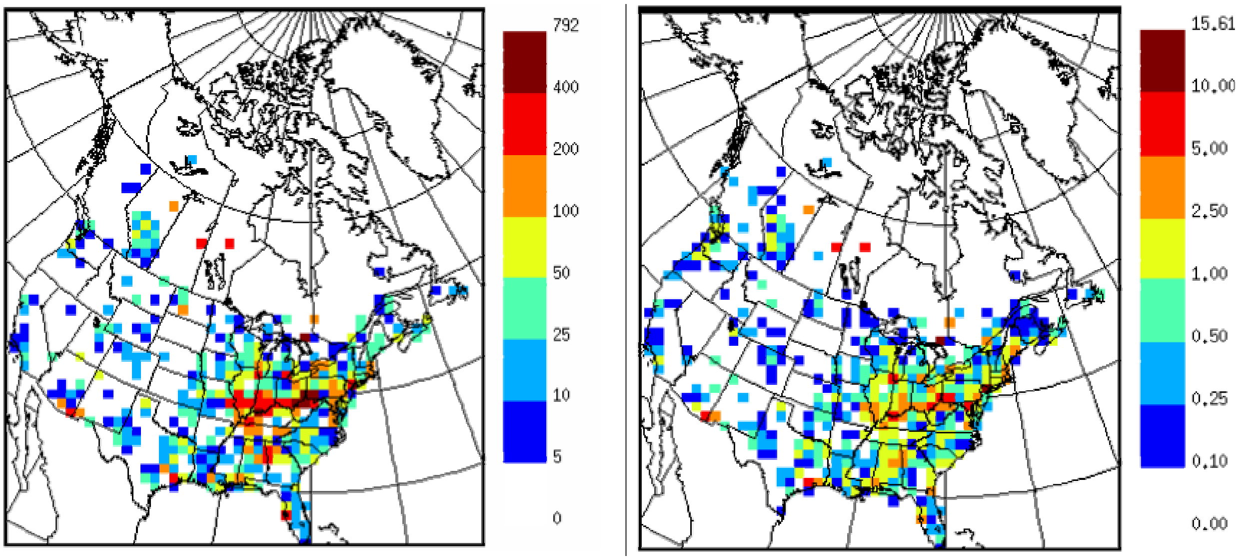

Figure 1. Spatial distribution of 1990 annual (a) SO_2 emissions (Ktonnes SO_2 y^{-1}) and (b) SO_4 emissions (Ktonnes SO_4 y^{-1}) on 127-km by 127-km ALSM grid.

The ALSM is a Lagrangian long-range transport and transformation model for SO_2 and $SO_4^=$ that has been used at MSC in studies of sulphur acid deposition in eastern North America for the past 20 years (e.g., Olson et al., 1982, 1983; Clark et al., 1989; Olson and Oikawa, 1989; RMCC, 1990, Environment Canada, 1997a). It consists of two components: a backward trajectory model requiring only meteorological input fields and a forward "moving-box" chemistry model with emissions and deposition. To run the ALSM, four-day-long, three-dimensional back trajectories are first calculated at six-hour intervals for each day (i.e., four trajectories per day) of the simulation period for each receptor site considered. The back trajectories are initiated from the 925-mb level and a three-hour integration time step is used. The horizontal grid associated with the ALSM is 52 by 58 grid points in size with 127-km by 127-km spacing between grid points on a polar stereographic projection of the Northern Hemisphere (see Figure 1). The one-layer chemistry box model then follows each pre-calculated four-day back trajectory forward in time from the end point to the starting point at the receptor. The sulphur chemistry is assumed to be linear and month- or season-averaged process parameterization coefficients are used (e.g., monthly dry deposition velocities, seasonal mixing heights). Gridded season-average SO_2 and $SO_4^=$ emissions are supplied on the 127-km by 127-k model grid. SO_2 and $SO_4^=$ concentrations in the moving box are assumed to be well mixed in the vertical at all times, and the layer is assumed to be capped by an inversion so that injections from above are not allowed. A constant transformation rate of 1% hr^{-1} is assumed for the oxidation of SO_2 to $SO_4^=$. Wet deposition is parameterized as the product of a scavenging ratio and six-hourly precipitation amounts.

2.2 1990 ALSM Simulation

The ALSM was run for the entire 1990 meteorological year using 1990 emissions. The required wind and precipitation fields were obtained from Canadian Meteorological Centre (CMC) archived analyses on a larger, 190.5-km, hemispheric polar-stereographic grid and then interpolated to the 127-km ALSM grid by bilinear interpolation. A set of 1990 gridded seasonal SO_2 and $SO_4^=$ emission fields were prepared using the 1990 Canadian and U.S. national criteria-air-contaminant emission inventories and the Canadian Emissions Processing System (Scholtz et al., 1999). Figure 1 shows the spatial distribution of SO_2 and SO_4 emissions on the ALSM grid. Most of the SO_2 emissions occur east of the Mississippi River, but large sources are also located in Texas, Arizona, Alberta, and Manitoba. The total annual SO_2 emissions for 1990 were 23.45 Mtonnes SO_2 y^{-1}, while primary SO_4 emissions were two orders of magnitude smaller, at 0.46 Mtonnes SO_4 y^{-1}. Each of the 3,016 (=52x58) ALSM grid points was treated as a receptor, and annual values at each receptor

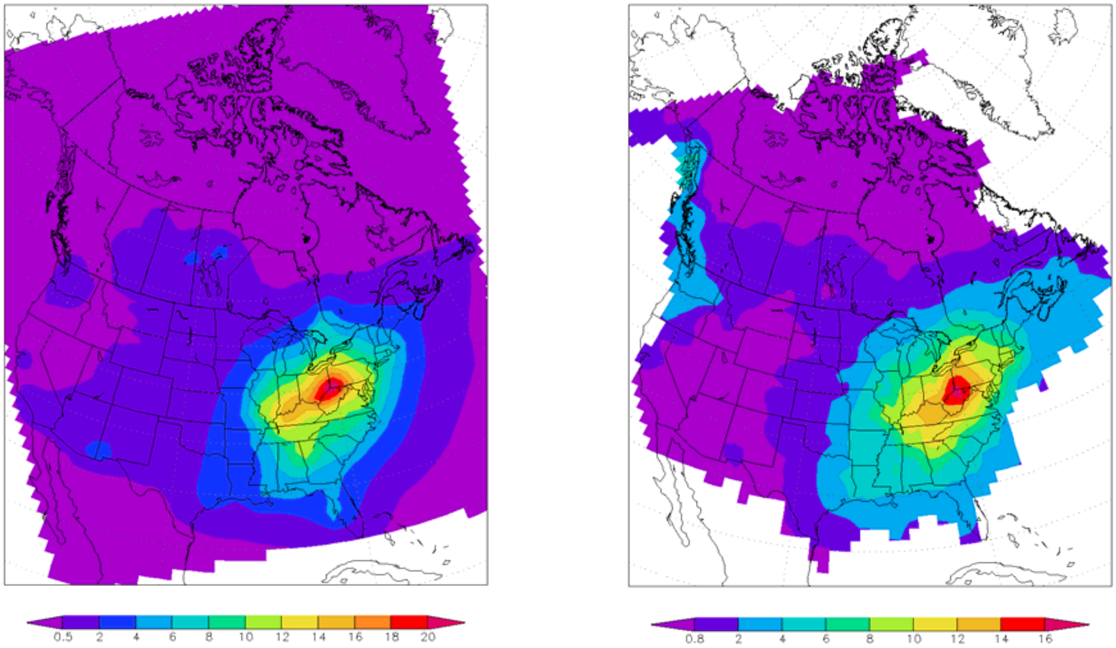

Figure 2. ALSM-predicted annual 1990 total-S (a) air concentration (µg S m^{-3}) and (b) wet deposition (kg S ha^{-1} y^{-1}) based on 1990 meteorology and 1990 emissions, where total sulphur S is calculated as $0.5*SO_2 + 0.3333*SO_4$. Contouring was performed with the GrADS visualization package.

were determined as the average of 1,460 trajectory values (=4x365) from the forward chemistry model. Eight quantities were calculated: (a) SO_2 air concentration; (b) SO_4 air concentration; (c) wet sulphur concentration in precipitation; (d) SO_2 dry deposition; (e) SO_4 dry deposition; (f) SO_2 wet deposition; (g) SO_4 wet deposition; and (h) precipitation.

Figure 2 shows the predicted spatial distribution of two quantities derived from the ALSM-predicted annual values for the “full grid” of 3,016 receptors, namely total-sulphur air concentration and total-sulphur wet deposition. These contoured fields were produced using OACRES, the Cressman inverse-square-weighting objective analysis function of the GrADS visualization package. The two fields are quite similar and broadly reflect the distribution of SO_2 and SO_4 emissions shown in Figure 1. Maxima of both total-sulphur air concentration and total-sulphur wet deposition are located over the Ohio Valley region of eastern North America. The secondary maximum in wet deposition predicted to occur in the Pacific Northwest is due to the high levels of precipitation that occur there (see Figure 3a).

2.3 1990 ALSM Performance Evaluation

To evaluate ALSM performance for the 1990 annual simulation, data sets of 1990 air-chemistry and precipitation-chemistry measurements were obtained from MSC’s NAtChem database (see http://www.msc.ec.gc.ca/natchem/index_e.html). Three air-chemistry networks (CAPMoN, CASTNet, IMPROVE) and nine precipitation-chemistry networks (CAPMoN, NADP, and seven Canadian provincial networks) were considered. In calculating observed annual values from the available daily and weekly measurements, one completeness criterion was applied for the air-chemistry data: a station must have ≥75% of its data as valid and not missing in the summary period. Eight of the 75 available air-chemistry stations were screened out by this criterion. For the precipitation-chemistry data, two completeness criteria were applied: first, precipitation coverage length (percentage of days with measured precipitation plus zero precipitation days in the summary period) for a station must be ≥ 90%, and second, a station must have had ≥70% of its data as valid and not missing in the summary period. 85 of the 402 available precipitation-chemistry stations were screened out by these criteria for annual values (i.e., 402 stations have quarterly summary data, 317 have annual summary data). Finally, in order

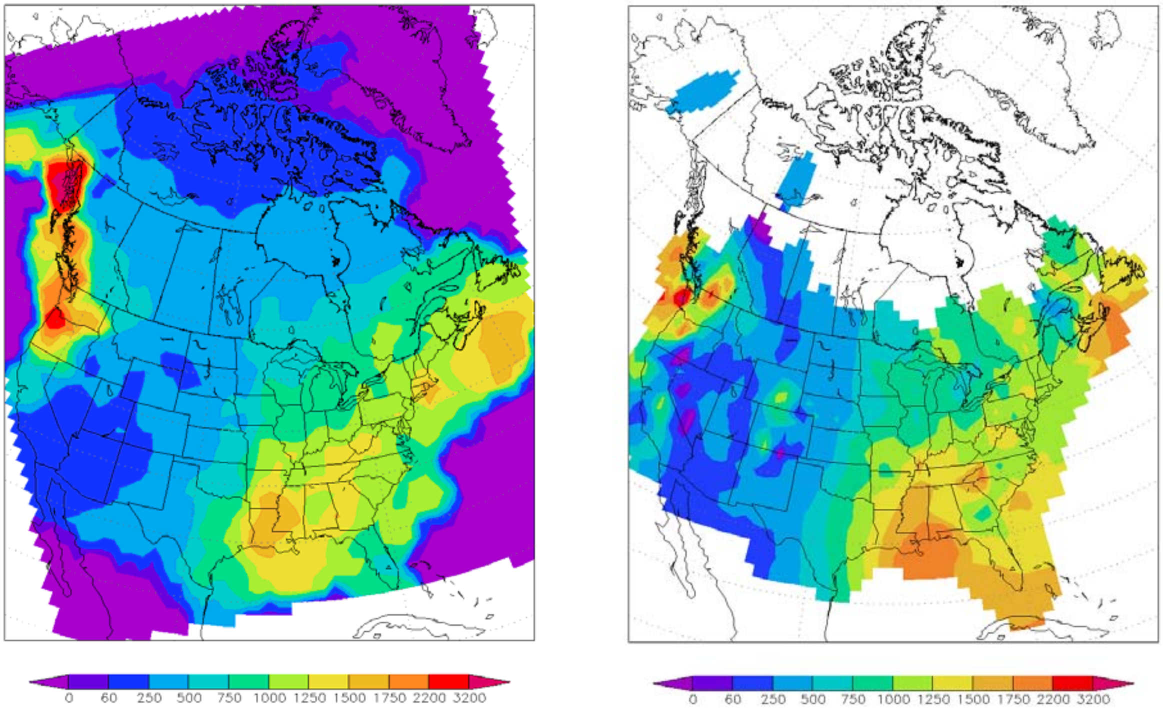

Figure 3. Annual precipitation (mm y^{-1}) for (a) 1990 from ALSM input files based on CMC analyses of 6-hourly accumulated precipitation and (b) for 2001-2003 period based on measurements from 265 precipitation-chemistry stations.

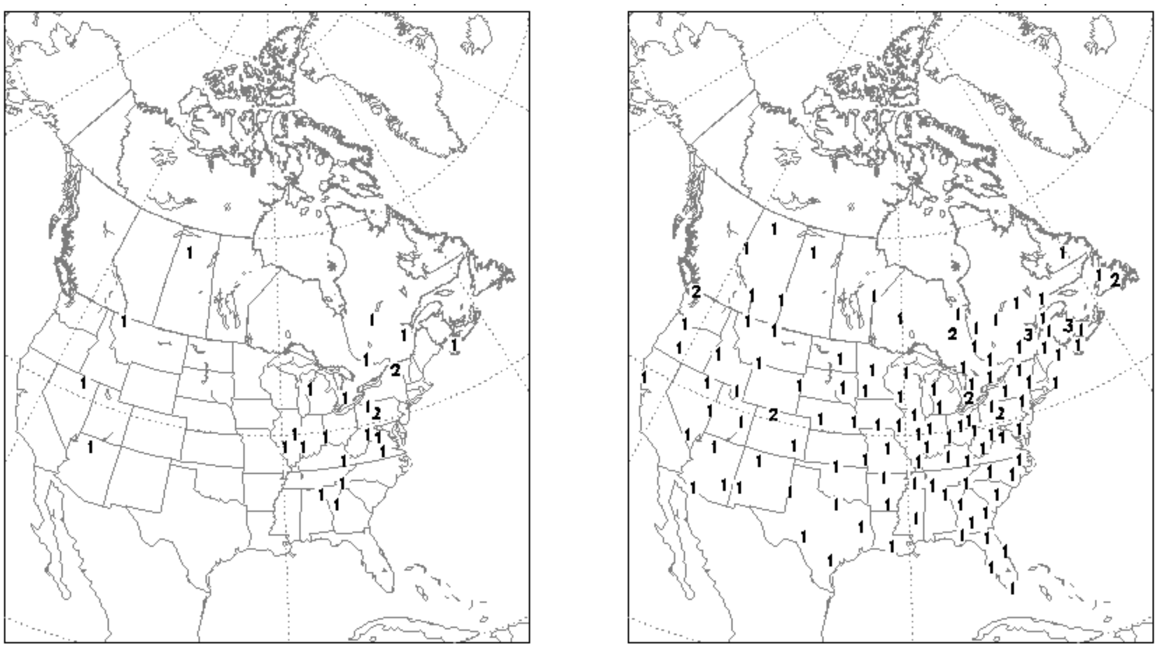

Figure 4. Locations of (a) 24 receptors with valid filter-chemistry data and (b) 114 receptors with valid precipitation-chemistry data considered in scatterplots in Figures 5 and 6, respectively, for 1990 annual evaluation. The number plotted at each receptor site indicates the number of measurement stations with valid data within a 20-km radius of that receptor location.

to compare the point measurements to model predictions, values for all samplers located within 20 km of one of a set of 200 ALSM receptors (see next section) were averaged together. As a result, ALSM predictions could be compared with air-chemistry measurements for 24 receptors (mostly located in eastern North America) and with precipitation-chemistry measurements for

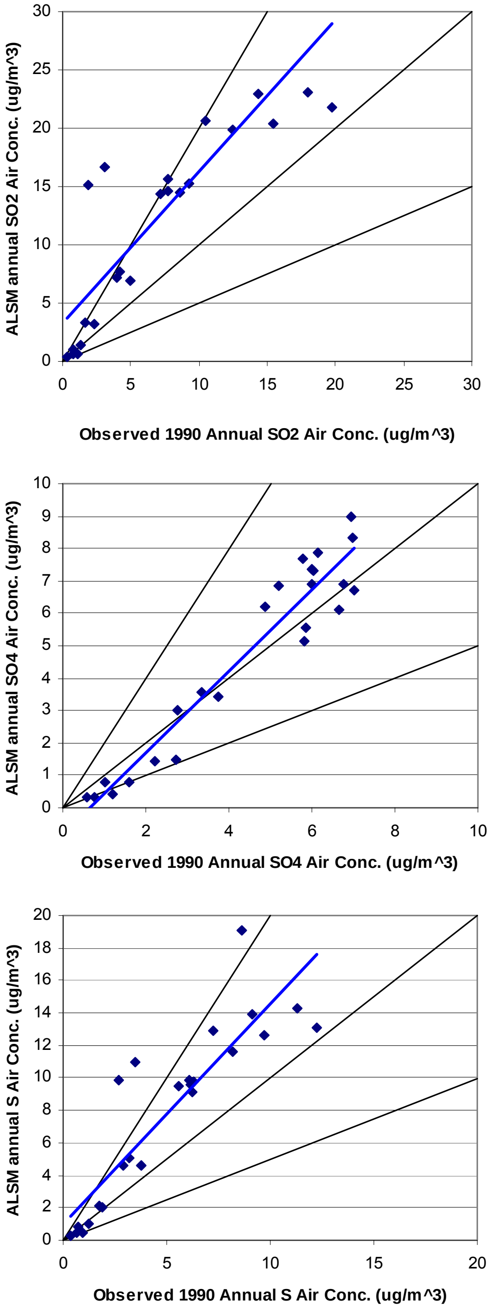

Figure 5. Scatterplots of 1990 predicted vs. observed annual ambient (a) SO_2 air concentration (μg SO_2 m^{-3}), (b) SO_4 air concentration (μg SO_4 m^{-3}), and (c) total-S air concentration (μg S m^{-3}) for 24 receptors.

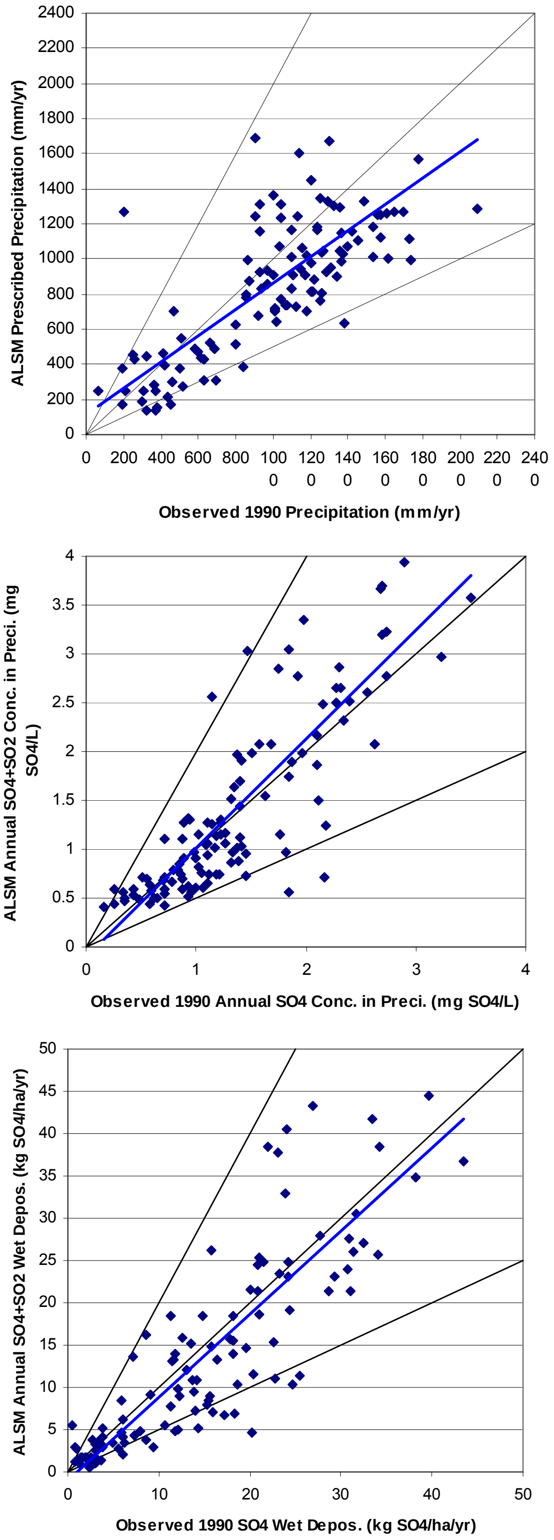

Figure 6. Scatterplots of 1990 predicted vs. observed annual (a) precipitation (mm y^{-1}), (b) total-S concentration in precipitation (mg SO_4 L^{-1}), and (c) total-S wet deposition (kg S ha^{-1} y^{-1}) for 114 receptors.

114 receptors spanning much of North America (see Figure 4).

Figure 5 shows scatterplots of 1990 predicted vs. 1990 observed annual ambient SO_2, SO_4, and total S air concentrations. The ALSM is biased high for annual SO_2 air concentrations but not for annual SO_4 air concentrations, and the scatterplot for total-S air concentration is in between. The overprediction for SO_2 may at least in part be attributable to the so-called “home-grid-cell problem”, in that SO_2 emitted anywhere in a model grid cell is assumed to disperse immediately throughout the grid cell, whereas in the real world a source will influence even a nearby receptor only intermittently depending upon the wind direction. The squared correlation coefficient (R^2) values for these three scatterplots are 0.72, 0.92, and 0.79, respectively. Figure 6 shows corresponding scatterplots of 1990 predicted vs. 1990 observed annual precipitation, total-S concentration in precipitation, and total-S wet deposition. Of these three quantities, the R^2 value is lowest for precipitation (0.59) compared to total-S concentration in precipitation (0.71) and total-S wet deposition (0.73). Interestingly, the ALSM annual precipitation for 1990 tends to be lower than the 1990 observed precipitation at the 114 precipitation-chemistry stations considered here, and this negative bias is also seen in the total-S wet deposition scatterplot, whereas the total-S concentration in precipitation, which is less

Table 1. Annual and Quarterly Evaluation Statistics for ALSM Predictions vs. 1990 Observed Values of Ambient SO_2 Air Concentration, Ambient SO_4 Air Concentration, Total-Sulphur Concentration in Precipitation, and Total-Sulphur Wet Deposition.

Species and Period	No. of Stations	Model Mean	Observed Mean	Mean Bias	RMSE	R Square	Slope m	Y-intercept b
1990 SO2 Air Concentration (ug SO2/m^3)								
Annual	24	12.484	7.083	5.401	7.346	0.720	1.303	3.254
Quarter 1	24	18.612	9.852	8.760	11.805	0.643	1.335	5.460
Quarter 2	25	9.956	5.499	4.457	5.848	0.762	1.401	2.250
Quarter 3	24	9.495	4.876	4.619	6.272	0.729	1.428	2.531
Quarter 4	25	13.596	9.307	4.289	6.687	0.687	0.989	4.389
1990 SO4 Air Concentration (ug SO4/m^3)								
Annual	24	4.727	4.418	0.309	1.043	0.918	1.252	-0.815
Quarter 1	24	4.829	3.088	1.741	2.632	0.712	2.102	-1.661
Quarter 2	25	4.212	5.016	-0.804	1.125	0.906	1.048	-1.044
Quarter 3	24	5.976	7.203	-1.227	1.558	0.957	0.887	-0.416
Quarter 4	25	4.257	2.750	1.507	2.091	0.838	1.816	-0.737
1990 S Concentration in Precipitation (mg S/L)								
Annual	114	1.417	1.367	0.049	0.516	0.709	1.116	-0.109
Quarter 1	118	1.089	1.206	-0.117	0.507	0.512	0.620	0.341
Quarter 2	117	1.640	1.563	0.077	0.734	0.670	1.212	-0.255
Quarter 3	111	1.787	1.778	0.009	0.919	0.626	1.047	-0.075
Quarter 4	110	1.012	1.017	-0.005	0.499	0.321	0.562	0.440
1990 S Wet Deposition (kg S/ha/y)								
Annual	114	12.061	14.778	-2.716	6.366	0.733	0.837	-0.314
Quarter 1	118	1.992	2.716	-0.725	1.589	0.502	0.536	0.535
Quarter 2	117	3.707	4.348	-0.641	2.605	0.627	0.851	0.007
Quarter 3	111	3.747	4.572	-0.825	2.598	0.691	0.821	-0.004
Quarter 4	110	2.261	2.733	-0.472	1.549	0.572	0.668	0.435

dependent on precipitation amount, shows a slight positive bias.

Table 1 summarizes observed and predicted seasonal behaviour for the four quarters of 1990. On a quarterly basis, SO_2 ambient air concentrations were observed and predicted to be highest in the first quarter (Jan.-Mar.) and lowest in the third quarter (Jul.-Sep.), while SO_4 ambient air concentrations were observed and predicted to be highest in the third quarter (Jul.-Sep.) and lowest in the fourth quarter (Oct.-Dec.). Like SO_4 ambient air concentration, total-S concentration in precipitation was highest in the third quarter and lowest in the fourth quarter. Total-S wet deposition, on the other hand, was also highest in the third quarter but was lowest in the first quarter. Except for the first quarter, the R^2 values were higher for SO_4 ambient air concentration, a secondary pollutant, than for SO_2 ambient air concentration, a primary pollutant. For total-S concentration in precipitation and total-S wet deposition, the annual R^2 values were higher than any of the quarterly values.

3. RECENT ALSM APPLICATIONS

3.1 Generation of 1990-Based Source-Receptor Matrices

The results of the performance evaluation described in Section 2.3 demonstrated that the ALSM had considerable skill in simulating that meteorological year. Given that positive outcome, the ALSM was next used to generate a set of annual sulphur-specie SRMs for the 1990 meteorological year as described in this section.

3.1.1 General methodology

The ALSM has been used in the past to construct atmospheric source-receptor matrices (SRMs) for sulphur species for three different meteorological years: 1978; 1980; and 1985 (Olson et al., 1983; Lam et al., 1998). The term "matrix" refers to the simple mathematical form of the linear source-receptor framework:

$$\mathbf{c} = T\,\mathbf{e}\,, \qquad (1)$$

where **c** is a one-dimensional column vector of concentration or deposition values for a set of receptors, T is a two-dimensional transfer matrix or source-receptor matrix, and **e** is a one-dimensional column vector of emissions from a set of source regions (e.g., Young and Shaw, 1986; Hidy, 1994). Each row of T is associated with a particular receptor and each column of T is associated with a particular source region. For SRMs to be practical tools, both the representation of sources (i.e., emissions) and receptors (i.e., concentrations and deposition) must be simplified. Figure 7 shows the division of North America into 40 source regions, 15 in Canada and 25 in the U.S, that was used for the earlier studies. The smaller size and greater number of source regions on the eastern half of the continent reflects both the higher emissions in that region and the focus of acid deposition control measures on that region. However, the location of emissions within these source regions, that is, the subregional emissions "structure", is not uniform but rather is determined by the gridded set of emissions shown in Figure 1.

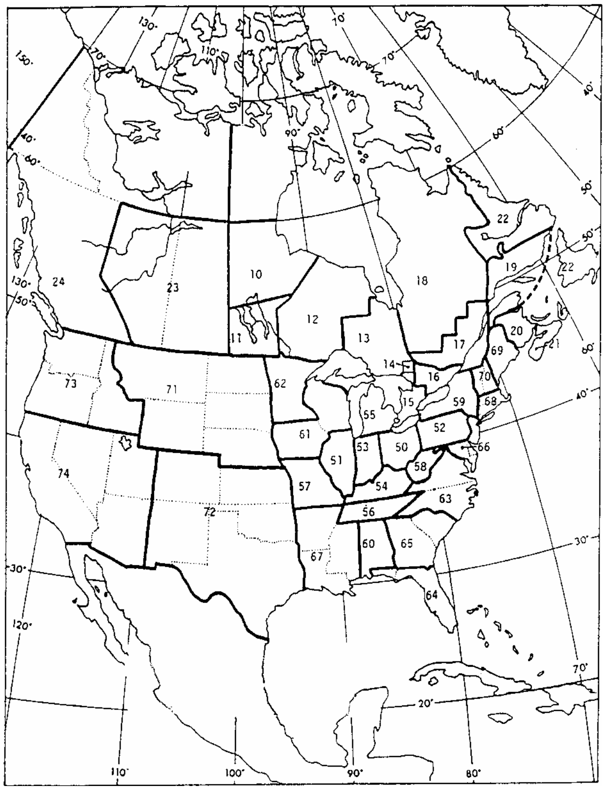

Figure 7. Location of 40 source regions used to construct ALSM-derived SRMs. 15 of these source regions are located in Canada (IDs 10 to 24) and 25 are located in the U.S. (IDs 50 to 74). Note that most of the source-region boundaries follow existing provincial and state boundaries.

To construct SRMs, the ALSM had to be run once for the set of all source regions and then once for each individual source region, that is, 41 times for the set of source regions shown in Figure 7. For an individual source region run, emissions from all of the other source regions are assumed to be zero (e.g., Olson et al., 1983). The result gives the contribution of the one source region considered to the set of receptors and corresponds to one column of the SRM, T.

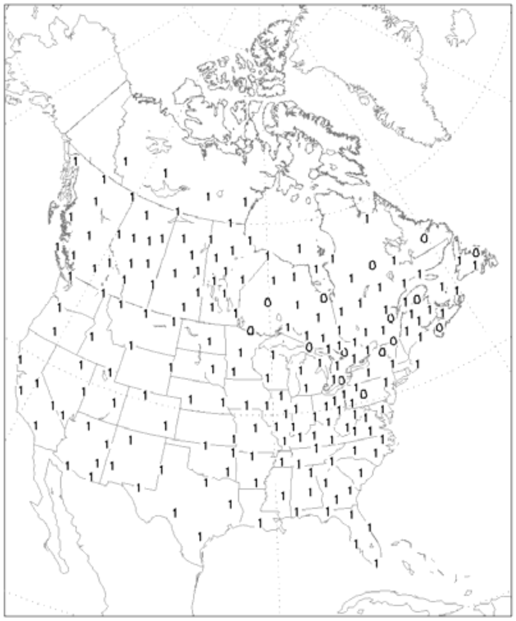

Figure 8. Location of 15 receptors considered for earlier MSC SRMs and new expanded set of 200 receptors, where original receptors are denoted by a '0' symbol and new receptors by a '1' symbol.

Note that any SRM can be expressed in one of three different forms: *actual-value* matrix; *unit-emission* matrix; and *percent-contribution* matrix. The actual-value matrix form is used with emission vectors of actual emissions and produces estimates of concentrations or depositions that would be expected from those emissions. The unit-emission matrix form is used with emission vectors of unit emissions and indicates the potential contribution of each source region to a receptor for the same amount of emissions. This matrix form can be obtained from an actual-value matrix by dividing each column of the matrix by the actual emissions value for the associated source region. The percent-contribution matrix form of T gives the percentage contribution of each source region to the concentration or deposition at a receptor for a set of actual emissions. This matrix form can be derived from an actual-value matrix by multiplying each element of the actual-value matrix by the actual emissions for the source region associated with that element and dividing by the actual concentration or deposition for the receptor associated with that element.

3.1.2 Expanded set of receptors for 1990 SRMs

The SRMs previously developed with the ALSM only considered 15 receptor sites in eastern North America, 12 located in southeastern Canada and three located in the northeastern U.S. (see Figure 8). The original decision to consider only 15 receptors was dictated by computer constraints and the use of these 15 sites in generating later SRMs was then retained for methodological consistency. However, having only 15 receptors is very limiting. One limitation is that for many effects data sets such as lake-chemistry data sets, the aquatic measurement sites may be located hundreds of kilometers from the nearest atmospheric receptor site. The need for co-located atmospheric inputs then forces the use of horizontal interpolation, which will in turn introduce additional uncertainty due to interpolation error. A second limitation is that 15 irregularly spaced data points are not enough to permit the drawing of spatially contoured fields such as those shown in Figure 2. Both of these limitations would be addressed if a larger set of receptor sites with both greater geographic coverage and higher spatial density (i.e., smaller between-site spacing) were to be considered.

Accordingly, an expanded set of 200 receptors distributed across most of Canada and the continental U.S. has been developed. The locations of these 200 receptors are shown in Figure 8. This new receptor set includes the original set of 15 receptors but adds another 80 receptor sites in Canada and 105 receptor sites in the U.S. Two criteria that were applied in choosing this expanded set of receptor sites were (a) to favour locations where air-quality measurement stations are located and (b) to minimize sampling errors in representing current observed concentration and deposition fields by locating more receptors where observed gradients occur. Of these 200 receptors, 151 are located at current precipitation-chemistry or air-chemistry station sites, an advantage for model performance evaluation. The density of receptors is greatest in eastern North America, where the highest regional air concentrations and deposition of sulphur species are measured (e.g., Figure 2).

To generate the new 1990-based SRMs, the same ALSM configuration and input files described in Section 2.2 were used, except that the ALSM was run for all of 1990 for the set of 200 irregularly-spaced receptors shown in Figure 8 rather than the 52x58 grid of regularly-spaced receptors, and it was run 41 times rather than just once. For each ALSM run, predicted values of SO_2 and SO_4 ambient air concentration, dry deposition, concentration in precipitation, and wet deposition were available four times per day at each receptor. The 1,460 values for each species for each receptor were then averaged to obtain annual averages. In effect, each of the 40 source-region-specific runs contributed one column to each of the 1990-based annual SRMs. The 41st run was needed to calculate the percent-contribution matrices.

In terms of Equation 1, the resulting 1990-based SRMs (T) have 200 rows and 40 columns, the concentration and deposition vectors **c** have 200 elements, and the emission vectors **e** have 40 elements.

As discussed in Section 2.2, Figure 2 is based on predicted values at all 3,016 grid points on the ALSM 52x58 computational grid. We can test how representative the set of 200 receptors is for this full grid by "sampling" such 3,016-point "full" fields at the 200 receptor sites shown in Figure 8 with bilinear interpolation and then plotting contoured spatial fields using only these 200 data points, Figure 9 shows one such comparison, where the 1990 annual SO_2 air concentration field predicted by the ALSM is plotted in Figure 9a and the corresponding 1990 annual SO_2 air concentration field based on 200 data points is plotted in Figure 9b. Qualitatively, the two patterns agree very well. Quantitatively, the sampled 1990 annual SO_2 air concentration field based on the 200 receptor values is within ± 3.0 μg SO_2 m^{-3} of the full-grid field; the relative differences associated with the largest actual differences of –2.5 and 3.0 μg SO_2 m^{-3} are –10% and 18%, respectively. The sampled 1990 annual SO_4 air concentration field (not shown) is within ± 0.6 μg SO_4 m^{-3} of the corresponding full-grid field, and the relative differences associated with the largest actual differences of –0.33 and 0.56 μg SO_4 m^{-3} are –4% and 7%, respectively. [Figure 9a for 1990 annual SO_2 air concentration can also be compared with Figure 2a for 1990 annual total-sulphur air concentration; the two fields are broadly similar, but the total-S field, which is the sum of a primary and a secondary pollutant, is somewhat smoother.]

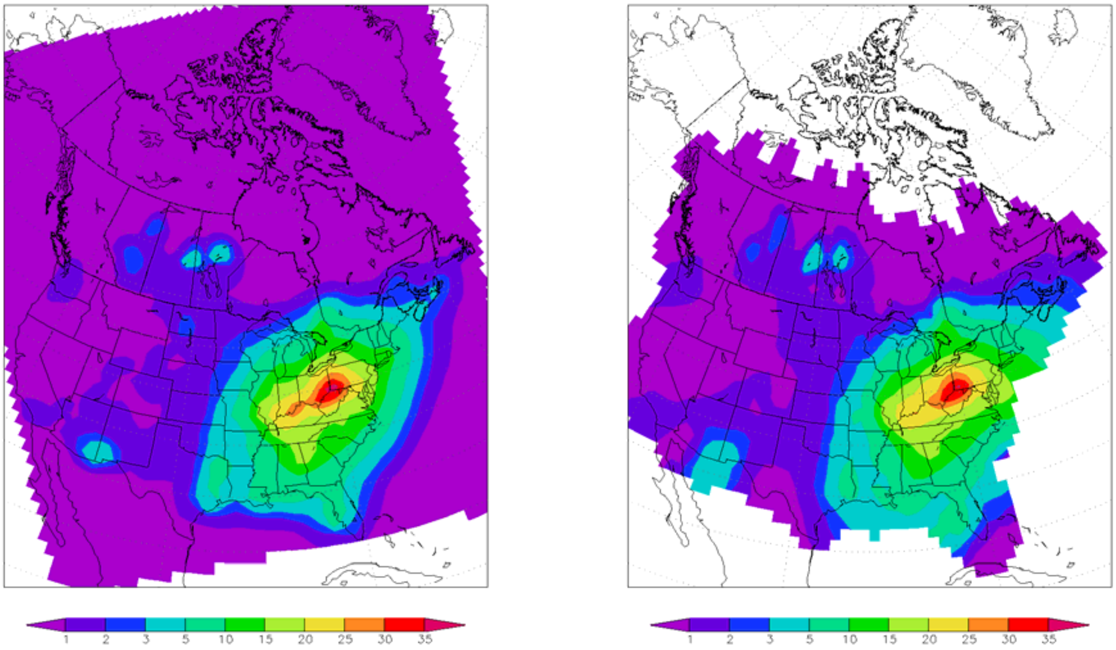

Figure 9. Annual 1990 SO_2 air concentration fields (a) predicted by the ALSM for the full set of grid points and (b) obtained by horizontal interpolation from 200 point values extracted from full field. Units are μg SO_2 m^{-3}.

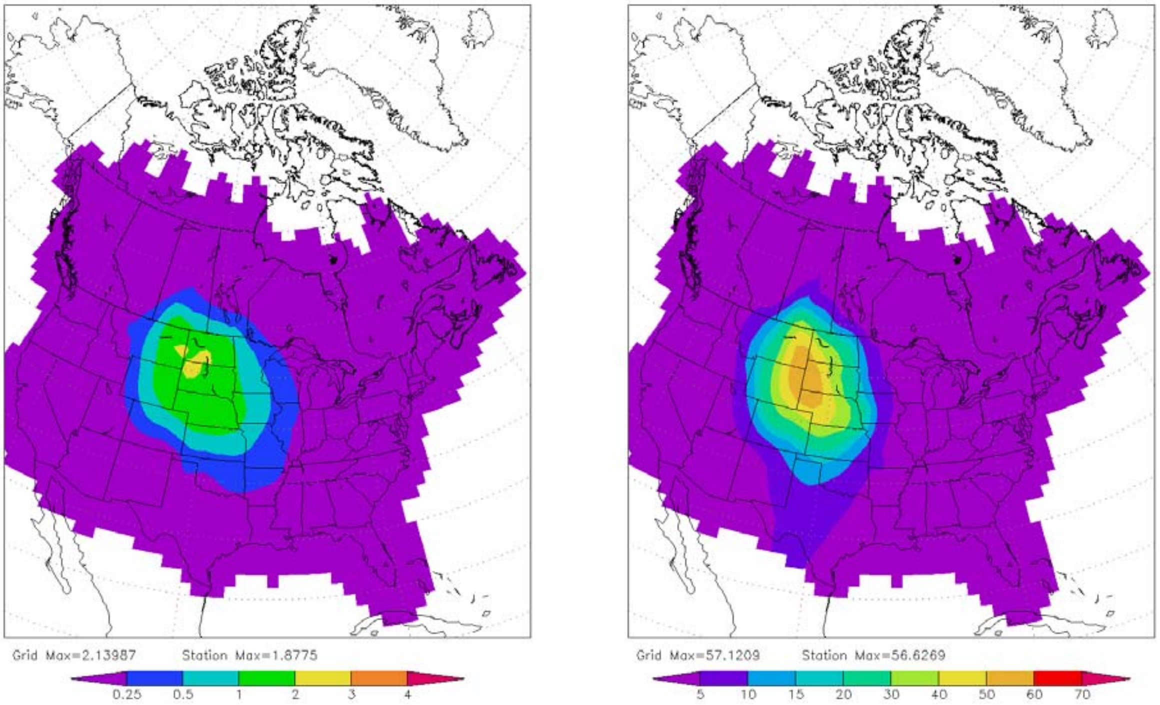

Figure 10. (a) SRM-predicted annual total-S air concentration (μg S m^{-3}) for SO_2 emissions from source region 71 (U.S. states of North Dakota, South Dakota, Nebraska, Wyoming, and Montana assuming 1 MT of SO_2 emissions (as S) and zero emissions from all other source regions and (b) percent contribution of SO_2 emissions from source region 71 in year 2002 to the annual continental total-S air concentration field.

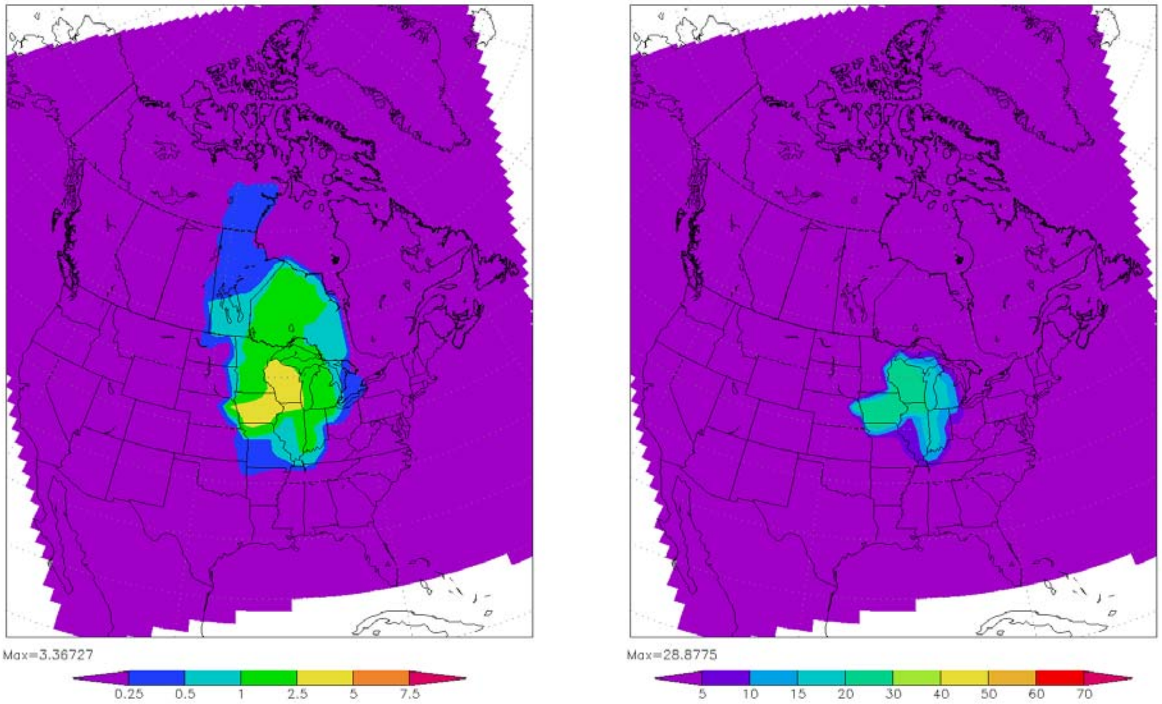

Figure 11. SRM-predicted contributions to annual total-S air concentration (μg S m^{-3}) at the receptor located at (a) Wellston, Michigan assuming 1 MT of SO_2 emissions (as S) from each of the 40 source regions and (b) percent contribution of SO_2 emissions from each of 40 source regions to Wellston receptor for actual levels of 2002 SO_2 emissions.

3.1.3 Visualization of SRM structure

As illustrated by Figure 9b, the 40x200 SRMs can be used with an emission vector to calculate concentration or deposition values at the 200 receptors (Equation 1), and these values can then be contoured to show the spatial distribution of the predicted quantity. Useful insights can also be gained, however, by contouring the individual rows and columns of T, the SRM itself.

For example, Figure 10 compares columns from two different SRMs for the same source region, source region 71, which consists of the five mid-western and western U.S. states of North Dakota, South, Dakota, Nebraska, Wyoming, and Montana. The contoured column from the first SRM (Figure 10a) is taken from the annual total-sulphur air concentration *unit-emission* matrix. The contoured column from the second SRM for source region 71, shown in Figure 10b, is taken from the 2002 annual total-S air concentration *percent-contribution* matrix. This matrix is based on actual 2002 emissions and shows the percentage of the annual total-S air concentration at each receptor that is contributed by source region 71. The difference in patterns between panels 10a and 10b can be explained by whether neighbouring source regions had higher or lower SO_2 emissions densities in 2002 than source region 71. If the adjacent region had a higher emissions density than source region 71, then the contribution of source region 71 to receptors in that region would be lower than to receptors in an adjacent low-emissions-density region (e.g., west Texas).

Figure 10 has a source-region-oriented perspective. Figure 11, on the other hand, provides a receptor-oriented perspective. It compares rows for the same receptor taken from two different SRMs. The receptor selected for this figure is located at Wellston, Michigan near the Lake Michigan shoreline. Figure 11a is based on the annual total-S air concentration *unit-emission* matrix and shows the source regions that would have the greatest influence on annual total-S air concentration at Wellston if they each had the same level of SO_2 emissions. Figure 11b, on the other hand, is based on the 2002 annual total-S air concentration *percent-contribution* matrix. It shows the source regions predicted to make the greatest contribution to annual total-S air concentration at Wellston based on their actual 2002 SO_2 emissions. The resulting set of source regions is quite different from the set shown in Figure 11a. For example, the actual contribution of the source regions in Canada to the north of Michigan is less than their potential contribution at an assumed level of emissions because their actual SO_2 emissions in 2002 were much smaller. Similar plots can be made for each of the other 198 receptors.

An Eulerian acid deposition model, the U.S. EPA's RADM model, which uses a grid with 80 km spacing, was used a decade ago to estimate the percent contribution to total-sulphur deposition of a different set of 53 (smaller) source

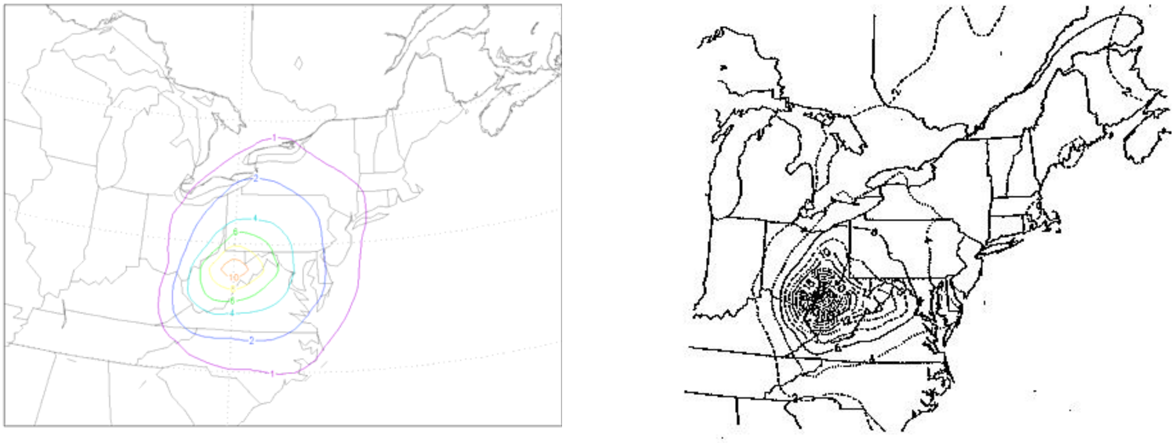

Figure 12. Percent contribution to total-S deposition predicted by (a) ALSM for 1990 emissions from ALSM/IAM source region region 58 (West Virginia) and (b) RADM for 1985 emissions from RADM source region 20 (OH/WV/KY border). Panel (b) has been taken from U.S. EPA (1995).

regions in the eastern U.S. for base year 1985 and future year 2010 (U.S. EPA, 1995). To the extent that source regions for this study and the U.S. EPA study can be matched, there is qualitative agreement between the percent-contribution fields predicted by ALSM and RADM. For example, Figure 12 compares the regions of influence for total-S deposition of ALSM source region 58 (West Virginia) for 1990 emissions and RADM source region 20 (OH/WV/KY border area) for 1985 emissions. The influence patterns are similar in shape, and both figures display a tighter gradient to the west of the source region than to the east and an elongated gradient to the northeast. On the other hand, RADM predicts both the local and the long-range contributions of the OH/WV/KY border area to be greater in magnitude than the ALSM does for the state of West Virginia.

3.2 1990-Based SRM Predictions for 2002

During the period from 1990 to 2002, SO$_2$ emissions decreased in both eastern Canada and the eastern U.S. in response to the requirements of SO$_2$ emission control legislation in each country (the 1985 Eastern Canada Acid Rain Control Program and the 1990 U.S. Clean Air Act Amendments, respectively). Based on province- and state-level emissions data obtained from Environment Canada and the U.S. EPA, 2002 SO$_x$ emissions (where SO$_x$ is a weighted sum of SO$_2$ and SO$_4$) equals were calculated for the 40 source regions shown in Figure 7. As summarized in Table 2, total annual SO$_x$ emissions in North America in 1990 were 23.8 Mtonnes SO$_2$ y^{-1}, whereas the corresponding value for 2002 was 16.2 Mtonnes SO$_2$ y^{-1}, a 32% decrease overall. The geographic distribution of Two of these 2002 SRM-predicted fields, annual total-S air concentration and annual total-S wet deposition, are shown in Figure 13a and 14a and can be compared directly to the corresponding ALSM-predicted fields for 1990 shown in Figure 2. The impact of the SO$_2$ emission reductions over this period is evident from comparing the three figures.

It is also of interest to compare the 2002 SRM-predicted fields with measurements as was done in Section 2.3 for the 1990 predicted fields. One additional consideration for this comparison is that the SRM prediction for 2002, while based on 2002 SO$_x$ emissions, is also based on 1990 meteorology, and it is well known that interannual variations in meteorology can cause significant

Table 2. 1990 and 2002 SOx Emissions for 40 North American Source Regions (MT SO$_2$ y^{-1})

Source Regions	**1990 SOx Emissions** (MT SO2)	**2002 SOx Emissions** (MT SO2)	**1990-2002 /1990** % chge
NMN 10	0.500	0.378	24
SMN 11	0.010	0.004	63
NWO 12	0.010	0.019	-93
NEO 13	0.050	0.011	78
SUD 14	0.693	0.281	59
SWO 15	0.396	0.257	35
SEO 16	0.035	0.027	22
SLV 17	0.195	0.148	24
NQU 18	0.150	0.062	58
GBY 19	0.050	0.001	98
NBK 20	0.185	0.141	24
NSP 21	0.184	0.169	8
NFL 22	0.066	0.054	18
ASK 23	0.671	0.614	9
BCA 24	0.102	0.139	-36
OHO 50	2.364	1.156	51
ILL 51	1.139	0.594	48
PEN 52	1.310	1.005	23
IND 53	1.808	0.874	52
KEN 54	0.924	0.532	42
MCH 55	0.477	0.438	8
TEN 56	0.893	0.452	49
MSU 57	0.885	0.338	62
WVR 58	0.968	0.534	45
NYK 59	0.605	0.448	26
ALA 60	0.676	0.562	17
WIO 61	0.638	0.515	19
MIN 62	0.129	0.138	-7
VNC 63	0.763	0.819	-7
FLD 64	0.700	0.567	19
GSC 65	1.135	0.816	28
MDJ 66	0.604	0.505	16
ALM 67	0.703	0.666	5
MCR 68	0.352	0.204	42
MAN 69	0.073	0.037	49
VNH 70	0.080	0.064	20
WNE 71	0.472	0.527	-12
WSE 72	1.721	1.601	7
WNW 73	0.222	0.152	32
WSW 74	0.855	0.323	62
Cdn Totl	**3.297**	**2.306**	**30**
US Tot'l	**20.496**	**13.867**	**32**
NA Total	**23.792**	**16.173**	**32**

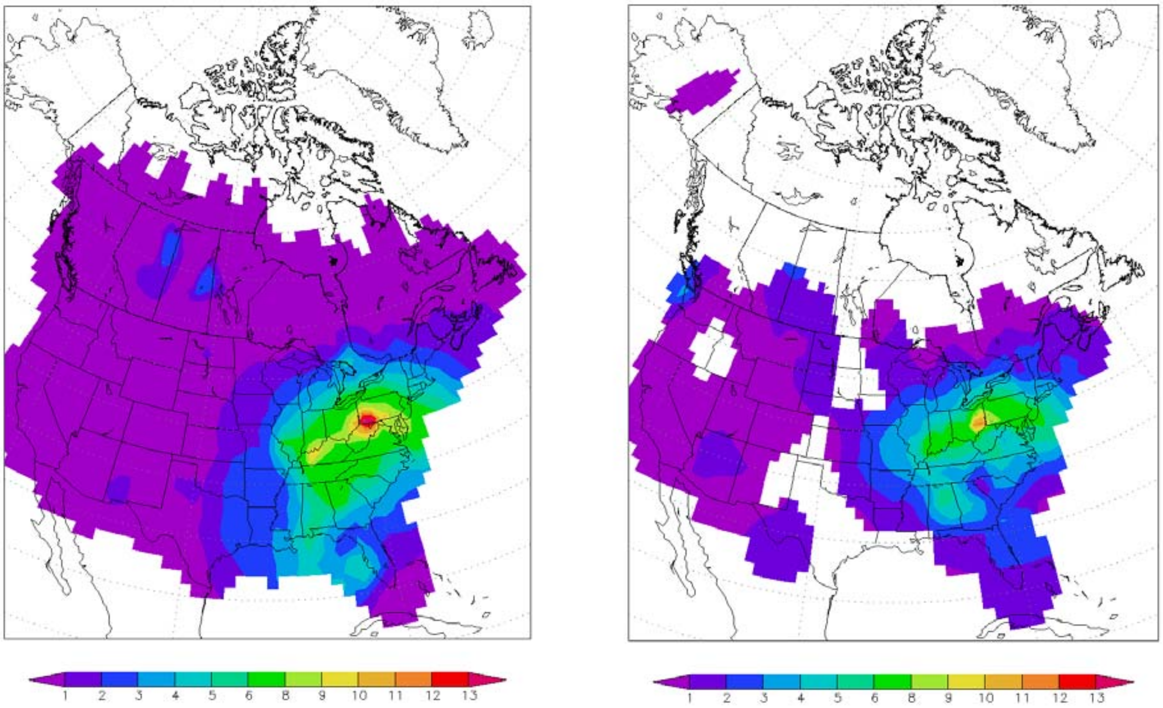

Figure 13. (a) Like Figure 2a, except for SRM-predicted 2002 annual total-S air concentration (μg S m^{-3}) based on 1990 meteorology and 2002 SO$_x$ emissions; (b) observed mean 2001-2003 annual total-S air concentration (μg S m^{-3}) based on measurements from 103 CAPMoN and CASTNet filter-chemistry stations. Note also the change in scale from Figure 2a.

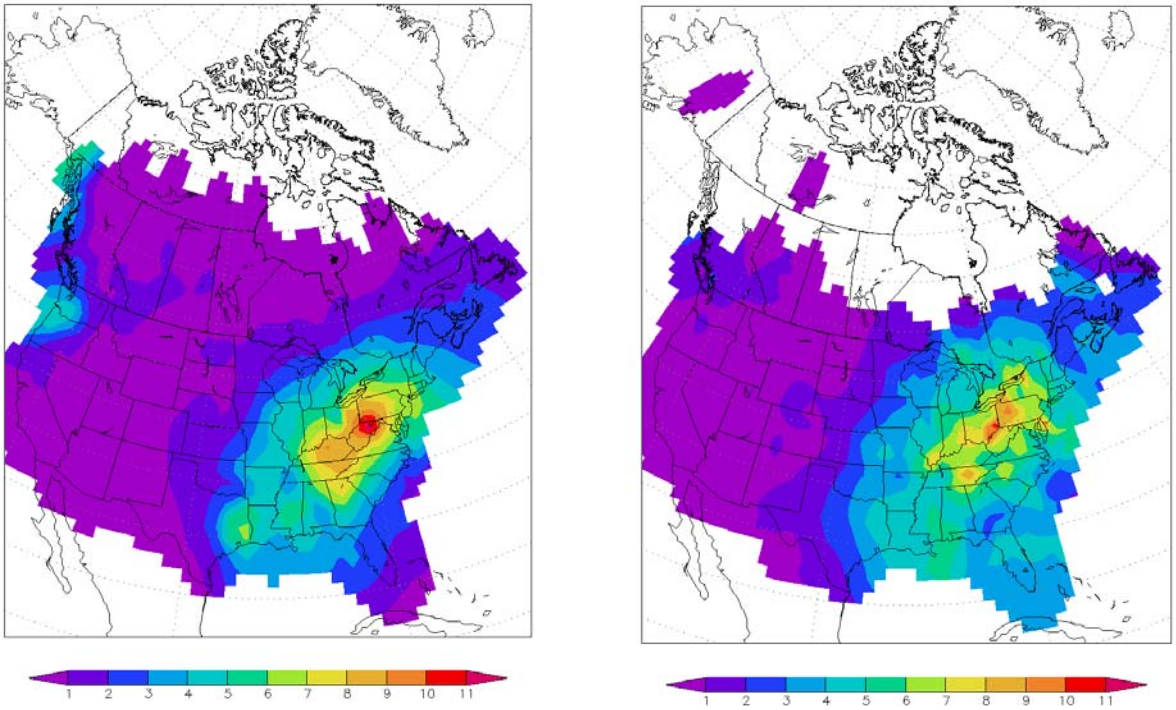

Figure 14. (a) Like Figure 2b, except for SRM-predicted 2002 annual total-S wet deposition (kg S ha^{-1} y^{-1}) based on 1990 meteorology and 2002 SO$_x$ emissions; (b) observed mean 2001-2003 annual total-S wet deposition (kg S ha^{-1} y^{-1}) based on measurements from 265 Canadian and U.S. precipitation-chemistry stations. Note also the change in scale from Figure 2b.

variations in air concentrations and deposition (e.g., Smith and Hunt, 1978; Brook and Johnson, 2000). To minimize the impact of interannual variations in meteorology, annual air concentration and deposition values for each available air- and precipitation-chemistry measurement station with at least two complete years of data were averaged for the three-year period 2001-2003 so that the impact of using a single meteorological year would be determined by its difference from a pattern closer to climatology, i.e., the 2001-2003 average, rather than its difference from another single meteorological year. Accordingly, air- and precipitation-chemistry measurements were obtained from the NAtChem database for years 2001-2003 for the same networks as used for the 1990 evaluation (see Section 2.3).

Figure 13 also compares the SRM prediction for 2002 annual total-S air concentration with the observed mean 2001-2003 annual total-S air concentration field, and Figure 14 compares the SRM prediction for 2002 annual total-S wet deposition with the observed mean 2001-2003 annual total-S wet deposition field. The broad-scale agreement between the predicted and observed fields is reasonable. Note that the plot of observed annual total-S air concentration in Figure 13b is based on only 103 observed values (total-S deposition in Figure 13a is based on 265 observed values), so that it is based on a set of observations of limited spatial coverage and resolution.

Figure 15 shows scatterplots of 2002 SRM-predicted vs. observed mean 2001-2003 annual ambient SO_2, SO_4, and total-S air concentrations. As in Figure 5, the SRM-based predictions are biased high for annual SO_2 and total-S air concentrations and are biased low for annual SO_4 air concentrations. The R^2 values for the three panels of Figure 15 are 0.72, 0.91, and 0.82 for annual ambient SO_2, SO_4, and total-S air concentrations, respectively.

Figure 16a shows a scatterplot of SRM annual precipitation (based on 1990 CMC precipitation analyses) vs. observed mean 2001-2003 annual precipitation for precipitation-chemistry measurement stations within 20 km of one of the 200 receptors. Interestingly, the correlation is reasonably good (R^2 value of 0.60) even though the periods being compared are different, suggesting that 1990 was not an unusual year meteorologically speaking. This

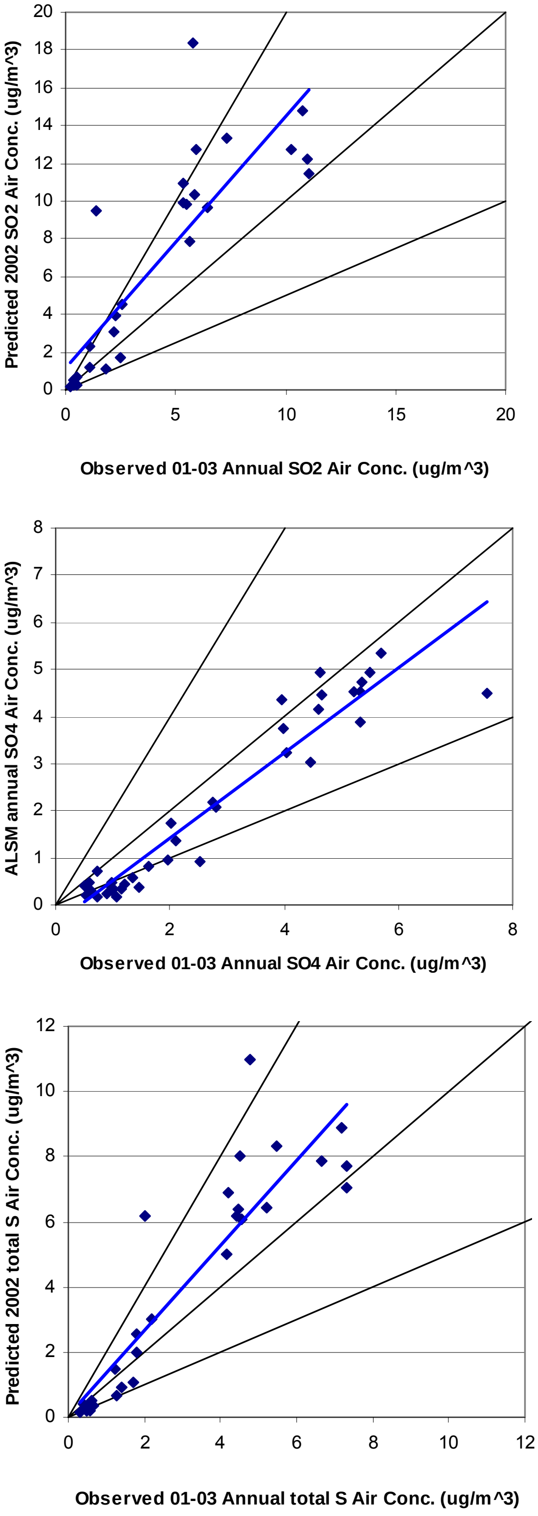

Figure 15. Scatterplots of 2002 SRM-predicted vs. observed mean 2001-2003 annual ambient (a) SO_2 air concentration (µg SO_2 m^{-3}), (b) SO_4 air concentration (µg SO_4 m^{-3}), and total S air concentration (µg S m^{-3}) for 28, 36, and 28 receptors, respectively.

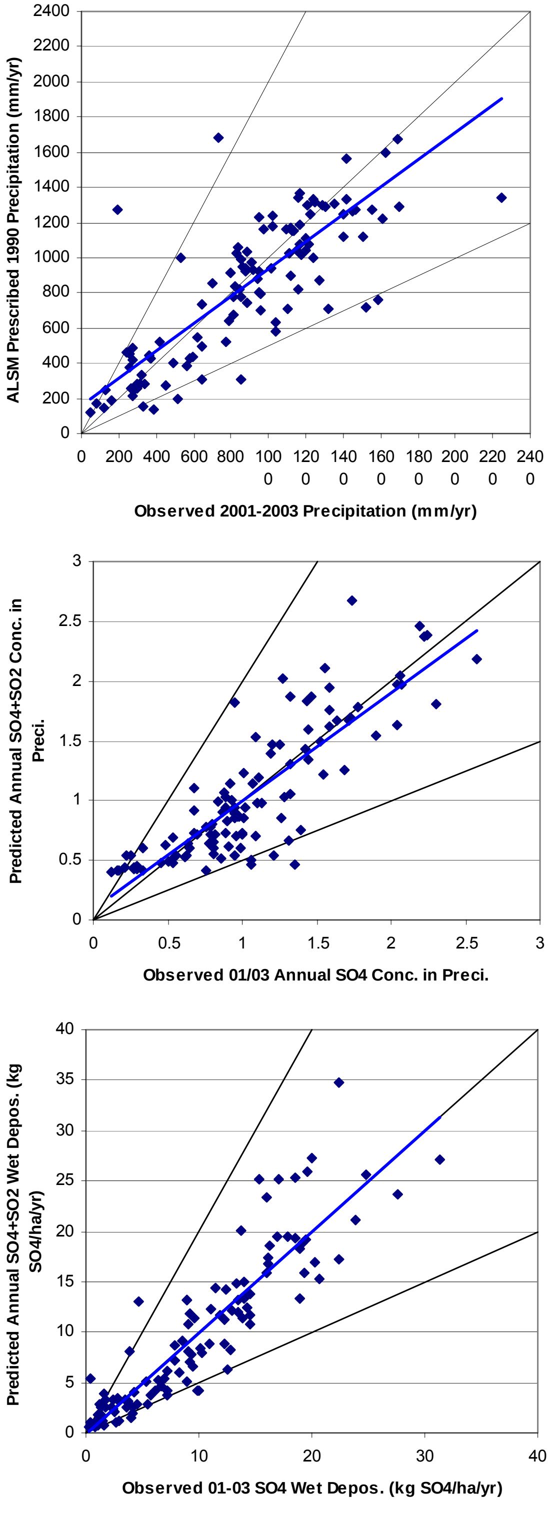

Figure 16. Scatterplots of 2002 SRM-predicted vs. observed mean 2001-2003 annual (a) precipitation (mm y^{-1}), (b) total-S concentration in precipitation (mg SO_4 L^{-1}), and (c) total-S wet deposition (kg S ha^{-1} y^{-1}) for 111 receptors.

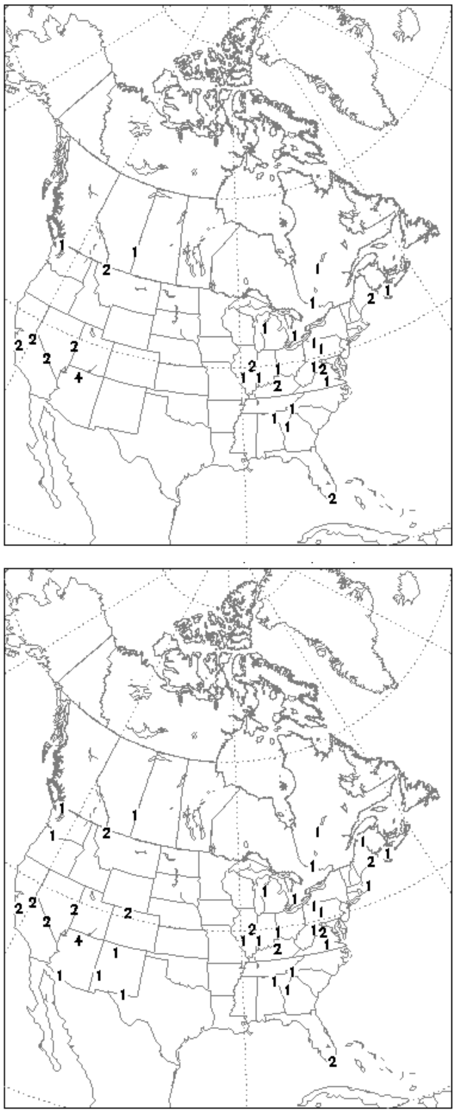

Figure 17. Locations of (a) 28 receptors with valid SO_2 filter-chemistry values (b) 36 receptors with valid SO_4 filter-chemistry values considered in scatterplots in Figure 15 for 2001-2003 annual evaluation. The number plotted at each receptor site indicates the number of measurement stations with valid data within a 20-km radius of that receptor location. The plot of the 111 receptors with valid annual precipitation-chemistry measurements is very similar to Figure 4b.

suggestion is supported by comparing the ALSM gridded 1990 annual precipitation field with a contoured observed mean 2001-2003 annual precipitation field based on precipitation measurements from 265 precipitation-chemistry stations across North America (Figure 3). Agreement between the broad-scale patterns for the two annual precipitation fields is good.

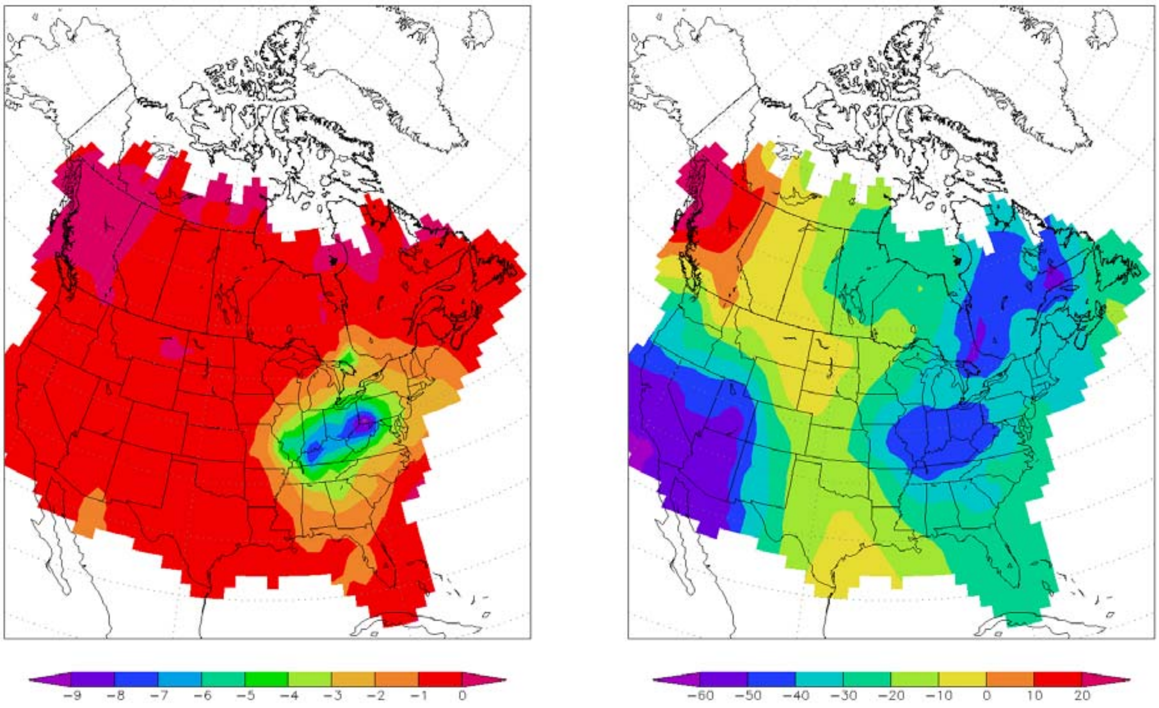

Figure 18. Plots of (a) actual difference and (b) percent difference in predicted annual total-S air concentration ($\mu g\ S\ m^{-3}$) between SRM predictions for 1990 and 2002 SO_x emissions.

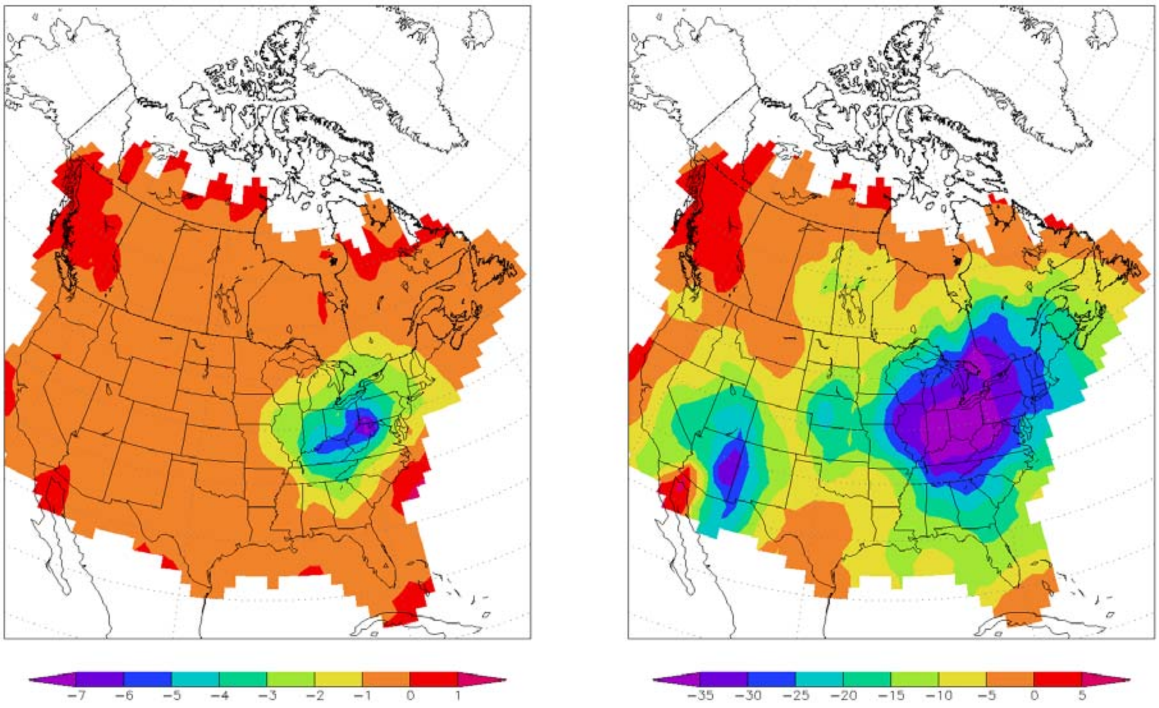

Figure 19. Plots of (a) actual difference and (b) percent difference in predicted annual total-S wet deposition ($\mu g\ S\ m^{-3}$) between SRM predictions for 1990 and 2002 SO_x emissions.

Figures 16b and 16c show the corresponding scatterplots of ALSM predictions of annual total-S concentration in precipitation and annual total-S wet deposition for 2002 emissions vs. observed mean 2001-2003 annual values of these two quantities. The comparison is good, in fact slightly better than the comparison for 1990 shown in Figure 6, with R^2 values of 0.72 and 0.82, respectively. The locations of the receptors and measurement stations considered in Figures 15 and 16 are shown in Figure 17.

3.3 1990-Based SRM Predictions of 1990-2002 Changes

While it is important to evaluate to evaluate CTM or SRM predictions against measurements for a particular period or periods (e.g., 1990, 2001-2003), it is also important to evaluate model predictions of atmospheric *changes* due to the impact of changes in emissions against measurements of these atmospheric changes since an important application of these models is for future-year emission scenarios. The availability of air- and precipitation-chemistry measurements for both 1990 and 2002 and knowledge of the emission changes over this period (Table 2) make the latter evaluation possible.

Figures 18 and 19 show the SRM-predicted impact of the SO_x emission changes on atmospheric concentration and deposition between 1990 and 2002: Figure 18 shows the actual difference and the relative difference for annual total-S air concentration (i.e., Figure 2a vs. Figure 13a) and Figure 19 shows the same quantities for annual total-S wet deposition (i.e., Figure 2b vs. Figure 14a). The most striking reduction has occurred over the Ohio Valley states and southern Ontario, where significant reductions in SO_2 emissions have occurred (e.g. source regions 14-16 and 50-59 in Table 2). A marked relative reduction was also predicted over the southwestern U.S., but the absolute reduction is small for that region.

Turning to scatterplots, of the 24 observation-model air-chemistry pairs available for 1990 (Figure 4a) and the 28 observation-model pairs available for 2001-2003 (Figure 15a), 19 pairs belong to both periods and thus allow observed *changes* to be calculated and compared to model- predicted *changes*. Figure 20 presents scatterplots of the observed changes

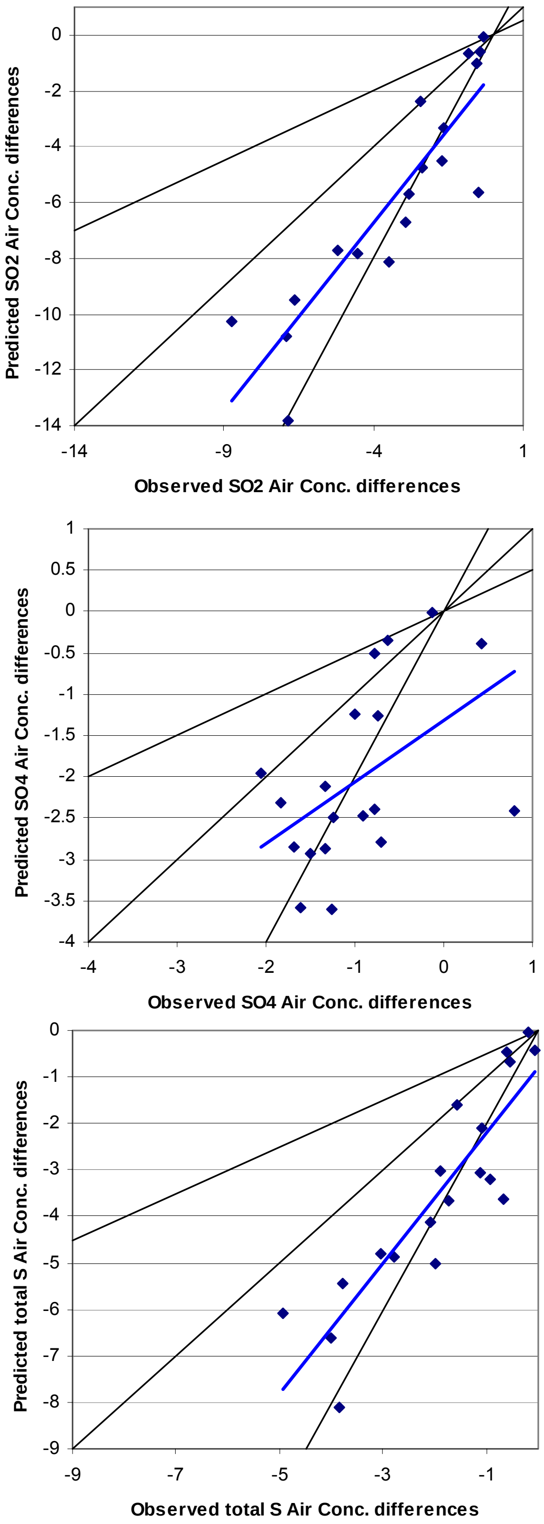

Figure 20. Scatterplots of ALSM predicted *changes* vs. observed *changes* for 1990-2002 period in annual ambient (a) SO_2 air concentration (μg SO_2 m^{-3}), (b) SO_4 air concentration (μg SO_4 m^{-3}), and (c) total-S air concentration (μg S m^{-3}) at 19 receptors.

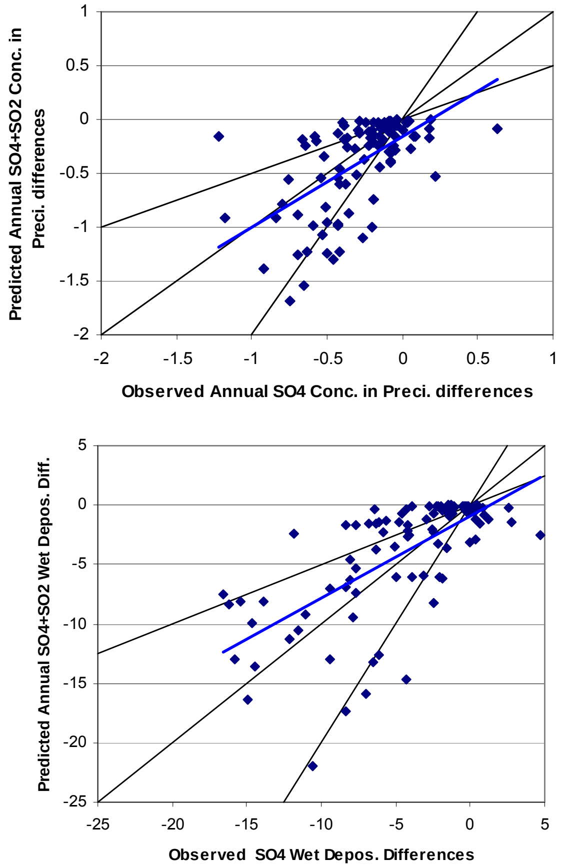

Figure 21. Scatterplots of ALSM predicted *changes* vs. observed *changes* for 1990-2002 period in annual (a) total-S concentration in precipitation (mg SO_4 L^{-1}) and (b) total-S wet deposition (kg S ha^{-1} y^{-1}) at 96 receptors.

from 1990 to 2001-2003 in annual ambient SO_2, SO_4, and total-S air concentrations vs. SRM-predicted changes due to the differences between 1990 and 2002 SO_2 emissions (see Table 2). There is more scatter evident in this figure than in Figures 5 or 15, with more data points lying outside the 1:2 and 2:1 lines, but a direct relationship is still evident, suggesting that the model predicted changes in sulphur air concentrations with some skill. The R^2 values for the three panels in Figure 20 are 0.80, 0.25, and 0.78, respectively. The two outliers (observed increases) in Figure 20b are for receptors located in Arizona and Alabama.

Of the 114 observation-model precipitation-chemistry pairs available for 1990 (Figure 6) and the 111 observation-model pairs available for 2001-2003 (Figure 16), 96 pairs belong to both periods. Figure 21 presents scatterplots of the observed changes in annual total-sulphur concentration in precipitation and annual total-sulphur wet deposition vs. SRM-predicted changes due to the differences between 1990 and 2002 SO_x emissions. The R^2 values for the two panels are 0.34 and 0.47, respectively.

In fact for about 10% of the data points, the observations indicate that total-S concentration in precipitation and total-S wet deposition increased from 1990 to 2001-2003 in spite of the general decrease in SO_2 emissions. Most of these data points turn out to be associated with receptors located in the low-concentration/low-deposition region west of the Mississippi River, where the year-to-year fluctuations that occur will be relative to a lower mean level. There are also a number of stations for which decreases were observed for which the model predicted little change. One contributing factor is likely the limitation that interannual meteorological variability is not considered by the 1990-based SRMs, both in terms of flow patterns and precipitation. There are also uncertainties with the estimates of SO_2 emissions used in the model. Overall, though, the ALSM shows skill in predicting changes in air concentrations and deposition of sulphur species resulting from changes in SO_2 emissions.

4. LAGRANGIAN INORGANIC AEROSOL MODEL

4.1 Earlier Lagrangian Nitrogen Model

Due to the role played by nitric acid and particulate nitrate as acidifying species, the acid-deposition effects and policy communities would like to have annual SRMs for North America for both sulphur and nitrogen species. Such SRMs have been developed in the past by MSC using the ALSM (see above) for sulphur species and using using an extension of the ALSM, the AES Lagrangian Nitrogen Model (ALNM), for oxidized nitrogen species. The ALNM was used to calculate a nitrogen budget for eastern Canada and nitrogen source-receptor matrices for 15 receptors in eastern North America (Olson et al., 1990, 1992).

Six chemical species – three nitrogen species, one volatile organic compound (VOC) species, O_3, and OH – and six reactions were added to the ALSM to create the ALNM. The nitrogen species were (a) NO_2, (b) IN (inorganic nitrate; i.e., sum of HNO_3 and particulate nitrate), and (c) PAN (peroxyacetic nitric anhydride), and the VOC species is ALD (sum of all aldehyde precursors of PAN). PAN formation was treated as reversible, allowing for the reformation of NO_2. As a result, the chemical mechanism used, though simple, is nonlinear, since the equilibrium between NO_2 and PAN will depend upon the *total* concentrations of these two compounds contributed by all source regions. Other notable aspects of the ALNM are (a) the consideration of only a single lumped hydrocarbon species, ALD (although aldehydes are the most important class of organic compounds for nitrogen chemistry), (b) the assumption that the peroxyacetyl radical PA is always in steady state, (c) the assumption that there is no coupling between sulphur and nitrogen species, (d) the treatment of O_3 and OH as *prescribed* fields (spatially-uniform O_3 and OH concentrations are prescribed using monthly average values with month-dependent diurnal profiles), and (e) the neglect of reduced nitrogen species (i.e., ammonia and ammonium) (Bouchet and Moran, 2002).

The numerous simplifications made in the formulation of the ALNM have raised concerns over its suitability for simulating atmospheric nitrogen chemistry, which is complex. Bouchet and Moran (2002) investigated other approaches to generate SRMs for nitrogen species, including European work to develop SRMs for nitrogen species and for ozone (e.g., Bartnicki, 1999; EMEP, 1998; Simpson, 1992; Simpson et al., 1997). Their recommendation was that the AES Lagrangian Oxidant Model (ALOM), a Lagrangian chemical transport model with a detailed gas-phase chemistry mechanism previously used for summer-time ozone modelling (Environment Canada, 1997b) should be (a) extended to include particle sulphate, nitrate, and ammonium and their attendant process representations (aqueous-phase and heterogeneous chemistry; particle dry and wet deposition), (b) tested and evaluated, and then (c) used to create SRMs for both sulphur species and for oxidized and reduced nitrogen species. It would then be possible as well to compare the new SRMs generated for sulphur species by this new model, which has been named LIAM (Lagrangian Inorganic Aerosol Model), with those SRMs generated previously using the simpler ALSM.

4.2 LIAM Development

As recommended by Bouchet and Moran (2002), the ALOM code has been modified to add or upgrade a number of process representations. To date, the following steps have been completed:

1. Three bulk aerosol species (p-SO_4, p-NO_3, and p-NH_4) were added to the 46 species already considered by the ALOM gas-phase mechanism (Lurmann et al., 1986; Environment Canada, 1997b). To accommodate this insertion, several reactions involving p-NO_3 were removed from the gas-phase mechanism set.
2. A simple but nonlinear treatment of thermodynamic equilibrium for H_2SO_4, HNO_3, NH_3, p-SO_4, p-NO_3, and p-NH_4 was added following the approach of the EMEP Lagrangian Acid Deposition Model (Tsyro, 2001). The concentrations of $(NH_4)_2SO4$ and NH_4HSO_4 are assumed to be equal, so that they can be treated as a single pseudo-species, $(NH_4)_{1.5}SO_4$. The formation of $(NH_4)_{1.5}SO_4$ is assumed to take place instantaneously and irreversibly at each time step after the gas-phase reactions have been caluculated until there is either no NH_3 left or no H_2SO_4 left. If any NH_3 is left, it enters into equilibrium with HNO_3 to create or destroy NH_4NO_3. The equilibrium concentrations of NH_3, HNO_3 and NH_4NO_3 are calculated using the method described in Seinfeld and Pandis (1998, Section 9.4.3).
3. The treatment of SO_2 aqueous-phase conversion via H_2O_2 and O_3 oxidation as a pseudo-gas-phase reaction that is used in the EMEP MADE50 acid deposition model (EMEP, 2003) was adopted. This parameterization requires knowledge of fractional cloud volume and cloud liquid water content. At this time a cloud pH of 4.5 is assumed.
4. The particle dry deposition scheme of Zhang et al. (2001) was implemented for the removal of particles by dry deposition and sedimentation. This scheme requires information about the distribution of different land-use types on the model domain.
5. The gas-phase deposition scheme of Zhang et al. (2002), which uses SO_2 and O_3 as two “master” species for parameterizing the dry deposition velocities of other gas-phase species, was implemented in place of the original ALOM scheme, which, unlike the new scheme, did not account for deposition velocity dependence on land-surface characteristics.

Table 3. Basic characteristics of ALSM and LIAM.

Model Characteristic	ALSM	LIAM
Vertical Resolution	Lagrangian box model with one vertical layer	Lagrangian box model with 1.5 vertical layers
Horizontal Resolution	127 km	127 km
Time Step	3 hour	1 hour
Numerical Solver	Simple mean-value theorem	Gear solver
Chemical Species	SO_2 and SO_4	49 species, including 28 transported gas-phase species and p-SO_4, p-NO_3, and p-NH_4
Emissions	SO_2 and SO_4 from sfc sources	19 species from surface sources
Gas-Phase Chemistry	Monthly average chemical transformation rate is used for the oxidation of SO_2 to SO_4	ADOM-II gas-phase mechanism (Lurmann et al., 1986)
Aqueous-Phase Chemistry	Combined with gas-phase transformation	Simple SO_2 aqueous-phase chemistry mechanism
Heterogeneous Chemistry	None	Simple $(NH_4)_{1.5}SO_4$ and NH_4NO_3 equilibrium mechanisms
Dry Deposition	Prescribed monthly, spatially-uniform dry deposition velocities for SO_2 and SO_4	Zhang et al. (2001, 2002) dry deposition velocity schemes for gas and particulate species; depends on land-use
Wet Deposition	Wet deposition is treated as product of a constant scavenging ratio and analyzed daily precipitation amount and predicted air concentration	Precipitation is used to compute wet deposition for SO_2, SO_4, HNO_3, NH_4, $(NH_4)_{1.5}SO_4$, and NH_4NO_3

Table 3 provides a process-by-process comparison of the LIAM with the ALSM.

The addition of the new process parameterizations listed above required additional meteorological fields beyond those used by ALOM to be input to LIAM. ALOM already required temperature to be input in order to calculate gas-phase reaction rates, but relative humidity, which is needed along with temperature in the treatment of ammonium nitrate thermodynamic equilibrium, was diagnosed from the dewpoint depression, temperature, and pressure fields contained in the CMC meteorological archives. Data on low-level cloud cover were obtained from the ECMWF 40-year reanalysis project (ERA-40) data archives, and cloud liquid water content, which is not an ERA-40 field, was diagnosed using ERA-40 fields of low-level and middle-level cloud cover, total-column water vapour and total-column water, and NCEP low-level cloud base fields. These cloud-related fields are needed by the parameterization of SO_2 aqueous-phase conversion.

To date, different developmental versions of LIAM have been tested with data from two 6-day periods during the Eulerian Model Evaluation Field Study (EMEFS), which took place in eastern North America in 1988-1990 (e.g., McNaughton and Vet, 1996). One is a summer period (Aug. 1-6, 1988) and one is a spring period (Apr. 25-30, 1990). Work is continuing now on LIAM to add a new treatment of wet deposition, acquire emission files for all of 1990, and evaluate model performance for more time periods.

5. SUMMARY AND CONCLUSIONS

Lagrangian chemical transport models are prognostic, emissions-based numerical models that have been used extensively to predict present and future-year seasonal and annual acid deposition. Because they are simpler, less data intensive, and less demanding computationally than Eulerian models, LCTMs have been the preferred means for generating the reduced-form representations of long-term atmospheric dispersion, chemistry, and removal known as SRMs. This paper has described the adaptation of two regional LCTMs to simulate long-term sulphur and nitrogen ambient concentrations and deposition in North America.

The first model, the ALSM, is a veteran sulphur-cycle LCTM that has been extended to generate three types of sulphur-species SRMs for the 1990 meteorological year for 40 SO_2 emission regions and 200 receptors covering most of North America. First, the performance of the ALSM for a 1990 full-year simulation was investigated, and annual and quarterly results for the ALSM using 1990 emissions showed good agreement with 1990 observed air- and precipitation-chemistry station data. Second, the ALSM was run 41 times for the 1990 meteorological year for the 200 receptors to generate a set of 1990-based SRMs for 12 sulphur-specie fields. Third, SRM predictions for 2002 and for changes between 1990 and 2002 were evaluated against 1990 and 2001-2003 air- and precipitation-chemistry measurements, and the model showed skill for both evaluations. CTM evaluation against observed atmospheric changes due to changes in emissions is an important test since a common application of CTMs is to predict future-year air quality. And fourth, it was demonstrated that the new 1990-based SRMs generated by the ALSM have enough rows and columns that spatial plots of unit-emission SRM and percent-contribution SRM rows and columns provide useful insights into potential and actual source and receptor “footprints” for different regions of the continent.

The second LCTM is a new and more complex model called LIAM that is being developed from another Lagrangian CTM called ALOM to model sulphur, oxidized nitrogen, and reduced nitrogen concentrations and deposition. The ultimate objective is to use LIAM to generate SRMs for both sulphur and nitrogen species. Three new inorganic aerosol chemical components (SO_4, NO_3, NH_4) have been introduced into LIAM as well as new process treatments for ammonium nitrate thermodynamic equilibrium, SO_2 aqueous-phase conversion, and particle dry deposition. Some preliminary evaluations have been performed for LIAM simulations of two 6-day periods from the 1988-1990 EMEFS field study (not presented here).

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