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LONG RANGE TRANSPORT OF ACID RAIN
PRECURSORS

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ABSTRACT

A model of the long range transport of primary and secondary pollutants derived by Fay and Rosenzweig (1) is applied to the problem of the transport of acid rain precursors. The model describes the long term average (annual or seasonal) airborne pollutant concentration due to a single source. Because the chemical transformation and physical deposition processes are assumed to be linear in the concentrations, the contributions of many sources may be determined by superposition. Simplified forms of the source-receptor relation are derived for ranges of the model parameters which are appropriate to sulfur oxide species. Quantitative results of applying the model to airborne sulfates in the eastern U.S. are compared with more complex models.

NOMENCLATURE

D	Horizontal turbulent diffusivity
f_{si}	Fraction of secondary pollutant concentration due to source i
h	Height of atmospheric mixing layer
k_{si}	Ratio of secondary pollutant concentration to primary source strength, Eq. (14)
K_0, K_1	Modified Bessel functions of order 0 and 1
ℓ	Length scale defined by Eq. (4)
Q	Primary pollutant source strength
Q_i	Primary pollutant source strength of source i
r	Radial distance of source from receptor
s	Length scale defined by Eq. (10)
w	Mean wind speed
x	Streamwise distance of receptor from source
y	Normal distance of receptor from source
β	Mass of secondary pollutant formed per unit mass of primary pollutant
λ	Length scale defined by Eq. (3)
η	Length scale defined by Eq. (8)
τ	Inverse of rate constant for loss of primary pollutant
τ_c	Inverse of rate constant for conversion of primary to secondary pollutant
τ_s	Inverse of rate constant for loss of secondary pollutant
X_p	Concentration of primary pollutant
X_s	Concentration of secondary pollutant
X_{s0}	Concentration of secondary pollutant at $r = 0$

INTRODUCTION

Acid rain is the popular name for wet deposition to the earth's surface of acidic solutions in the form of rain, snow, sleet, fog, and mist. Acidic aerosols also are deposited slowly by gravity; this is termed dry deposition. The acidic content of these deposits is principally due to sulfates and nitrates, but other species of lesser importance may also be present. In the heavily industrialized regions of eastern North America and Western Europe where precipitation is most acidic, the sulfate and nitrate ions are predominantly anthropogenic in origin, having been formed in the atmosphere from NO and SO₂ precursors emitted as byproducts of the combustion of fossil fuels.

Because acid rain is found in rural areas downwind of industrialized regions, it is clear that precursors are transported in the atmosphere for long distances, of the order of hundreds of kilometers, before being deposited in wet form. During this period of travel, which may require a day or more, the precursors are oxidized to the acidic ions, SO₄²⁻ and NO₃⁻, via complex processes which are not well understood at the present time. The precise relationship between the amount of precursor emissions and the rate of wet acid deposition at remote distances from the emission sources is not known unequivocally because of the complexity of the intervening processes. It is the objective of long range transport models to provide quantitative information on such source-receptor relationships for use in acid rain control programs.

Models which describe the transport, transformation and deposition of air pollutants at long distances from the source (of the order of 10³ km) are of two types: Lagrangian and Eulerian. The former utilize air parcel

trajectories computed from historical meteorological data to relate source emissions to receptor effects, while the latter describe average flow properties within an Eulerian grid. This paper is concerned with an Eulerian model averaged over a long time period (several months to a year) and utilizing the statistical properties of air parcel trajectories. Such a model has been termed a climatic model to distinguish it from episodic models which attempt to describe the temporal changes in air pollution over a period of several days within a large region but containing fine spacial resolution. Climatic models show less spatial and time resolution than do episodic models.

The transport and transformation of acid rain precursors occurs within a mixed layer at the base of the atmosphere whose height is of the order of a few kilometers. But because the transport occurs over hundreds of kilometers, the dispersion of the pollutants is primarily in the two lateral dimensions parallel to the earth's surface. While the most elaborate models include vertical mixing within the mixed layer as an element, most models, like ours, assume that the primary and secondary pollutants are well mixed vertically and hence the variables of interest, such as concentrations of airborne species and deposition rates, are functions of latitude and longitude only.

A critical element in any model is the specification of the rate processes for chemical transformation of primary precursors to secondary acidic species and deposition of either species to the earth's surface. These complex processes are represented by first order linear terms in the mass conservation equation for each species. While this cannot be precisely true, especially for the transformation processes, it may be a

sufficiently good approximation to the actual process to preserve the usefulness of a model for analytical or predictive purposes.

The long distance transport model discussed below was devised by Fay and Rosenzweig (1) to describe the long distance transport of primary and secondary pollutants. It provides for the conversion of primary to secondary pollutant species and the wet and dry deposition of both species as linear processes. By virtue of the linear approximation, the contributions from various sources can be added together, greatly augmenting the usefulness of the model. In this paper we extend and simplify the model for the purpose of evaluating acid rain control programs.

DISPERSION MODEL

The long distance dispersion model of Fay and Rosenzweig (1) assumes that the horizontal dispersion can be expressed by a turbulent transport model having a horizontal eddy diffusivity D which is constant throughout the flow field. Averaging over long times and assuming that the mean wind speed w is also constant in magnitude and direction everywhere, the conservation of mass of primary pollutant, whose mass concentration is χ_p , becomes

$$w \frac{\partial \chi_p}{\partial x} = D \left(\frac{\partial^2 \chi_p}{\partial x^2} + \frac{\partial^2 \chi_p}{\partial y^2} \right) - \chi_p / \tau \quad (1)$$

in which x and y are the streamwise and normal distances and τ^{-1} is the rate constant for loss of primary pollutant due to wet and dry deposition and conversion to secondary pollutant.

We next find a solution to Eq. (1) for a source of mass flux Q of primary pollutant located at the origin ($x=0, y=0$):

$$\chi_p = (Q/2\pi hD) \exp(x/\lambda) K_0\{r/\ell\} \quad (2)$$

in which h is the height of the mixing layer, r is the radial distance from the source to the receptor, $K_0\{z\}$ is the modified Bessel function of zero order and argument z , and the lengths λ and ℓ are defined by:

$$\lambda \equiv 2D/w \quad (3)$$

$$\ell^{-2} \equiv \lambda^{-2} + (D\tau)^{-1} \quad (4)$$

so that $\ell \leq \lambda$. Because the dispersion equation (1) is linear, we may superpose any collection of sources to determine the concentration χ_p at a chosen receptor location. Near the origin, χ_p varies in proportion to $\ln(r/\ell)$. This is a weak singularity which can be avoided in a practical calculation (1). Eq. (2) breaks down at $r = 0$ because Eq. (1) assumes perfect vertical diffusion at the source. At very large distances from the source, χ_p decreases exponentially with r , more rapidly in the upwind than in the downwind direction.

A mass conservation equation similar to Eq. (1) can be written for the secondary pollutant concentration χ_s :

$$w\partial\chi_s/\partial x = D(\partial^2\chi_s/\partial x^2 + \partial^2\chi_s/\partial y^2) - \chi_s/\tau_s + \beta\chi_p/\tau_c \quad (5)$$

in which τ_s^{-1} is the rate constant for loss of secondary pollutant due to both wet and dry deposition, τ_c^{-1} is the rate constant for conversion of primary to secondary pollutant (which must be less than τ^{-1}), and β is the mass of secondary pollutant formed per unit mass of primary pollutant. For a source of primary pollutant at the origin, Eqs. (2) and (5) can be solved to yield:

$$X_s = (\beta Q / 2\pi h D) \exp(x/\lambda) [K_0\{r/\ell\} - K_0\{r/\eta\}] / [(\zeta/\eta)^2 - (\zeta/\ell)^2] \quad (6)$$

in which the lengths ζ and η are defined by:

$$\zeta^2 \equiv D\tau_c \quad (7)$$

$$\eta^{-2} \equiv \lambda^{-2} + (D\tau_s)^{-1} \quad (8)$$

Note that both η and ℓ are less than λ , but ζ may be more or less than λ .

Fay and Rosenzweig (1) suggest the following values for the dimensional parameters of Eqs. (2) and (6): $w = 2\text{ms}^{-1}$; $D = 2 \times 10^6 \text{m}^2 \text{s}^{-1}$; $\tau = 8 \times 10^4 \text{s}$; $\tau_s = 1.6 \times 10^5 \text{s}$; $\tau_c = 2.4 \times 10^5 \text{s}$. The corresponding length scales are $\lambda = 2 \times 10^6 \text{m}$; $\ell = 3.9 \times 10^5 \text{m}$; $\zeta = 6.9 \times 10^5$; $\eta = 5.4 \times 10^5$. Thus the length scales are of the order of 100 km except for λ , which is an order of magnitude larger. As consequence, the factor $\exp(x/\lambda)$ varies more slowly than the Bessel functions in Eqs. (2) and (6), suggesting that the convective term in Eqs. (1) and (5) is not of great importance.

In Fig. 1 is reproduced Fig. 3 of Fay and Rosenzweig showing a comparison of the annual average of the secondary pollutant, airborne sulfate, as calculated (solid line) from Eq. (6) and as measured (dotted line through smoothed values) at monitoring stations indicated by the small circles. This comparison includes an assumed background level of $6 \mu\text{gm}^{-3}$. One can see that the agreement is satisfactory over the eastern half of the United States where substantial rain acidity has been observed (2).

It is interesting to determine the fraction of the primary pollutant which is ultimately deposited in the form of wet or dry deposition of

secondary pollutant. Since the rate constant for conversion of primary to secondary pollutant is τ_c^{-1} and the rate constant for deposition of primary pollutant is τ^{-1} , and these rates are the same everywhere throughout the flowfield, the ratio τ/τ_c must be the ratio of secondary to primary deposition rates. For the values of τ and τ_c quoted above for SO_2 emissions, τ/τ_c is 1/3. This may be compared with Golomb's (3) estimate that 0.18 of SO_2 emissions in the eastern U.S. is wet deposited as sulfate. Galloway and Whelpdale (2) estimate that dry deposition is about the same as wet deposition. Thus the quoted value of 1/3 for τ/τ_c is compatible with these estimates.

It is possible to simplify the form of Eq. (6) if $|r/\lambda - r/\eta| \ll 1$ or $r \ll |\lambda^{-1} + \eta^{-1}|^{-1}$. Using the values of λ and η quoted above, this would require that $r \ll 1.4 \times 10^6$ m. But at distances as great or greater than this limit χ_s would be very much smaller than its value near the primary source, and hence of little practical interest. In this limit Eq. (6) takes the form:

$$\chi_s = (\beta Q / 4\pi h D) (s/\tau)^2 [\exp(x/\lambda)] (r/s) K_1\{r/s\} \quad (9)$$

in which K_1 is the modified Bessel function of order one and the length s is:

$$s \equiv (\lambda + \eta)/2 \quad (10)$$

and has a value of 4.7×10^5 m if the values of λ and η are those quoted above. If $\lambda \gg s$ the exponential factor in Eq. (9) can be neglected without much loss of accuracy in determining χ_s .

The distance-dependent factors (the last two) of Eq. (9) depend only upon the normalized distance r/s . Fig. 2 shows how these factors

decrease as a function of r/s , ultimately decaying exponentially according to the asymptotic limit:

$$(r/s) K_1\{r/s\} \approx (\pi s/2r)^{1/2} \exp\{-r/s\} \quad (11)$$

Note, however, that the secondary pollutant concentration is nearly uniform near the primary source ($r=0$) and does not substantially decay until r/s exceeds unity.

Of particular interest is the concentration χ_{s0} of secondary pollutant at the source ($r=0$) of the primary pollutant. In this limit Eqs. (6) and (9) reduce to, respectively,

$$\chi_{s0} = (\beta Q/2\pi h D) \ln (\ell/\eta) / [(\zeta/\eta)^2 - (\zeta/\ell)^2] \quad (12)$$

$$= (\beta Q/2\pi h D) (s^2/2\zeta^2) \quad (13)$$

where Eq. (11) is the equivalent of Eq. (12) of Fay and Rosenzweig (1).

SOURCE APPORTIONMENT

Source apportionment is a methodology for determining the fraction of the concentration χ which is due to each source i (of strength Q_i) among a collection of contributing sources. Our linear model may be used to determine the fractions f_{si} of secondary pollutant which are caused by the primary sources Q_i . First we determine the transfer coefficients k_{si} relating the receptor concentration to the source strength:

$$k_{si} \equiv \chi_s / Q_i \quad (14)$$

using Eq. (6) or (9) to evaluate χ_s / Q_i . Then the source apportionment fraction f_{si} is found from:

$$f_{si} = k_{si} Q_i / \sum_j k_{sj} Q_j \quad (15)$$

Note that the fractions f_{sj} are independent of the absolute value of x_s as determined by the leading factor in Eq. (6) or (9) and depend only upon the distance related factors (as illustrated in Fig. 2) and, of course, the primary source strengths Q_i .

To illustrate the usefulness of the source apportionment fractions, we show in the first column of Table 1 the percentage of annual average ambient sulphate at a receptor located in the Adirondack mountains as calculated from Eqs. (14) and (15) of this paper. The sulfur sources considered are those in a 31 state region bordering on and east of the Mississippi River (4). Ten states or groups of states (14 states all told) are listed in rank order of their contribution to the Adirondack sulfate level. Their cumulative contribution is more than 80% of the total from the 31 states. It can be seen from the list that the major contributors are the nearby states in the northeast region of the U.S. Nearly half of all the ambient sulfate from the 31-state group is caused by the states which share a border with New York (including, of course, New York itself).

Table 1 also shows a comparison with similar calculations based on results from models which were reviewed by the U.S. - Canada Regional Modeling Subgroup (5). Of these models, MOE is a climatic model similar to that of this paper; ASTRAP, ENAMAP and UMACID are trajectory models; MEP and AES are Lagrangian models and CAPITA is a Monte Carlo model. Despite the quite different features of these models, the principal results are quite similar; i.e., the predominant effect of nearby sources and the negligible contributions of the more distant ones. The implications of these source apportionment analyses for acid rain control strategies are discussed by Fay and Golomb (6).

The last column of Table 1 lists the geometric mean of all eight entries.

CONCLUSION

The climatic model of dispersion of acid rain precursors described in this paper is an easy one to apply to the determination of the relative contributions of various sources to the ambient concentrations of secondary pollutants. Like most other linear models, it makes use of the principle of superposition to determine source-receptor relationships.

The relationship of secondary pollutant level to primary source strength, distance and orientation to the average wind involves the use of several parameters characterizing the importance physical and chemical processes. Assumed values of these parameters determine the quantitative results but the qualitative features of the model are related to the model assumptions regarding the transport, transformation and deposition of pollutants.

An example of the determination of the source apportionment fractions of air-borne sulfate at an Adirondack receptor shows the dominant influence of nearby sources compared with distant sources. These features are quantitatively similar to those derived from seven other models of greater complexity.

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TABLE 1
 Comparison of Model Predictions for % of Ambient Sulphate
 at Adirondack Receptor⁺

Model Source State	This paper	MOE*	ASTRAP*	ENAMAP*	UMACID*	MEP*	AES*	CAPITA*	Mean and S.D.
PA	17.4	13.2	18.1	19.7	15.9	23.6	19.5	18.6	18.3 ± 3.0
OH	14.8	16.2	15.9	26.7	20.9	17.4	18.8	17.7	18.6 ± 3.8
NY	10.5	9.4	24.2	9.3	12.4	23.4	13.3	10.1	14.1 ± 6.2
IN	7.6	9.5	7.8	9.7	8.1	5.1	7.2	8.9	8.0 ± 1.5
WV	6.6	5.2	4.9	7.9	5.7	5.6	6.7	8.9	6.4 ± 1.4
MD/DE/NJ/DC	6.4	3.4	4.2	2.9	3.5	5.5	4.0	3.1	4.1 ± 1.2
MA/CT/RI	5.8	2.9	1.3	2.7	4.7	3.6	2.6	1.7	3.2 ± 1.5
MI	5.2	7.8	3.9	7.3	7.2	6.1	9.0	5.9	6.6 ± 1.6
IL	3.9	6.5	4.0	2.7	5.1	2.3	6.0	5.4	4.5 ± 1.5
KY	3.4	3.5	3.7	4.4	3.0	1.7	2.1	3.8	3.2 ± 0.9
Other	18.4	32.4	12.0	6.7	13.5	5.5	10.8	15.9	14.4 ± 8.5

+ Sources in 31 state region only (4)

* Data from (5)

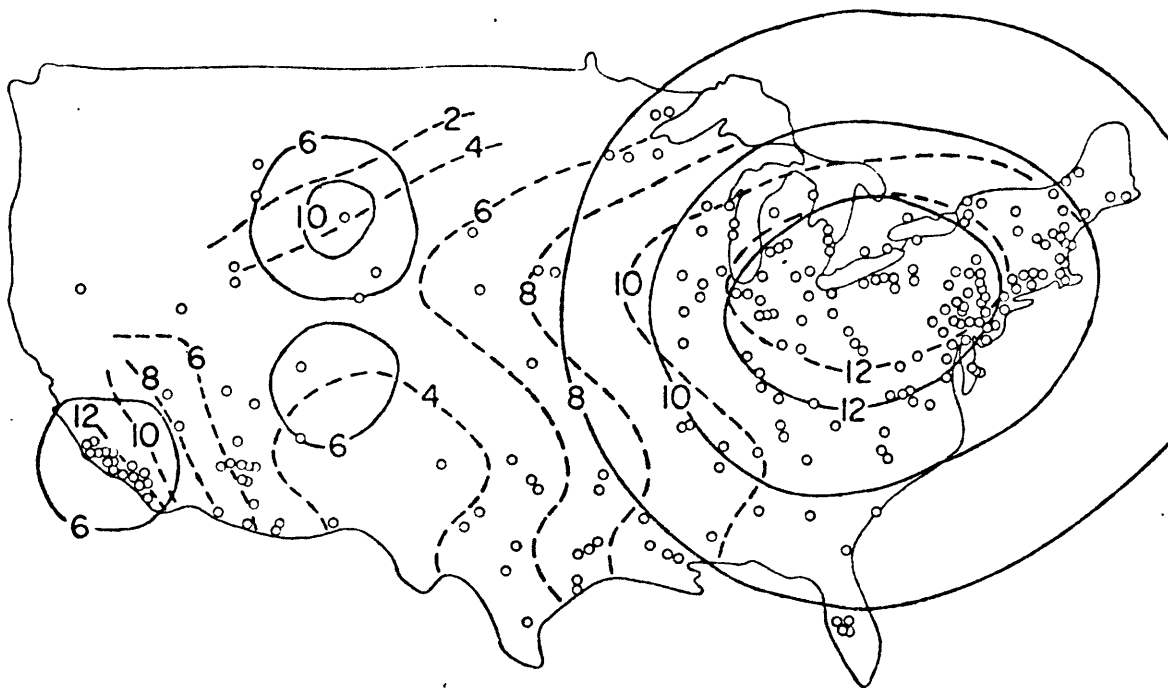


Fig. 1 A comparison of the annual average sulfate concentration ($\mu\text{g m}^{-3}$) in the U.S. as calculated (solid line) by Fay and Rosenzweig (1) and as measured (dotted line through smoothed values) at monitoring stations indicated by small circles. From (1).

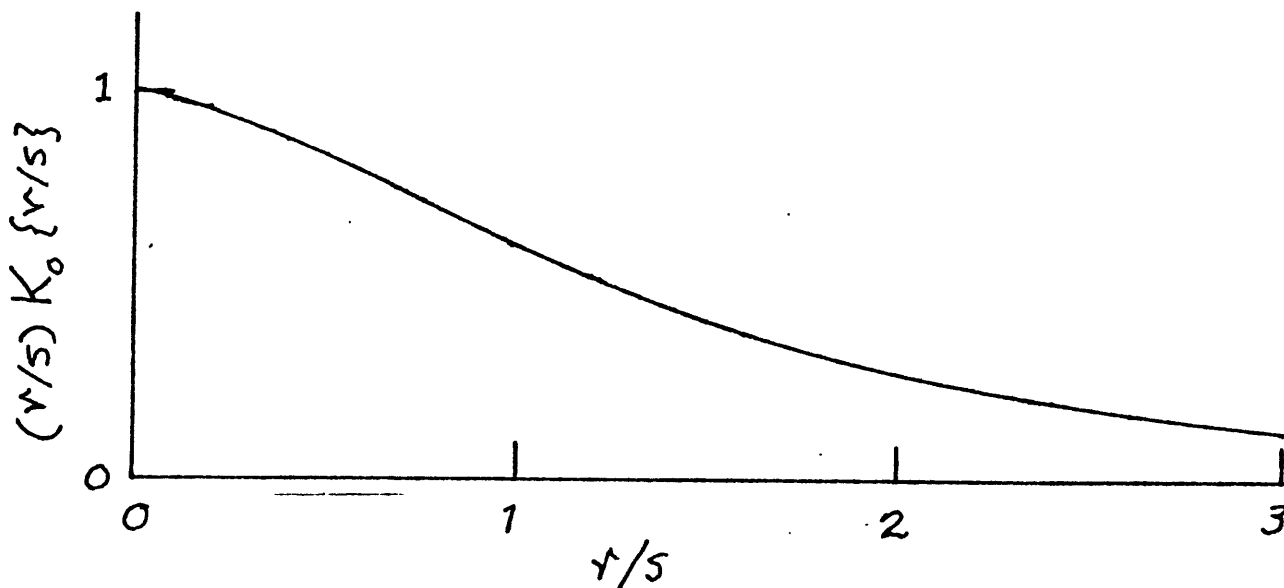


Fig. 2 Space dependent factor of secondary pollutant concentration (Eq. 9).

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