

DEPOSITION OF SEMI-VOLATILE AIR TOXIC POLLUTANTS TO THE GREAT
LAKES: A REGIONAL MODELING APPROACH

by

Jason K.S. Ching*, Francis S. Binkowski*, and O. Russell Bullock, Jr.*

Atmospheric Sciences Modeling Division

Air Resources Laboratory

National Oceanic and Atmospheric Administration

Research Triangle Park, NC 27711

Jason Ching, Atmospheric Modeling Division, National Exposure Research Laboratory,
(MD-80), Research Triangle Park, NC 27711 (919) 541-4801/(FAX (919) 541-1379.

** On assignment to the National Exposure Research Laboratory, U.S. Environmental Protection Agency*

DISCLAIMER

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

A modeling approach is described that will be able to predict wet and dry deposition of toxic airborne semi-volatile organic compounds (SVOCs) applicable on a regional scale. In principle, these compounds cycle between the aerosol or the gas phases depending primarily on their vapor pressure and the ambient temperature and aerosol particle concentration. This study outlines an approach using as its modeling framework the U.S. Environmental Protection Agency's (USEPA) Regional Particulate Model (RPM) which predicts size distribution and the chemical composition of secondary formed aerosol particles. These particles provide sites for the condensation or volatilization of these semi-volatiles. Partitioning of ambient SVOCs between gas and particles based on formulations of Pankow (1993) are proposed and discussed and a requirements plan presented. It is demonstrated that the approach can handle a wide range of volatility characteristic of various compounds. Examples of the use of the RPM for relatively low volatility organochlorines and relatively high volatility persistent aromatic hydrocarbon pollutants are presented.

Key Words: Semi-Volatile Organic Compounds

Toxics deposition

Modeling Toxics

Great Lakes pollution

Great Waters Study

INTRODUCTION

Toxic air pollutants generally have long atmospheric residence times and therefore can be transported great distances from their sources. During transport, these pollutants are removed from the atmosphere via dry deposition and wet deposition processes. Once deposited from the atmosphere, the pollutants enter terrestrial and aquatic systems where they can adversely affect the health of the ecosystem by causing undesirable mutations and/or cancer in vulnerable species. Many of these pollutants can bioaccumulate causing ecological problems for decades. Semi-volatile pollutants, those that coexist in the atmosphere in both the gas and particle phases, can revolatilize back to the atmosphere after deposition, thereby extending the atmospheric transport scale. Toxic pollutants deposited to farmlands, grasslands and water bodies can enter the human food chain and contribute to adversely increasing human health problems. Recognizing the health hazards of toxic air pollutants, Congress in 1990 passed the Clean Air Act Amendments (CAAA-90), which in part require the USEPA to quantify the relative atmospheric loadings and identify the major sources of 189 particulate, gaseous and semi-volatile toxic pollutants to the "Great Waters", including the Great Lakes. Extensive routine and intensive monitoring studies, compilations of air emission inventories, as well as the development and application of an appropriate regional atmospheric model, specifically for targeted toxic air pollutants, are necessary to conduct the mandated assessments. Research and modeling results are to be presented to Congress on a biennial basis. A general overview, statement and discussion of the problem, issues associated with and current knowledge about environmental hazards and technical aspects of loadings and deposition of toxic pollutants are presented in the first of such reports (USEPA, 1994),

This paper focuses on the scientific modeling issues and the approach to develop a regional atmospheric model specifically designed for semi-volatile toxic pollutants. The approach calls for an adaptation of the existing RPM, an Eulerian model based on the USEPA Regional Acid Deposition Model (RADM). Deposition of such pollutants is modeled for both gas and particle phase pollutants.

CURRENT MODELING ASSESSMENTS

Current regional atmospheric models for aerosols are considered "screening-level" models. That is, due to the lack of data and knowledge, these models do not consider all the relevant atmospheric chemistry and particle dynamics processes or do not include detailed simulations of the processes. Consequently, model calculations of atmospheric deposition may yield our current best estimate, but it is accompanied by an uncertainty of unknown magnitude.

Such a screening-level model, the Regional Lagrangian Model of Air Pollution (RELMAP), (Eder et al., 1986) was recently applied to calculate the 1989 annual atmospheric deposition of anthropogenically emitted trace metals (i.e., arsenic, cadmium, chromium, lead and nickel) to Lake Superior (Clark, 1993). One of the main result of that study is a demonstration of the large spatial extent to which toxic pollutants can be transported in the atmosphere. Two examples of models results are shown in Figure 1 which show that significant lead (Pb) and Chromium (Cr) emissions can be transported across spatial scales exceeding 1000 km. Indeed, for cadmium, chromium and nickel, the most significant sources (those contributing 77%, 40%, and 50%, respectively, of the total annual atmospheric deposition to Lake Superior) were in excess of 800 km from Lake Superior. Semi-volatile pollutants can very likely be

transported across even greater transport distances due to recycling between deposition and revolatilization between the atmosphere and the earth's surface.

THE CHALLENGE:

When modeling regional-scale deposition of air toxics, it is noted that the deposition is cumulative over long-term periods, the processes involved from the point of release to deposition are numerous and complex, and the inventory of emissions and their temporal and spatial distributions are largely incomplete. Significant progress has been made, recently, in developing state-of-science regional scale air pollution deposition models for applications to specific environmental pollutant issues such as oxidants (Lamb, 1983), and acid deposition (Chang et.al., 1990; NAPAP, 1991). In principle, such models can be adapted for use in studies of toxic deposition to large water bodies such as the Great lakes, however, the modeling of air toxics presents additional complications and challenges.

Many of the 189 toxic pollutants cited in the CAAA-90 list are semi-volatile, that is, their vapor pressure permits a residence state in the atmosphere as either aerosols or gas phase depending on the ambient temperature. In low temperature conditions, semi-volatile toxics seek to condense upon existing aerosols. However, when the temperature increases, the SVOC compound volatilizes from the aerosol. Regional-scale air toxics models must be able to ascertain the phase state of such compounds when dealing with their transport and deposition when humidity and temperature undergo large temporal and spatial variations. Cycling between the gas and aerosol states can occur diurnally and in conditions of air mass modification. Deposition to the earth's surface is different for gases and particles. During transport, the host

aerosol particles can undergo complex changes in both their chemical constituents, moisture content and size distribution. The gas-to-particle attachment (and vaporization) is complicated by the degree of wetness of the aerosol surfaces (Graedel et.al., 1981). Additionally, models must recognize and treat the vertical exchange of toxic pollutants between air and water surfaces. Highly polluted water bodies may, under some meteorological conditions, be sources of toxic pollutants to the atmosphere, the opposite of deposition (Hornbuckle et al., 1994). Further, toxic compounds can revolatilize from land and vegetative surfaces effectively extending the overall transport scale of the problem (Pankow 1993).

THE APPROACH:

The USEPA is developing a toxic air and gas exchange model to predict the concentrations and deposition of SVOC toxic pollutants in both the gas and particulate states on regional-scales. The modeling approach under consideration is based on an adaptation of a regional-scale aerosol model, the RPM, a state-of-science Eulerian framework model (Binkowski and Shankar, 1995). The RPM is also itself, an adaptation of the RADM (Chang et al., 1990). Briefly, RADM predicts hourly gridded fields of wet and dry deposition of acidic compounds and the vertical and horizontal distribution of their ambient precursors. Typical grid sizes used in RADM are 80km in the coarse mode and 27km in a finer scale version but even finer grid resolution is anticipated. Typically, the vertical structure is characterized by 6 or 15 layers. The model applies all known, important and relevant processes to the preprocessed hourly meteorological and emissions data to obtain the desired fields. The RPM further computes the chemical composition and size distribution of the secondary sulfur and nitrogen species. In

turn, the RPM can provide for toxics modeling applications, gridded hourly requisite information on the size, chemical composition and moisture content of airborne particles, to serve as sites for the condensation and volatilization of SVOC. The current modeling domain for RPM is shown in Figure 2. The SVOC model would be applicable to such a modeling region. Details of the model follows with a brief summary of the major features of the RPM and the method by which the SVOC's are partitioned between the gas and particulate states.

Description of RPM:

Within most of eastern north America, sulfate is considered as the predominant aerosol species. Sulfur dioxide emissions are oxidized by hydroxyl radicals to sulfuric acid in the presence of water vapor resulting in a non-ideal aqueous sulfuric acid solution. Absorption of ammonia gas neutralizes the solution toward an ammonium sulfate solution. If the solution is not fully neutralized, the formation of aerosol nitrates, other than dissolved nitric acid, is inhibited. When the sulfuric acid solution is fully neutralized, and ammonia gas is still available, ammonium nitrate may be present in solution. In addition to the formation of sulfate through the oxidation of sulfur dioxide, small amounts of sulfates (taken as sulfuric acid) are directly emitted from sulfur sources. Sulfate is also produced in cloud droplets by the aqueous oxidation of dissolved sulfur dioxide. When the relative humidity exceeds that for particle crystallization, typically about 30 to 40% depending upon the degree of neutralization, (Spann and Richardson, 1985; Rood et al., 1989), the particles are assumed to exist as a non-ideal multi-component ionic aqueous solution of sulfates and nitrates. Organic and elemental carbon are currently treated as non-ionic constituents of the solution. All particles are presently assumed to be

chemically identical internal mixtures.

The gas-to-particle transformation in RPM currently occurs as condensation upon existing particles. The formation of new particles by nucleation will be added in the future. In addition to particle growth through condensation, coagulation of pairs of small particles to form a larger particle is also included. Finally, aerosol swelling and shrinking in response to relative humidity is included as an equilibrium process. Pilinis et al. (1989) show that the response to a change in relative humidity occurs very rapidly, on the order of microseconds. Thus, RPM treats this effect of relative humidity as an equilibrium process. The particle size distribution in RPM is represented by two log-normal distribution functions or modes. Following the nomenclature of Whitby (1978) and Whitby et al. (1991), the smaller mode is designated the "nuclei" mode and consists of particles that are freshly emitted from sources as well as those formed by gas-to-particle transformation. The larger mode is designated the "accumulation" mode and consists of aged particles. Total particle number, surface area and volume are provided for each mode as well as the distribution of these quantities within each mode as a function of particle diameter. The geometric mean diameter and geometric standard deviation within each mode are variable, thus allowing the size distribution to respond to the growth, coagulation, and swelling/shrinking processes.

Dry deposition of gas phase pollutants is parameterized in both RADM and in RPM where the deposition of a pollutant i , given by its concentration, C_i , is computed using deposition velocity ($V_{d,i}$) parametric formulations, ie., $F = V_{d,i} * C_i$. $V_{d,i}$ is in turn computed as the inverse sum of resistances to deposition due to the nature of the underlying surface, the viscosity of the sublayer and from vegetative stomata. Requisite information to compute these

resistances are contained in the RADM/RPM modeling framework. Deposition by aerosol particles are also computed using a deposition velocity parameterization dependent on particle size distribution, a key output of the RPM. Wet deposition is computed as the product of the scavenging coefficient with the precipitation rate for each vertical column above the surface grid that contain precipitation.

Input emissions inventory and the meteorological fields for RPM is the same as that used by the RADM for the National Acid Precipitation Assessment Program (NAPAP). Placet et al. (1990) discuss the NAPAP approach to emissions; Chang et al. (1990) shows how the NAPAP emissions are input into RADM. In addition, an inventory of primary particle emissions is currently under development by EPA to support activities associated with PM-10 and a potential fine particle standard. Meteorological information for the RADM/RPM models is provided by a meteorological processor based upon a numerical weather prediction model, MM4 with four-dimensional data assimilation (Stauffer et al., 1991). Further, RPM incorporates the nesting features of RADM (Pleim et al., 1991).

Proposed Treatment of SVOCs in RPM:

SVOCs can exist as vapors or adsorbed onto atmospheric aerosol particles depending upon atmospheric conditions. Pankow, (1987) shows how to distribute the SVOCs between the vapor and particle phases by using a partition function which depends upon the atmospheric temperature, total aerosol particle surface area, and characteristics of the SVOC of interest, (e.g. vapor pressure).

An additional complication to modeling the behavior of SVOCs in the atmosphere is that

SVOCs can also be adsorbed onto and revolatilized from the ground surface (soil, vegetation, etc.). Pankow (1993) has developed a simple model for SVOCs which are no longer emitted but are observed to have a seasonal trend in concentration (Hoff et al., 1992a,b). In a preliminary study of this process, Pankow (1993) proposed a simple coefficient for partitioning the SVOCs between the atmosphere and the earth's surface of the form:

$$K_m = \underline{K}_m \exp(Q_m/RT)$$

where \underline{K}_m is assumed to be independent of compound and temperature, and Q_m is an enthalpy of desorption from the surface and is assumed to be dependent upon specific compounds. Pankow (1993) used field data to estimate appropriate values for compounds which are no longer being emitted but have long residence times. He used a box model to explain the seasonal behavior of SVOCs. Pankow's (1993) model illustrates the importance of the ground surface as a sink for SVOCs, but does not yet provide sufficient information for inclusion into RPM. The parameters of the partitioning coefficient must be determined for different land covers and water surfaces as well as a large group of SVOCs which are being currently emitted. Then estimates of the transport and partitioning between air, the surface and aerosol particles of selected SVOCs could be made to show how differences in land use affects the partitioning and what transport patterns might be related to these differences.

For the present, however, only partitioning between vapor and particle phases will be discussed. Following Pankow (1987), SVOCs may be partitioned between the vapor and particle phases by use of a partition function:

$$\phi = cS_t / (P_0 + cS_t)$$

where S_t is the total aerosol surface area concentration ($\text{cm}^2 \cdot \text{cm}^{-3}$) and P_0 is the vapor pressure (atm). The coefficient of S_t is given by:

$$c = RTN_s \exp[j/RT]$$

$$j = Q_1 - Q_v$$

R is the universal gas constant, T is the ambient temperature (Kelvin), and N_s is a measure of the surface area required for sorption. Pankow (1987) shows that N_s is typically about 4×10^{-10} (moles cm^{-2}) and is not a strong function of compound over the classes of SVOCs considered such as organochlorines (OCs) to polycyclic-aromatic hydrocarbons (PAHs). Q_1 and Q_v are the enthalpies (kcal mole^{-1}) for desorption directly from the aerosol particle surface and of vaporization of the pure liquid SVOC, respectively. Pankow (1987) also shows $1 < j < 4$, and the approximate values of j are 1.5 for OCs, and 3 for PAHs.

For the current approach, it is assumed that the partitioning of SVOCs is to sulfate aerosol particles. SVOCs can also partition to soot particles. The initial modeling approach requires no specific distinction on the composition of particles. It is assumed that sulfate particles act as a surrogate for all other particles for which the SVOCs would have an affinity. Moreover, soot particles are likely to coagulate into sulfate dominated aggregates as air mass ages, or as currently assumed in RPM, the sulfate would condense on other ambient particulates including soot, so that tracking sulfates as a means to follow particulate SVOCs, while not mechanistically correct, may work. Further refinements may be necessary as the investigation

continues.

The deposition of SVOCs that are in the particle phase will be computed as the host particles to which they have become attached, and will follow the parametric formulations for such particles. The assumption requires the mass of attached SVOC to be much smaller than the inorganic host particle. With typical sulfate concentration in the microgram range, and SVOC in the nano-pico gram range, this assumption is generally acceptable. Similarly, wet scavenging of SVOCs attached to ambient aerosols can be assumed to be scavenged along with the host particles. The problem is somewhat more complex for deposition of SVOCs in the gas phase. For such compounds, stomatal resistances are generally unknown, and surrogate resistances for pollutant having similar properties will need to be substituted. This is an area needing further research. The "stickiness" of the particles to the ground will depend on the temperature of the ground. Warmer surfaces are less likely to retain an SVOC molecule as seen in the Pankow (1993) relationship for K_m above. Additionally, significant loadings of dissolved SVOC's in water bodies can be released back into the atmosphere so that during special conditions the net flux is upward. A two-film gas exchange model similar to that of Hornbuckle et al. (1994) will be used to estimate instantaneous fluxes of SVOC's across the air/water interface. This technique will estimate the balance between deposition and volatilization based on the air and water pollutant concentrations, the Henry's Law constant of the pollutant, and separate parametric estimates of the mass transfer rate (length/time) across the stagnant-air and stagnant-water layers on each side of the interface. Scavenging coefficients for gas phase SVOCs are also largely unknown, and parameterizations for surrogate gases will need to be entered for gas phase SVOCs.

PRELIMINARY RESULTS

The particular meteorological episode chosen is for the 72 hour period beginning at 00Z on July 17, 1985. During this period, a cold front oriented southwest to northeast moved southeastward through the eastern portion of the modeling domain. More information about this simulation is contained in Binkowski and Shankar (1993). Figures 3 and 4 provide sample outputs from the model. The upper left panel of Figure 3 shows the temperature at the four grid cells identified in Figure 2. Each grid cell is 80 km on a side and the results given are for the lowest 180 m of the atmosphere. The aerosol particles consist only of sulfate, ammonium, and water for this case. The lower left panel of this figure shows the aerosol surface area concentration ($\text{mm}^2 \text{cm}^{-3}$). Its variation is seen to exceed in two orders of magnitude. The behavior of C , the coefficient of the Φ function of temperature for a typical summer period is shown in the right hand panels of Figure 3. Values of P_0 are about 3.3×10^{-8} atm for OCs and 1.2×10^{-10} atm for PAHs. The vapor pressures vary as:

$$\log (P_0) = A + B/T.$$

Hinckley et al. (1990) tabulate values of A and B for selected SVOCs. The values used here are $A = 12$, $b = -5000$ for PAH's and $A = 12$ and $B = -4300$ for OCs. These values approximately represent benzo[a]pyrene and *cis*-chlordane respectively.

Figure 4*a,b* shows how P_0 varies with time for a typical summer period. Figure 4*c,d* shows the partition function, ϕ . The partition function generally tracks the total surface area shown in Figure 3. Even after accounting for the differences in the logarithmic and linear scales,

there appears to be some slight amplification of the surface area signal by the partition function.

The function shows that low vapor pressure SVOCs like higher molecular weight PAHs reside primarily on the particles. Higher vapor pressure SVOCs like the OCs exist primarily as vapors.

An example of the spatial distribution of the parametric fields are shown in Figures 5 and 6. The total surface area of ambient aerosols as depicted in Figure 5*b* indicates elevated values in the southeastern United States. Much of the aerosols in this region are subject to high relative humidities. As a result, the water fraction of the aerosols is large. The horizontal distribution of aerosol area concentration ranges over three orders of magnitude in the eastern half of the United States. The spatial pattern for the partition function, Φ , shows that for one of the organochlorines, the pollutant is primarily in the vapor phase, with as much as 4% attached to particles in different regions of the model domain. In contrast, Figure 6*b* indicates that more than 90% of the PAH congener modeled is particle bound, but some spatial variation exists due to the spatial distribution of aerosols. This set of simulations show that the model can handle the full range of Φ values from 0 to 100%. As the various pollutants differ greatly in their thermodynamic properties, especially their vapor pressures, intermediate values of Φ for different pollutants will be able to be modeled on an episodic basis.

Practical Considerations:

The study of the response of SVOCs to hypothetical control strategies for anthropogenic emissions would be a primary objective for application of the RPM adapted to address toxic pollutants. Typically, such analyses would be performed on an annualized basis. However, RPM provides predictions on an episodic basis, i.e., gridded fields of SVOC concentrations and

deposition are computed on a hourly bases for a period of several days. In order to obtain estimates of seasonal or annual averaged concentrations and deposition for the SVOCs, the model can be utilized in a manner analogous to that developed for the NAPAP Assessment Study (NAPAP Vol I (Report 3) 1991). In that study, RADM was run for a series of 30 meteorological episodes of 72 hr duration. By using a set of weight functions reflecting the climatological occurrence of each type of episode, the 30 cases were combined into an annual average. This particular annual average referred to acidic deposition, but other averages could be constructed.

For each episode, the toxics calculations would be initiated with RPM simulations for the various scenarios over a set of aggregation meteorological cases and the resulting output and meteorological data files archived. Subsequently, the emissions inventory for the SVOC species and the parameters values of P_0 , Q_v , Q_b , Q_m , K_m , and ϕ for gas to particle and gas to surface partitioning would be introduced and applied to the RPM results for aerosol particle distributions and the appropriate meteorological information as inputs. Depositional losses of SVOCs would be tracked as proportional to particle losses. This is justified on the basis that most of the SVOCs of interest are either chemically inert or very slowly reacting. The concentrations of these species are about 3 orders of magnitude (nanograms as opposed to micrograms) less than the aerosol particle species considered in RPM. Thus, it is not likely that they would change the chemical behavior or size distribution of these particles.

DISCUSSION AND CONCLUSIONS

Modeling air concentrations of SVOCs and the specific problem of their deposition to the

Great Lakes is an extremely challenging problem due to the numerous, diverse and complex scientific and computational issues involved, many of which are as yet unaddressed. The approach of utilizing a regional-scale state-of-science model for particles as applied to this problem shows promise. It has great potential as a tool for predicting fate and transport of SVOCs far from their sources. Clearly, much new information is needed to fully develop this approach for assessments, including information on vertical exchange processes between water and air. Furthermore, other processes not discussed in any detail in this paper that need further research include the role of clouds as both transporters and as aqueous chemical transformers, and the resuspension of pollutants from various land uses. Also, the input data requirements are formidable, including emissions inventories and boundary conditions. Finally, use of such state-of-science approaches will be computationally demanding. Using a combination of complex models to provide benchmark testing of other more simpler approaches or screening type models such as RELMAP may be a practical interim approach. As an outline of the approach using RELMAP for example, from the modeled sulfate concentration field, and given a mode particle size, the number density of sulfate particles is computed. Subsequently, the total surface area, S_T , is determined, and the Φ function for the particular SVOC of interest is computed. Additionally, RPM could be used to investigate upper and lower bounds for characteristic meteorological conditions. Alternatively, aggregation techniques similar to that used in the RADM assessments efforts could be utilized to calculate longer than episodic deposition/exchange fields such as seasonal and annual averages.

REFERENCES

Binkowski, F.S. and U. Shankar. 1995. *The Regional Particulate Model: Part 1, Model description and preliminary results.* In press J. Geophys. Res.

Eder, B.K., D.H. Coventry, T.L. Clark, and C.E. Bollinger. 1986. RELMAP, A Regional Lagrangian Model of Air Pollution User's Guide, EPA/600/8-86/013. U. S. Environmental Protection Agency, Research Triangle Park, NC.

Chang, J.S., F.S. Binkowski, N.L. Seaman, D.W. Byun, J.N. McHenry, P.J. Samson, W.R. Stockwell, C.J. Walcek, S. Madronich, P.B. Middleton, J.E. Pleim, and H.L. Landsford. 1990. The Regional Acid Deposition Model and Engineering Model, NAPAP SOS/T Report 4. *National Acid Precipitation Assessment Program, Acidic Deposition: State of Science and Technology, Volume I.* 722 Jackson Place, NW, Washington, DC.

Clark, T.L. 1993. Model assessment of the annual atmospheric deposition of trace metals to Lake Superior. *Proceedings, First UN/ECE Workshop on Emissions and Modeling of Atmospheric Transport of Persistent Organic Pollutants and Heavy Metals, Durham, NC.*

Graedel, T.E., and Weschler, C.J. 1981. *Chemistry within aqueous atmospheric aerosols and raindrops.* Reviews of Geophysics and Space Physics. **19(4):** 505-539.

Hinckley, D.A., T.F. Bidleman, W.T. Foreman, and J.R. Tuschall. 1990. *Determination of vapor pressures for nonpolar and semipolar organic compounds from gas chromatographic retention data*. J. Chem. Eng. Data. **35**: 232-237.

Hoff, R.M., D.C.G. Muir, and N.P. Grift. 1992a. *Annual cycle of poly-chlorinated biphenyls and organohalogen pesticides in air in southern Ontario. 1. Air concentration data*. Environ. Sci. Technol. **26**: 266-275.

Hoff, R.M., D.C.G. Muir, and N.P. Grift. 1992b. *Annual cycle of poly-chlorinated biphenyls and organohalogen pesticides in air in southern Ontario. 2. Atmospheric transport and sources*. Environ. Sci. Technol. **26**: 276-283.

Hornbuckle, K. C., J. D. Jeremlason, C. W. Sweet and S. J. Eisenreich. 1994. *Seasonal variations in air-water exchange of polychlorinated biphenyls in Lake Superior*. Environ. Sci. Technol. **28**: 1491-1501.

Lamb R.G. 1983. A regional scale (1000km) model of photochemical air pollution. Part I. Theoretical consideration. EPA/600/3-83/035. US Environmental Protection Agency, Research Triangle Park, NC 27711, 230 pages.

National Acid Precipitation Assessment Program (NAPAP) 1991. Acidic deposition: State of Science and Technology, Vol I Emission, Atmospheric processes and deposition. 722 Jackson

Place, NW. Washington DC 20503.

Pankow, J.F. 1987. *Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere.* Atmos. Environ. **21**: 2275-2283.

Pankow, J.F. 1993. *A simple box model for the annual cycle of partitioning of semi-volatile organic compounds between the atmosphere and the earth's surface.* Atmos. Environ. **27A**: 1139-1152.

Pilinis, C., J.H. Seinfeld, and D. Grosjean. 1989. *Water content of atmospheric aerosols.* Atmos. Environ. **23**: 1601-1606.

Placet, M., R.E. Battye, F.C. Fehsenfeld. 1990. Emissions Involved In Acidic Deposition Processes, NAPAP SOS/T Report 1, In: *National Acid Precipitation Assessment Program, Acidic Deposition: State of Science and Technology, Volume I.* 722 Jackson Place, NW, Washington, DC.

Pleim, J.E. J.S. Chang, and K. Zhang. 1991. *A nested grid atmospheric chemistry model.* J. Geophys. Res. **96(D2)**: 3065-3084.

Rood, M.J., M.A. Shaw, T.V. Larson, and D.S. Covert 1989. *Ubiquitous nature of ambient metastable aerosol.* Nature **337**: 537-539.

Spann, J.F. and C.B. Richardson. 1985. *Measurement of the water cycle in mixed ammonium acid sulfate particles.* Atmos. Environ. **19**: 819-825.

Stauffer, D.R. and N.L Seaman. 1990. *Use of four-dimensional data assimilation in a limited area mesoscale model. Part I: Experiments with synoptic scale data.* Mon. Wea. Rev. **118**: 1250-1277.

Stauffer, D.R., N.L Seaman, and F.S. Binkowski 1991. *Use of four-dimensional data assimilation in a limited area mesoscale model. Part II: Effects of data assimilation within the planetary boundary layer.* Mon. Wea. Rev. **119**: 734-754.

U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards.
Deposition of Air Pollutants to the Great Waters, First Report to Congress.(EPA 453/R-93-055) 1994. Research Triangle Park, NC 27711.

Whitby, K.T.1978. *The physical characteristics of sulfur aerosols.* Atmos. Environ. **12**: 135-159.

Whitby, E.R., P.H. McMurry, U. Shankar, and F.S. Binkowski. 1991. Modal Aerosol Dynamics Modeling, Rep. 600/3-91/020, Atmospheric Research and Exposure Assessment Laboratory, US Environmental Protection Agency, (NTIS PB91-161729/AS), Research Triangle Park, NC.

FIGURE CAPTIONS

Figure 1. Relative contributions to 1989 RELMAP-calculated atmospheric deposition of (a) lead and (b) chromium to Lake Superior as a function of transport distance and sector.

Transport ranges are defined in the abscissa where 1=0-100km, 2= 101-200km, etc.

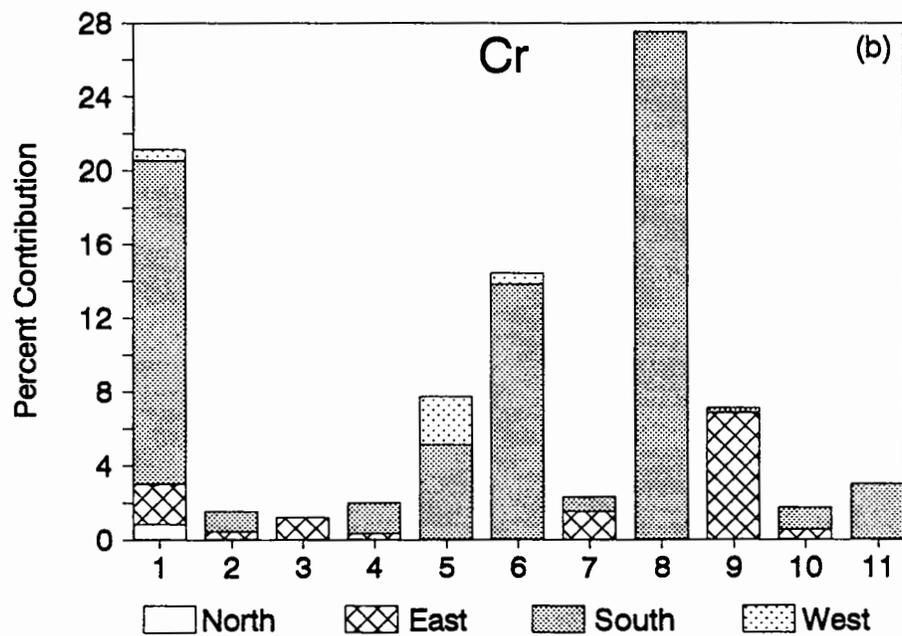
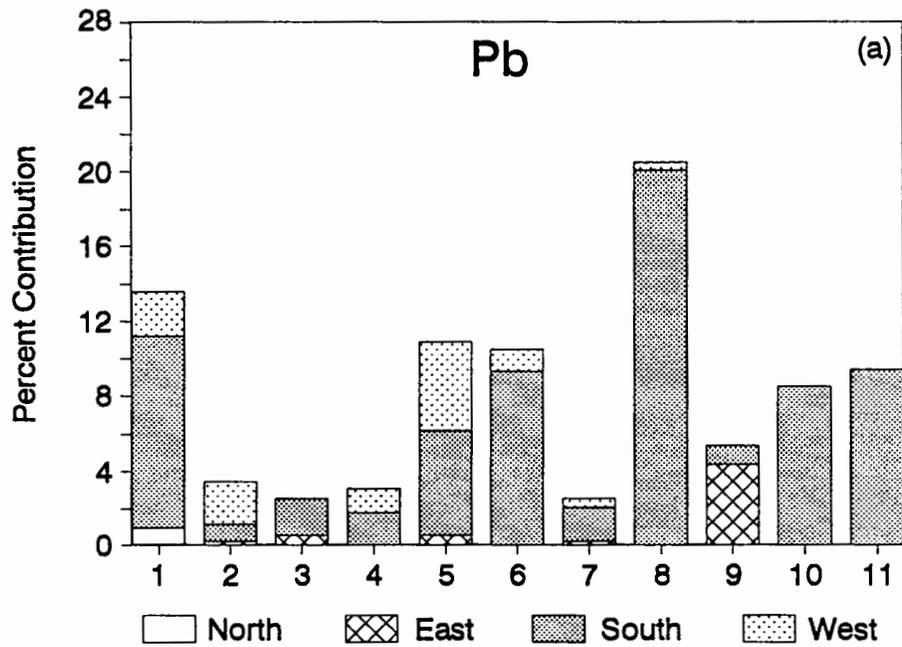
Figure 2: Modeling domain used by the RPM in this study. The grid cells shown here are 80 km on a side.

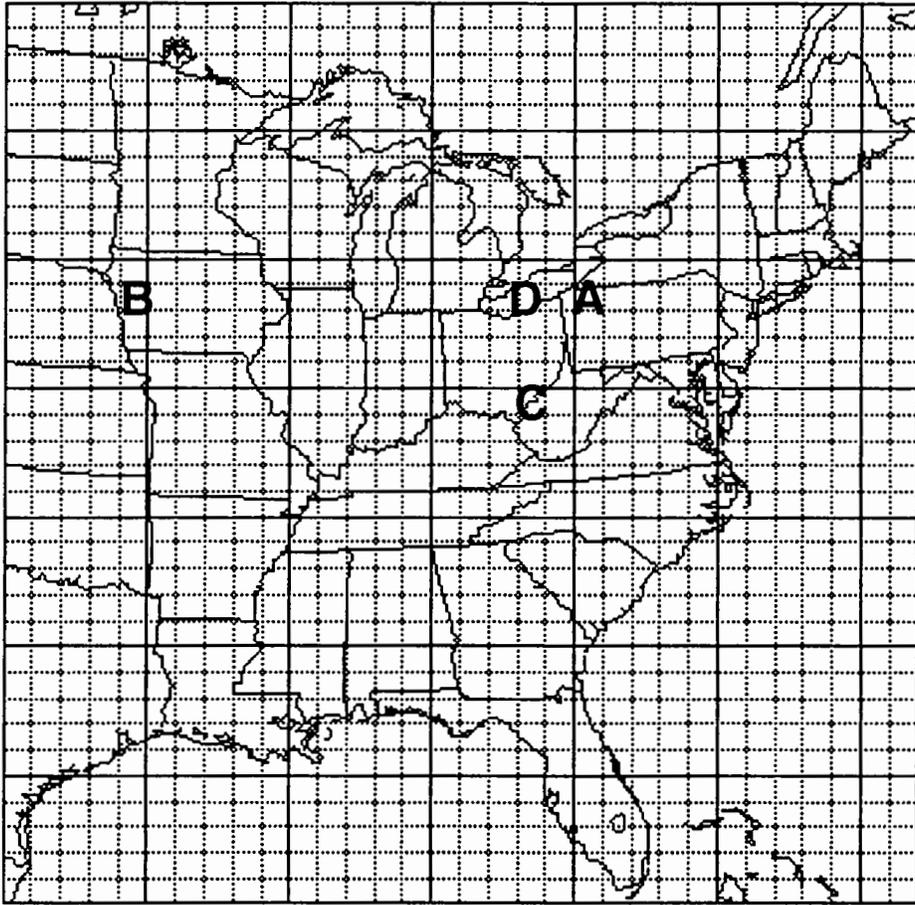
Figure 3.(a) Simulated temperature (K) and (b) aerosol surface area ($\text{mm}^2 \text{cm}^{-3}$) from RPM. The behavior of coefficient "C" for (c) PAH, and (d) OC used in this study. Note scales are different for PAH and OC. Cell "A" is the light solid line, "B" the bold solid line, "C" the dashed line, and "D" the hatched line.

Figure 4 The behavior of vapor pressure for the (a) PAH and (b) OC; and for the partition function for (c) PAH and (d) OC examples in this study. The line style for each of the four grid cells is the same as in Figure 3. Note the differences in the scales for each panel.

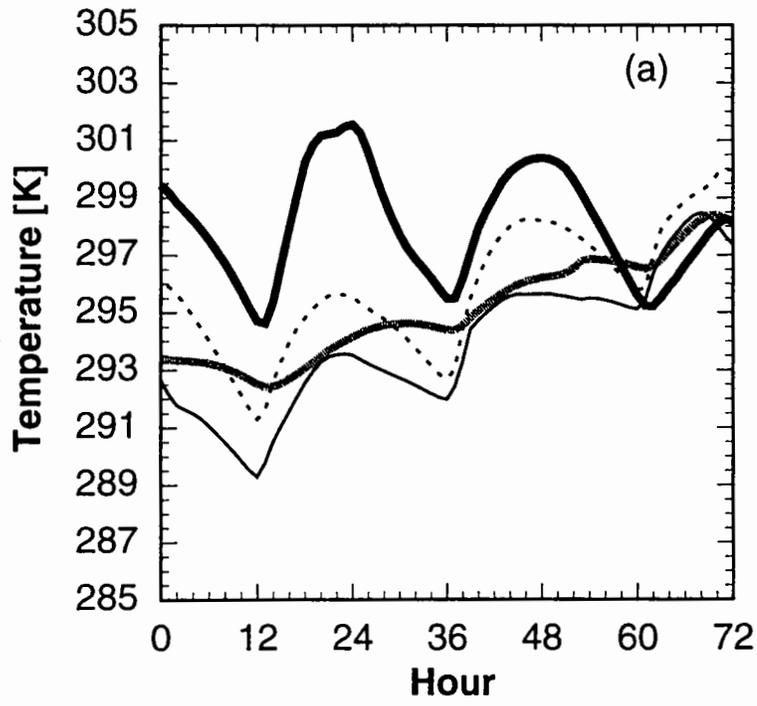
Figure 5. Modeled outputs of surface layer fields of (a) relative humidity and (b) total aerosol surface area for 1700 GMT July 17, 1985.

Figure 6. Modeled surface layer fields of the partition function, Φ , for the same simulation as in Figure 5 for (a) organochlorine, OC, and (b) polycyclic aromatic hydrocarbon, PAH.

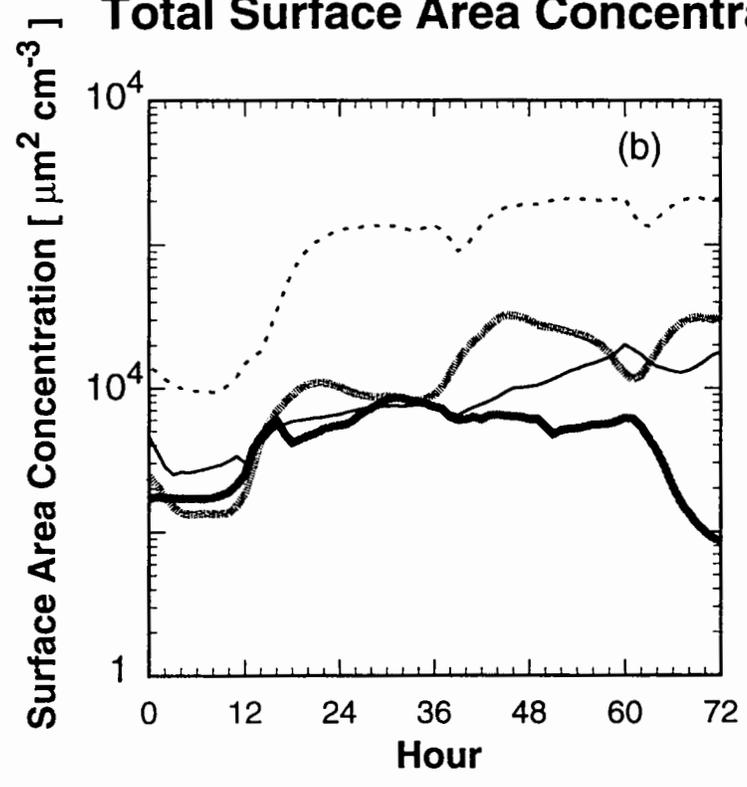




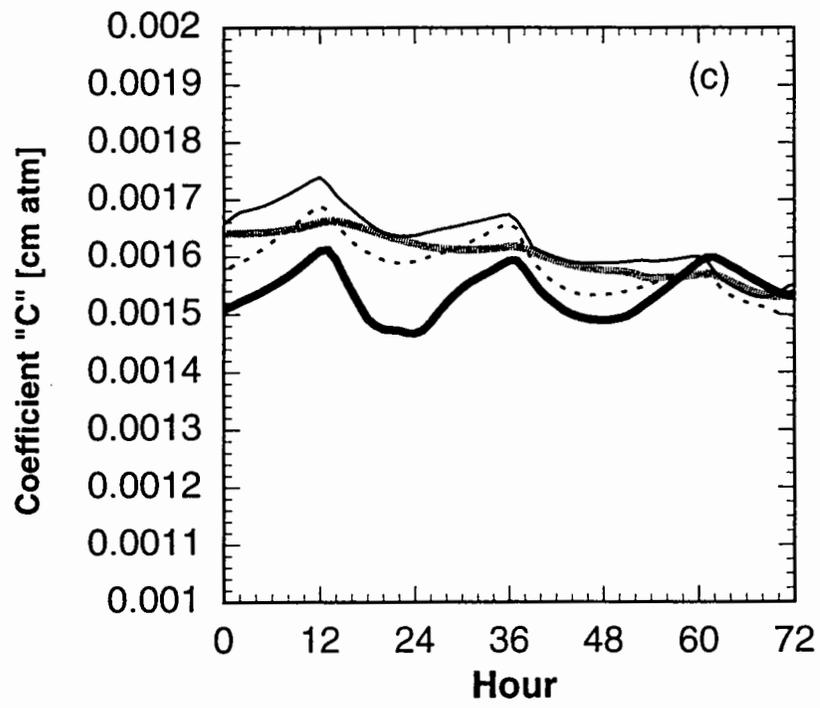
Cell Temperature



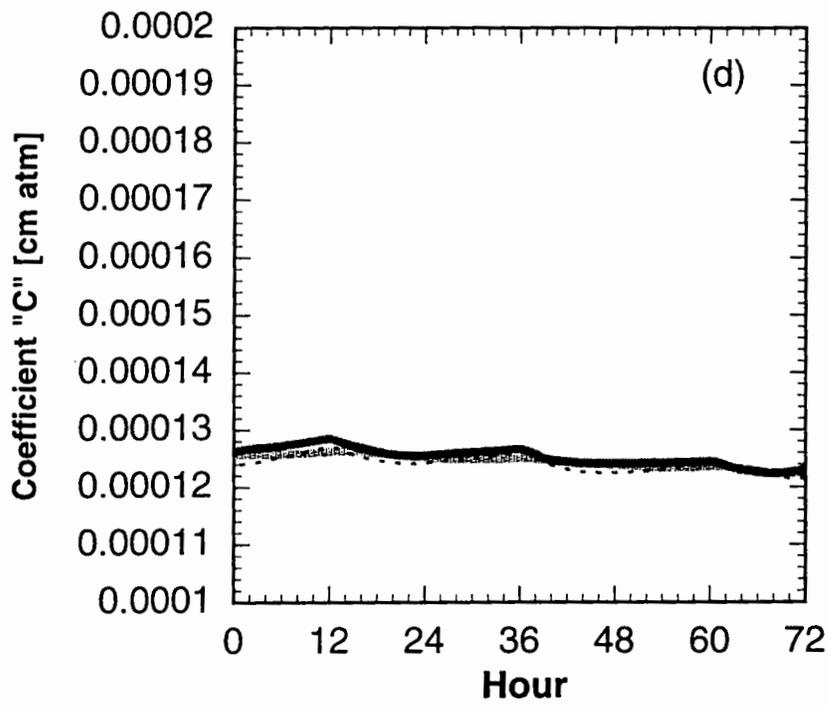
Total Surface Area Concentration



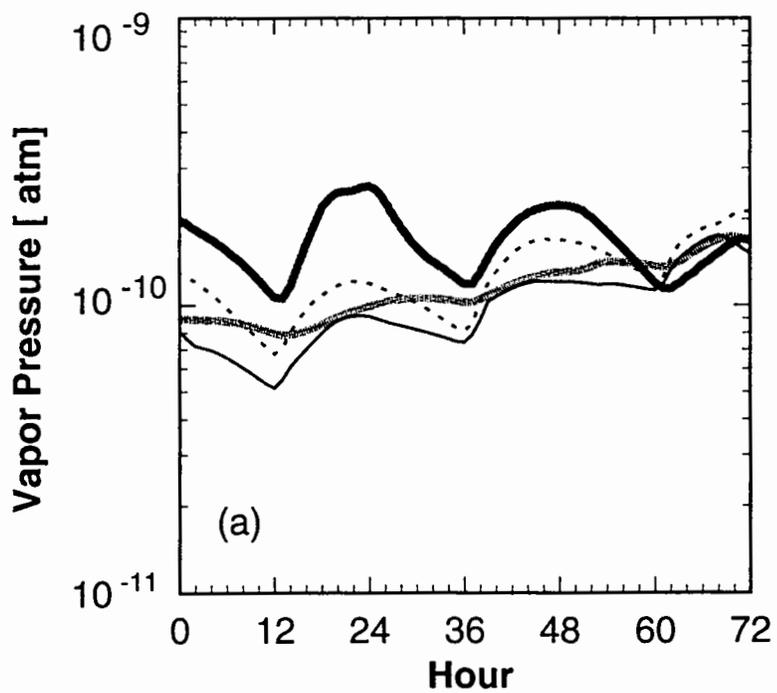
Coefficient "C" for PAH



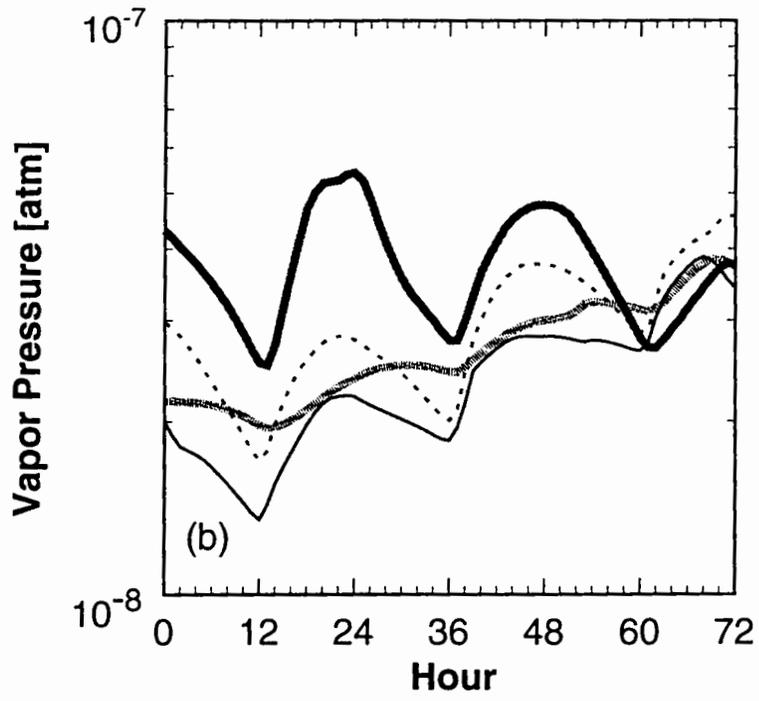
Coefficient "C" for OC



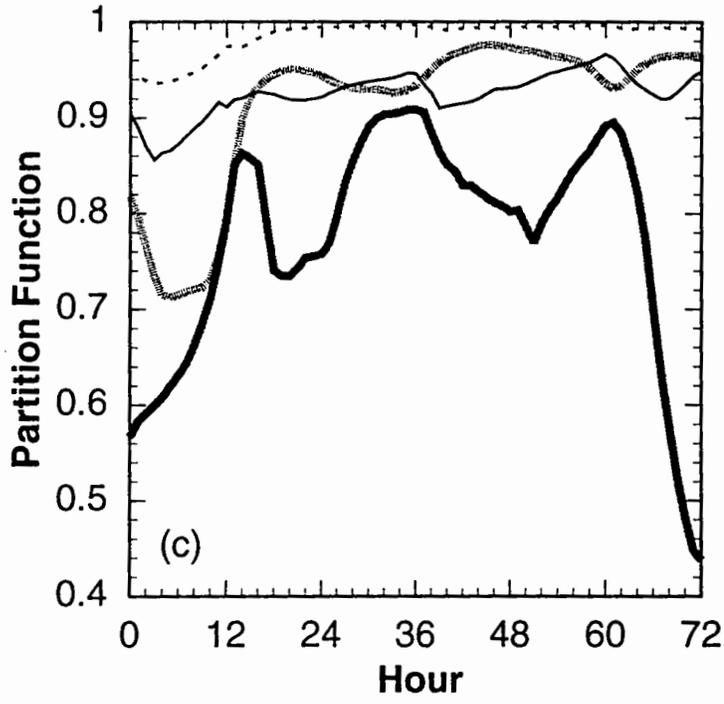
Vapor Pressure for PAH



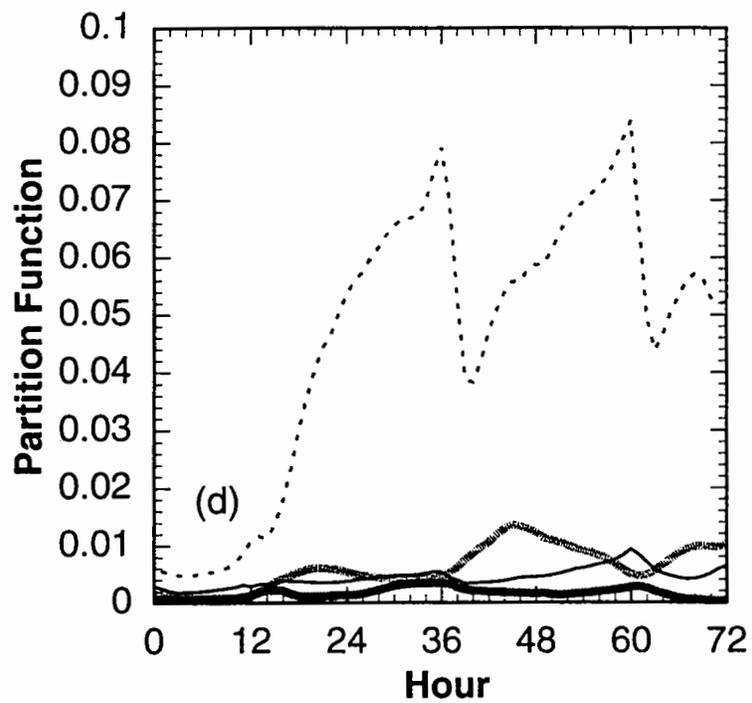
Vapor Pressure for OC

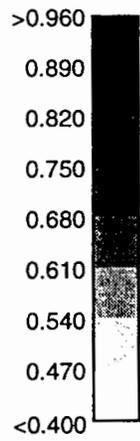


Partition Function ϕ for PAH



Partition Function ϕ for OC



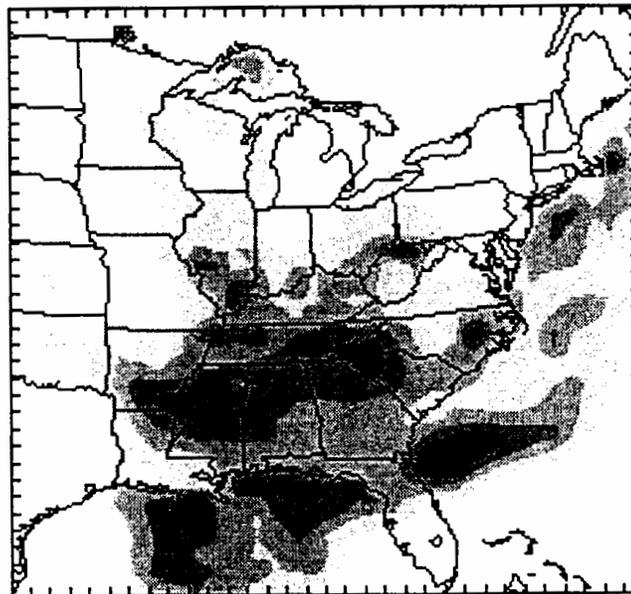
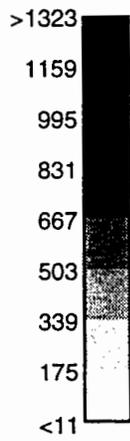


(a)

Fractional
Relative
Humidity

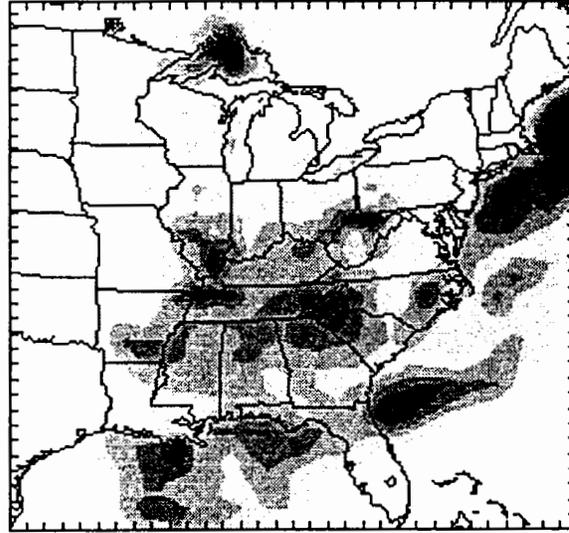
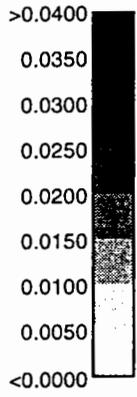
7/18/85 17 GMT

$[\mu\text{m}^2 \text{ cm}^{-3}]$



(b)

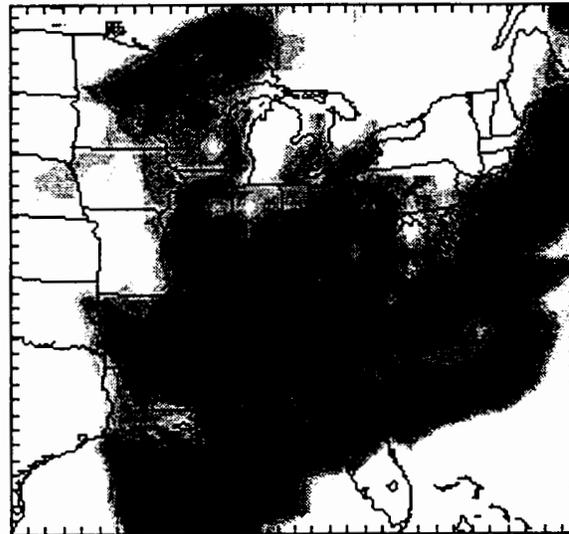
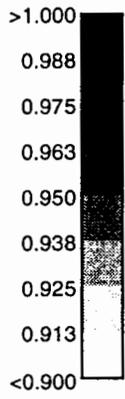
Total
Aerosol
Surface
Area
Concentration



(a)

Partition
Function
 Φ_{OC}

7/18/85 17 GMT



(b)

Partition
Function
 Φ_{PAH}

TECHNICAL REPORT DATA

1. REPORT NO. EPA/600/A-95/132		2.	
4. TITLE AND SUBTITLE Deposition of Semi-Volatile Air Toxic Pollutants to the Great Lakes: A Regional Modeling Approach		5. REPORT DATE	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Ching, J.K.S., F.S. Binkowski, and O.R. Bullock, Jr.		8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Office of Research and Development National Exposure Research Laboratory Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS SAME AS 9.		13. TYPE OF REPORT AND PERIOD COVERED Proceedings, FY-95	
		14. SPONSORING AGENCY CODE EPA/600/9	
15. SUPPLEMENTARY NOTES			
16. ABSTRACT A modeling approach is described that will be able to predict wet and dry deposition of toxic airborne semi-volatile organic compounds (SVOCs) applicable on a regional scale. In principle, these compounds cycle between the aerosol or the gas phases depending primarily on their vapor pressure and the ambient temperature and aerosol particle concentration. This study outlines an approach using as its modeling framework the U.S. Environmental Protection Agency's (USEPA) Regional Particulate Model (RPM) which predicts size distribution and the chemical composition of secondary formed aerosol particles. These particles provide sites for the condensation or volatilization of these semi-volatiles. Partitioning of ambient SVOCs between gas and particles based on formulations of Pankow (1993) are proposed and discussed and a requirements plan presented. It is demonstrated that the approach can handle a wide range of volatility characteristic of various compounds. Examples of the use of the RPM for relatively low volatility organochlorines and relatively high volatility persistent aromatic hydrocarbon pollutants are presented.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS	b. IDENTIFIERS/ OPEN ENDED TERMS	c. COSATI	
18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES	
	20. SECURITY CLASS (This Page)	22. PRICE	

X:ARSTO... NEEDS TO