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Deposition of S and NO_x Nitrogen to the Great Lakes Estimated with a Regional Deposition Model

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■ Atmospheric loading of anthropogenic S and NO_x N to the Great Lakes is estimated with a regional deposition model. Dry deposition calculations include the effects of the wet surface and the predominant seasonal atmospheric boundary-layer structure over the lakes, i.e., strong stability in spring and summer and strong instability in autumn and winter. Modeling results are generally consistent with objective analyses of observed deposition. Best agreement is shown for the lower lakes; the model appears to underestimate deposition to Lake Superior, particularly for S. The analyses themselves contain large uncertainties, especially for Lake Superior, because all monitoring is over land and dry deposition monitoring is also both sparse and indirect. Examination of S and N mass budgets for Lake Superior indicates that the atmospheric pathway plays an important role in total loading and that the atmospheric pathway is more important for N than for S. An examination of modeled and observed S deposition trends during the 1980s illustrates the difficulty in separating possible emission-related trends in deposition from meteorologically induced variability and uncertainties in modeling or analysis when the emission changes are relatively small.

Introduction

The Great Lakes, together with their land drainage areas, form a combined basin of approximately 7.5×10^5 km^2, with the lakes covering one-third of the area. Atmospheric deposition to the Great Lakes ecosystem is an issue of continuing concern (*1*), because wet or dry deposition directly to the lakes is believed to constitute the major input mechanism for many nutrients and toxic substances (*2-4*). Atmospheric deposition to the land basins and subsequent collection in runoff may be a significant additional input. Horizontal mixing within each lake reduces any gradient in cumulative deposition loading, particularly dry, that might otherwise occur downwind of sources near the shore; thus, integrated deposition across the various lakes and land basins should be the most useful measure of loading.

While deposition of heavy metals and toxic organic compounds is the most critical issue in atmospheric loading to the Great Lakes, monitoring data for those pollutants are generally insufficient for reliable estimation of atmospheric loading. An alternate approach is to estimate such loading with models; modeling has the important additional advantage of potential use with future emission scenarios. However, for most toxic substances, significant difficulties occur in determining model emissions input, in quantifying and parameterizing removal processes, and in verifying model output. In contrast, the intensive investigation of acidic deposition during the last decade has produced a wealth of observational data and regional deposition modeling studies for SO_x and NO_x. Thus, in this

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initial modeling study we calculate deposition of S and N from anthropogenic emissions of oxides of S and oxides of N to each of the Great Lakes and to their runoff basins. Ultimately, we wish to apply similar modeling techniques to estimate loading of heavy metals and toxic organic compounds as their emission inventories are developed and refined and as removal processes are better understood.

First, we exercise a regional atmospheric deposition model to calculate large-scale, seasonal and annual patterns of average air concentrations and cumulative wet and dry deposition. We integrate the deposition fields over the lakes and basins to calculate total deposition loading, after adjusting dry deposition to the lakes to take into account significant lake effects on dry deposition velocities. Then we compare our modeled estimates with integrated spatial analyses of deposition produced from extrapolation of observations taken over land and evaluate the significance of the atmospheric loading pathway by comparison with estimates of loading via tributaries and runoff. Finally, to demonstrate the potential of the modeling approach for examining past trends in deposition, we exercise the S model for each year of the period 1980–1988 and compare wet deposition results with the trends from objectively analyzed monitoring data.

Method

The first step in our approach is to calculate seasonal average air concentrations of SO_2, SO_4^{2-}, combined NO/NO_2 (as NO_2), and combined NO_3^-/HNO_3 (as NO_3^-), and cumulative wet and dry deposition of S and NO_x N for a grid that includes all of the Great Lakes basin. (Here we use NO_x N to mean all deposited nitrogen resulting from anthropogenic emissions of NO or NO_2, irrespective of speciation when deposited.) For this calculation we use the Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model (*5*). ASTRAP, which has been applied extensively in the modeling of long-range transport and deposition of acidifying pollutants (*6–8*), is a long-term Lagrangian (trajectory) model in which all chemistry is simplified to linear, first-order approximations. Concentration and deposition patterns from different sources are thus additive, a key factor in the efficiency of the model.

ASTRAP uses gridded wind and precipitation fields, updated several times daily, to calculate horizontal trajectories initiated at 6-h intervals. Seasonal ensembles of trajectories from each virtual source on a grid are described statistically. Wet deposition is a function of the total airborne burden and the 6-h precipitation total; wet removal events are statistically combined separately from nonprecipitation cases. A separate one-dimensional (vertical) numerical integration takes into account emission height, vertical mixing, dry deposition, loss to the free troposphere, and linearized chemical transformation. The rates of key parameterizations such as the profile of eddy diffusivities, dry deposition velocities, and chemical transformations are prespecified to vary diurnally and seasonally but not daily or horizontally. The trajectory and vertical integration statistics are combined with an emission inventory to calculate seasonal cumulative deposition and average air concentrations directly rather than by summing or averaging short-term simulations; annual results are produced by combining seasonal simulations. Calculations are made separately for SO_x and NO_x.

Although ASTRAP is highly parameterized, long-term regional deposition simulations for eastern North America are similar to observed fields and to aggregated results from a sophisticated episodic Eulerian model, particularly for wet deposition (*9*). This may be because spatial distributions of emissions and synoptic-scale wind and precipitation patterns, the controlling factors in long-term, regional-scale deposition of S and NO_x N, are described adequately in both models.

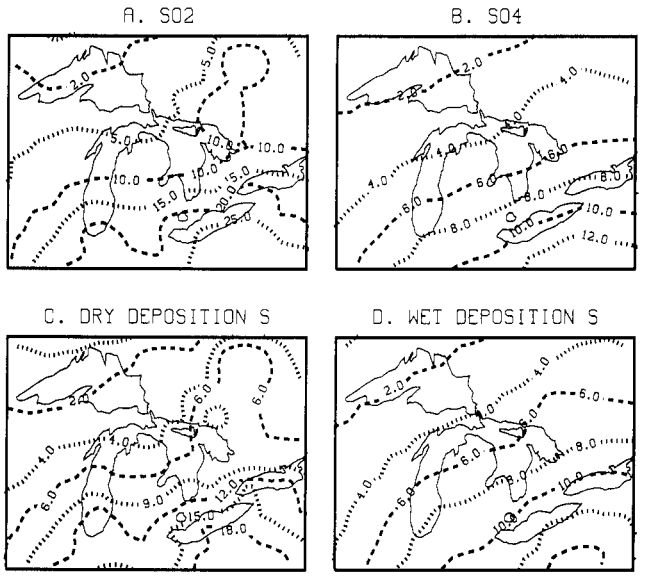

Figure 1. Annual average surface air concentrations ($\mu g/m^3$) and cumulative deposition (kg/ha) for 1985 from ASTRAP simulations with anthropogenic SO_x emissions.

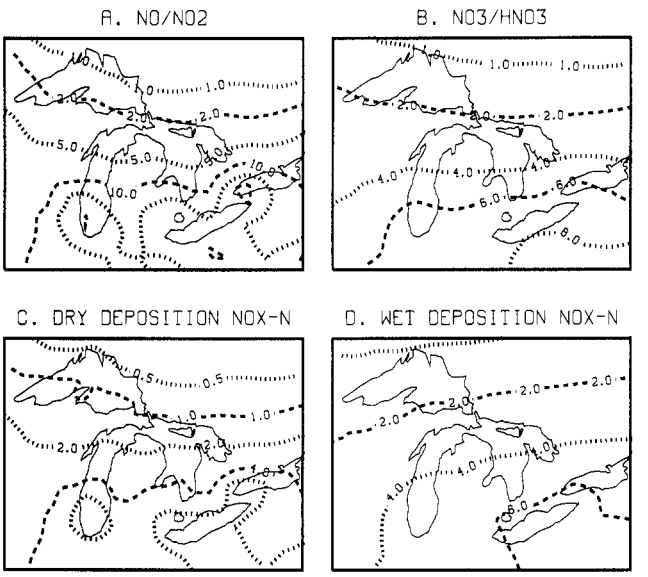

Figure 2. Annual average surface air concentrations ($\mu g/m^3$) and cumulative deposition (kg/ha) for 1985 from ASTRAP simulations with anthropogenic NO_x emissions.

For this study, anthropogenic SO_x and NO_x emission inventories for the United States and Canada have been resolved seasonally, horizontally in cells approximately 120 km on a side, and vertically in 6 layers to 800 m. Meteorological analyses over North America and adjacent waters include 1000- and 850-mbar wind fields from numerical analysis, updated 4 times daily, and precipitation fields updated twice daily. Regional-scale, annual average air concentrations and cumulative deposition simulated with emissions and meterology for 1985 (the year for which spatial details of emissions are best known) are shown in Figures 1 and 2. Most of the regional fields have maxima in the upper Ohio River Valley and decrease from southeast to northwest across the Great Lakes, with local maxima near isolated large-point sources and large urban centers.

ASTRAP regional-scale simulations normally are produced for a grid of Canadian Meteorological Centre (CMC)

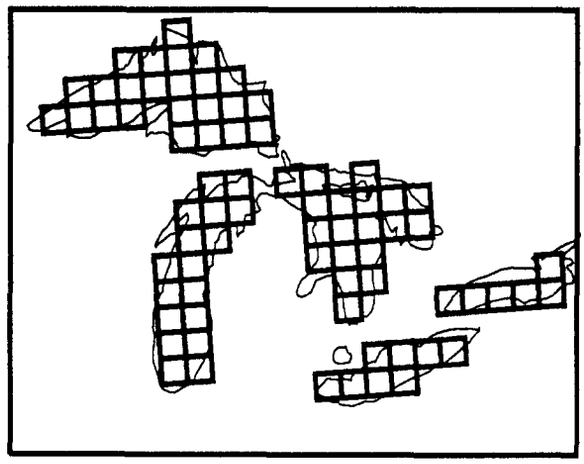

Figure 3. Gridded representation of the Great Lakes in ASTRAP simulations.

spacing, which increases with latitude from ~112 to 120 km over the Great Lakes basin. Such grid spacing is coarse relative to the shorter horizontal dimensions of the lakes, particularly Ontario and Erie, whose north–south extents are equivalent to about one grid length. To improve depiction of the irregularly shaped lakes and basins with a denser grid, the ASTRAP seasonal air concentration and deposition fields shown in Figures 1 and 2 cover a 26 × 24 grid of $^1/_2$ CMC spacing. (Because of the resolution limitations in input data and model structure, the real resolution of model output with the denser fields is only marginally improved.) The grid cells in the finer grid are coded 0–10, with 1–5 representing the lakes in hydrological order and 6–10 representing their respective basins. The portions of the grid outside the Great Lakes basin are coded 0. The lakes are described by combinations of cells ranging in number from 6 for Lake Ontario to 24 for Lake Superior, as shown in Figure 3. A cell represents 1.25–1.45 × 10^4 km^2, with the cell area a function of the sine of the latitude.

The integrated seasonal wet deposition for each lake and basin and the dry deposition for each basin are determined by first multiplying the modeled seasonal deposition rate for each of the cells that depict the feature by the area represented by the cell and summing the resulting deposition totals. Then the lake or basin total is adjusted by the ratio of the actual size of the lake or basin to its size as represented by the combination of grid cells to eliminate areal biases resulting from the discrete depiction of the lakes and basins.

The lack of horizontal variability of dry deposition velocities in ASTRAP has important implications for our modeling study. It is well known that the atmospheric boundary layer over the lakes can differ strongly from that over nearby land (*10*). Because of the vertical mixing processes and the large thermal capacities of the lakes, their surfaces heat and cool much more slowly than the surrounding land surface. The lakes undergo little diurnal or day-to-day variation in surface temperature; the annual cycle accounts for most of the water temperature variation. In spring and summer, the lakes are cool relative to the surrounding land. When warm air typical of the season is advected over the water, cooling of the lower atmospheric boundary layer results in the development of a very stable layer. Dry deposition to the lakes is then strongly limited by atmospheric resistance to vertical transfer; at the same time, the surface heating of nearby vegetated land surfaces and the resulting thorough atmospheric mixing may produce large daytime dry deposition velocities over land. The opposite case is common in autumn and winter, when the lakes often are a strong source of both heat and moisture to the lower layer of passing air masses, particularly cold, dry polar air. The lower layer becomes unstable and vertical mixing increases; thus, dry deposition processes are enhanced. This simplified description of the atmospheric boundary layer over the lakes does not always apply. Episodic incursions of relatively warm air masses in autumn and winter and relatively cool air masses in spring and summer may undergo little change during advection over the lakes.

The lakes affect dry deposition rates in other ways as well. Surface wetness increases deposition rates for soluble gases but reduces deposition rates for hydrophobic substances. Wind speeds tend to be higher over water than over nearby land. Although dry deposition rates are enhanced if winds become sufficiently strong to produce breaking waves, increases in wind speed shorten transit time over the lake, a factor that tends to reduce total deposition to the lake. When the land is warmer than the lakes and the synoptic-scale wind field is sufficiently weak, lake-breeze circulations form and make calculations of air parcel trajectories and residence times in regional models problematic.

Horizontal variations in dry deposition velocities cannot be treated directly in the basic structure of ASTRAP. The parameterizations in regional ASTRAP simulations are meant to apply to the whole of eastern North America, which is primarily agricultural or forested. If model simulations of dry deposition over land are unbiased, then without adjustment ASTRAP should overpredict dry deposition to the lakes when the surface boundary layer over the lakes is strongly stable (spring and summer) and underpredict dry deposition when the surface boundary layer is highly unstable (fall and winter). We seek to improve our estimates of seasonal dry deposition loading to the lakes by multiplying averaged dry deposition velocities specified for the lakes by the seasonal average air concentrations over the lakes as calculated in ASTRAP. The dry deposition fields over the lakes are then integrated as is done for wet deposition. Because the air concentrations are calculated in ASTRAP with dry deposition velocities different from those specific to the lakes, this approach deviates somewhat from mass consistency in that increased (decreased) dry deposition velocities should lead to decreased (increased) air concentrations. For instance, the mean concentration in a well-mixed boundary layer 1.0-km deep would be about 7% less after 4.0 h for a dry deposition velocity of 1.0 cm s^{-1} than for a dry deposition velocity of 0.5 cm s^{-1}. However, any errors arising from this method of model adjustment should be small, because overwater transit time typically is no more than a few hours.

The major difficulty in this approach is in determining the seasonal average overwater deposition velocities, particularly for nitrogen species that are combined in ASTRAP simulations because of the need to parameterize chemistry simply. Because air concentrations are combined for NO and NO_2 and for NO_3^- and HNO_3, their deposition velocities must also be combined. Although ASTRAP simulations of wet and dry deposition of total NO_x N appear to be reasonably accurate when they are aggregated annually over states and provinces (*9*), deposition velocities are quite different for NO and NO_2, and for NO_3^- and HNO_3 (*11–13*). Deposition velocities for NO are usually near zero and often negative over land (i.e., indicative of upward fluxes from natural sources). NO_2 deposition velocities are appreciable, although generally less than those for SO_2. Nitric acid is deposited essentially as rapidly as it can diffuse to the surface, while the de-

Table I. Mean Dry Deposition Velocities Used in Regional ASTRAP Simulations (*5*) and Mean Dry Deposition Velocities Estimated for the Great Lakes (cm/s)

	winter	spring	summer	autumn
ASTRAP				
SO_2	0.30	0.40	0.45	0.30
SO_4^{2-}	0.12	0.20	0.23	0.15
NO/NO_2	0.20	0.25	0.30	0.16
NO_3^-/HNO_3	0.40	0.30	0.60	0.30
over lake				
SO_2	0.60	0.20	0.20	0.50
SO_4^{2-}	0.30	0.10	0.10	0.25
NO/NO_2	0.40	0.15	0.15	0.30
NO_3^-/HNO_3	1.00	0.30	0.30	0.75

position of nitrate particles is much slower and depends on particle size. The assumptions in ASTRAP as to the ratios of NO to NO_2 and NO_3^- to HNO_3 are not explicit, but they may be implied in the choices of regionally representative removal parameterizations for the combined species. Thus, the weighting of individual overwater deposition velocities, which in themselves are uncertain, to produce deposition velocities suitable for use with the air concentrations of species lumped in ASTRAP must be largely subjective. The seasonally averaged dry deposition velocities used in regional ASTRAP simulations and those applied in recalculation of dry deposition to the lakes are shown in Table I. The variation in seasonal overwater dry deposition velocities input to the model is less than that of the analytical estimates of lake-specific monthly means (*10*) for three reasons: first, seasonal averaging dampens somewhat the analytical minima and maxima, which generally last for only 1 or 2 months; second, the minima and maxima tend to occur near the spring–summer and autumn–winter transitions, respectively, and thus affect the averages of two seasons; and third, the same model parameterization is applied to each of the lakes, although the analytical estimates for each lake are somewhat different. Lake-specific deposition velocity adjustments in the model were not felt to be justified at this stage because of the many uncertainties in the approach.

Results

Objective analyses of Great Lakes deposition with which ASTRAP calculations can be compared include wet S and NO_x N deposition for 1980–1984 (ref 14, hereafter VA), extended through 1986 for S as presented later, and both wet and dry deposition for 1985–1987 (ref 9, hereafter SS) for S and NO_x N, interpolated from regional wet deposition analyses and extrapolated from dry deposition monitoring data. For both studies, adaptations of the analysis method developed by Krige (*15*) were used. The SS analyses adjusted wet deposition to remove the estimated contribution from natural sources by subtracting assumed background concentrations of 2 μmol/L of SO_4^{2-} and 1 μmol/L of NO_3^-. Overall, about 7% of wet deposition was attributed to natural sources, with the natural contribution ranging from 4% for Lake Erie to 12% for Lake Superior. No such adjustment was made in the VA estimates. The model simulations in this study estimate only the deposition associated with anthropogenic emissions.

Comparisons between 1985–1986 VA, 1985–1987 SS, and 1985–1987 ASTRAP values for S and 1983 VA, 1985–1987 SS, and 1985 ASTRAP values for NO_x N are shown in Tables II and III, respectively. Neither modeling nor observational estimates treat deposition perturbations over the lakes that are associated with mesoscale effects. If the estimated contribution from natural sources is taken into account, the model results are similar to the VA estimates of wet S deposition for the lower lakes but are considerably lower for the upper lakes, particularly Lake Superior, for which the model estimate is lower by about a factor of 3. The model estimates of average annual wet S deposition to the lakes during 1985–1987 are very similar to those of SS for the lower lakes, about one-third lower for Lakes Huron and Michigan, and lower by a factor of ~2 for Lake Superior. Thus, the gradient in wet S deposition over the lakes is considerably steeper in ASTRAP results than in the objective analyses of the terrestrial monitoring data. This results in part from the linear nature of the ASTRAP model, which leads to overprediction when available oxidants are limited relative to pollutant loading; this condition probably holds at times over the lower lakes, particularly in winter near major sources. A second possible cause for the discrepancy is the assumed rate of deposition from natural sources; if the rate is larger than assumed, then the modeled and adjusted observed gradients become more similar. In addition, as will be seen in a later section, the analysis of observations has greater relative and absolute uncertainty for the upper lakes, particularly Lake Superior, because observations, all over land, are sparser and because the lakes are larger. For wet NO_x N deposition to either lakes or basins, on the other hand, all methods produce fairly similar results. Because ASTRAP has generally simulated regional patterns of wet deposition of S and NO_x N equally well across eastern North America

Table II. Annual S Deposition Estimates (kt/year)

deposition region	wet[a]	wet[b]	wet[c]	dry[b]	dry[c]	total[b]	total[c]
lakes							
Superior	41	29	13	18	15	47	28
Michigan	43	38	28	33	43	71	71
Huron	51	45	30	22	36	67	66
Erie	34	25	26	21	48	46	74
Ontario	22	17	18	10	27	27	45
total	191	154	115	105	169	258	284
basins							
Superior	60		16		18		34
Michigan	87		51		74		125
Huron	116		67		81		148
Erie	74		63		94		157
Ontario	56		57		65		122
total	393		254		332		586
Great Lakes basin total	584		369		501		870

[a] Analysis of observations from 1985 to 1986 (ref 14 or VA). [b] Analysis of observations from 1985 to 1987 after subtraction of estimated contribution to wet deposition from natural sources (ref 9 or SS). [c] ASTRAP regional simulations for 1985–1987 with dry deposition over the lakes calculated with dry deposition velocities specific to the Great Lakes.

Table III. Annual NO_x N Deposition Estimates (kt/year)

deposition region	wet[a]	wet[b]	wet[c]	dry[b]	dry[c]	total[b]	total[c]
lakes							
Superior	21	16	12	9	7	25	19
Michigan	20	20	24	22	25	42	49
Huron	28	22	23	17	14	39	37
Erie	13	12	17	11	18	23	35
Ontario	8	9	11	5	11	14	22
total	90	79	87	65	75	144	162
basins							
Superior	30		15		8		23
Michigan	38		43		35		78
Huron	60		46		25		71
Erie	35		42		40		82
Ontario	21		34		25		59
total	184		180		133		313
Great Lakes basin total	274		267		208		475

[a] Analysis of observations from 1983 (ref 14 or VA). [b] Analysis of observations from 1985 to 1987 after subtraction of estimated contribution to wet deposition from natural sources (ref 9 or SS). [c] ASTRAP regional simulations for 1985 with dry deposition over the lakes calculated with dry deposition velocities specific to the Great Lakes.

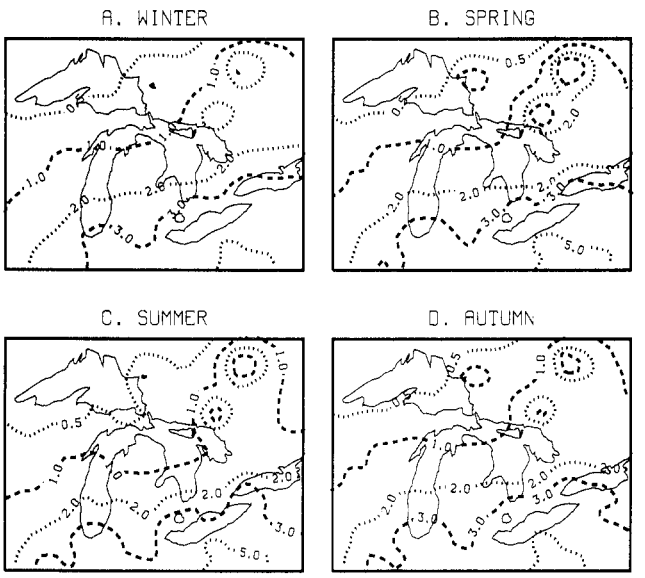

Figure 4. Cumulative seasonal dry deposition (kg/ha) of anthropogenic emissions of S from ASTRAP simulations before overwater adjustment.

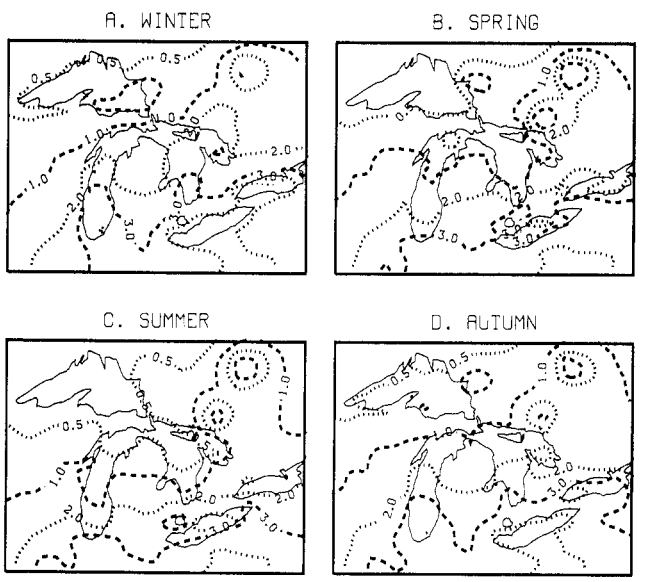

Figure 5. Cumulative seasonal dry deposition (kg/ha) of anthropogenic emissions of S from ASTRAP simulations after overwater adjustment.

(5), the better agreement between model and observations in the upper lakes for NO_x N wet deposition is somewhat surprising. It may be due in part to a more accurate parameterization of the contribution from natural sources.

VA estimated wet deposition only. SS did not estimate loading to the lake basins; however, they did estimate both dry and wet deposition to the lakes. SS dry deposition estimates over the eastern United States and the Great Lakes combined information from five dry deposition monitoring sites on land including one site near Chicago, with objective analyses of the average air concentrations of the dry depositing species for a period of ~5 weeks and were admittedly highly uncertain over the lakes. SS made no adjustment over the Great Lakes to dry deposition estimated from observations over land, although they recognized its desirability, because they analyzed annual data rather than seasonal data. The ASTRAP dry S deposition estimates are 40% higher than those from SS before adjustment and 60% higher after adjustment. The large seasonal effects of the dry deposition adjustment for S, responsible for the differences between Figures 4 and 5, tend to cancel somewhat in annual loading estimates. NO_x N dry deposition estimates are very consistent between this modeling study and the observational analysis of SS; accounting for lake effects increases NO_x N dry deposition estimates by about 25%.

Modeled wet and dry deposition loadings to the Great Lakes have marked seasonal variations, particularly in the case of S deposition, but the patterns are of nearly opposite phase; therefore, seasonal variations in total deposition are smaller. While year-to-year variability was considerable during 1985–1987, 39% and 7% of modeled wet S deposition occurred in summer and winter, respectively, while the corresponding values for dry S deposition were 10% and 55% in summer and winter, respectively. The wet deposition loading in winter is probably underestimated because of the inadequate capture of lake-effect snows by precipitation networks. For modeled NO_x N deposition in 1985, seasonal wet deposition contributions ranged from 20% in winter (probably underestimated) to 33% in autumn, while seasonal dry deposition ranged from 9% in summer to 42% in winter.

Relative Importance of the Atmospheric Pathway to Total Loading. Although the focus of this paper is on how to estimate the atmospheric input to the Great Lakes and their basins, it is also of interest to compare the magnitude of the atmospheric loading with that from industrial and municipal discharge and from runoff and tributary inputs. The latter may also be influenced by atmospheric input through deposition to the land basin

Table IV. Estimates of Annual S and NO_x N Loading for Lake Superior

	wet dep loading,[a] kt	wet dep + dry dep loading,[b] kt	tributary and industrial/ municipal loading,[c] kt	atmos share total loading,[d] kt
S	47	34	178	16
NO_x N	20	19	35	35

[a] Annual wet deposition estimate for 1980–1983 from ref 17. [b] Total (wet + dry) annual atmospheric deposition of N from 1985 anthropogenic NO_x emissions from this study. [c] Estimated annual loading of total N for 1983 (*17*). [d] Fraction of total loading attributed to direct atmospheric deposition.

and subsequent runoff and through direct input to the tributaries. Quantification of all loadings to the lakes is essential for producing contaminant mass balance in the lakes, evaluating potential control strategies, and predicting the rate of recovery of the lakes if control options are exercised. A comparison of estimates of the magnitude of the atmospheric input with estimates of input from other sources provides an indication of how accurately each term needs to be determined. If the atmospheric input is a minor constituent of the total loading, there is little need to strive for high accuracy in its estimate. If on the other hand the atmospheric loading appears to be dominant, an accurate estimate is highly desirable and information on major sources and source regions is critical.

Our estimation of the importance of atmospheric loading as presented in Table IV is intended to be illustrative rather than comprehensive, as we examine only Lake Superior (*16*, *17*). For the Great Lake most remote from industrial areas, direct atmospheric loading of S is estimated to equal about one-sixth of total loading. However, we have not yet taken into account several factors: (1) our estimate of additional wet S deposition from natural sources was 12% of that from anthropogenic sources; (2) some of the S deposition to the watershed, which is estimated to equal ~120% of that to the lake itself, also reaches the lake; and (3) SO_x emissions decreased and climatological conditions varied during the period. ASTRAP simulations that include emissions and meteorological variation (*18*) indicate that average annual deposition of anthropogenic S to the Great Lakes during 1973–1983 was 28% greater than during 1985. If we scale our atmospheric loading estimate by 1.12 × 1.28 = 1.43 to get 49 kt of S and assume that atmospheric deposition to the watershed could have contributed between 0 and 1.2 × 49 = 59 kt of the 178-kt S loading from tributaries and runoff, then atmospheric deposition of S could ultimately account for 22–48% of the S loading to Lake Superior, depending upon how much of the tributary input is assumed to result from terrestrial deposition.

Defining an input budget for NO_x N is more complicated than for S because of the larger number of significant species for the former, and because N is such an actively cycled nutrient. Our estimation of total atmospheric deposition includes dry deposition of NO_x (primarily NO_2), HNO_3, and particulate NO_3^-, and wet deposition of all those species (unspecified but presumably mostly as NO_3^- in solution), but we do not attempt to simulate either wet or dry deposition of NH_4^+ or NH_3. Budget studies cited above (*16*, *17*) examine NO_3^- separately from total Kjeldahl N. We chose to use loading estimates for total N, but we recognize that it is an overestimate for our purposes to the extent that it includes NH_3 or NH_4^+. Direct atmospheric loading from anthropogenic NO_x N emissions is estimated to be a major source (35%) of N to Lake Superior, even without considering factors similar to those discussed for S deposition. The third factor would be less important for N than for S, because anthropogenic emissions of NO_x during 1985 decreased relative to the 1973–1983 average only two-thirds as much as did S emissions (*19*, *20*). Although retention within the watershed would likely be greater for N than for S, if we pursue the logic of the earlier argument then the total atmospheric deposition to the basin could account for 41–92% of N loading to Lake Superior. A study of the trend in nitrate concentration in Lake Superior from 1906 to 1976 (spring concentrations increased from 75 ppb N to 311 ppb N) attributed the increase to atmospheric loading (*21*).

The loading estimates were also used in a simple mass balance model for Lake Superior to evaluate the reasonableness of the estimated atmospheric input (*17*). We can take a similar approach, shown in Table V, with our estimates of deposition. Losses to sediment, long-term accumulation in the biota, and degradation are assumed to be negligible. The change in the mass budget for the lake is assumed to equal the total loading to the lake (sum of total atmospheric deposition, tributary, industrial, and municipal input) minus the material outflow through the St. Mary's Channel. Annual input is assumed to be constant between 1973 and 1983, years for which lake concentrations are available. Net accumulation is divided by lake volume to estimate the change in concentration, which can be compared with measured concentration changes in Lake Superior over the decade. The measured lake concentration of SO_4^{2-} expressed in equivalent S increased from 1.00 in 1973 to 1.15 mg/L in 1983, while our predicted end concentration is slightly lower at 1.12 mg/L. For N the measured lake concentration increased from 0.368 in 1973 to 0.405 mg/L in 1983, while our prediction of the increased level is somewhat lower at 0.391 mg/L. Despite the crudeness in the assumptions and the uncertainties in all parameter values the agreement is fairly good, particularly when one considers that the factors mentioned in the preceding paragraphs would tend to adjust the predicted values upward.

Uncertainties in the Modeling Approach. Because the specified deposition velocities to the Great Lakes are independent of the modeled air concentrations, they are associated with independent uncertainties in estimated dry deposition loading to the lakes. Several factors in addition to the lumping of species, discussed earlier, contribute to uncertainties in dry deposition velocities. The same seasonal averages are applied to each lake, even though they have somewhat different annual cycles of mean conditions (*10*). A range of low-level stabilities and resulting deposition velocities occur during each season, but stable conditions are much more common in spring and summer and unstable conditions in fall and winter. The extent and

Table V. Concentrations of S and N in Lake Superior As Observed and Predicted from Mass Balance Considerations

	lake vol, 10^{12} m^3	wet dep + dry dep, kt/year	other loading, kt/year	outflow, kt/year	1973 lake conc, mg/L	1983 lake conc, mg/L	pred 1983 conc, mg/L
S	11.8	34	178	77	1.00	1.15	1.12
N	11.8	19	35	27	0.368	0.405	0.391

Table VI. Modeled Wet S Deposition Trend (kt/year)

deposition region	1980	1981	1982	1983	1984	1985	1986	1987	1988
lakes									
Superior	18	17	16	26	22	19	8	13	16
Michigan	34	31	27	43	39	35	21	28	28
Huron	42	43	34	46	42	40	20	31	36
Erie	33	34	27	32	34	30	20	28	29
Ontario	23	25	19	21	23	21	14	19	22
total	150	150	123	168	160	145	83	119	131
basins									
Superior	22	20	20	32	27	22	10	16	20
Michigan	63	57	49	80	72	65	38	51	52
Huron	92	92	74	100	93	84	47	69	79
Erie	78	79	64	78	79	73	49	66	67
Ontario	71	76	58	65	70	65	45	60	67
total	326	324	265	355	341	309	189	262	285
Great Lakes basin total	476	474	388	523	501	454	272	381	416

Table VII. Modeled Dry S Deposition Trend (kt/year)

deposition region	1980	1981	1982	1983	1984	1985	1986	1987	1988
lakes									
Superior	17	20	17	25	23	15	15	15	17
Michigan	43	46	45	54	54	46	42	41	42
Huron	37	46	36	45	45	39	36	34	39
Erie	49	52	46	48	53	46	50	49	47
Ontario	30	32	27	27	31	26	30	26	30
total	176	196	171	199	206	172	173	165	175
basins									
Superior	20	22	19	25	25	17	18	20	20
Michigan	75	78	75	89	87	74	73	75	72
Huron	87	96	77	91	95	82	79	81	83
Erie	93	98	88	94	100	94	94	95	91
Ontario	73	73	65	61	68	66	68	60	69
total	345	367	324	360	375	333	332	331	335
Great Lakes basin total	521	563	495	559	581	505	505	496	510

variation of ice cover have not been taken into account.

Uncertainties in modeled air concentrations over the lakes or in modeled deposition to the land basins arise from the simplified model parameterizations of complex atmospheric processes in ASTRAP and from uncertainties in model input. Uncertainties in the parameterizations are less critical here where the combined effects of all sources are being simulated than they would be in examining the effect of changing the emissions of a single source, because the parameterizations are based upon long-term, regional-scale field data under more or less current conditions.

Model input data uncertainties can be related to either emissions or meteorology. The emissions fields were well described for seasonal or longer totals in 1985, with somewhat greater uncertainties for other years examined here. Meteorological observations input to preprocessors are made over land; thus, meteorological analysis over the lakes requires either spatial interpolation in which the meteorological effects of the lakes are not resolved or extensive calculations with a meteorological model sufficiently detailed to produce mesoscale variations associated with the lakes, such as lake breezes and increased wind speeds due to decreased surface roughness. A detailed modeling approach is more correct but is rarely feasible for long-term simulations. The lakes also have mesoscale effects on precipitation. Lake-effect snows are usually confined to the lakes and nearby downwind shores and may be missed entirely by the precipitation networks, while the relative coolness of the lakes in the spring and summer may weaken precipitation systems passing over the lakes. The mesoscale effects can often be detected by weather radar, but such data are rarely used to improve the routine spatial analyses of precipitation produced from precipitation measurements in gauges.

Uncertainty is examined here only qualitatively because modeling estimates cannot be fully verified with observational data. Dry deposition monitoring takes place only at a few research sites, most of which are outside the basin. The uncertainties in measurements and the difficulties in extrapolating site values to regional scales are discussed in (*9*). Wet deposition of S and NO_x N is adequately monitored on the regional scale. However, wet deposition is not monitored over the lakes themselves. Unrepresentative siting and problems with network procedures contribute to the uncertainties in "observed" deposition (*14*).

Modeled Trends in Deposition. An important test of the suitability of a deposition model is its performance in trend simulation. Model evaluation requires deposition observations, which are available for the Great Lakes region in reasonable density (at least for the lower lakes) since 1980. Availability of emission inventories and suitable sets of wind and precipitation analyses for 1980–1988 allow us to model the S deposition trends over the Great Lakes basin during the 9-year period. Intrastate emission variations are known most accurately for 1985. For emission input to the calculations for other years, scaling factors based upon statewide emission inventory trends (*19*) are applied to the intrastate patterns for 1985. Spatial and seasonal details of the temporal trend in Canadian emissions are more uncertain (*20*), but they are included to the extent possible.

Results from ASTRAP simulations are shown in Tables VI and VII. Corresponding estimates of annual deposition produced from observational analyses of precipitation-weighted concentrations and average precipitation for the period 1980–1984 (*14*) are extended through 1986 and presented in Table VIII. For consistency, only observa-

Table VIII. Wet S Deposition Estimated from Observations (kt/year)[a]

deposition region	1980	1981	1982	1983	1984	1985	1986
lakes							
Superior	78 (36)	45 (13)	44 (11)	41 (8)	40 (5)	45 (4)	36 (5)
Michigan	57 (17)	55 (11)	46 (7)	45 (4)	42 (4)	43 (3)	44 (3)
Huron	75 (11)	68 (9)	65 (6)	58 (4)	59 (3)	56 (3)	47 (3)
Erie	34 (2)	36 (2)	33 (2)	28 (1)	35 (1)	35 (1)	33 (1)
Ontario	23 (2)	23 (2)	22 (1)	16 (1)	20 (1)	21 (1)	22 (1)
total	267	227	210	188	196	200	182
basins							
Superior	119 (58)	62 (14)	64 (14)	60 (9)	59 (5)	70 (5)	58 (4)
Michigan	119 (39)	113 (18)	92 (11)	87 (6)	83 (6)	91 (3)	90 (3)
Huron	158 (21)	139 (13)	136 (8)	116 (7)	120 (4)	115 (3)	104 (3)
Erie	99 (4)	100 (4)	92 (3)	74 (3)	85 (3)	93 (2)	88 (2)
Ontario	71 (4)	75 (3)	70 (3)	56 (2)	64 (2)	66 (2)	69 (2)
total	566	489	454	393	411	435	409
Great Lakes basin total	833	716	664	581	607	635	591

[a] Values in parentheses are pooled standard deviations.

tions from the major networks are used in the observational analyses. The uncertainties shown for the analyses are probably understated, because the method cannot fully take into account such factors as mesoscale meteorological variations over the lakes or siting biases. The uncertainties for the upper lakes are much higher for the first two years, when observations were sparser. Both modeled and analyzed results indicate that the deposition was less at the end of the period than at the beginning. There is very little agreement in year-to-year variations, but the year-to-year variations in the observed values are generally nonsignificant. A minimum in deposition, particularly in modeled results, is seen in 1986; summer, the season during which wet S deposition normally peaks, was very dry in the Great Lakes basin (*22*). Modeled wet S deposition was at a maximum in 1983. Although summer of 1983 had slightly less precipitation than normal in the Great Lakes basin (*23*), spring and autumn were much wetter than normal (*24*, *25*). In contrast, the observational analyses indicated a secondary minimum in 1983. Meteorologically induced variability is confounded with emission-induced variability in the deposition trend and makes the detection of any deposition trend related to the relatively small emission changes, about 10% during the period (*19*, *20*), problematic. The normalized trend in total anthropogenic emissions of SO_x in the United States and Canada is shown in Figure 6 to be smoother than the observational analyses and much smoother than the modeled deposition trend.

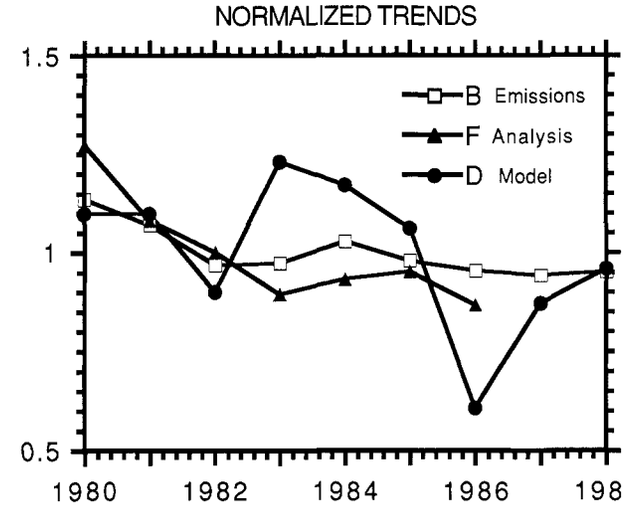

Figure 6. Normalized trends in total S emissions from the Great Lakes states and Ontario (*19*, *20*), wet deposition to the Great Lakes from analysis of observations (*14*), and ASTRAP simulations of wet deposition to the Great Lakes.

Summary and Conclusions

Model simulations of wet deposition of S and NO_x N to the Great Lakes basin show general agreement with analyses of observations, although actual wet deposition remains uncertain because of the lack of monitoring data over water. Model simulations and data analyses show greatest agreement in wet S deposition for the lower lakes and least agreement for Lake Superior, for which the modeled value is much lower than the observational analysis. This difference is thought to be due in part to nonlinear processes not treated in the model and in part to uncertainties in adjustment for the contribution from natural sources; in addition, the analysis of observations has the greatest relative uncertainty there because of the interpolation necessary over the largest Great Lake. Model simulations of dry deposition are much more difficult to evaluate because of the lack of direct monitoring even in the land areas of the basin and because lake effects would be expected to be much greater for dry deposition than for wet deposition. Modeled dry S deposition is about 60% higher than extrapolated observations from a few research sites on land outside the basin. Dry NO_x N deposition estimates from model simulations before overwater adjustment are quite close to those from extrapolation of the limited research site data outside the basin, but the modeled gradient of deposition is steeper. Taking lake effects into account increases modeled estimates of dry NO_x N deposition by 25%.

Comparisons with estimates of other loading terms for S and N to Lake Superior indicates that direct deposition of anthropogenic emissions to the lake is important but not dominant (16% and 35% contributions to S and N inputs, respectively) for the mass budget of both elements. However, when one allows the deposition of natural emissions, meteorological and emission variability, and runoff of terrestrial deposition, then deposition to the basin becomes more significant (22–48% and 41–92% contributions for S and N, respectively) and gives support for an atmospheric source of the increasing nitrate concentrations in Lake Superior.

Model simulations of the trend in S deposition during the period 1980–1988 indicate considerably more variability than occurred in the annual emission totals. This appears to be the result of large variations in meteorological conditions, particularly precipitation, and illustrates the difficulty in detecting the effect of minor emission changes over a relatively short period with statistical confidence. There is little agreement in year-to-year

variations between model estimates and analysis of observations, although both indicate a long-term decrease.

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