The Transport and Deposition of Persistent Toxic Substances to the Great Lakes

III. Modeling the Atmospheric Transport and Deposition of Persistent Toxic Substances to the Great Lakes

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by

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Preface

This report was commissioned by the IJC International Air Quality Advisory Board. It is the first in a series of five closely related reports prepared for the Board which examine a set of persistent toxic substances identified in the Binational Virtual Elimination Strategy (BVES). The first report deals with the long range atmospheric potential for these compounds. The second analysis deals with the status and capabilities of available emissions inventories for BVES compounds. This report, the third in the series, deals with modeling the atmospheric transport and deposition of BVES compounds to the Great Lakes. The fourth study concerns the monitoring of these compounds in the Great Lakes region. The fifth report is a summary of the first four reports.

These reports were prepared as background documents for the IJC-sponsored Joint International Air Quality Board and Great Lakes Water Quality Board Workshop on Significant Sources, Pathways and Reduction/Elimination of Persistent Toxic Substances, held May 21-22, in Romulus Michigan.

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1. Introduction

A. Overall Scope of this Analysis

Atmospheric deposition is an important pathway for the entry of many pollutants to the Great Lakes. This report describes a number of attempts to model the atmospheric fate and transport of pollutants emitted to the air.

This analysis is primarily limited to U.S. and Canadian *government* modeling efforts which have *considered one or more of the compounds or groups of compounds listed in Table 1* with the Great Lakes as receptors.

In a *few* cases, particularly relevant *non-governmental* modeling efforts, efforts for *other compounds*, and/or analyses looking at *receptors other than the Great Lakes* have been included, but, comprehensive coverage of these other types of analyses was beyond the scope of this analysis.

B. Compounds Being Considered

The IJC International Air Quality Advisory Board selected a target list of 27 chemicals or chemical groups to be considered in this analysis, including twelve Level I substances or groups and fifteen Level II substances or groups.

> Level I substances are the 11 Critical Pollutants identified by the IJC's Great Lakes Water Quality Board, plus two additional Critical Pollutant identified by the Lake Superior LaMP and the Lake Ontario Toxics Management Plan (octachlorostyrene and chlordane).
>
> Level II Substances are those substances identified by the Canada-Ontario Agreement respecting the Great Lakes Basin Ecosystem (COA) as "Tier II" chemicals, plus additional substances of concern identified by LaMP and RAP processes and the Great Lakes Water Quality Guidance in the U.S.

A list of the compounds or groups included is given in Table 1, with the Level indicated in parentheses following the name of the compound.

Table 1. Compounds Considered in this Analysis

(Level indicated in Parentheses)

METALS / ORGANOMETALLICS

Alkylated Lead (I)
  including, but not necessarily limited to:
    tetra-, tri- and di-ethyl lead,
    tetra-, tri- and di-methyl lead

Mercury and Mercury Compounds (I)
  including, but not necessarily limited to:
    elemental mercury, mercury dichloride
    monomethyl mercury, and
    particulate mercury

Cadmium and Cadmium Compounds (II)
  including, but not necessarily limited to:
    cadmium, cadmium oxide
    cadmium dichloride, cadmium sulfide

Tributyltin Compounds (II)

ORGANOCHLORINE BIOCIDES

Aldrin / Dieldrin (I)
DDT / DDD / DDE (I)
Mirex (I)
Toxaphene (I)
Endrin (II)
Heptachlor / Heptachlor Epoxide (II)
Hexachlorocyclohexanes (α,β,δ, and γ) (II)
Methoxychlor (II)
Pentachlorophenol (II)
Chlordane (I)

INDUSTRIAL / MISCELLANEOUS

Octachlorostyrene (I)
3,3'-Dichlorobenzidene (II)
4,4'-Methylene bis (2-Chloroaniline) (II)
4-Bromophenyl Phenyl Ether (II)
Hexachloro-1,3-Butadiene (II)

CHLOROBENZENES

1,4-dichlorobenzene (II)
Tetrachlorobenzenes (several congeners) (II)
Pentachlorobenzene (II)
Hexachlorobenzene (I)

POLYCHLORINATED DIBENZO-P-DIOXINS & DIBENZOFURANS

2,3,7,8-TCDD and 2,3,7,8-TCDF (I)
1,2,3,7,8-PeCDD (I)
1,2,3,4,7,8-HxCDD (I)
1,2,3,6,7,8-HxCDD (I)
1,2,3,7,8,9-HxCDD (I)
1,2,3,4,6,7,8-HpCDD (I)
OCDD (I)
1,2,3,7,8-PeCDF (I)
2,3,4,7,8-PeCDF (I)
1,2,3,4,7,8-HxCDF (I)
1,2,3,6,7,8-HxCDF (I)
1,2,3,7,8,9-HxCDF (I)
2,3,4,6,7,8-HxCDF (I)
1,2,3,4,6,7,8-HpCDF (I)
1,2,3,4,7,8,9-HpCDF (I)
OCDF (I)

POLYCHLORINATED BIPHENYLS (PCB'S)

PCB's (I) [an attempt is being made to do the analysis on a congener specific basis; there are more than 200 PCB congeners]

POLYCYCLIC AROMATIC HYDROCARBONS

Dinitropyrenes (several congeners) (II)
Benzo[a]Pyrene (I)

plus PAH's as a group (II)
including but not limited to
Phenanthrene, Anthracene
Benz[a]Anthracene, Perylene
Benzo[g,h,i]Perylene

For this analysis, the following additional PAH's were added, consisting of the remaining compounds in the EPA's 16-PAH list and the ATSDR 17-PAH list:

Naphthalene, Acenaphthene
Acenaphthylene, Fluorene, Pyrene
Fluoranthene, Chrysene,
Benzo[b]Fluoranthene, Benzo[j]Fluoranthene
Benzo[k]Fluoranthene, Benzo[e]Pyrene
Dibenz[a,h]Anthracene,
Indeno[1,2,3-c,d]Pyrene

C. Overview of Atmospheric Modeling of Persistent Toxic Substances

In atmospheric modeling of pollutants, an attempt is made to estimate the transport and fate of pollutants which are emitted to the air. Often the objective is to understand and/or predict the atmospheric concentrations and/or deposition of one or more pollutants at a given location or locations arising from specific emissions sources.

General reviews of air pollution modeling include those by Hanna *et al.* (1982), Seinfeld (1986), RMCC (1990), NAPAP (1991), U.S. EPA (1996c), Dennis *et al.* (1996), and McQueen *et al.* (1996a). Reviews of long-range atmospheric transport modeling include those by Eliassen (1980), Fisher (1983), Voldner *et al.* (1986), and Sandroni (1987). Reviews of phenomena associated with the fate and transport of persistent organics in the atmosphere include those by Harkov (1986), Schroeder and Lane (1988), Bidleman (1988), de Voogt and Jansson (1993), and Wania and Mackay (1996). Recent reviews of the modeling of mercury in the atmosphere include those by Petersen (1996) and Petersen *et al.* (1996).

The following might describe an ideal modeling analysis:

- the emissions of all sources of a given pollutant are well characterized (geographical resolution; temporal resolution; etc.);
- the atmospheric fate and transport of these emissions is accurately modeled, including accurate characterizations of meteorological processes, micro-chemical (e.g., reaction with hydroxyl radical) and micro-physical processes (e.g., vapor/particle partitioning), and deposition processes (and possible re-emission processes, e.g., the grasshopper effect).
- the total concentrations and deposition to a given receptor are predicted (and compare well with measured values), and, the contributions to the total loading at a given receptor from individual sources and/or source regions are quantified.

There have been many different approaches to modeling the atmospheric fate and transport of air pollutants. Most can be classified as being either a Lagrangian or Eulerian framework.

In a Lagrangian model, pollutant fate and transport is mathematically characterized relative to the trajectory of air parcels. The coordinate system for pollutant dispersion moves along with a given air parcel. Lagrangian models are typically used in attempts to estimate the impact of a given source on downwind receptors. When multiple emissions sources are involved, calculations can be made for one source at a time, or, for all sources together. An advantage of many Lagrangian models is that they can require less computational resources than Eulerian approaches, all things being equal. There are difficulties in using Lagrangian models for simulations in which complex atmospheric chemistry must be considered and in which the interaction of emissions from different sources is important. In Lagrangian-based models, it is possible to consider emissions from multiple sources at the same time. When this is done, however, the process of keeping track of source-receptor relationships becomes numerically difficult.

In the Eulerian approach, pollutant fate and transport is estimated everywhere in the modeling domain relative to a fixed coordinate system. Pollutants from all sources being considered are mixed together in grid cells which cover the modeling domain. During each time step in an Eulerian model, the movement and dispersion of the pollutant is modeled by estimating the behavior of the pollutant *within* each grid cell and estimating the movement of pollution *from each cell to adjoining cells*. In contrast to Lagrangian models, this type of framework is ideal for situations where the interaction of emissions from different source is important. Perhaps the classical example of this situation is the problem of estimating concentrations of tropospheric ozone. In this situation, volatile organic compounds (VOC's) and nitrogen oxides emitted from many disperse sources are mixed together in the atmosphere and participate in a complex set of chemical and photochemical reactions. Ozone is formed during these reactions. To predict the concentration of ozone in such a situation, it is necessary to simulate behavior of the pollutants from all significant sources *at the same time*.

The mathematical formulations of deposition processes used Lagrangian and Eulerian models are often very similar, and in some cases are essentially identical.

Some general statements can be made about modeling the atmospheric behavior of most or all of the compounds listed in Table 1. First, on an absolute basis, they are generally present at very low concentrations, e.g., on the order of a few parts per million or less in the atmosphere. Because these compounds are relatively toxic, there can be adverse toxicological and environmental effects even at these low concentrations. The ambient concentrations of these compounds will generally be so low that the *interactions* of Table 1 pollutants *emitted from different sources* will not be significant.[1] Thus, for most or all of the compounds listed in Table 1, it may be possible to model their fate and transport with Lagrangian as well as Eulerian approaches.

There is an important caveat to the above statement, however. It regards the problem of simulating the interaction of pollutants at the earth's surface, especially in regard to vapor-phase dry deposition and re-emission processes. In these processes, the transfer of pollutant between the atmosphere and the surface is governed by the degree to which the instantaneous local situation departs from thermodynamic equilibrium. The degree of departure from equilibrium is dependent on the *total*

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[1]. For example, 2,3,7,8-TCDD emitted from one facility will not interact significantly with dioxin emitted from another facility. The concentrations in the atmosphere will be so dilute, reaction rates will be negligible.

concentration of the pollutant in the local atmosphere *and* the *total* concentration of pollutant in (and/or on) the particular materials at the earth's surface at the location of interest. The net direction of transfer will depend on the relative concentrations in the two phases. The rate of this net transfer will depend on the degree of thermodynamic imbalance and the motion, diffusion and mixing processes in *each* of the two phases (e.g., the rate of turbulent mixing and diffusion of pollutant in the each phase, etc). For example, the instantaneous rate of deposition of vapor-phase pollutant to a Lake at a given time and location depends not only on the concentration of the pollutant in the gas phase of the atmosphere immediately above the water surface; it also depends on the concentration of the same pollutant in the water near the surface.

The implication of the above considerations for modeling the fate and transport of persistent toxic pollutants is the following. *If* the compound's re-emission from the earth's surface after being deposited is an important process (e.g., re-emission from a water body or a terrestrial surface), then, it is likely that an estimate of the net direction of the transfer and the rate of the transfer between the atmosphere and the earth's surface will depend on the *total* instantaneous concentrations of the pollutant in the atmosphere above the surface and at surface itself. This means that past deposition and re-emission and the impacts of *other* sources may affect the fate and transport behavior impact of any given source. In a sense, this complicated situation is similar to the situation described above in modeling the problem of tropospheric ozone. In both situations, an accurate simulation only appears to be possible when all sources are considered together. Finally, these re-emissions situations, it may be necessary to couple the atmospheric model with a model of the surface media (e.g., surface water, soil, etc.).

The problem of incorporating the above so-called "grasshopper effect" into air pollution models is an area of current research interest. This topic is discussed in a series of articles by Wania and Mackay (1993ab, 1995, 1996).

An overall summary of the general components of many modeling systems that attempt to simulate the atmospheric fate and transport of pollutants is given in Table 2.

Table 2. General Components of Many Modeling Systems for Simulation of the Atmospheric Fate and Transport of Persistent Toxic Substances

Emissions Inventory

- the inventory must be geographically and temporally resolved
- information on the speciation of pollutants emitted is often necessary (e.g., elemental mercury vs. $HgCl_2$, etc.)
- physical form of pollutant when emitted (e.g., vapor and/or particle?; particle size distribution?; physical and chemical characteristics of emitted particles?)
- emissions conditions are needed (height, temperature, velocity, etc.)
- re-emissions of previously deposited material from the surface may be important to consider

Characterization of the Dynamic Meteorological Environment

- details of three-dimensional wind movement at many different scales can be important (large scale motions, mesoscale dynamics, short-range phenomena, small-scale turbulent mixing);
- the dispersion and diffusion of the emitted pollutant in the atmosphere must be characterized over all relevant length scales

Characterization of the Spatially & Temporally Varying Micro-Physical and Micro-Chemical Environment

- temperature; humidity
- clouds; precipitation
- physical & chemical nature of the atmospheric aerosol
- concentration of hydroxyl radical & other reactants
- intensity & spectral distribution of electromagnetic radiation
- detailed characteristics of the earth's surface

Characterization of the Interaction of the Pollutant Being Modeled with the Micro-Physical and Micro-Chemical Environment

- vapor/particle partitioning
- partitioning to cloud water; precipitation
- reaction rates with hydroxyl radical and other reactants in vapor phase, particle phase
- rates of droplet phase reactions
- rate of photolytic transformation
- deposition and re-emission phenomenon

Model Output

- predicted atmospheric concentration (from all sources) at a given locations at given times
- predicted deposition (from all sources) to a given receptor at a given time at a given location
- source-receptor relationships, e.g., the amount of deposition at a given receptor at a given time attributable to the contribution of a given source's emissions

Model Evaluation

- comparison of predicted concentrations and deposition with measured values

2. Brief Descriptions of Modeling Analyses

A. RELMAP

RELMAP (the Regional Lagrangian Model of Air Pollution) began as the Lagrangian puff model EURMAP developed by SRI International. EURMAP was created for the Federal Environment Office of the Federal Republic of Germany to model ambient concentrations, wet and dry deposition patterns, and transfer coefficients of SO_2 and $SO_4^=$ between sources and receptors throughout western and central Europe. The European model was adapted by SRI and refined by EPA for application to eastern North America in the late 1970's and early 1980's. The mid-1980's version of the model (Eder, 1986) was configured to simulate ambient concentrations, deposition, and source-receptor relationships for SO_2, $SO_4^=$, coarse (2.5 µm < diameter < 10 µm) and fine (diameter < 2.5 µm) particulate matter. Further description of the incorporation of particulate matter into the model is provided by Eder (1987).

RELMAP's modeling domain was originally a 45x30 array of grid cells across Eastern North America (size: 1° latitude x 1° longitude). The model has four vertical layers, from the surface up to the top of the mixed layer or planetary boundary layer (typically about 700-1500 meters). Its domain has been extended and its grid size made smaller in recent years.

An initial validation test of RELMAP was performed in which its predictions of sulfur concentrations and deposition were compared against measured values for 1980 at approximately 65 sites across Eastern North America (Clark *et al.*, 1987). This study suggested that improvements could be made to RELMAP, especially in its prediction of wet deposition, and these were carried out. A summary of improvements and refinements made to RELMAP has been presented recently by Bullock (1994).

Applications of RELMAP to BVES compounds are described below.

i. Atmospheric Transport of Heavy Metals to Lake Michigan

RELMAP was used to predict the transport of several heavy metals (arsenic, cadmium, chromium, lead, and nickel) from their emissions sources in Eastern North America to Lake Michigan for 1985 (Clark, 1992ab). An air emissions inventory for U.S. and Canadian sources of these compounds was used as input to the model. Runs were made under two scenarios: in one set of simulations the size of particle with which each metal was associated in the atmosphere was assumed to be 0.5 µm in diameter; in another set, the diameter was assumed to be 5 µm. Estimates of wet and dry deposition of each metal to Lake Michigan were reported. While RELMAP is capable of producing results for source-receptor relationships, these results are not available for this set of calculations (Bullock, 1997a).

Clark compared his model predictions with the semi-empirical measurement-based loading estimates of Strachan and Eisenreich (1988) for total lead deposition to Lake Michigan. RELMAP predicted approximately 20% more lead deposition, and this was attributed to the contribution of urban plumes (a contribution generally considered to be not well represented by the Strachan and Eisenreich estimates, which were based on samples taken in relatively rural locations).

ii. Fate and Transport of Mercury Air Emissions in the United States

RELMAP was recently used to model the fate and transport of mercury emitted to the air from sources in the continental U.S. (Bullock *et al.*, 1997; U.S. EPA, 1996a). Modifications to RELMAP to simulate mercury fate and transport were primarily based on Lagrangian models of atmospheric mercury in Europe (Petersen *et al.*, 1995). Three forms of mercury were modeled: elemental mercury, divalent mercury, and particulate mercury. A geographically resolved anthropogenic emissions inventory for the three forms of mercury was estimated for the general time period from 1990-1993 (U.S. EPA, 1996b) and was used as input to RELMAP. The global background arising from anthropogenic and natural emissions were accounted for by using a background concentration of elemental mercury vapor of 1.6 ng/m^3. Meteorological data for 1989 were used for the simulation. The modeling domain for the simulations was between 25 and 55 degrees north latitude, and between 60 and 130 degrees west longitude. The grid resolution was set to ½ degree longitude and ⅓ degree latitude, approximating a 40-km square. The modeling domain thus encompassed the entire continental U.S., southern Canada, northern Mexico, and portions of the Pacific and Atlantic oceans, including portions of the Gulf of Mexico.

Results have been reported for geographically resolved ambient concentrations and wet and dry deposition predicted to arise from the inventoried anthropogenic emissions. For the year-long simulation, of the total of 224 metric tons of mercury that were estimated to have been emitted from anthropogenic sources in the continental U.S., 78 metric tons were predicted to be deposited to the surface somewhere in the model domain (as described above), 145 metric tons were advected out of the model domain, and 0.6 metric tons of the emitted mercury remained suspended in the air within the model domain at the end of the simulation. The total deposition of mercury in the model domain, including that arising from global background sources, was estimated to be 111 metric tons for the year-long simulation.

Detailed deposition fields were estimated that would allow the total deposition to each of the Great Lakes to be estimated. These estimates are not available at this time, but, presumably could be made.

RELMAP can be used to generate source-receptor results. However, in this analysis, source-receptor results were not obtained. Insufficient resources were available for the data accounting task of a source-receptor analysis for mercury (Bullock, 1997b).

It might be possible to numerically aggregate sources and receptors, lessening the geographical resolution of the “saved” results and making the numerical requirements of the source-receptor analysis more practical.

In a related study, short-range modeling of mercury emissions from typical facilities predict that a minimum of 75% (maximum of 99.5%) of emitted mercury is carried in the atmosphere *outside* of a 50 km local-impact modeling domain (U.S. EPA, 1996a), with the fraction depending on the speciation of emissions, the height of the source, and the characteristics of the local weather. This local impact modeling was done using COMPDEP, an EPA short-range gaussian-plume-type model. These results are consistent with the view that regional and long-range transport of mercury is significant.

iii. Fate and Transport of Dioxin Air Emissions in the United States

In a preliminary analysis, RELMAP was recently used to estimate fate and transport of the 17 toxic 2,3,7,8-substituted PCDD/F congeners. A geographically resolved emissions inventory for 1985 was and meteorological data for 1989 were utilized for the simulation.

Vapor/particle partitioning of individual PCDD/F congeners was treated using the approach of Junge (1978), using subcooled liquid vapor pressures, as suggested by Bidleman (1988). A constant value of the aerosol surface area (used in the estimation of the vapor/particle partitioning) of 3.5e-6 cm^2/cm^3 was used, corresponding to a value believed to be typical of “background + local sources”. Average ambient temperatures were estimated for the vapor/particle partitioning calculation based on latitude and season. In this analysis, dioxins and furans were treated as chemically inert species.

Comparison of preliminary model predictions with ambient measurements suggested that the emissions inventory needed improvement (Bullock 1997a). Because it was only a preliminary study, there are no results available at this time.

There are plans to continue this work modeling PCDD/F with RELMAP, with additional refinements to model algorithms and emissions inventories (Cleverly, 1997).

B. ASTRAP

The Advanced Statistical Trajectory Regional Air Pollution model (ASTRAP) was initially developed by J.D. Shannon at the Environmental Research Division of Argonne National Laboratory (Shannon: 1981, 1985, 1997a). It has been extensively used for acid transport/deposition research (e.g, Shannon and Voldner: 1982, 1992; Shannon and Lesht, 1986). ASTRAP was originally developed at the Argonne National Laboratory, and it has undergone further development and application there and at Environment Canada's Atmospheric Environment Service.

Given a geographically resolved emissions inventory, ASTRAP attempts to predict ambient concentrations and wet and dry deposition for specified receptors. It is a long-term, statistical Lagrangian model. Horizontal dispersion is estimated by computing the statistical variability of the trajectory centerlines of a series of puffs emitted from each of a set of virtual sources. Wet deposition for each trajectory is generally estimated as a function of the half-power of the precipitation rate encountered by the puff's centerline. Dry deposition, vertical dispersion, and loss to the free troposphere (i.e. transport of material out of the "top" of the model domain) are assumed to vary with puff age using time- and location-dependent parameterizations (e.g., dry deposition velocity is a parameterized as a function of the time of day, the season, and whether the puff is over land or water). The program-generated source-receptor relationships for the grid of virtual sources are combined with a geographically resolved emissions inventory to estimate the concentration and deposition at all specified receptors in the modeling domain.

Detailed source-receptor estimates can be obtained with ASTRAP. However, source-receptor relationships have not been reported [and are not otherwise available (Shannon, 1997b)] in the examples discussed below of its application to one or more of the persistent toxic compounds of Table 1.

i. Atmospheric Transport of Toxaphene to the Great Lakes

Voldner and Schroeder (1989) used the ASTRAP model to simulate the atmospheric transport of toxaphene from sources in the U.S. to the Great Lakes (usage in Canada was believed to be negligibly small) for 1976 and 1980. The simulations were based on 1980 meteorological data obtained from the Canadian Meteorological Center spectral model at 1000 and 850 mb, at a temporal resolution of 6 hours and a spatial resolution of 127 x 127 km (precipitation fields had a temporal resolution of 12 hours). Emissions of toxaphene were estimated for U.S. states based on use patterns for 1976 and 1980.

In the simulations, approximately 60% of the emitted toxaphene was deposited somewhere in the U.S. or Canada, and about 40% left the continent, primarily over the east coast. Detailed source-receptor results linking source regions with each of the Great Lakes or their basins were presumably calculated during the simulation but were not reported. A few source-receptor results linking emissions in one state to deposition in another state were presented. For example, for emissions in Texas, 20% were predicted to be deposited in that state, 5% in Oklahoma, 3% in Missouri, 2% in Illinois, and 1% in the state of Michigan.

The total wet and dry deposition to each of the Great Lakes and their basins were given. A brief summary of the results [total predicted deposition (wet + dry)] of the analysis is given below in Table 3. In this table, for brevity, only the total predicted deposition (wet + dry) is given.

Voldner and Schroeder faced a typical set of difficulties in performing their modeling analysis, i.e., uncertainties in the emissions inventory and fate processes, and lack of ambient measurements for validation purposes. They state: “Because of the considerable uncertainty in the emissions inventory and in the physical/chemical properties of toxaphene present in ambient air, as well as the insufficiency of suitable environmental measurements of this pesticide, the accuracy of the computed deposition amounts to the Great Lakes and their basins is difficult to verify.”

In spite of these difficulties, a reasonable agreement between predicted and measured ambient air and rain concentrations was reported.

Table 3. Summary of Predicted Toxaphene Deposition to the Great Lakes arising from Emissions in the U.S.(*) (Voldner and Schroeder 1989)

Lake	Total Deposition to Lake (metric tons)	Total Deposition to Basin (metric tons)	Fraction of Emissions Deposited to Lake	Fraction of Emis. Deposited to Basin
1976 (total emissions = 7700 metric tons)				
Superior	15	19	0.0019	0.0025
Michigan	23	45	0.0030	0.0058
Huron	19	35	0.0025	0.0045
Erie	13	44	0.0017	0.0057
Ontario	8	22	0.0010	0.0029
Total Great Lakes	78	165	0.0101	0.0214
1980 (total emissions = 3600 metric tons)				
Superior	8	14	0.0022	0.0039
Michigan	10	19	0.0028	0.0053
Huron	8	15	0.0022	0.0042
Erie	5	18	0.0014	0.0050
Ontario	3	10	0.0008	0.0028
Total Great Lakes	34	76	0.0044	0.0099

* Emissions in Canada believed to be negligible

ii. Atmospheric Transport of Mercury to the Great Lakes

In a similar modeling analysis, Shannon and Voldner (1995) used the ASTRAP model to simulate the atmospheric transport of mercury from sources in the U.S. and Canada east of about 95 °W. The emissions inventory used was for 1985, with a geographical resolution of 100-127 km (depending on latitude). Anthropogenic and "natural" emissions sources were included. The simulations were based on meteorological data in the year-long period from December 1988 through November 1989, obtained from the Canadian Meteorological Center spectral model. Wind fields at 1000 and 850 mb, with a temporal resolution of 6 hours and a spatial resolution of 381 km were used; precipitation fields with a temporal resolution of 12 hours and a spatial resolution of 127 km were utilized.

In the simulations, it was found that approximately 78% of the predicted mercury deposition to the Great Lakes was due to estimated emissions of divalent mercury (e.g., mercury dichloride, $HgCl_2$). Detailed source-receptor results linking source regions with each of the Great Lakes or their basins were presumably calculated during the simulation but were not reported. A reasonable agreement between predicted and measured ambient air and rain concentrations and independently estimated loadings to the Great Lakes was found.

The total wet and dry deposition to each of the Great Lakes and their basins were given, arising from anthropogenic emissions of elemental mercury, divalent mercury, and particulate mercury, as well as from emissions from natural sources. Anthropogenic sources were estimated to account for over 80% of the predicted deposition to the Great Lakes, with natural and global background sources contributing on the order of 15% of the predicted deposition. An abbreviated summary of the results for anthropogenic sources in the modeling domain (eastern U.S. and Canada) is given in Table 4.

Table 4. Summary of Predicted Mercury Deposition to the Great Lakes arising from Anthropogenic Emissions from Sources in the U.S. and Canada for 1985 East of 95 °W longitude (Shannon & Voldner 1995)

Lake	Total Deposition to Lake (kg)	Total Deposition to Land Basin (kg)	Fraction of Emis. Deposited to Lake	Fraction of Emissions Deposited to Land Basin
1985 (total anthropogenic emissions = 490,000 kg Hg)				
Superior	345	373	0.0007	0.0008
Michigan	1012	1544	0.0021	0.0032
Huron	644	1298	0.0013	0.0026
Erie	1060	2342	0.0022	0.0048
Ontario	834	2014	0.0017	0.0041
Total Great Lakes	3895	7571	0.0079	0.0155

iii. Atmospheric Transport of Lead to the Great Lakes

An analysis of atmospheric transport of lead to the Great Lakes has also been carried out using the ASTRAP model (Voldner *et al.*, 1993). Only *total* lead was modeled; i.e., alkylated lead compounds (one of the compounds of Table 1) were not considered separately. Source-receptor relationships were not reported.

Wet and dry deposition of total lead to each of the Lakes and their associated land basins were estimated for each of the years from 1970-1990. Dramatic declines in the predicted deposition over the time period simulated were consistent with the decrease in lead emissions accompanying the phase out of leaded gasoline usage. The model-predicted direct deposition to the Great Lakes decreased from 5200 metric tons/year in 1970 to only 250 tons/year in 1990.

The model-predicted deposition to Lake Superior during 1990 (40 metric tons/year)[2] was consistent with the depositions estimated empirically using observed ambient air and rain concentrations (67 metric tons/year). Other sources of lead to Lake Superior were considered in an attempt to construct a mass balance. The total direct contribution from the atmosphere to Lake Superior (40 - 67 metric tons/year) was greater than the total of 30 metric tons/year estimated to be contributed by other pathways (e.g., runoff, tributaries, industrial discharges, sewage treatment plants).

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[2]. The direct deposition to Lake Superior in 1970 was estimated to have been 800 metric tons/year.

C. Global Chemical Transport Model

The Canadian global spectral model (Ritchie, 1991) is a three-dimensional air transport model. The model has been used to simulate the global distribution of radionuclides emitted from the Chernobyl accident (Pudykiewicz, 1990), the global distribution of sulfate aerosol from the volcanic eruption of Mt. Pinatubo (Pudykiewicz and Dastoor, 1995) and the transport of sulfur to the arctic (Dastoor and Pudykiewicz, 1996). The model uses meteorological measurements and simulates the three-dimensional dynamics of the atmosphere in between measurements using primitive equations. The dispersion of emitted pollutants in the atmosphere is estimated using a semi-Lagrangian approach as described by Smolarkiewicz and Pudykiewicz (1992). The equations of atmospheric and pollutant motion are integrated vertically through 20 layers from the surface up to a height of 20 km and with a horizontal grid size of 2.8° latitude/longitude. The model includes a relatively detailed treatment of condensation and cloudiness (Dastoor, 1994).

i. Global Distribution of Hexachlorocyclohexane

The Canadian Global Spectral Model has been recently used to model the global distribution of alpha- and gamma-hexachlorocyclohexane (lindane) (Pudykiewicz and Koziol, 1997; Pudykiewicz and Dastoor, 1996).

In simulations completed to date, only emissions from the oceans have been considered. The emissions of α-HCH and γ-HCH from the ocean were estimated from measured concentrations in seawater. In these initial simulations, the concentration of HCH in the air is assumed to be zero at the beginning of the simulation, and the global dispersion of HCH from ocean emissions is simulated.

Results from this initial modeling include a time series of predicted atmospheric concentrations at particular locations in the Arctic (e.g., at Tagish and Alert) and maps showing the global distribution of HCH at various times after the beginning of the simulation arising from ocean emissions. Detailed source-receptor relationships are not currently reported by the model.

ii. Future Work

A description of future work and planned improvements to the model was kindly provided by Pudykiewicz and Koziol (1997):

- the use of a global use inventory of HCH (Li *et al.*, 1996) to estimate a global emissions inventory for HCH for use as additional emissions input to the model;

- refinements of model algorithms for estimating wet deposition (current algorithms believed to underestimate rate of wet deposition);

- include the characterization of the interaction of semivolatile pollutants with snow;

- include the reaction of hydroxyl radical with HCH using reaction rate constants predicted using the Atmospheric Oxidation Program (Meylan and Howard, 1996)[3];

- improve the characterization HCH in the water column in the Arctic Ocean;

- improve the characterization of the ice cover in the Arctic, which is believed to be currently underestimated in the model;

- add the capability of the model to simulate vapor/particle partitioning of semivolatile compounds in the atmosphere;

- compare the results from the improved model with measurements of HCH in the Arctic;

- extend the model to other compounds; e.g. within a few years, PCB's may be able to be included.

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[3]. Meylan and Howard of the Syracuse Research Corporation (SRC: Syracuse, New York) have utilized the structure-activity relationships of Atkinson and colleagues — including the latest update (Kwok and Atkinson, 1995) — to create the Atmospheric Oxidation Rate Program. A few changes to Atkinson's methodology were made which are believed to improve the accuracy of the estimates (Meylan and Howard, 1996).

D. REMSAD

The Regulatory Modeling System for Aerosols and Deposition (REMSAD) is a relatively new model; work started on it about 2 years ago and it is currently undergoing development. It is an Eulerian model based on the Urban Airshed Model (UAM), a regional air quality model. It is designed to be a flexible analytical system to support regulatory decisions, by allowing the deposition of toxic pollutants to selected receptors (the Great Lakes and Chesapeake Bay, for example) under current conditions and under different regulator scenarios to be estimated (Axelrad, 1997; Guthrie *et al.*, 1995). A user's guide for REMSAD has recently been made available (SAI, 1996).

It is currently envisioned that the model will be used to develop *overall* deposition estimates to particular receptors, e.g., the Great Lakes, arising from the combined affect of all modeled emissions sources. It would be possible, however, to numerically tag emissions of a given pollutant from different sources or source regions and develop estimates of source-receptor relationships (Axelrad, 1997).

The model is currently being configured to simulate the atmospheric behavior of dioxin, mercury, cadmium, polycyclic organic matter, and atrazine. Work is underway to simulate the transport and deposition of some or all of these compounds to the Great Lakes and other Great Waters. There are no results available at the present time; results are expected in perhaps 1-2 years.

E. HYSPLIT

HYSPLIT was developed at National Oceanic and Atmospheric Administration (NOAA) for operational medium and long-range transport modeling of accidental releases of radioactive materials. The development, validation, and operation of HYSPLIT are described elsewhere (Draxler *et al.*: 1991ab; Draxler: 1987, 1992, 1994), and so, as with the other models described in this report, only a brief description will be given here. It is currently undergoing extensive additional development at NOAA by Roland Draxler.

HYSPLIT is a Lagrangian model, in which puffs of pollutant are emitted from user-specified locations, and are then advected, dispersed, and subjected to destruction and deposition phenomenon throughout the model domain. It has been used to simulate many different atmospheric processes, including sulfur transport and deposition in the U.S. (Rolph *et al.*: 1992, 1993) and dispersion of pollutants from Persian Gulf oil fires (Draxler *et al.*, 1994; McQueen *et al.*, 1994).

HYSPLIT uses gridded meteorological data computed by an external model. The data used are a combination of concurrent and short-range predictions generated by NOAA's Nested Grid Model (NGM), a primitive-equation meteorological simulation model. The data provided to HSYPLIT from the NGM include wind speed and direction, the amount and type of precipitation, the temperature, the humidity, and other meteorological data.

HYSPLIT is being used by many researchers around the world, and there are many applications that could be discussed here. Moreover, HYSPLIT has been and will continue to be utilized as an air pollution research tool by Roland Draxler and colleagues at NOAA.

As an example of the use of HYSPLIT, the work done by the author and his colleagues at the Center for the Biology of Natural Systems (CBNS) at Queens College in simulating the atmospheric fate and transport of dioxins, furans, hexachlorobenzene will be discussed below. The developer of HYSPLIT, Roland Draxler, provided the HYSPLIT model for this work and assisted in its modification to simulate atmospheric phenomena of PCDD/F and HCB.

i. Transport and Deposition of Dioxins, Furans, and Hexachlorobenzene from Sources in the U.S. and Canada to the Great Lakes

Fate and transport modeling of emitted PCDD/F is commonly done in conjunction with risk assessments for proposed, potentially major sources, such as municipal waste incinerators. In most if not all cases, Gaussian Plume-based models are used, and these are typically applicable only out to approximately 50 km from the source. Procedures for modeling the short-range transport of PCDD/F and similar compounds in the atmosphere have been recommended by the U.S. EPA (1990, 1993, 1994A). This type of analysis is of course valuable because the locations of the most intense potential impact are generally within this range. Mass balances are not generally computed or reported in these studies. Analysis of typical results suggests that on the order of 90 - 99% of the emitted dioxin can be transported outside the 50 km region surrounding the source. These results and a general consideration of the physical/chemical properties of PCDD/F and its atmospheric behavior suggest that PCDD/F is capable of regional and long-range atmospheric transport.

Modeling of long-range transport of PCDD/F in the atmosphere has been relatively limited. Rappe *et al.* (1989) and Tysklind et al.. (1993) compared measured atmospheric concentrations of PCDD/F at locations in Sweden to modeled back-trajectories of the air masses sampled, and found evidence that long-range atmospheric transport of these compounds was occurring. Van Jaarsveld and Schutter (1993) modeled the long-range transport and deposition of dioxins in portions of Europe by adapting a Lagrangian model developed originally for analysis of acidic deposition.

In an attempt to estimate the transport and deposition of dioxins, furans, and hexachlorobenzene from sources in the U.S. and Canada to the Great Lakes, the HYSPLIT model was used (Cohen *et al.*, 1995). In the version of HYSPLIT that was used (Version 3.2, 1994), data from the NGM were supplied for 2-hour intervals, on a 33 x 28 grid, with spacing approximately 180 km, at the surface and at 6 atmospheric layers, up to a height of 3000 meters.

In this analysis, a geographically-resolved PCDD/F and HCB emissions inventory for the U.S. and Canada was developed. There were substantial difficulties in obtaining information for the inventory, and, it was recognized that there were significant uncertainties in the emissions inventory used. Consequently, calculations were carried out using a range of estimated emissions. For PCDD/F, the calculations were done for each of the seventeen 2,3,7,8-substituted toxic congeners (shown in Table 1) and for homologue groups (e.g., total TCDD, total PeCDD, etc.).

Vapor/particle partitioning was included in the simulations. As a simplifying assumption, the characteristics of the background aerosol were assumed to be constant throughout the modeling domain. The ambient temperature at any given location was used in the estimation vapor/particle partitioning. Chemical transformation and deposition processes were estimated for both vapor and particle fractions of a given pollutant in the atmosphere at any given time and location.

Several sensitivity analyses have been performed in conjunction with this modeling analysis. One such analysis examined the effect of the above assumption regarding the constancy of the atmospheric particulate in the simulation. It was found that while the predicted deposition to the Great Lakes from a given source is somewhat sensitive to variations in the atmospheric particulate surface area, it is not overwhelmingly so. Variations of a factor of 10 higher or lower than the default value changed the predicted deposition by no more than a factor of 2.

HYSPLIT was used to estimate the transfer coefficients (i.e., the fraction of emissions from a given source that are predicted to be deposited in a particular Lake) for a series of PCDD/F congeners and HCB at a series of “standard” source locations. To reduce needed computational resources, interpolation methods were developed and validated to: (a) estimate transfer coefficients for PCDD/F congeners that were not explicitly calculated; and (b) estimate transfer coefficients for source locations other than the “standard” locations for which explicit simulations were run. The analysis was done for the entire year 1993.

Relatively good agreement was found between predicted and measured concentrations of atmospheric PCDD/F at Dorset, Ontario.

Agreement between measured and predicted atmospheric concentrations of HCB could not be obtained in this analysis, which considered only sources in the U.S. and Canada. The atmospheric lifetime of HCB is estimated to be on the order of years and it is known to be globally distributed. Thus, it is perhaps not surprising that this limited modeling analysis could not simulate real-world HCB concentrations.

A similar problem is faced in the atmospheric modeling simulations of mercury; here the impact of global emissions can also be significant. In mercury models with limited geographical scope, a “background” concentration of mercury arising from global sources is sometimes used.

With the above methodology, detailed source-receptor results were obtained. Estimates of the contribution to each Great Lake for more than 1300 individual sources or area-source regions for HCB and for each PCDD/F congener were developed. In this analysis, only direct deposition to the Lakes was considered. Indirect flux to the Lakes as a result of deposition to the watershed was not included.

The results for PCDD/F will be discussed here. Approximately half of the predicted atmospheric deposition of dioxin was linked to sources in states and provinces immediately adjoining the Great Lakes; the other half was associated with sources in the rest of the U.S. and Canada. Sources in Mexico and the rest of the world were not considered; if they had been included, it is expected that they would have made a lesser but perhaps not insignificant contribution to the total predicted loadings.

In Figure 1, an example of the cumulative relationship between the sources’ distance from a particular Lake (in this case Lake Michigan) and the relative dioxin contribution (on a total TEQ basis[4]) is shown. For this lake (similar to other Lakes), it was found that about half of the cumulative dioxin deposition comes from sources about 300 miles (480 kilometers) or less from the center of the Lake — that is, located in the U.S. states and the province of Ontario that border the Lake. The remaining half of the total deposition comes from sources as far as 1,500 miles (2,400 kilometers) away.

The extent to which the different sources contribute to the dioxin deposited in the Great Lakes was found to depend not only on the amounts they emit and their distances from the lakes, but also on their geographic location. A higher percentage of the dioxin emitted from sources to the south and west of the lakes is deposited in them than from the sources to the north and east. Figure 2 illustrates this effect in the case of Lake Michigan, again, on a total TEQ basis.

Another illustration of the effect of the weather pattern in influencing the efficiency with which a given source contributes dioxin to a given receptor is given in Figure 3, again with Lake Michigan as the example. For this purpose the entire U.S. and Southern Canada area was divided into 20,000 squares (each 270 square miles in area). Using the air pollution model, the percent of dioxin emitted from each square's center point that would be transported through the atmosphere and deposited in Lake Michigan was estimated (i.e., the "air transfer coefficient" was estimated for a series of potential source locations to a given receptor, Lake Michigan). In Figure 3, the results for a particular congener (2,3,4,7,8-pentachloro-dibenzofuran) are shown. The figure maps the geographic distribution of six successive ranges of air transfer coefficient. It shows that dioxin transport and eventual deposition to Lake Michigan is most efficient for sources to the west and southwest of the Lake, and least efficient for sources to the northeast and southeast of the lake. This reflects the general southwest-to-northeast and west-to-east weather pattern.

In Figure 4, an estimate of the contribution of sources in States/Provinces adjoining each Lake relative to that from the rest of the U.S. and Canada is shown.

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[4]. Dioxin congeners with chlorines in at least the 2,3,7,8 positions show evidence of the greatest toxicity. Out of the 210 different CDD/F congeners, only 17 have such a chlorine configuration, and the evidence suggests that these have varying degrees of toxicity. The toxicity of each congener can be expressed in terms of its estimated, approximate potency relative to that of the most toxic congener (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) by multiplying by its estimated "Toxic Equivalency Factor" or TEF. The overall dioxin content of a mixture of dioxin and furan congeners is often summarized by multiplying the amount of each congener by its TEF and then summing over all the congeners to get the total Toxic Equivalents (TEQ) in the mixture. The meaning of a result expressed as "TEQ" is that the total overall toxicity of the mixture is presumed to be equivalent to the stated amount of "pure" 2,3,7,8-TCDD.

Figure 1. Effect of Distance of Sources on Cumulative Deposition of Dioxin in Lake Michigan

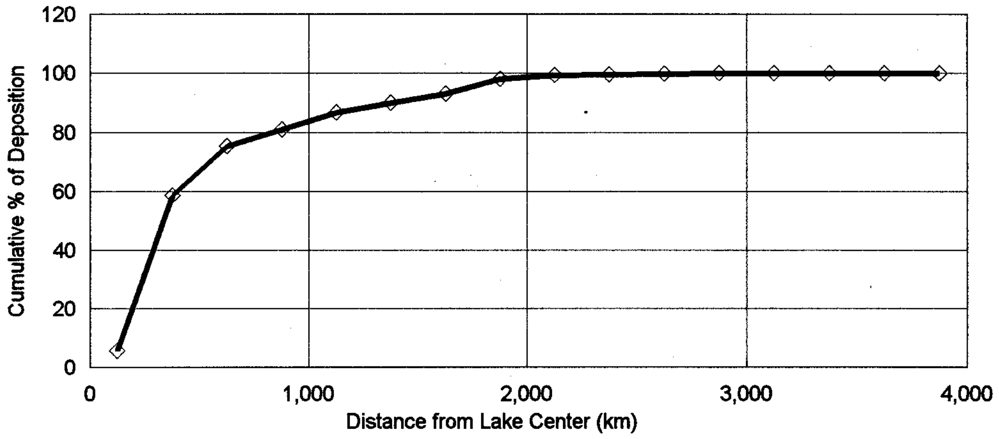


Figure 2. Relation Between the Directional Orientation of Dioxin Sources and their Emissions and Deposition in Lake Michigan

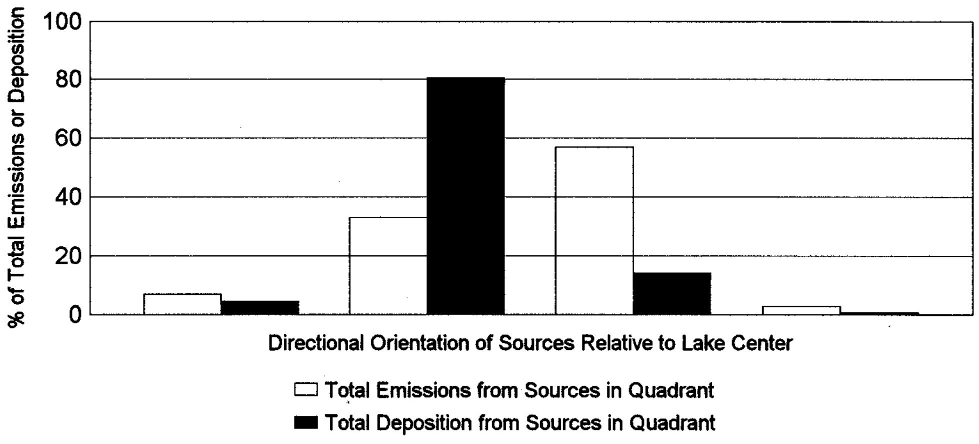


Fig. 3: GEOGRAPHIC DISTRIBUTION OF AIR TRANSFER COEFFICIENTS FOR 2,3,4,7,8-PeCDF.
Percent of Emissions Deposited in Lake Michigan in 1993.

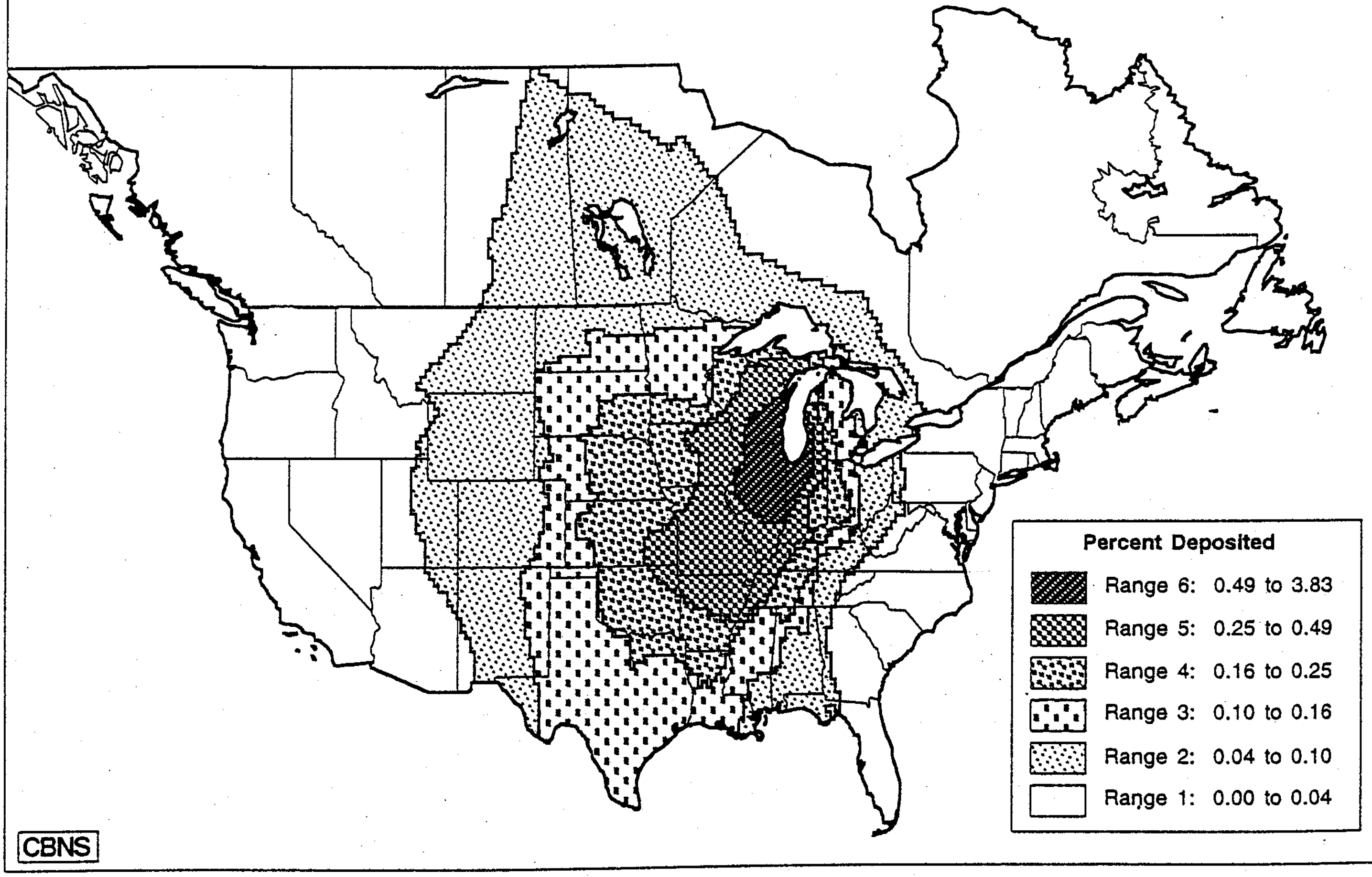
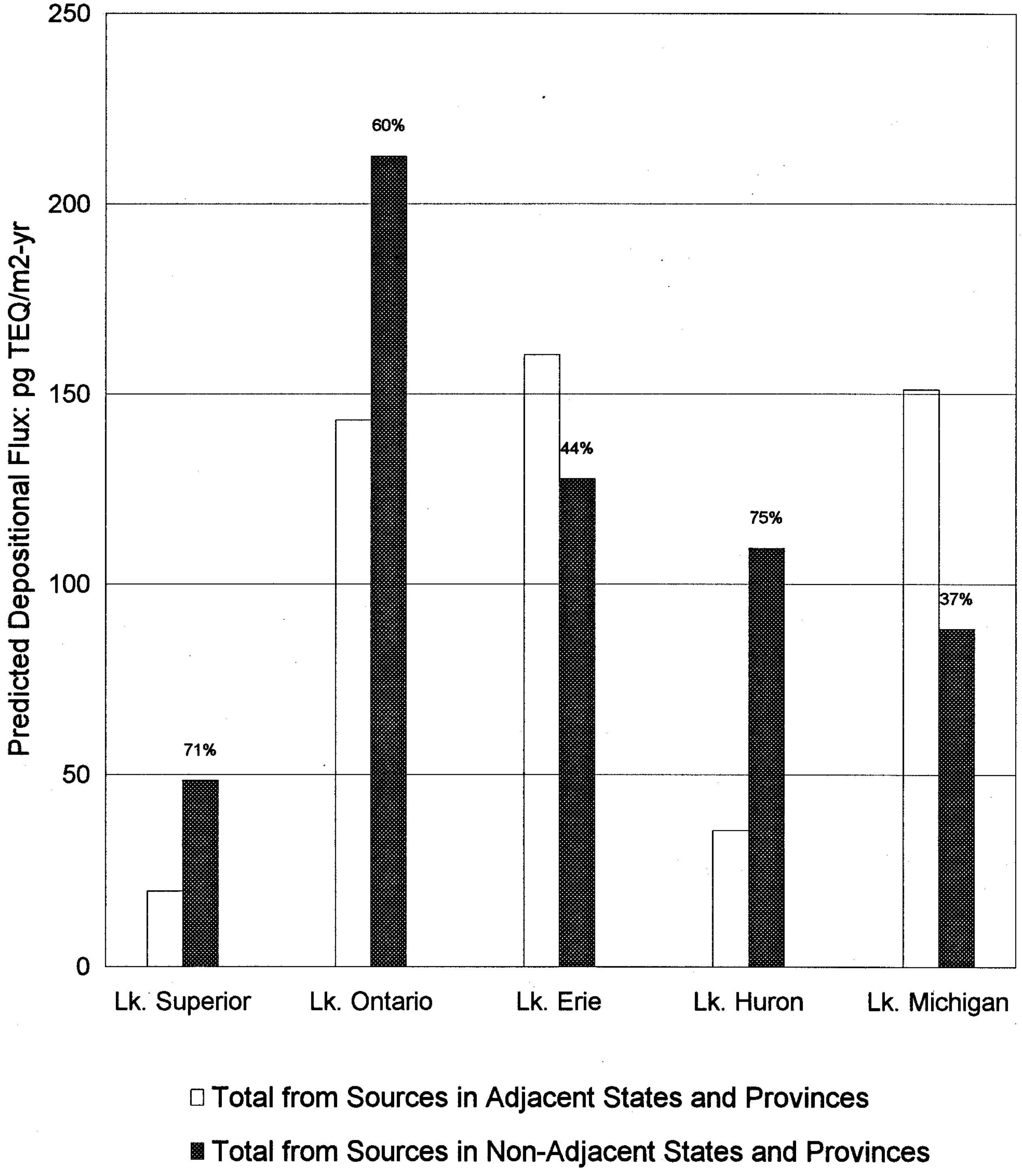


Figure 4. Predicted Depositional Flux of Atmospheric PCDD/F to the Great Lakes From Sources in Adjacent vs. Non-Adjacent States and Provinces, 1993



ii. Transport and Deposition of Dioxins and Furans from Sources in the U.S. and Canada to the Dairy Farms in Wisconsin and Vermont

Building upon the work described above, HYSPLIT is currently being used to study the short-, medium-, and long-range transport of dioxin from specific sources and source regions to dairy farms in Wisconsin and Vermont. Measurements of dioxin in the air above the farms, in the crops, and in cow's milk at the farms are also being made. These data will be used to test the validity of the modeling methodology and to develop new information on deposition of dioxin to agricultural crops. The work is a collaborative project involving the Center for the Biology of Natural Systems at Queens College, the New England Environmental Policy Center (director: Jean Richardson), and the University of Wisconsin Department of Dairy Science (Randy Shaver and others). The estimation of the full set of source-receptor relationships between known sources and the farms will be attempted. One goal of this study is to estimate the relative contribution of short-, medium-, and long-range air transport to the contamination of dairy feed crops by dioxin.

iii. Atmospheric Fate and Transport of Endocrine-Disrupting Biocides

In another current project using HYSPLIT at CBNS, the long-range transport and deposition of biocides suspected of being endocrine disruptors will be simulated. It is anticipated that atrazine will be simulated initially; other compounds may be added to the analysis later. In this work, a geographically and temporally resolved emissions inventory will be developed. The HYSPLIT model will be applied to simulate the atmospheric transport and fate of emitted material. The validity of the overall modeling methodology will be tested against an existing set of measurements of biocides in rainwater. Predictions of the loadings to particular receptors (e.g., the Great Lakes, drinking water reservoirs, and agricultural sites) will be made. Details of the source-receptor relationships for key receptors will be presented.

iv. Future Work at CBNS Using HYSPLIT

To extend the work described above, several refinements and improvements to the modeling methodology are planned. These include the following:

- Increasing the accuracy of emissions inventories;
- Refinements to fate and deposition algorithms;
- An attempt to include the grasshopper effect;
- Evaluation of the accuracy of the short-range modeling analysis (improve if necessary);

- Use of a new version of HYSPLIT, being developed by Roland Draxler of NOAA;

- Additional model evaluation tests;

- For improved estimates of deposition to the Great Lakes, attempt to link the atmospheric model to a Lake model; this is especially crucial for compounds for which gas exchange is important;

- Analysis of a range of other compounds that are emitted from specific sources, are transported through the air, and are deposited in the Great Lakes and other receptors.

F. ADOM

The development of ADOM, the Acid Deposition and Oxidant Model, began in 1982, sponsored by the Ontario Ministry of the Environment (now OMOEE), Environment Canada's Atmospheric Environment Service (AES), the Umweltbundesamt of the (then) Federal Republic of Germany, and the Electric Power Research Institute. Summaries of the development and evaluation of ADOM for its initial use with acidic deposition are given by Venkatram *et al.* (1988, 1992), Fung *et al.* (1991, 1992), ERT (1984, 1985), ENSR (1990), and RMCC (1990). ADOM has been used, for example, to evaluate the environmental impacts of different emissions reductions scenarios (Misra *et al.*, 1989).

ADOM is an Eulerian model which considers meteorology and transport, cloud physics, aqueous and gas phase chemistry, and wet and dry deposition processes. Grid sizes in simulations with ADOM have been on the order of 127 km in the horizontal, and in the vertical, 12 layers from the ground surface up to a height of 10 km. The vertical layers are unevenly spaced. The model uses thinner vertical layers in the planetary boundary region of the atmosphere to better simulate the expected higher concentration gradients near the earth's surface. There are eight layers in the region from the surface up to a height of 2000 meters.

The first complete version of ADOM, ADOM I, was tested against measurements in two different acid deposition episodes in April 1981 (Venkatram *et al.*: 1988, 1992). Precipitation was monitored at a network of 37 stations in the eastern U.S. and Canada. The modeling domain for ADOM's simulations was 30-60 °N Latitude and the eastern part of the U.S. and Canada (ranging from east of 94°W in the South to east of 110°W in the North). For one of the events, approximately 90% of the predicted sulfate and 60% of the predicted nitrate wet deposition values were within a factor of 2 of the measured values. For the second modeled event, more than 90% of the predicted sulfate and about 75% of the predicted nitrate wet deposition values were within a factor of 2 of the measured values.

ADOM has also been evaluated in its ability to simulate an ozone episode in the northeastern U.S. and southern Ontario in June 1983 (Venkatram *et al.*, 1992) and in the 1987 Across North America Tracer Experiment (ANATEX). A revised version of the model, ADOM II, was evaluated along with RADM (discussed below) in the 1988 Eulerian Model Evaluation Field Study (EMEFS) (Fung *et al.*, 1992).

A program has been underway to use ADOM to simulate the atmospheric transport and fate of mercury. This work will be described below.

i. Atmospheric Transport and Fate of Mercury

ADOM was adapted to simulate mercury in the atmosphere (Bloxam *et al.*, 1991). Mercury was considered to exist in three different forms in the atmosphere: (a) elemental mercury (Hg^o); (b) particulate mercury; and (c) divalent mercury ($HgCl_2$ or HgO).

An anthropogenic emissions inventory of mercury for the eastern U.S. and Canada was used as an input to the simulation. To complete the emissions inventory, the rate of "natural" emissions of mercury from soils or vegetation were assumed to be a function of temperature.

Initial modeling assumptions assumed no *net* effect of gas-phase chemistry, i.e., oxidation and reduction reactions were assumed essentially cancel out. In the aqueous phase (i.e., inside atmospheric water droplets), the oxidation of Hg^o by O_3 to give HgO was included in the model. Dry deposition was modeled using deposition velocities, with divalent mercury species assumed to dry deposit at rates similar to HNO_3, particulate Hg assumed to deposit at rates similar to sulfate. Dry deposition of elemental mercury was assumed to have a seasonally dependent deposition velocity to forest surfaces, with no dry deposition to other surfaces.

Typical values of atmospheric mercury measured at remote atmospheric sites were used as "boundary" conditions, i.e., for the concentration of mercury in air entering the model boundaries.

The model was used to simulate a 5-day period in April 1981, and the predicted air and rain concentrations of mercury were compared against the limited ambient measurement data that were available. Comparison of general concentration levels (not location-specific) were reported in this initial analysis. It was found that:

- Predicted atmospheric concentrations of Hg^o were generally in the range of 1-4 ng/m^3, except near regions of intense emissions. These results were consistent with typical measured concentrations away from source areas.

- Predicted air concentrations of particulate mercury were in the range of 0.01 to 0.05 ng/m^3, the same order of magnitude of the limited available measurement data (~0.06 ng/m^3 in New England; ~0.02 ng/m^3 in Wisconsin).

- Predicted concentrations of mercury in moderate to heavy precipitation (2- 20 ng/liter) were of the same order of magnitude as measured, long-term average concentrations (10-20 ng/liter).

As discussed in the Introduction, source-receptor relationships are not generally estimated in these types of models. However, a few sensitivity tests were performed using the model which yield interesting information about such relationships. For example, it was reported that when anthropogenic emissions were doubled, concentrations in source regions increased by 70-80% (i.e., they almost doubled), while concentrations at remote sites increased by 10-20%. An increase in the boundary concentrations by 50% (i.e., simulating a higher global background concentration) resulted in only a 10% increase in concentrations near sources, and a 30-50% increase in remote concentrations. These results give some information about the relative importance of local, regional, continental, and global air transport in affecting the atmospheric mercury concentrations at a given location.

Bloxam (1997) describes a second set of mercury simulations made with ADOM, in which the model attempted to simulate a 31-day period in August 1988. Again, it was found that predicted atmospheric concentrations of elemental mercury and the predicted wet deposition of mercury were in the range of observed data. Predicted particulate mercury concentrations were slightly less than the few measurements available for comparison. In the modeling simulations, most of the divalent mercury emitted was either dry-deposited or wet-deposited within several hundred kilometers of its emissions location. The predicted mercury deposition rates were found to be particularly sensitive to assumptions regarding the dry deposition of elemental mercury.

Work on adapting ADOM to simulate mercury is continuing. A summary of numerical modeling of atmospheric mercury, including that in ADOM is given by Petersen, Munthe and Bloxam (1996). A refined tropospheric chemistry module for the model, including cloud mixing, scavenging, chemistry and wet deposition, has recently been constructed and tested (Petersen *et al.*, 1996, *submitted for publication*).

G. RAMS

The Regional Air Modeling System (RAMS), developed at Colorado State University, is currently being used at NOAA's Air Resources Laboratory to address a number of air pollution issues (McQueen et al., 1996ab). RAMS is a model that simulates complex meteorology at highly resolved spatial and temporal scales. As a meteorological simulation tool, it is analogous to the MM5 model, used, for example in Models-3 (discussed below), and the Nested Grid Model (NGM), used in conjunction with HYSPLIT (discussed above).

One of the primary functions of the use of RAMS at NOAA is to allow the dispersion of a toxic release to be quickly modeled in an emergency situation (e.g., Draxler et al., 1993). In a practice exercise, RAMS was evaluated in its ability to simulate a complex meteorological episode in the vicinity of a nuclear power plant in the Susquehanna River valley, Pennsylvania (McQueen et al., 1995). In this study, a series of simulations was made with RAMS in which the grid size and terrain resolution were varied. It was found, perhaps not surprisingly, that with the highest terrain resolution, the best results were obtained with the smallest horizontal grid size tested (2.5 km) and the highest vertical model resolution (in the first of 24 vertical layers, the model layer closest to the ground surface was only 12 meters thick).

Fate and transport phenomena of air pollutants are, of course, highly influenced by the complex, three-dimensional characteristics of atmospheric motion. As a particular example, the dry deposition of vapor and particulate pollutants to any location on the earth's surface will depend intimately on the local, detailed meteorology (e.g., three-dimensional wind fields, temperature, humidity, etc.).[5] Most of the regional and long-range model applications discussed in this report use meteorological descriptions specified on relatively coarse grid scales, e.g., horizontal resolutions are typically on the order of 100 km or greater. For example, in the application of the HYSPLIT model to study PCDD/F and HCB transport to the Great Lakes, a horizontal grid size of 180 km was used with 6 vertical layers to a height of 5000 meters. Clearly, in these types of simulations, many details of the motion of the atmosphere are not explicitly characterized.

With a model such as RAMS, atmospheric motion is simulated on a relatively fine scale. Consequently, phenomena such as dry deposition can be treated in more detail than with models with coarser grids. The computational requirements for such fine-scale modeling simulations are very high; it is not currently practical to carry out long-term simulations over large model domains with such fine grids. Nevertheless, such simulations are necessary to accurately characterize local dispersion and to provide insight, for example, into deposition phenomena. After carrying out detailed

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[5]. Dry deposition will also depend on the physical-chemical properties of the pollutant and the nature of the earth's surface at any particular location.

calculations and ground-truthing exercises with a fine-scale model, one is in a better position to assess the validity of various approximations made in coarser-scale models.

i. Micro-Meteorological Characteristics of Dry Deposition to the Chesapeake Bay

In an effort particularly relevant to subject of this report, RAMS is being used to investigate dry deposition to the Chesapeake Bay (McQueen et al., 1997a, 1997b; Valigura et al., 1996). Initial results of this research have shown that accurate characterization of dry deposition phenomena at the surface require a relatively fine grid scale (e.g., horizontal resolution of 5 km or less; near-surface vertical resolution of 12 meters). The requirements are even more restrictive for situations in which the atmosphere's thermal stratification is stable, i.e., when the water is colder than the air. The compound currently being investigated in this research, nitric acid, is not one of those in Table 1. However, while there are, of course, some pollutant-specific influences, dry deposition phenomena for all air pollutants to water surfaces are fundamentally similar. Thus, this research is providing insights into the micro-meteorological aspects of atmospheric deposition that will likely be useful in modeling the deposition of any of the pollutants of Table 1 to the Great Lakes.

H. RADM

The Regional Acid Deposition Model (RADM) is an Eulerian model originally developed to study acid deposition phenomena. It was developed to support the National Acid Precipitation Assessment Program (NAPAP). The development, application, and evaluation of RADM for this application is reviewed by Chang *et al.* (1990), Dennis *et al.* (1990ab), and Dennis (1997).

RADM has continued to undergo additional application, evaluation, development and refinement (e.g., Pleim *et al.*, 1991; Poppe *et al.*, 1992; Stein, 1992; Dennis *et al.*, 1993; Middleton *et al.*, 1993; Pleim and Ching, 1993; Cohn and Dennis, 1994; McHenry and Dennis, 1994; Spence and McHenry, 1994; Byun and Dennis, 1995; Jang *et al.*, 1995ab; Zimmermann and Poppe, 1996). RADM has been used to simulate the fate and transport of sulfur and nitrogen species, as well as the generation of tropospheric ozone through photochemical reactions of nitrogen species and volatile organic compounds (VOC's).

To simulate meteorological processes, RADM uses the Mesoscale Meteorological Model (MM4). This model uses weather observations and the output from other models to estimate a self-consistent simulated three-dimensional field for wind, temperature, precipitation, and other meteorological variables. The output data of MM4 are used as input to RADM. Similar to other Eulerian models, attempts are made to simulate each of the following processes in each grid cell, for pollutants, precursors, and reactants:

- Emissions into the cell
- Transport of compounds into the cell from other cells
- Transport of compounds from the cell into other cells
- Dispersion of compounds
- Chemical transformation of compounds
- Wet deposition phenomena
- Dry deposition phenomena

The vapor-phase surface-level dry deposition algorithms that have been used in RADM closely follow those presented in Wesley (1989).[6]

To estimate source-receptor relationships for sulfur simulations, a method of numerically "tagging" emitted material from specific sources was developed (McHenry

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[6]. These algorithms were also used as the basis for the mathematical formulation for gaseous dry deposition in the development and application of HYSPLIT at NOAA (e.g., Draxler 1994) and in the use of HYSPLIT to simulate the atmospheric fate and transport of dioxin (Cohen *et al.*, 1995).

et al., 1992). Recently, Dennis (1997) has developed an approach for elucidating source-receptor relationships in RADM simulations for nitrogen species.

i. Nitrogen Deposition Airshed of the Chesapeake Bay Watershed

RADM has recently been used to estimate the geographical extent of the nitrogen deposition airshed of the Chesapeake Bay watershed (Dennis, 1997).

RADM version 2.61 was used in this analysis. In the east-west direction, the domain included the eastern half of the continental U.S. and Canada; in the north-south direction, the domain extended from below the southernmost regions of the U.S. to the lower portion of Hudson Bay in Canada. [Approximate latitude and longitude ranges can be estimated from the domain maps given in Dennis (1997): the modeling domain in the analysis extended from approximately 25-52 °N latitude and from approximately 65-100 °W longitude.]

Horizontally, the grid cells used were 80km x 80km, a grid size frequently used in RADM applications. Vertically, the model uses 15 logarithmically spaced layers from the earth's surface up to a height of 16 km. The model domain contains 19,950 cells (35 x 38 x 15). To estimate annual averages for a particular emissions scenario, 30 five-day and 3 ten-day simulations were run. The results from the 30 five-day simulations are combined in a weighted average based on the estimated weather patterns for 1982-1985.

To estimate source-receptor relationships, the emissions from a small subregion were reduced by 50% and the resulting deposition was compared with that estimated when the emissions from the subregion were at full strength.[7] For each source, the deposition was normalized against the total deposition attributed to the source in the model domain. The average distances over which 25%, 50%, and 75% of the deposition occurred from a particular source region were estimated.

Nine particular source regions were studied in this way.[8] For the sources simulated, it was found that approximately 25% of the deposition occurred within 100-150 km of the source, 50% of the deposition occurred within 150-350 km of the source, and 75% of the deposition occurred within 250-800 km of the source (as might be expected, the distances were longer in the prevailing wind direction).

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[7]. A sensitivity test of the reduction percentage was conducted. It was found that the inferred source-receptor relationships were not significantly affected by the reduction percentage used in the numerical experiments (Dennis, 1997).

[8]. Dennis (1997) reports that approximately 65 total CPU hours on a Cray C90 computer were required for each scenario examined. Thus, it would appear that for the base case analysis and the nine source regions examined, approximately 650 CPU hours on the Cray C90 were required.

The “range of influence” of a particular source or source region was operationally defined to be the region in which 75% of the deposition from the source in the model domain occurs. In the simulations performed this range of influence was found to be on the order of 700-800 km in the prevailing wind direction, consistent with a travel time of approximately 1-1.5 days (Dennis, 1997). Similar range-of-influence results have been found for sulfur emissions/deposition in a study using the “tagged” species approach with RADM (U.S. EPA, in press, as cited by Dennis, 1997).

I. MODELS-3

Models-3 is a "third generation" air pollution modeling system being developed by the U.S. EPA (Novak *et al.*, 1995; Appleton, 1996; Dennis *et al.*, 1996). A preliminary version of the model has been prepared, but the full system is still under development. A fully operational system is scheduled to be in place by the end of 1997.[9]

Models-3 is being constructed using at least the following models as a base: (a) RADM (described above); (b) the Regional Oxidant Model (ROM) (Lamb, 1983ab; Young et al., 1989); and (c) the Urban Airshed Model (UAM) (e.g., Scheffe and Morris, 1993). Meteorological processes will be simulated using the Meteorological Mesoscale Model Version 5 (MM5), developed by researchers at the Pennsylvania State University and the National Center for Atmospheric Research (NCAR). Models-3 is being designed as a powerful decision support tool, to enable a wide range of policy-related air pollution questions to be addressed. It is being constructed as a highly flexible system that will be able to be applied to a range of pollutants over various geographical length scales.

i. Transport and Fate of Atrazine Emitted in the U.S. and Canada, including Atmospheric Deposition to Lake Michigan

Of direct relevance to the subject of this analysis, it is planned that Models-3 will be used to simulate the fate and transport of Atrazine emitted from agricultural uses in the United States and Canada. This analysis will be conducted in conjunction with the Lake Michigan Mass Balance Study (Bullock 1997a). In this analysis, a geographically resolved emissions inventory will be estimated based on a biocide-emissions model developed at the ORTECH Corporation (Scholtz *et al.*, 1993, 1994). Meteorological data to drive the emissions model is currently being prepared by NOAA-EPA researchers. It is anticipated that Models-3 will be use to simulate particular emissions episodes. The modeling predictions will be compared against ambient measurements of Atrazine made in the measurement-phase of the Lake Michigan Mass Balance Study. Atmospheric deposition to the Lake will also be simulated. This analysis is expected to be completed by 1998. Mercury may also be simulated using Models-3 in conjunction with the Lake Michigan Mass Balance Study.

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[9]. A similar comprehensive modeling system is being developed under the auspices of the Electric Power Research Institute (EPRI) by the Consortium for Advanced Modeling of Regional Air Quality (CAMRAQ) (Hansen *et al.*, 1994; Zannetti *et al.*, 1995).

J. BACK-TRAJECTORY CALCULATIONS

Back trajectory calculations are sometimes used in attempts to estimate the relative importance of different sources and/or source regions to the concentrations and/or deposition at a given receptor (e.g., Keeler *et al.*, 1990; Keeler and Pierson, 1994).

In this type of analysis, back-trajectories for low-level and high-level concentration measurement events are estimated. High-concentration events are assumed to result when air parcels arrive at the measurement site from regions with significant sources of the given pollutant; low-concentration events are presumed to result when air parcels that arrive at the measurement site from regions without significant sources of the pollutant. The distance between a known or hypothesized source location and the measurement site obviously influences the potential extent of its noticeable impact in the measured concentrations; dispersion, deposition, and chemical transformation will all generally serve to lower the atmospheric concentration of pollutant with increasing distance from any given source, and these processes are dependent on the physical-chemical properties of the particular pollutant and the detailed nature of the atmospheric environment encountered by the polluted air parcel in between the source and the measurement site.

A few examples of this type of analysis are given below.

i. NO_x sources to the Chesapeake Bay

The HYSPLIT model has been used to analyze potential source regions for NOx in the Chesapeake Bay region (results reported in Valigura *et al.*, 1996). Back-trajectories for low and high measured concentration events were estimated. High concentration events appeared to result from air parcels that arrived at the measurement site from regions with significant sources of NOx; low concentration events appeared to result from air parcels that arrived at the measurement site from regions without significant sources of NOx.

ii. Mercury sources to Michigan

A back-trajectory analysis is being used to assess the sources of mercury in Michigan. Ambient mercury (vapor and particulate form) and mercury in precipitation is being measured at at least three sites. Initial results for back-trajectories of high-concentration precipitation events have been published (Hoyer *et al.*, 1995). It was found that the highest mercury concentrations in precipitation were generally associated with air parcels that arrived at the measurement sites from the west, southwest, south, and southeast. There were some exceptions; occasionally, there were high concentrations of mercury in precipitation from air trajectories from the north and east of the sites.

iii. Trace Elements, including Cadmium, on the northern shore of Lake Ontario

Principal component analysis has been combined with back-trajectory calculations in an attempt to assess the potential sources of trace metals at Point Petre, one of the five master IADN sampling sites, on the northern shore of Lake Ontario (Blanchard, Hopper and Hoff, 1997). It was found that the sampling events associated with the highest levels of generalized anthropogenic emissions corresponded to air trajectories that passed over the heavily populated regions to the south and west of Point Petre. The authors report that the noticeable contribution of cadmium and arsenic from trajectories coming from the north is consistent with the locations of large known sources of these pollutants (smelters).

iv. Trace Elements, including Cadmium, at Dorset, Ontario

A back trajectory analysis was performed on a data-set of measured trace elements in ambient particulate and precipitation at Dorset, Ontario. In this analysis, a range of elements were measured. The results for cadmium will be briefly presented here, as that is one of the compounds being considered in this analysis. The analysis of back-trajectories calculated for high-measurement precipitation events suggested that there are only a few source areas which contribute strongly to the cadmium in precipitation at Dorset, Ontario. Particular source regions suggested by the analysis included:

- an area around Lake Champlain and across Northern Vermont (which the authors noted does not have any obvious, known sources of cadmium);
- Ottawa and Montreal, which the authors stated could be associated with incineration and other urban sources of cadmium;
- An area in Pennsylvania and near Atlanta Georgia, which the authors stated could be associated with metal industries.

Due to a lack of emissions inventory data, the authors acknowledged that is was difficult to verify whether source locations suggested by the analysis did indeed correspond to large known sources.

v. Unusually High Dust Events in Illinois

Back trajectory analysis was used in an attempt to explain unusually high dust levels observed in ambient measurements during a particular period in 1979 at two sampling sites in Illinois (Gatz and Prospero 1996). The available evidence strongly suggested that the origin of the dust in this event was the Saharan desert in North Africa.

vi. Polychlorinated Biphenyls and Organohalogen Pesticides to Southern Ontario (at Egbert, Ontario)

Back trajectory analysis was used in conjunction with measurements at Egbert, Ontario to attempt to estimate source regions of PCB's and several organohalogen pesticides (Hoff *et al.*, 1992ab). It was found that events in which high concentration of pesticides were measured corresponded to air flowing from the south, especially the southern U.S. and the Carribean. The concentration of PCB's appeared to be only weakly dependent on source regions, and more dependent on the ambient temperature. As the authors concluded, this is evidence of significant emissions and re-emissions (i.e., the grasshopper effect) occurring over widely dispersed areas.

K. Hybrid-Receptor Modeling Approach

The Hybrid-Receptor modeling approach combines measured atmospheric concentrations and meteorological observations in a Lagrangian modeling context (Keeler and Samson, 1989).

Measured concentrations at sites upwind of a given receptor are projected forward in a Lagrangian simulation to estimate the impact at the receptor for air parcels originating at the measurement site. In this situation, the downwind impact at the receptor is equivalent to the impact of a hypothetical source at the sampling point. The hypothetical source emits pollution at a rate such that the concentration in the air in the vicinity of the source location would be the same as the measured atmospheric concentration.

For measured concentrations downwind of the receptor of interest, an upwind virtual source is numerically constructed which can account for the measured concentrations. In these cases, the impact on the receptor is estimated by simulating the fate and transport of material emitted from the virtual source.

i. Dry Deposition of Semivolatile Organic Compounds to Lake Michigan

As part of the Lake Michigan Urban Air Toxics Study (LMUATS) (Keeler 1994), the Hybrid-Receptor approach was used to estimate the dry deposition flux of a range of semivolatile organic compounds to Lake Michigan (Pirrone *et al.*, 1995b).

Of the organic pollutants listed in Table 1, estimates for the following compounds were reported in Pirrone *et al.* (1995b): hexachlorobenzene, γ-HCH, dieldrin, a range of PCB's (including homologue group totals, e.g., monochloro-PCB's, dichloro-PCB's, etc.), and the following 11 PAH's: Benzo[a]Pyrene, Benzo[e]Pyrene, Fluorene, Pyrene, Fluoranthene, Chrysene, Dibenz[a,h]Anthracene, Indeno[1,2,3-c,d]Pyrene, Anthracene, Benz[a]Anthracene, and Benzo[g,h,i]Perylene.

Trans-nonachlor was also measured in the organics series. Additional organic compounds from Table 1 measured in LMUATS (but not discussed in Pirrone *et al.*, 1995b) included Mirex, Aldrin, DDT, 1,4-dichlorobenzene, Hexachloro-1,3-butadiene, Naphthalene, Acenaphthylene, Phenanthrene, and Benzofluoranthenes.

Ambient air samples were collected at three sites:

(1) on a building roof at Illinois Institute of Technology in Chicago, Illinois
(2) at South Haven, MI, a rural site 3 km from the eastern shore of Lake Michigan
(3) onboard a research ship located on Lake Michigan 5-10 km offshore of Chicago.

Total (vapor + particle) concentrations of pesticides, PAH's and PCB's were measured. Water concentrations were not measured for any of the semivolatile organics during the study, so, the estimation of the vapor-phase dry deposition was somewhat uncertain. However, the authors judged this uncertainty to not be overly significant, reporting that water concentrations have been found to be somewhat constant over space and time in Lake Michigan.

The Hybrid-Receptor modeling methodology was modified to account for vapor/particle partitioning of semivolatile organic compounds in the atmosphere.

As might be expected, ambient concentrations and deposition *flux* (e.g., g/m^2-sec) decreased with distance from a hypothetical or virtual source as air parcels moved across Lake Michigan. This analysis found that the largest part of the decrease is due to dispersion and not due to loss of material due to deposition of pollutant to the Lake.

ii. Dry Deposition of Trace Elements to Lake Michigan

A similar approach was used to estimate the dry deposition flux of a range of trace elements to Lake Michigan (Pirrone *et al*., 1995a; Keeler, 1994). None of the compounds listed in Table 1 were reported by Pirrone *et al.* (1995a). Total particulate lead was measured (but no separate measurements were made for alkylated lead compounds). No measurements were reported for cadmium or tin. Vapor- and particle-phase mercury measurements were made in LMUATS (Keeler, 1994).

iii. Dry Deposition of Trace Elements to Lake Erie

Using the Hybrid-Receptor approach, Keeler and Pirrone (1996) estimated the dry deposition flux of Cd, Mn, V, As, Se, and Pb to Lake Erie.

Ambient measurements were made at two sites in the Detroit metropolitan area for 10 days during April 1992: (a) downtown Detroit, downwind of a heavily industrialized area; and (b) a mixed residential/industrial area downwind of a large municipal waste incinerator. In March 1994, 18 days of measurements were made at the downtown Detroit site (a) to characterize the levels of trace elements in particulate matter with diameters less than 2.5 μm and with total suspended particulate matter.

The particle size distributions of each trace element in the atmosphere measured by Holsen *et al*. (1993) and Pirrone *et al*. (1995a) were used to estimate deposition velocities to Lake Erie.

The predicted deposition flux along a particular trajectory that traversed Lake Erie on March 7, 1994 from the sampling site in downtown Detroit decreased dramatically with distance during the over-water transport. However, this decrease was predominantly due to atmospheric dispersion; deposition of the particle-associated pollutants accounted for only 5-20% of the overall decrease during over-water transport.

iv. Dry and Wet Deposition of Trace Elements to the Rouge River Watershed

Using the Hybrid-Receptor modeling approach, Pirrone and Keeler (1996a) estimated the deposition flux of Cd, Cr, Ni, Pb, and Hg to the Rouge River watershed. The Rouge River flows into the Detroit River which flows into Lake Erie.

Ambient measurements of the trace elements in total suspended particulate matter were made at five sites in the southeast side of the Rouge River watershed from 1982 to 1992 (Pirrone *et al*., 1995c). Meteorological parameters were measured at several sites in the watershed area, and were used in the modeling. The Hybrid-Receptor modeling approach was modified in this analysis to include deposition due to aerosol scavenging by precipitation. Scavenging ratios were based on measured ground-level air concentrations and precipitation concentrations measured during an 18-day study in March 1994. The model of Pirrone and Keeler (1993) was used to estimate dry deposition velocity. Trends in emissions of the trace metals in the watershed area were compared with trends in the estimated deposition fluxes; emissions and deposition of cadmium, chromium, and nickel vary from year to year, but show a slight *upward* trend from 1982 to 1992. Emissions and deposition of lead in the watershed show a downward trend from 1982-1992, largely due to the phasing out of leaded gasoline usage. Mercury emissions and deposition show an increase from 1988 to 1992.

3. Summary and Concluding Observations

A. Scope of the Analysis

This analysis has dealt with models that have, will, or could attempt to estimate the atmospheric transport and fate of one or more of the BVES persistent toxic substances emitted to the air, with particular emphasis on deposition to the Great Lakes basin. A summary of the models considered in this analysis is given in Table 5.

The focus of this analysis has been on modeling efforts undertaken by government agencies in the U.S. and Canada which address the above topic, and an attempt has been made to comprehensively describe the universe of such efforts. The relevant universe of such government efforts was assembled in the following through (a) discussions with members of the International Air Quality Advisory Board (which includes representatives from the USEPA, NOAA, Environment Canada Atmospheric Environment Service, Ontario Ministry of the Environment, and others agencies and institutions), (b) discussions with government researchers (a list is provided in the Acknowledgments section of this report), and (c) review of the literature

Despite the intention to be comprehensive, it is recognized that relevant efforts may have been inadvertently omitted. For the most part, non-governmental modeling efforts have not been included. This is recognized as a limitation of the analysis. An attempt was made, however, through review of the literature, to include particularly relevant modeling analysis that has attempted to link air emissions sources to atmospheric deposition to the Great Lakes for one of the persistent toxic substances being considered. A few such efforts that were found have been included.

B. General Observations

The ideal modeling situation might be described in the following way:

- the emissions of all sources of a given pollutant are well characterized;

- the atmospheric fate and transport of these emissions is accurately modeled, including accurate characterizations of meteorological processes, micro-chemical (e.g., reaction with hydroxyl radical) and micro-physical processes (e.g., vapor/particle partitioning), and deposition processes (and possible re-emission processes, e.g., the grasshopper effect).

- the total concentrations and deposition to a given receptor are predicted (and compare well to measured values), and, the contributions to the total loading at a given receptor from individual sources and/or source regions are quantified.

Table 5. Summary of Modeling Analyses Considered

#	**Model**	**Reference(s) and/or principal contact(s)**	**Compounds Considered**	**Source Regions**	**Receptor Regions**	**Type of Results Available *(or Expected to be Available)***
Eulerian Approaches						
1	Global Chemical Transport Model	Pudykiewicz and Koziol, 1997; Pudykiewicz and Dastoor, 1996	α-HCH, γ-HCH	global oceans; future work will include terrestrial emissions	global, including, but not limited to the Arctic	predicted atmospheric concentrations now available; *deposition results available or soon to be available*
2	REMSAD	Axelrad, 1997; Guthrie et al., 1995; SAI, 1996	PCDD/F, Mercury, Cadmium, Polcyclic Organic Matter, Atrazine	U.S. (planned); possibly others	Great Lakes, Chesapeake Bay, possibly other receptors	*results for concentrations and deposition expected to be available in 1-2 years*
3	ADOM	Bloxam et al., 1991; Bloxam, 1997; Petersen et al., 1996	Mercury	Eastern U.S. and Canada	Eastern U.S. and Canada	concentrations and deposition; *additional results expected*
4	RAMS (Meteorological)	McQueen et al., 1997a, 1997b; Valigura et al., 1996	Nitric Acid	(not modeled)	Chesapeake Bay	detailed estimates for dry deposition
5	RADM	Dennis, 1997	Nitrogen compounds	Eastern U.S. and Canada	Chesapeake Bay and Watershed	concentrations; deposition; source-receptor relationships
6	MODELS-3	Novak et al., 1995 Dennis et al., 1996 Bullock, 1997a	Atrazine (+ others)	U.S. and Canada	Lake Michigan (+ others)	*concentrations; deposition; source receptor relationships (?)*

Table 5. Summary of Modeling Analyses Considered

#	Model	Reference(s) and/or principal contact(s)	Compounds Considered	Source Regions	Receptor Regions	Type of Results Available *(or Expected to be Available)*
Lagrangian Approaches						
7	RELMAP	Clark, 1992ab	Cadmium (a)	U.S.	Lake Michigan	Deposition to Lake Michigan
8		Bullock et al., 1997b; U.S. EPA 1996c	Mercury	U.S.	U.S.	Atm. Conc. & Deposition in U.S.
9		Bullock 1997ac; Cleverly 1997	PCDD/F	U.S.	U.S.	Atm. Conc. & Deposition in U.S.
10	ASTRAP	Voldner and Schroeder, 1989	Toxaphene	U.S.	Great Lakes	Total predicted deposition; a few source-receptor relationships presented
11		Shannon and Voldner, 1995	Mercury	Eastern U.S. and Canada	Great Lakes	Total predicted deposition
12		Voldner et al., 1993	Lead	U.S. and Canada	Great Lakes	Total predicted deposition
13	HYSPLIT	Cohen et al., 1995	PCDD/F and HCB	U.S. and Canada	Great Lakes	Atmospheric concentrations and predicted deposition; source receptor relationships
14		CBNS, Queens College, ongoing work	PCDD/F	U.S. and Canada	Dairy Farms in Wisconsin and Vermont	*Atmospheric concentrations and predicted deposition; source receptor relationships*
15		CBNS, Queens College, ongoing work	Endocrine-Disrupting Biocides	U.S. and Canada	Drinking water reservoirs in the midwest and northeast	

Table 5. Summary of Modeling Analyses Considered

#	Model	Reference(s) and/or principal contact(s)	Compounds Considered	Source Regions	Receptor Regions	Type of Results Available *(or Expected to be Available)*
Receptor-Oriented Approaches						
16	Back-Trajectory Approach	Valigura et al., 1996	NO2	U.S. and Canada	Chesapeake Bay	Information about source regions contributing to observed concentrations at the receptor location
17		Hoyer et al., 1995	Mercury	U.S. and Canada	Michigan	
18		Blanchard, Hopper, and Hoff, 1997	Cadmium (a)	U.S. and Canada	northern shore of Lake Ontario	
19		Gao, et al., 1996	Cadmium (a)	U.S. and Canada	Dorset Ontario	
20		Gatz and Prospero, 1996	dust	U.S. and Canada	Illinois	
21		Hoff et al., 1992ab	PCB's and organochlorine biocides	U.S. and Canada	Egbert Ontario	
22	Hybrid-Receptor Modeling Approach	Keeler, 1994; Pirrone et al., 1995b	Semivolatile Organic Compounds	Great Lakes region	Lake Michigan	deposition arising from hypothetical "virtual" sources that could explain observed atmospheric concentrations at particular locations.
23		Keeler, 1994; Pirrone et al., 1995a	Trace Elements		Lake Michigan	
24		Keeler and Pirrone, 1996	Cadmium (a)		Lake Erie	
25		Pirrone and Keeler, 1996a	Cadmium, Mercury		Rouge River Watershed	

Notes: (a) Other heavy metals also considered; the only BVES compound included, however, was cadmium

None of the modeling analysis discussed in this report have reached this ideal situation yet, although work continues toward these goals.

The following recurring themes have emerged from this analysis.

i. Emissions Inventories

For essentially all of the modeling efforts considered, significant uncertainties in the emissions inventory have been acknowledged. This remains a difficult problem. In another report in this series, emissions inventories in the U.S. and Canada for the persistent toxic substances considered are discussed. *While many efforts are underway to improve the quality of emissions inventories, there do not appear to be accurate inventories currently available at present for most or all of the substances being considered.*

- for some compounds, there appears to be no emissions information available;
- for some compounds for some sources in some source regions, available inventory information appears to be confidential and unavailable to the public, independent researchers, or even government researchers who might want to explicitly calculate *and present* source-receptor relationships for specific emissions sources.
- for some pollutants, existing inventories have insufficient geographical and/or temporal resolution to be useful for modeling;
- for some pollutants, there appears to be no way to assess the accuracy of existing inventories, because of insufficient documentation of inventory details and/or of quality assurance/quality control procedures;
- for some pollutants in some source regions, there are ongoing efforts to improve the above situation;
- the above statements are based upon the information that could be obtained in the course of this research from the relevant government regulatory agencies (e.g., the U.S. EPA, Environment Canada, etc.); it is possible that additional information exists at these or other institutions but was not identified in the course of this research; if such additional information does exist, then perhaps it will come to light in the further review and discussion of this issue.

The physical and chemical situation which atmospheric fate and transport models are attempting to simulate is extremely complex, and the scientific understanding of many important processes is somewhat limited. Thus, a range of assumptions and simplifications are made. Comparison of model results against real-world measurements help assess the validity of these approximations. In these comparisons, a fundamental question frequently arises: If model predictions do not match measurements, is the discrepancy the cause of a inaccuracies in the simulation or in the inventory? In most cases, it is fairly difficult (or impossible) to determine the answer to this question *a priori*.

For these reasons, many modelers feel that it is premature to even attempt to model most or all persistent toxic substances at this time because of the lack of accurate emissions inventories. Basing an analysis on an inaccurate inventory is very risky, as successful validation against real-world measurements is unlikely. Resources for research are generally very scarce; failure of modeling efforts can result in the withdrawal of resources. Thus, the question of whether an emissions inventory is accurate or not is a very serious one, in regards to its potential use as an input to an air pollution model. Thus, it is important to examine the quality assurance and quality control approaches associated with a given inventory. Unfortunately, these types of inventory details are rarely, if ever, available.

ii. Pollutant-Specific Micro-Physical and Micro-Chemical Processes

With varying degrees of accuracy, each of the models considered in this analysis is or could be capable of simulating the atmospheric fate and transport of most or all of the persistent toxic substances being considered (Table 1). However, for most of the pollutants considered, there are significant uncertainties in basic physical-chemical properties, chemical reaction rates (and concentrations of reactants), rates of atmospheric photolysis, vapor/particle partitioning phenomena, and/or wet and dry deposition processes.

These uncertainties will limit the accuracy of the use of any of the models considered here (or any other model) to predict atmospheric fate and transport of persistent toxic substances.

Research to develop greater understanding in these uncertain areas should be continued and supported at the highest possible level. In these efforts, laboratory and field measurements should play a very important role.

Accurate air pollution models are only really possible to create after these basic underlying phenomena are elucidated. Models can be thought of as the scientific culmination of the process of attempting to understand environmental processes. For a given phenomenon, the course of scientific knowledge might progress through the following steps: (1) measurements are made; (2) theories are developed to explain the measurements; (3) the theories are tested for their predictive ability. Only after a large body of experimental and theoretical scientific work has been performed which leads to a relatively complete understanding of a particular phenomenon can such a process be included in any meaningfully accurate way in an air pollution model. In this sense, models can be seen as an overall test of the scientific understanding of the environment and the behavior of a given pollutant within it.

Thus, given an accurate emissions inventory, *if* the scientific understanding of atmospheric dynamics, pollutant dispersion, physical/chemical transformations and deposition processes were known perfectly, it would be possible to accurately predict concentrations and deposition at any desired receptor. We may perhaps be closest to this ideal with the fate and transport of atmospheric sulfur and nitrogen pollutants. However, for most or all of the persistent toxic substances considered here, the scientific community is in the early stages of attempting to construct comprehensive models of atmospheric fate. Future modeling efforts will hopefully be able to incorporate additional scientific findings regarding fundamental atmospheric phenomena.

iii. Characterization of Atmospheric Motion and Pollutant Dispersion

Relative to uncertainties which exist in the two areas discussed above (emissions inventories and pollutant-specific chemical/physical atmospheric processes), most model architects would consider the meteorological aspects of the simulation as being the most well understood. This is not to say that improvements are not needed in this area. For example, the characterization of clouds and precipitation is believed to need improvement (e.g., McQueen *et al*., 1996).

Different models treat meteorological and dispersion phenomenon with different approaches; there are differences in horizontal and vertical resolution (grid size) and in the numerical and physical sophistication of the simulations.

In the future, it may be possible to compare the predictions of different models (as discussed below). These comparison might would might yield information on the relative accuracy of different approaches. In particular, it would be useful to gain insights into the tradeoffs in accuracy among models of varying computational intensity.

iv. Model Evaluation

In overall model evaluation tests, predicted concentrations and deposition estimates are compared against actual measurement data collected at specific locations at specific times.

Tests of model validity must be made. It is essentially impossible to know *a priori* if enough of the physics and chemistry of a given situation have been characterized accurately enough without checking the results against real-world measurements.

There are often very little data against which to compare model predictions. However, for many of the compounds in Table 1, a particularly valuable data set for model validation is that which has been and will be provided by the IADN measurement program. There are other important monitoring programs, as well, and for the Great Lakes region, these are summarized in a separate report in this series (Cohen and Cooney, 1997). In many cases, measurements at locations relatively distant from intense sources are the most useful for model evaluation purposes, especially for comprehensive models covering large geographic areas. In such exercises, the available geographical resolution of the model and of the emissions inventory are often insufficient to accurately characterize phenomena close to intense sources.

With many uncertainties in different model components, it can be difficult or impossible to determine the causes for poor model performance.

As with any numerical simulation, there are tradeoffs between the resolution and sophistication of the calculation and the computational resources required to carry out the analysis. Some of the models described here are probably only practical to run in mainframe super-computer environments; some of the models described here can be run on a personal computer.

A useful exercise that might be carried out in the future for some or all of the pollutants considered here would be side-by-side model analyses, using the same emissions inventories and validation data. This type of inter-comparison analysis has been carried out in the past; example of model inter-comparison studies include those for:

- global distribution of radionuclides emitted from the Chernobyl accident (Klug *et al.*, 1992);
- sulfur transport and deposition in the U.S. and Canada (Clark *et al.*,1987,1989);
- transport of atmospheric tracers in the U.S. (Carhart *et al.*, 1989); and
- transport of tetroons (tracer balloons) in the U.S. (Clarke *et al.*, 1983).

v. Modeling Results, including Source-Receptor Relationships

The ultimate outputs of most models are the total predicted atmospheric concentration (from all sources) and deposition at given locations at given times arising from emissions input into the model.

Most models are capable of determining source-receptor relationships, e.g., the amount of deposition at a given receptor at a given time attributable to the contribution of a given source's emissions. Lagrangian-based models, in particular, are generally inherently capable of generating such results. In some cases, however, Eulerian models might be able to be configured to develop such estimates (e.g., by treating emissions of a given chemical from a given source as a different “species” than emissions of the same chemical from a different source); at the present, however, this is not generally done. There is one example discussed in this report involving the use of an Eulerian model to determine source-receptor relationships for nitrogen deposition to the Chesapeake Bay (RADM).

Although the Lagrangian models considered here were inherently capable of producing source-receptor results, no such results could be identified for inclusion in this analysis (with one exception) for various reasons. The only such results that could be obtained in the course of this analysis were the results for dioxin and hexachlorobenzene from sources in the U.S. and Canada to the Great Lakes (Cohen *et al.*., 1995).

Some of the reasons for the paucity of available results for source-receptor relationships may include the following:

- keeping track of source-receptor relationships can require substantial computational resources; thus, this is not attempted in many modeling exercises;
- in some cases, there may be a reluctance to specify source-receptor relationships because of actual or perceived uncertainties in the emissions inventory;
- in some cases, there may be a hesitance to specify source-receptor relationships because of the politically sensitive nature of ascribing a specific adverse environmental effect to a particular source.

C. Overall Concluding Remarks

The use of atmospheric models to trace the movement of persistent toxic substances from emissions sources to receptors is essential to understand the problem of pollution of the Great Lakes through the atmospheric pathway. The elucidation of source-receptor relationships is a necessary pre-requisite to developing and implementing approaches to reducing or virtually eliminating such pollutant input to the Great Lakes.

There have been a number of worthwhile modeling analyses conducted to date, and there are a number of promising modeling efforts currently ongoing. Nevertheless, the current state of knowledge and ability of such efforts is somewhat limited due to the following factors:

- uncertainties in emissions inventories;
- uncertainties in pollutant-specific atmospheric fate processes;

- for many pollutants, there are very few or no ambient measurements against which to test the overall validity of models;

- most modeling analyses done to date and most of those underway (that could be identified in this analysis) appear to be focused on estimating the *total* impact from all sources combined, and do not appear to be focused on elucidating specific source-receptor relationships.

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