



Project Summary

Improved Parameterizations for Surface Resistance to Gaseous Dry Deposition in Regional-Scale, Numerical Models

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Methods for estimating the dry deposition velocities of atmospheric gases in the United States and surrounding areas have been improved. The improvements have been incorporated into a revised module of computer coding for use in numerical models of atmospheric transport and deposition of pollutants over regional scales. As before, the dry deposition module computes deposition velocities for five seasonal categories and 11 landuse types specified in a landuse map. The key improvement is the computation of bulk surface resistances according to three distinct pathways of mass transfer: to the upper portions of vegetative canopies, to the lower portions of canopies or structures, and to the ground (or water surface). This approach replaces the previous technique of providing simple tables for looking up bulk surface resistances. With the surface resistances divided explicitly into several pathways, the bulk surface resistances for a large number of gases can be computed in addition to those for gases considered in the previous module (SO_2 , O_3 , NO_x , and HNO_3), if estimates of the effective Henry's Law constants and appropriate measures of the chemical reactivity of the various substances are known. This has been accomplished successfully for H_2O_2 , HCHO , acetaldehyde (to represent other aldehydes), methyl hydroperoxide (to represent organic peroxides), peroxyacetic acid, HCOOH (to represent organic acids), NH_3 , PAN, and HNO_2 . Other factors considered include surface temperature, stomatal response to en-

vironmental parameters, the wetting of surfaces by dew and rain, and the covering of surfaces by snow. Surface emission of gases and variations of uptake characteristics by individual plant species within the landuse types are not considered explicitly.

This Project Summary was developed by EPA's Atmospheric 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

Dry deposition of gases from the atmosphere provides a primary means of cleansing the atmosphere and delivering chemical doses to surface components. Numerical simulation of dry deposition is important in evaluating the relationships between emissions in one area and deposition in another. The dry deposition module of the Regional Acid Deposition Module (RADM) has been used to compute the dry deposition velocities for SO_2 , O_3 , NO_x (defined as the sum of NO and NO_2), sulfate (in submicron particles), and HNO_3 in the United States and southern Canada. The basis for the parameterizations of the deposition velocities were micrometeorological formulas and, for SO_2 , O_3 , and NO_x , tables of resistances to uptake. The purpose of the present work is to put these tables on a more solid scientific footing, within a framework that enables logical extension to additional gaseous

substances such as H₂O₂, HCHO, other aldehydes, organic peroxides, peroxyacetic acid, organic acids, PAN, NH₃, and HNO₂. Other improvements include a more explicit means to evaluate changes in surface resistances caused by the effects of surface wetness associated with dew and rain.

Procedures

The general approach commonly used in resistance models of dry deposition of gases is summarized by the following formula:

$$v_d = (r_a + r_b + r_c)^{-1} \quad (1)$$

where v_d is the deposition velocity, which can be multiplied by the concentration at a specific height to produce the deposition rate; r_a and r_b are gas-phase resistances to vertical transport, which are computed by conventional means; and r_c is the bulk surface resistance and is the focus of this work. In the previous version of the dry deposition module, the estimates of r_c for SO₂ and O₃ were obtained from simple tables for looking up surface resistances for each of the 11 landuse types specified in a computerized landuse map (urban land, agricultural land, range land, deciduous forest, coniferous forest, mixed forest including wetland, water, barren land, non-forested wetland, mixed agricultural and range land, and rocky open areas occupied by low-growing shrubs). The tables were duplicated for each of five seasonal categories (midsummer, autumn, late autumn, winter with snow, and transitional spring). The values of r_c for NO_x were calculated with a simple function of the values for O₃, and values of r_c for HNO₃ were assumed to be very small in all cases.

The improved procedures for the revised module divide the bulk surface resistance into component resistances for three major pathways of mass flux, as is shown in Figure 1. To implement this model, a table of numerical values of the component resistances (except for r_m) is provided for the landuse types and seasonal categories specified above. The component resistances are as follows:

- (i) r_s , the leaf stomatal resistance for water vapor (the table lists minimum values, and an algorithm is supplied to compute r_s as a function of solar irradiation and surface temperature);
- (ii) r_m , plant mesophyll resistance (computed entirely from algorithms);
- (iii) r_{lu} , resistance at the outer surfaces of leaves in the upper canopy;
- (iv) r_{dc} , a gas-phase dynamic resistance from the top of the canopy to the sur-

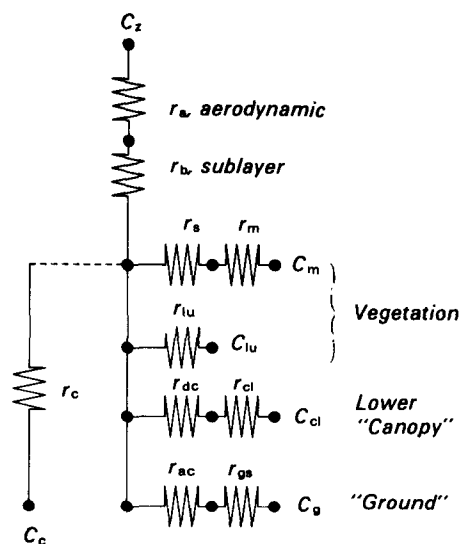


Figure 1. Schematic diagram of pathway resistances used in the dry deposition module.

- face in the lower parts of the canopy (or structure);
- (v) r_{cl} , surface resistance at lower parts of the canopy or structure, with separate values listed for SO₂ and O₃;
- (vi) r_{ac} , an aerodynamic resistance from the top of the canopy to the surfaces at the ground beneath the canopy;
- (vii) r_{gs} , surface resistance at the ground (soil surface, leaf litter, exposed water, etc.), with separate values listed for SO₂ and O₃.

All resistances represent bulk surface characteristics and can be combined by series and parallel additions, analogously to Ohm's law, to compute the overall surface bulk resistance r_c . Of course, the table of values itself constitutes a look-up table, by landuse type and seasonal category, and superficially may appear to be needlessly complicated as compared to the previous look-up tables. This is not the case, however, because the new table allows a more thorough scientific approach and more versatility.

The versatility of the present approach becomes evident when the effects of surface wetness caused by dew and rain are considered. For example, recent experiments have shown that the presence of dew tends to increase uptake of SO₂ by vegetation and to slightly reduce O₃ surface removal, whereas wetting by rain decreases SO₂ uptake and slightly increases O₃ removal. This is easily taken into account by manipulating the values for r_{lu} and r_s . In addition, generalized formulas describe the increase of uptake resistances caused by cold surface conditions.

The scheme represented by Figure 1 also represents a fairly rigorous procedure to estimate the bulk surface resistances for many substances in addition to SO₂ and O₃, whose surface resistance components are fairly well known because of the large number of relevant observations taken in the field and laboratory. Sulfur dioxide is readily soluble in water at near-neutral pH, which is typical of the interior of plant leaves and of many other biological substrates. Ozone, on the other hand, is weakly soluble in water but is much more reactive in terms of oxidizing power, which seems to be a crucial factor affecting uptake by many types of natural surfaces. To take solubility into account, the effective Henry's Law constant at a pH of seven for the substance of interest is compared to the constant for SO₂. The ratio of the two constants is applied in formulations that allow evaluation of the effect of solubility on resistances of the plant mesophyll, outer surfaces of leaves in the upper canopy, and exposed surfaces in the lower portions of the structure or canopy and at the ground. A similar scaling approach involving O₃ takes into account the chemical reactivity of a substance. In this case, a measure of chemical reactivity is derived from the negative log of electron activity for half redox reactions in neutral aqueous solutions and from the overall, second-order, aqueous reaction rates with S(IV). A substance can be classified as highly reactive (as reactive as O₃), slightly reactive, and nonreactive. Numerical values assigned to each of these classifications are used in the formulations for many of the component resistances for r_c , those resistances noted above to be affected by solubility.

Results and Conclusions

The values of r_c for SO₂, O₃, NO₂, NO, and HNO₃ estimated with these procedures are nearly the same as those found with the previous dry deposition module. The uptakes of SO₂, O₃, and NO₂ by healthy vegetation during the daytime are controlled by stomatal resistances. Ozone surface resistances tend to be smaller than those for SO₂, and the differences are accentuated for surfaces that are rather inactive biologically, such as senescent vegetation and surfaces typical of winter and autumn landscapes. The surface resistance for HNO₃ is always small, in accordance with its very large value of Henry's Law constant. A value of r_c near 10 s m⁻¹ should be assumed for HNO₃ and other substances whenever r_c is nearly zero, in order to avoid unrealistic estimates of extremely high deposition velocities over unusually rough surfaces.

Consistent with experimental observations, the resistances for NO₂ for surfaces other than sunlit vegetation appear to be quite large, a result of the relatively low solubility and chemical reactivity of NO₂. The resistances for NO indicate practically no surface uptake. It is recommended that the sum of NO and NO₂ should be considered, not either alone, because rapid in-air chemical reactions can change the vertical fluxes of each of these substances but do not change the sum of the two fluxes. Another factor that should be considered for these nitrogen oxides, as well as NH₃, is that surface emissions due to biological activity can obviate the usefulness of the air-surface exchange rates estimated with the present scheme. More realistic estimates would be produced if an internal concentration corresponding to a compensation point, typically a few ppbV, were assumed for C_m, C_{lu}, C_{cl}, or C_g in Figure 1, rather than the value of zero implied when deposition velocities are used with air concentrations to estimate fluxes.

The resistances computed for other substances are predictions that usually have few, if any, supporting field data. Hydrogen peroxide has the unusual properties of being both moderately soluble in water and a strong oxidizing agent. Rapid removal takes place at wet surfaces, and moderately rapid deposition occurs over vegetation. Many surfaces that may seem somewhat inert, such as those in unharvested agricultural areas, remove H₂O₂ fairly efficiently. Solubility alone is highlighted in the surface resistances calculated for formaldehyde (HCHO), formic acid (HCOOH, or ORA to represent organic acids), and acetaldehyde (CH₃CHO, or ALD to represent aldehydes other than HCHO). Formaldehyde is taken up rather rapidly at liquid water surfaces and by sunlit vegetation, but has much less interaction with soils and senescent vegetation. The rather large solubility of formic acid allows it to be taken up rapidly at many different types of surfaces. Variations on the same theme are seen for NH₂ and HNO₂.

The remaining three substances, methyl hydroperoxide (CH₃O₂H, or OP to represent several organic peroxides), peroxyacetic acid [CH₃C(O)O₂H, or PAA], and peroxyacetyl nitrate [CH₃(O)O₂NO₂, or PAN], have slightly limited solubility and are moderately reactive as oxidants. PAN is the least soluble and thus has the largest surface resistance of the three substances for sunlit green vegetation, although the low solubility of PAN is offset somewhat by its relatively higher reactivity. This behavior of

PAN is consistent with laboratory observations.

In conclusion, the dry deposition module, which is available along with the landuse map in computer-compatible form, provides a means to estimate the dry deposition velocities for many substances. Limitations include the fact that the module categorizes all surfaces by only 11 landuse types and considers only five general seasonal categories. Estimates of dry deposition velocities are probably not very accurate for short periods of time or for a particular small area. Rather, the estimates are intended for long-term averages over at least several weeks and for rather large areas, over which the individual variations of plant species composition and factors such as soil moisture content are smoothed. For vegetation, uptake resistances by individual plant species have not been identified, and the influence of varying amounts of leaf area (green or senescent) has not been tied explicitly to a measurable quantity such as LAI (leaf area index). The following factors are considered in a general fashion: vegetation height, aridity or soil moisture content, surface temperature, and variations of leaf stomatal resistance with solar radiation and temperature. A number of factors that can strongly influence air-surface exchange are not considered. These include the differences between sea water and fresh water, the effects of fog or impacting cloud water at high elevations, soil alkalinity or acidity, and natural surface emissions.

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The complete report, entitled "Improved Parameterizations for Surface Resistance to Gaseous Dry Deposition in Regional-Scale, Numerical Models," (Order No. PB 88-225 099/AS; Cost: \$14.95, subject to change) will be available only from:

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