



Project Summary

Long-Range Transport and Transformation of SO₂ and Sulfate: Refinement, Application, and Verification of Models

Teizi Henmi and Elmar R. Reiter

A three-layer model of long-range transport/transformation of SO₂ and sulfate, which includes dry and wet deposition, was refined and applied to calculate patterns of 24-hour concentration and deposition amounts over the northeastern United States bounded by 35-45° N latitude and 75-95° W longitude for 2 separate days. Meteorologically, the model is driven by routine upper-air observations of the National Weather Service. The model was modified to reduce computer requirements and to produce monthly average concentrations. It was applied for 2 months over a larger area extending into Canada, bounded by 35-53° N latitude and 62-95° W longitude. Sulfur budgets and comparisons of observed and calculated SO₂ and sulfate concentrations are presented and discussed.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

There is growing concern by the public, scientists, government, and

international organizations about the consequences of SO₂ pollution and especially about the increasing acidity of precipitation. Current opinion is that this type of pollution threatens human welfare and the environment. Precipitation with increasing acidity has been observed especially over the northeastern United States and Scandinavia. The annual average pH of the Adirondack Lakes has dropped from 6.5 in the 1930s to 4.8 today; more than 90 of these lakes are completely devoid of fish. It is generally recognized that precipitation acidification involves long-range transport and transformation of sulfur and nitrogen oxides and other man-made pollutants. Cloud and precipitation physics also play a role in lowering the pH of rain. Attempts at mathematical simulation of the total process have been hampered by a lack of detailed knowledge about various subprocesses and basic input information (e.g., rate constants, meteorological and pollutant emissions data, etc.). Over the last several years research in this project has focused on constructing a practical mathematical model of long-range transport and transformation of SO₂ and sulfate, developing and incorporating improved knowledge about critical subprocesses, and applying the model to study air quality over the

eastern United States and nearby Canada. This report describes refinements to earlier modeling efforts (EPA reports 600/4-78-003 and 600/4-79-068) as well as application and verification of the models.

The basic model may be described as a Lagrangian, forward-trajectory type, which generates average 24-hour concentrations over a grid of 1-degree (1/2 degree on a suitable computer) longitude/latitude spacing. It uses routine rawinsonde observations of the National Weather Service to keep track of pollutants in three diurnally varying layers:

- the daytime, ground based stable layer,
- the daytime (largely convective) mixing layer, and
- the layer at night that extends from the top of the stable layer to the top of the most recent daytime mixed layer.

For this long-range transport model it is assumed that pollutants in the various layers are distributed vertically in a uniform manner; lateral diffusion depends mainly on wind shear. Constant transformation rates of SO₂ to sulfate are employed, one each for daytime and nighttime in accordance with sunlight effects. Dry and wet removal of SO₂ and sulfate are modeled through use of the deposition velocity concept.

Results

This report describes improvements and modifications to the earlier model. Vertical temperature profiles along each trajectory were analyzed objectively to determine the vertical limits of the three layers. Trajectory computations were increased to four per day (every 6 hours), were run for 48 hours, and were composed of 3-hour segments. The latest information on rates of transformation and on dry and wet deposition were incorporated into the model. A major accomplishment (in terms of required computer capacity) was the development of a much more efficient routine to interpolate concentrations along trajectories to grid points. A similar scheme was used for precipitation rates measured at weather stations.

The improved model was applied to calculate geographic distributions of 24-hour average concentrations and dry and wet deposition amounts of SO₂ and sulfate over the region bounded by 35-45° N latitude and 75-95° W longitude, which encompasses the Ohio

River basin. January 25 and July 11, 1976, were chosen for computations because observed concentrations were relatively abundant on those days. Sixty point sources of SO₂, each with an emission rate of more than 10⁵ tons/year, were estimated to account for 90 percent of total SO₂ emissions in the region. Precipitation data were available for 81 stations. The modeling applications indicated that removal of SO₂ from the atmosphere by precipitation (assumed proportional to precipitation rate) is relatively inefficient, whereas the amounts of sulfate were substantial. But data for verification are not available. Comparisons of observed and calculated SO₂ and sulfate concentrations indicated that calculated SO₂ concentrations generally were too low and sulfate too high, suggesting that the rate used in the model for transformation of SO₂ to sulfate was too high. Table 1 shows correlation coefficients between observed and calculated concentrations; all are significant at the 99.9 percent confidence level. Although calculated and observed concentrations were related statistically, the correlations were not particularly high; for SO₂ they were disappointingly low. This was attributed in part to the too-high transformation rate and to the use of observed concentrations in urban areas where the impact of *nearby* (unaccounted for) small sources could be large. Table 2 shows the sulfur budget for the region that was modeled. More than 50 percent of the emitted sulfur was transported out of the region on

both dates. Less than 10 percent was removed from the atmosphere by precipitation, compared to 30 percent in our earlier model, a consequence of revising the formula for wet removal.

The model described in the foregoing paragraphs was applied in a climatological mode after some modifications, largely to reduce the computing time. Trajectories from each SO₂ source were begun every 6 hours, and were based on 3-hour time segments; they were pursued for up to 3 days, and were based on average winds for only one layer, the seasonal average afternoon mixing layer. The vertical distribution of pollutants was assumed uniform in the mixing layer. The lateral distribution was assumed to depend on the deviation of each trajectory from an average trajectory from each source (meander) and on the vertical wind shear. Puffs of SO₂ were formulated with a Gaussian distribution along and across each trajectory segment. Based upon data for January, 1977, for 72 major SO₂ sources in the eastern United States and southeastern Canada, the four average dispersion components (meander and shear, along and across trajectories) displayed some interesting characteristics. The greatest dispersion component out to 72 hours was meander along trajectories, followed by meander across trajectories (which had many of the smallest standard deviations), shear along trajectories, and finally shear across trajectories. For all components the rate of increase of dispersion tended to become small by 72 hours.

Table 1. Correlation Coefficients (*r*) Between Observed and Calculated 24-Hour Average Concentrations

	January 25, 1976	July 11, 1976
SO ₂	<i>r</i> = 0.68 (N = 162)	<i>r</i> = 0.44 (N = 216)
Sulfate	<i>r</i> = 0.77 (N = 155)	<i>r</i> = 0.85 (N = 86)

Table 2. Calculated Sulfur Budget (Tons) for Region Modeled (Sulfur Emission = 24,492 Tons)

	Jan 25, 1976	July 11, 1976
Removal by Wet Deposition	808	2,015
in SO ₂	90	129
in Sulfate	718	1,886
Removal by Dry Deposition	10,167	7,495
in SO ₂	9,240	6,406
in Sulfate	927	1,089
Total Deposition	10,975	9,510
Amount Exported	13,517	14,982

Calculations of concentration, transformation, dry, and wet deposition all were handled in a straightforward manner as in the basic model. The climatological model was run for the regions bounded by 35-53° N latitude and 62-95° W longitude for the months of January, 1977, and March, 1979. In order to compute sulfur budgets the region was broken into four subregions: United States, Canada, Great Lakes, and Atlantic Ocean. Monthly precipitation amounts from approximately 700 stations were used to calculate wet deposition amounts of SO₂ and sulfate. Emissions of SO₂ for 72 point sources, each with an annual emission rate of at least 10⁵ tons, were used as inputs to the model.

Figure 1 shows the distribution of average SO₂ concentrations for January 1977. The highest concentrations tended to occur in the general vicinity of greatest emissions, i.e., along the Ohio River basin and northward into Canada (north of Lakes Erie and Huron). The general pattern of SO₂ concentrations in Figure 1 is similar to that for sulfate and for dry and wet deposition amounts of SO₂ and sulfate—and to the general patterns for March, 1979. For January, 1977 observed average concentrations of SO₂ and sulfate were available for more than 90 and 60 locations, respectively, in the United States. The respective correlations with observed

concentrations were 0.538 and 0.477, significant at the 99 percent level. As for the basic model, the correlation coefficients were not impressive. Observed SO₂ and sulfate concentrations for March, 1979 were not available.

The climatological model was used also to estimate monthly mass budgets of sulfur for subregions of the area that were studied. The results for January, 1977 and March, 1979 indicate that:

- The budgets for the 2 months were different, due to differing meteorological conditions.
- During January, 1977, inflow of sulfur to Canada from the United States was only 23 percent of the total sulfur over southeastern Canada, but during March, 1979, it was 40 percent.
- Less than 3 percent of the total sulfur over the northeastern United States was imported from Canada in both months.
- Major portions of sulfur were removed from the atmosphere by wet and dry deposition.
- Of the total sulfur emitted by the northeastern United States and by southeastern Canada, less than 10 and 3 percent, respectively, were transported to the Atlantic Ocean, much less than in other estimates.

Finally, the climatological model was used to calculate the acidity (pH) of precipitation. Since it has been shown

that there is a significant correlation between the pH and the concentration of sulfate in precipitation, it was assumed that the pH of precipitation could be expressed as the wet deposition amount of sulfate (as generated by the model) divided by the volume of precipitation per unit area (based on observed precipitation amounts). For March, 1979, the average pH of precipitation samples measured at each of 17 stations in the United States was compared to corresponding calculated pH values; the correlation coefficient was 0.825, significant at the 99 percent confidence level.

Recognizing that the acidity of precipitation is dependent on ions other than sulfate, available data on nitrates and ammonium were utilized to evaluate previously proposed formulations, some also involving additional ions in precipitation in ratios found in sea water. Clearly, the matter of precipitation acidity is extremely complicated, but the results of evaluations indicate that inclusion of nitrogen oxides in the long-range transport model will improve pH predictability.

Conclusions

The correlations between calculated and observed concentrations of SO₂ and sulfate for the basic model (24-hour average concentrations) and for the climatological model (monthly average concentrations) are statistically significant, but in both cases there is much more scatter than desirable. Some possible causes of discrepancies are as follows:

- SO₂ annual emission data were used rather than more specific, shorter term values.
- SO₂ emissions less than 10⁵ tons/year were neglected. Such small sources that are relatively close to a receptor may have a large impact on concentrations there.
- Measured values of SO₂ and sulfate used in this study may be unreliable.
- Model parameters such as dry and wet deposition velocities and the transformation rate of SO₂ to sulfate likely can be improved.
- Under certain conditions (e.g., at fronts and in the vicinity of cols) trajectory calculations may be inaccurate.
- Small-scale, close-to-the-source dispersion is neglected entirely.

In spite of these difficulties the modeled patterns of concentrations and

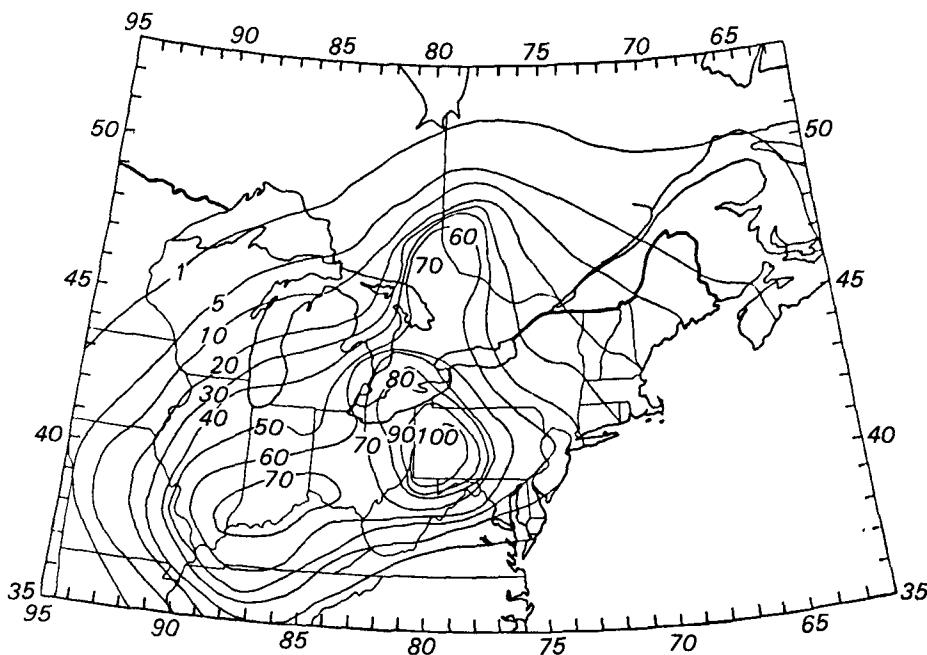


Figure 1. Distribution of SO₂ concentrations (µg/m³) for January 1977.

deposition amounts are not unreasonable, and were used to calculate sulfur budgets for the northeastern United States and southeastern Canada. The results show that major portions of the emitted sulfur were removed by wet and dry deposition. For the sulfur over Canada the contribution transported from the United States was substantial, whereas that from Canada to the United States was small. Only a small fraction of the total emitted sulfur was transported to the Atlantic Ocean.

The basic objective of this project, to develop reasonable working models that include the essential features of long-range transport/transformation/dispersion/deposition, has been achieved. Future incorporation into the models of new knowledge about the basic phenomena involved (especially, nitrogen oxides transformation to nitrates) and the use of more appropriate input information will permit improvements in the modeling results.

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The complete report, entitled "Long-Range Transport and Transformation of SO₂ and Sulfate: Refinement, Application, and Verification of Models," (Order No. PB 82-101 759; Cost: \$9.50, subject to change) will be available only from:

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