

US EPA ARCHIVE DOCUMENT

## CHAPTER IV SCIENCE AND TOOLS

In addition to the environmental progress discussed in Chapter II and the program progress discussed in Chapter III, there has been significant advancement since the *Second Great Waters Report to Congress* in the development and use of new scientific methods and tools needed to understand the problem associated with Great Waters pollutants of concern. This includes improved understanding and assessment capabilities in some areas and a clearer picture of remaining uncertainties and future research needs in other areas.

This chapter highlights recent advancements in scientific research, as well as new and improved monitoring and modeling capabilities and databases that are improving our understanding of and abilities to address public health and environmental risks posed by the pollutants of concern in the Great Waters. Unlike Chapter II, which focuses on the results of new research and monitoring for the purpose of defining the overall problem, the discussion in this chapter focuses on developments and new findings that improve our understanding of more narrow issues related to pollutant emissions, transport, loadings, and effects. It also discusses the status and directions of research and information sources that will be useful in future assessments of the Great Waters. Finally, the chapter identifies additional research and tools that are necessary to address remaining uncertainties related to atmospheric deposition in the Great Waters. This discussion is not intended to be comprehensive, but rather to highlight some of the key scientific advancements since the *Second Report to Congress*.



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## WHAT MAJOR ADVANCEMENTS HAVE OCCURRED SINCE THE SECOND REPORT?

This section summarizes a number of major advancements in scientific research, models, and databases that are and will be useful in better understanding atmospheric deposition of the Great Waters pollutants of concern. Recent developments in emissions inventories are presented first, followed by a discussion of changes in programmatic direction and progress of several ambient air and deposition monitoring networks and environmental monitoring networks. The last two main subsections provide a discussion of recent scientific advancements in environmental fate and transport modeling, and exposure and effects research and modeling.

### EMISSION INVENTORIES

#### *National Toxics Inventory*

Developing estimates of how much of a pollutant is being emitted is an important key to characterizing the extent of the air toxics problem in the U.S., including persistent, bioaccumulative toxics that are of concern to the Great Waters program. For about 20 years, EPA has routinely collected emissions inventory data for criteria pollutants, such as lead, carbon monoxide, and particulate matter. For air toxics, however, scientists have had to rely on indirect estimates of emissions that are based on emission factors and other imprecise methods. With the air toxics program in the CAA amendments of 1990 came a new focus on air toxics emissions inventories. This information can be used to estimate and characterize risk and develop strategies to reduce risks from air toxics. These pollutants are emitted by major, area, and mobile sources, and emission estimates from these sources can vary from the national-level to regional- and county-level estimates, and to facility- and process-specific emissions data that can be used in air dispersion models.

The dispersion and exposure modeling used to estimate and characterize risks from air toxics requires a model-ready emissions inventory. As a result, EPA has compiled and continues to update and refine the National Toxics Inventory (NTI). To date, EPA has compiled an inventory data set for the 1990 to 1993 period (called the 1993 NTI) and another for 1996. The 1993 NTI data, where available for Great Waters pollutants of concern, are presented in Chapter II to characterize emissions and sources on a national level. The NTI does not include emissions of air toxics from natural sources (e.g., plants, volcanoes).

The 1996 NTI was completed in early 2000, but was not available in time to be included in this report. It represents a substantial improvement over the 1993 NTI in that it is more complete in its coverage of pollutants and their sources, and it carries a higher degree of spatial resolution owing to its development from source-specific information (i.e., the “bottom-up” approach to inventory development) and contains HAP emission estimates for major (facility-specific), area, and mobile on-road and non-road sources. In these 1996 NTI efforts, a majority of the State and local air pollution control agencies have provided direct emission information or a critical review of EPA-developed emissions in a coordinated effort to develop the best inventory in the available timeframe. This approach provides estimates of emissions at the county-level of resolution (or better, in many cases), which subsequently allows the 1996 NTI to be used to develop screening-level modeling assessments of ambient concentrations and inhalation exposures down to the county-level. As such, the 1996 NTI represents the most recently verified and complete emissions inventory available for national assessments.

The EPA has been compiling the 1996 NTI using five primary sources of data:

- State and local toxic air pollutant inventories (developed by State and local air pollution control agencies);
- Existing databases related to EPA's air toxics regulatory program;
- The EPA's Toxic Release Inventory (TRI) database;
- Estimates developed using mobile source methodology (developed by EPA's Office of Transportation and Air Quality); and,
- Emission estimates generated from emission factors and activity data. (NOTE: While major sources were not estimated using emission factors and activity data, 30 area sources were in the 1996 NTI.)

Preference is given to State- and locally-generated information, where available. Where such data are not available, existing data from EPA's regulatory development databases are utilized. If neither of these data sources contains information for a known stationary source, EPA uses data from the TRI. The EPA also gives preference in inventory development to emissions data resulting from direct measurements over those generated from emissions factors and activity data.

The TRI database contains national inventory data submitted by individual facilities that meet certain reporting criteria. The TRI does not account for smaller sources within a source category that do not meet the reporting criteria. Although the TRI data are limited in source category coverage, in many cases, TRI data are used because they are the only available means to estimate emissions from certain source categories. For the missing States and for sources not included in the State inventories, MACT data, or the TRI, EPA estimated air toxic emissions using air toxic emission factors and corresponding activity data.

The compilation of such a large data set presents a significant challenge to EPA and introduces several limitations. In terms of consistency, the NTI is a composite of emissions estimates generated by State and local regulatory agencies, industry, and EPA. Because the estimates originated from a variety of sources and estimation methods, as well as for differing purposes, they vary in quality, included pollutants, level of detail, and geographic coverage. Also, the accuracy of emissions estimation techniques varies with pollutants and source categories. In some cases, an estimate may be based on few (or only one) emissions measurements at a similar source. The techniques used and quality of the estimates will vary between source categories (e.g., some have been better studied than others) and between major, area, and mobile source sectors. Another limitation of the NTI is that emissions from reservoir sources, such as volatilization from soils where chemicals were previously spilled or applied (in the case of pesticides), are either missing or poorly quantified. If such sources are a major component of the total emissions for a given chemical, NTI could under report total emissions for that chemical.

Future updates of the NTI are scheduled every 3 years. However, similar to other inventories, the NTI is dynamic and is subject to change (via periodic updates) as new, more reliable data become available for the year it represents. Further, EPA continues to work with the State and local agencies to promote consistency and accuracy in estimating and reporting emissions information for future years.



## ***The Great Lakes Regional Air Toxics Emissions Inventory***

Under the auspices of the Great Lakes Commission, the eight U.S. Great Lakes States and the Canadian province of Ontario have been engaged since the early 1990s in creating and updating a regional air toxics emissions inventory of the Great Lakes pollutants of concern – the Great Lakes Regional Air Toxics Emissions Inventory. The inventory covers 86 pollutants from point, area, and mobile sources. The emissions estimates are at the process level, and the data are model-ready. The inventory is compiled according to a regional protocol designed to provide data of consistent quality and format throughout the Great Lakes region. The inventory data are supplied to the NTI; data for the 1993 reporting year were released in the summer of 1998.

## **AMBIENT AIR AND DEPOSITION MONITORING NETWORKS**

Figure IV-1 displays the monitoring sites for all ambient air and deposition monitoring networks that measure Great Waters pollutants of concern in the regions of the Great Waters and throughout the U.S. and parts of Canada.

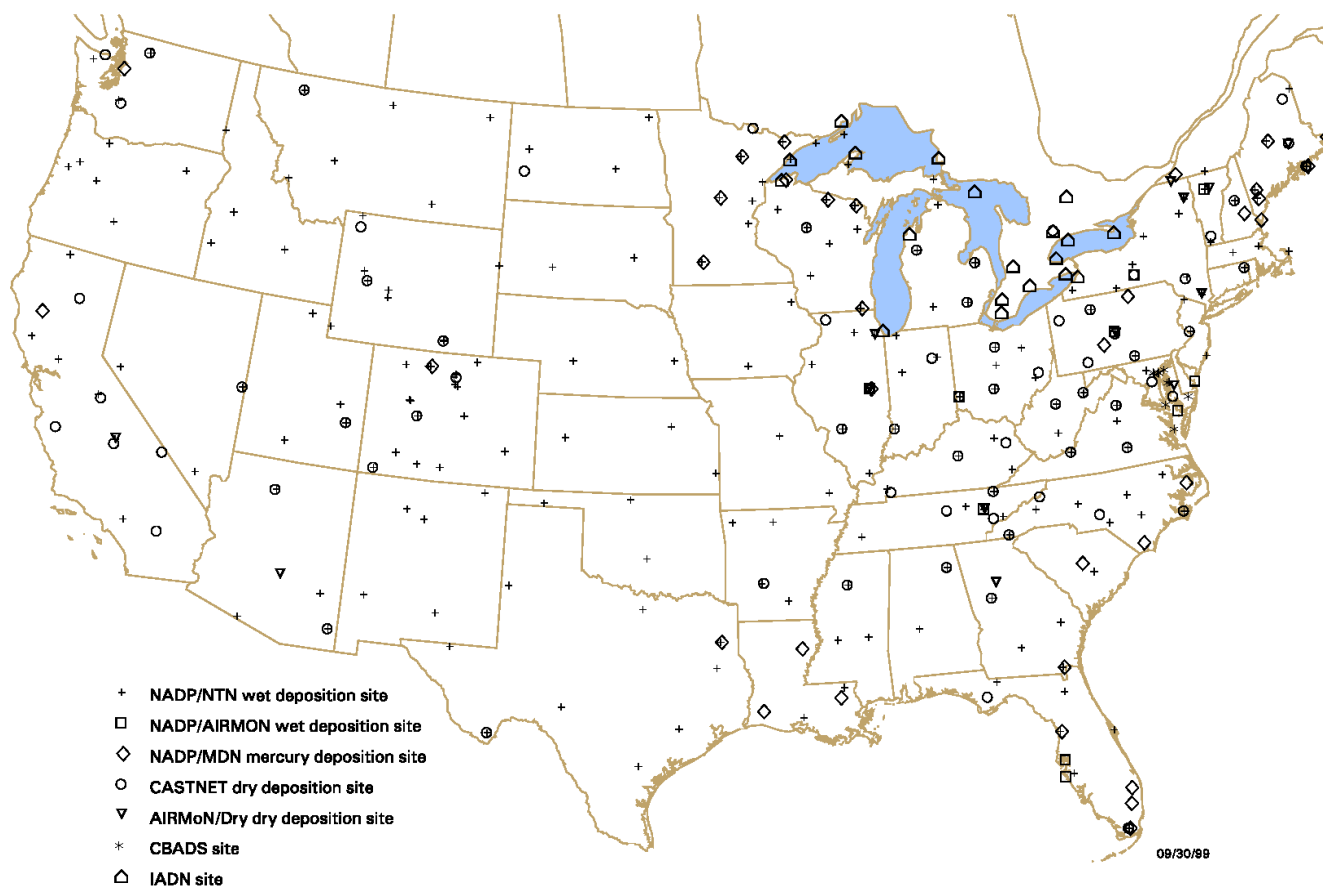
### ***National Atmospheric Deposition Program/National Trends Network***

The National Atmospheric Deposition Program (NADP) began in 1978 as a cooperative program between Federal and State agencies, universities, electrical utilities, and other industries to determine geographical patterns and trends in wet deposition of sulfate, nitrate, hydrogen ion, ammonium, chloride, calcium, magnesium, and potassium. The NADP was renamed as NADP/NTN (National Trends Network) in the mid-1980s when the program had grown to almost 200 monitoring sites (Figure IV-1). The monitoring sites are located in rural areas, and data are collected on a weekly basis. The collected data provide insight into natural background levels of pollutants. The network of NADP/NTN monitoring sites allows for the development of concentration and wet deposition maps to describe the trends and spatial patterns in the constituents of acid precipitation. The Mercury Deposition Network (MDN), which is another component of the NADP, measures mercury levels in wet deposition at over 40 NADP sites (U.S. EPA 1998l). The data that are currently available from NADP/NTN and NADP/MDN are presented in Chapter II to characterize the deposition of nitrogen and mercury, respectively.

### ***Clean Air Status and Trends Network***

The Clean Air Status and Trends Network (CASTNet) was initiated in 1987 to estimate dry acidic deposition, to provide data on rural ozone levels, and to determine the effectiveness of national emission control programs. The CASTNet is comprised of about 70 monitoring stations across the U.S. (Figure IV-1). Data on atmospheric concentrations of sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid are collected weekly, and ambient ozone concentrations are collected hourly. Most of the stations are operated by EPA's Office of Air and Radiation; 19 stations are operated by the National Park Service in cooperation with EPA (U.S. EPA 1998l).

**Figure IV-1**  
**Monitoring Sites of Ambient Air and Deposition Monitoring Networks**  
**Measuring Pollutants of Concern**



Does not display NADP/MDN mercury deposition monitoring site at St. Anicet in Canada.

## ***Atmospheric Integrated Research Monitoring Network***

Established in 1992, the Atmospheric Integrated Research Monitoring Network (AIRMoN), which is sponsored by the NOAA Air Resources Laboratory, conducts research on both wet and dry deposition based on measurements taken at a subset of NADP and CASTNet sites (Figure IV-1). The primary AIRMoN objectives are determining the effectiveness of emission controls mandated by the CAA, evaluating potential impacts of new sources of emissions on protected areas, and identifying source/receptor relationships in atmospheric models. One notable distinction of the AIRMoN-wet network is that sampling is conducted on a daily basis, whereas NADP/NTN data are collected on a weekly basis. Daily sampling allows for the application of source-receptor models to individual storm systems and reduces the storage artifact for ammonium. The AIRMoN-dry network has yielded direct measurements of dry deposition that have been used to support inferred dry deposition measurements at other NOAA and CASTNet stations. In the future, AIRMoN data will also be used to characterize spatial variability around current deposition stations, which will improve NOAA's ability to construct regional deposition loadings estimates.

## ***Integrated Atmospheric Deposition Network***

The Integrated Atmospheric Deposition Network (IADN) is a joint U.S.-Canada program begun in 1990 under a formal 6-year implementation plan. The IADN's mandate, which is derived from Annex 15 of the Canada-U.S. Great Lakes Water Quality Agreement of 1987, is to determine atmospheric loadings of toxic substances, including Great Waters pollutants of concern, to the Great Lakes and their temporal and spatial trends. The IADN collects data that can be useful in assessing the relative importance of atmospheric deposition. Under IADN, trends in pollutant concentrations in air and precipitation are assessed and loading estimates of atmospheric deposition and volatilization of pollutants are made every 2 years. The IADN network currently consists of one master station per Great Lake and 14 satellite stations (Figure IV-1). Stations are located in remote areas and do not assess urban sources of pollution. The satellite stations do not meet the original siting criteria but are subject to quality assurance and quality control requirements (U.S./Canada IADN Scientific Steering Committee 1998).

Detailed results from IADN are presented in Chapter II by pollutant group. General conclusions include the following:

- Levels in air and precipitation appear stable for current-use pesticides such as endosulphan, but levels for most other pesticides, PCBs, and lead are decreasing;
- Gas absorption appears to be the dominant deposition process for delivering semi-volatile organic compounds (SVOCs), including PCBs and PAHs, to lake surfaces, while wet and dry deposition dominate for the trace elements and higher molecular weight PAHs;
- For some IADN substances, like dieldrin and PCBs, the surface waters are behaving like a source since the amount that is volatilizing from the water is greater than the amount being deposited to the water;
- The lakes are sensitive to the atmospheric concentration of IADN chemicals, and this points out the fragility of these resources given that long-range transport from other regions may be a significant source of toxic pollutants; and,

- Air trajectory analyses indicate that many SVOCs are potentially originating from outside the Great Lakes basin, whereas trace metals and PAHs may be associated with local sources (U.S./Canada IADN Scientific Steering Committee 1998).

In 1998, the Second Implementation Plan for 1998 to 2004 was developed based on a review of the program from 1990 to 1996. No major changes are anticipated under the Second Implementation Plan. The IADN will continue surveillance and monitoring activities, related research, and provision of information for intergovernmental commitments and agreements. Additional work to be completed under the Second Implementation Plan is the development of a database for all U.S. and Canadian data. Potential modifications will be discussed in relation to the placement of satellite stations to assess urban inputs and air-water gas exchange, criteria for changes to the IADN chemical list, coordination with other research activities, quality assurance and control of IADN operations, and communication of IADN results (U.S./Canada IADN Scientific Steering Committee 1998, U.S. EPA 1998m).

### ***Chesapeake Bay Atmospheric Deposition Study***

The Chesapeake Bay Atmospheric Deposition Study (CBADS) network was established by a team of scientists from the University of Maryland, Virginia Institute of Marine Sciences, University of Delaware, and Old Dominion University. In June 1990, CBADS began collecting data from three rural (i.e., at least 50 km from urban areas) shoreline monitoring sites at Wye Institute and Elms Institute, Maryland, and Haven Beach, VA. Measured parameters included wet and dry deposition and gas exchange of elements (including lead and cadmium), individual PAHs, and total PCBs. Results of data collected from June/July 1990 to the end of 1991 were reported in the *1994 Chesapeake Bay Basin Toxics Loading and Release Inventory* (1994 TLRI) (Chesapeake Bay Program 1994) and in the *Second Report to Congress* (U.S. EPA 1997b). The 1994 TLRI results did not include any data on mercury or current-use agrichemicals, nor did it provide information on wet deposition to urban areas in the Chesapeake Bay watershed. An additional 21 months of CBADS wet deposition data were collected and reported in the 1999 TLRI (making the total study period from June/July 1990-September 1993). This new information on Great Waters pollutants of concern is presented in Chapter II by pollutant group.

Other atmospheric deposition studies were also reported in the 1999 TLRI, including data collected for wet deposition and loadings of mercury and agrichemicals; however, only initial data were available at the time of the report generation to estimate wet deposition loadings to urban areas. For the 1999 TLRI, urban wet deposition fluxes of metals, PAHs, PCBs, and mercury were assumed to be enriched two-, four-, ten-, and two-fold over regional background levels, respectively. Analysis of monitoring data collected by CBADS and other studies not included in the 1999 TLRI will be available for the next report.

### ***Air Toxics Monitoring***

The EPA is currently developing a concept for an air toxics monitoring network and beginning implementation. Ambient air toxics data would be useful to characterize ambient concentrations and deposition in representative areas, to provide data to support and evaluate dispersion and deposition models, and to establish trends and evaluate the effectiveness of strategies to reduce air toxics emissions. The goal is to build on monitoring already in place in State, local, and tribal programs as well as other national networks. For example, in the near future, fine particulate matter speciation monitors will provide ambient air measurements of several air toxic metals (including lead and cadmium compounds) at over 50 urban locations in the country. Rural and remote monitoring of these metals takes place as part of EPA's efforts to assess regional haze. As the air toxics network is phased in, the pollutants to be monitored are expected to include several of the compounds of concern to the Great Waters, such as



mercury, POM, and metals. Information about the monitoring strategy can be found at [www.epa.gov/ttn/amtic/airtxfil.html](http://www.epa.gov/ttn/amtic/airtxfil.html).

The EPA has also begun a research effort for ambient air monitoring of dioxin and dioxin-like compounds called the National Dioxin Air Monitoring Network (NDAMN). It is designed with several objectives:

- To provide data useful for calibrating regional-scale, long-range transport models used in estimating air concentrations of dioxin as a function of dioxin source emissions;
- To provide air monitoring capability for the occurrences and levels of dioxin-like compounds in areas where animal feeds (used to feed domestic livestock) are primarily grown;
- To provide for the long-term monitoring of dioxin-like compounds in different regions of the U.S. and over different seasons; and,
- To provide data on potential transboundary import of dioxins and furans into the U.S.

The network is being developed in phases. Phase 1 consists of up to 20 air monitoring stations; Phase 2 is expected to consist of about 30-40 stations. Additional information about the network can be found at [www.epa.gov/nceawww1/1page.htm](http://www.epa.gov/nceawww1/1page.htm).

## **OTHER ENVIRONMENTAL MONITORING NETWORKS AND DATABASES**

### ***The EPA's Environmental Monitoring and Assessment Program (EMAP)***

In 1988, the EPA Science Advisory Board (SAB) recognized a deficiency in the documentation of the status of the Nation's natural environment and recommended that EPA develop a program to monitor ecological status and trends in the U.S. The EPA responded with the initiation of the Environmental Monitoring and Assessment Program (EMAP) in 1989. The EMAP program also collaborates with other agencies, including NOAA.

The primary goal of EMAP is to “monitor the condition of the Nation's ecological resources, to evaluate the cumulative success of current policies and programs, and to identify emerging problems before they become widespread or irreversible” (U.S. EPA 1997i, j, k). Knowledge from the EMAP process will give decision makers the ability to make informed environmental management decisions, set rational priorities, and make known to the public the costs, benefits, and risks of

#### **Condition of the Mid-Atlantic Estuaries**

The EPA's Office of Research and Development and the Environmental Monitoring and Assessment Program (EMAP) issued a report, *The Condition of the Mid-Atlantic Estuaries Report*, that is the first in a series of State-of-the-Region Reports for the Mid-Atlantic. The report discusses the adequacy of current protective measures, the present condition of natural resources, and the extent and possible causes of ecological problems. These issues are addressed through the evaluation of the best available scientific information, including data from large sampling programs throughout the estuaries, and use of the latest scientific tools. Although the Mid-Atlantic estuaries are being impacted by human activities, active management by the States and EPA has had positive results. Future State-of-the-Region Reports for the Mid-Atlantic will address streams, forests, and other resources (U.S. EPA 1998b).

proceeding or refraining from implementing specific regulatory actions. Four operational objectives guide EMAP:

1. Estimate the current status, trends, and changes in selected indicators of the Nation's ecological resources on a regional basis with known confidence;
2. Estimate the geographic coverage and extent of the Nation's ecological resources with known confidence;
3. Seek associations between selected indicators of natural and anthropogenic stresses and indicators of ecological resources; and,
4. Provide annual statistical summaries and periodic assessments of the Nation's ecological resources.

These four objectives create an innovative approach for EMAP, which adopts a comprehensive, multimedia perspective of the Nation's natural resources rather than the traditional single-pollutant or single-location approach to environmental assessment.

The EMAP's strategy also includes the development of a Regional Environmental Monitoring and Assessment Program (R-EMAP) to test the effectiveness of the EMAP approach on answering questions about regional and local ecological conditions. The R-EMAP has three main objectives:

- C To evaluate and improve EMAP concepts for State and local use;
- C To assess the applicability of EMAP indicators at differing spatial scales; and,
- C To demonstrate the utility of EMAP for resolving issues of importance to EPA Regions and States.

Since 1990, EPA has funded at least two R-EMAP projects in each of the ten EPA Regions. One of these studies addressed mercury deposition levels and geographic trends in the Great Lakes region, as mentioned in Chapter II.

### ***National Sediment Inventory***

The EPA established the National Sediment Inventory (NSI) to prepare the first biennial National Sediment Quality Survey (NSQS) Report to Congress (U.S. EPA 1997i, j, k) (see also page III-8). National-level results from the NSQS on sediment contamination are presented in Chapter II. The NSI is intended to have applications far beyond supporting subsequent NSQS biennial reports. The NSI is the largest set of sediment chemistry and related biological data ever compiled by EPA. In addition to sediment chemistry data, the NSI includes tissue residue and sediment toxicity data.

The NSI includes data from ten existing Federal databases (see sidebar). Minimal data requirements for the NSI include monitoring program, sampling date, latitude and longitude coordinates, and measured units. Additional data fields such as sampling method and other quality assurance/quality control information are included when available. At present, the NSI contains approximately 2 million records for more than 21,000 monitoring stations across the country. More than 230 chemicals and chemical groups are included. Only data from 1980 to 1993 were used for the first NSQS. However, older data are available in the NSI.

**NSI Federal Databases**

- ì EPA's Storage and Retrieval System (STORET)
- í NOAA's Coastal Sediment Inventory (COSED)
- î EPA's Ocean Data Evaluation System (ODES)
- ï EPA Region IV Sediment Quality Inventory
- ò The Gulf of Mexico Program's Contaminated Sediment Inventory
- ñ EPA Region X/USACE Seattle District's Sediment Inventory
- ó EPA Region IX Dredged Material Tracking System (DMATS)
- ô EPA's Great Lakes Sediment Inventory
- õ EPA's Environmental Monitoring and Assessment Program (EMAP)
- ö USGS's Massachusetts Bay Data

Although the NSI provides broad geographic coverage, the 21,000 monitoring stations currently represented in the data are not randomly distributed. Most of the monitoring programs used to compile the NSI are located in areas with known or suspected contaminant impacts.

## ***National Contaminated Sediment Point Source and Non-point Source Inventories***

The EPA's mandate to investigate sediment contamination in the Nation's water included a directive to identify potential pollutant sources. With future biennial NSQS Reports to Congress, EPA will inventory point and non-point sources and estimate loadings. The first NSQS Report to Congress evaluated point sources (i.e., direct discharges to waterbodies) only (see also page III-8). The National Contaminated Sediment Point Source Inventory (U.S. EPA 1997k) provided a relative ranking of industrial categories and discharged chemicals for their potential contribution to sediment contamination. The EPA developed the "load score," a unitless index of the magnitude of potential sediment contamination based on chemical/facility-specific releases, physical and chemical properties, and potential environmental risks. A screening analysis of the load scores indicated that the point sources most likely to contribute to sediment contamination were sewerage systems, metals products and finishing, primary metals industries, industrial organic chemicals, public utilities, petroleum refining, and other chemical products. Metals were associated with higher load scores than other contaminant groups because point source releases are more prevalent. Additional analyses are needed to assess the bioavailability and toxicity of metals in sediments.

Although the NSQS did not inventory specific non-point sources, it examined the land uses in watersheds containing areas of probable concern (APCs) to identify potential relationships between sediment contaminants and human activities. In general, EPA found that diversified land uses were associated with diversified pollutants. However, a high percentage of agricultural land use corresponded with markedly higher contamination from pesticides. Most chemical classes increased with higher percentages of urban land use. The analysis suggested that mercury and PAHs in urban sediments may be attributable to atmospheric deposition from local sources.

Although the National Contaminated Sediment Point Source Inventory identified metals as the leading contaminants based on load scores, the NSQS identified PCBs, mercury, pesticides, and PAHs as most often responsible for contamination levels of concern in sediment (see also page II-73). This

suggests that non-point sources and historical releases (including atmospheric deposition) contribute largely to contamination in the Nation's waters.

## ***NOAA's National Status and Trends Bioeffects Assessments***

The National Status and Trends (NS&T) Program under NOAA (see page II-70) conducts bioeffects assessment studies, which include sediment toxicity surveys and the development of effect-based numerical guidelines for use in evaluating the toxicological relevance of sediment contamination, among other factors. The sediment toxicity surveys are conducted in coastal areas where data from NS&T's Mussel Watch and Benthic Surveillance Projects indicate the potential for substantial environmental degradation and biological effects. Bioeffects assessments have been or are being conducted in 16 coastal areas. Reports and data sets are available on the Internet for several of these locations at <http://seaserver.nos.noaa.gov/projects/bioeffects/page1.html>.

## **ENVIRONMENTAL TRANSPORT AND FATE**

### ***Available Environmental Transport and Fate Models***

#### **Models-3 Community Multi-Scale Air Quality (CMAQ) Modeling System**

The Models-3 community multi-scale air quality (CMAQ) modeling system is a flexible software system designed to simplify the development and use of environmental assessment and decision support tools for applications ranging from regulatory and policy analysis to understanding the interactions of atmospheric chemistry and physics. This newest generation of environmental modeling software has been under development for the past 7 years. Models-3, in combination with CMAQ, form a third generation air quality modeling and assessment system. First generation air quality models dealt with tropospheric air quality with simple chemistry at local scales using Gaussian plume formulation (i.e., the model assumes that the plume spreads from an emission source laterally and vertically in accordance with a Gaussian distribution) as the basis for prediction. Second generation models covered a broader range of scales (i.e., local, urban, regional) and pollutants, addressing each scale with a separate model and often focusing on a single pollutant. Third generation models treat multiple pollutants simultaneously up to continental scales and incorporate feedback between chemical and meteorological components. Models-3 has a unique framework and science design that enables scientists and regulators to build their own modeling systems to suit their needs. The CMAQ system has capabilities for urban to regional-scale air quality simulation of tropospheric ozone, acid deposition, visibility, toxics, and fine particles. The Models-3 framework contains components that assist the model developer with creating, testing, and performing comparative analysis of new versions of air quality models and enables the user to execute air quality simulation models and visualize the results. The overall goal of Models-3 is to simplify and integrate the development and use of complex environmental models, beginning with air quality and deposition models (U.S. EPA 1998e). It is expected that the Models-3 framework and CMAQ will be useful tools for research related to the Great Waters program.

The initial public release of the Models-3 framework occurred in June 1998. This framework provides a unifying foundation for continued evolution of environmental modeling and assessment tools with the ability to extend the capabilities beyond the current air quality implementations. One area of investigation has been a basic integration of the Chesapeake Bay Water Quality Model (CBWQM) into the Models-3 framework to explore multimedia model linkages. Future development toward a fourth generation system will extend linkages and process feedback to include air, water, land, and biota to

provide a more holistic approach to simulation of transport and fate of chemicals and nutrients throughout an ecosystem (U.S. EPA 1998e).

### **Total Risk Integrated Methodology (TRIM)**

The Total Risk Integrated Methodology (TRIM) is a comprehensive framework for characterizing human health and ecological risk. It is being designed by EPA's Office of Air Quality Planning and Standards (OAQPS) for use in CAA programs (e.g., the Residual Risk Program) as a way to consistently estimate the impacts of air pollutants. The TRIM will have the following characteristics: (1) ability to perform multimedia assessments; (2) ability to perform human health and ecosystem risk assessments; (3) ability to perform multipollutant assessments; (4) capability to address uncertainty/variability; and, (5) ability to provide a readily available, user-friendly tool that will assist in risk management decisions (U.S. EPA 1999e).

The EPA is attempting to create a system that is scientifically defensible, flexible, and user friendly. The format of input data sets to TRIM are consistent with Models-3. When complete, TRIM will contain three separate modules, including (1) fate and transport, (2) exposure, and (3) risk characterization. The most complex module is the multimedia fate and transport module, which is entitled TRIM.FaTE. This is the module on which EPA has been concentrating most of its effort (U.S. EPA 1999e).

The TRIM.FaTE module is a multimedia, chemically mass-balanced model. In the model, the ecosystem scale of interest (landscape) is divided into compartments. The model tracks the mass of the pollutant transported between compartments (rather than a set of one-way fate algorithms). The model is being designed so that a wide variety of pollutants can be addressed. The TRIM.FaTE module will have the capability to (1) simulate steps in a time series and (2) resolve mass distribution spatially. A prototype version of TRIM.FaTE has been developed by EPA; however, significant work remains on this module, including comparisons of output to monitoring data for case studies and other model evaluation exercises. A version of TRIM, including TRIM.FaTE, is expected to be released in 2000 (U.S. EPA 1999e).

### **Models for Atmospheric Mercury**

Because of the need to identify the emission reductions required to meet water quality and other criteria, systems are being developed that use emissions data with atmospheric chemistry and transport models and meteorological models. A report, *A Computer-Based Framework to Model Acceptable Loadings of Mercury to the Atmosphere to Protect Water Quality*, was prepared for EPA Region IV by Nicola Pirrone and Gerald J. Keeler, at the University of Michigan (Pirrone and Keeler 1997). This report discusses the coordination of available computer models for atmospheric mercury – its transport, chemical-physical dynamics, and deposition (wet and dry) to water surfaces and terrestrial receptors. The analysis of model capabilities and critical data inputs is applicable nationwide. In addition, some specific discussions are provided for the South Florida Everglades in comparison to forested watershed and lake systems.

This report presents a framework linking models that relate data on mercury emissions into the air to subsequent mathematical modeling of atmospheric transport, chemistry, and deposition processes (Pirrone and Keeler 1997). The modeling framework is designed so that regulatory agencies can define target load reductions from local and regional sources that are needed to meet water quality goals. In order to correctly relate water quality criteria and bioaccumulation of mercury in the food chain to the atmospheric and other inputs, this modeling framework needs to be coupled to an aquatic modeling system utilizing mercury transport and fate processes in similar timeframes. The set of models in the



framework will need inputs including watershed-specific information or default assumptions and chemical species released from the major pollutant sources, along with meteorological data and mesoscale models (such as RAMS from Colorado State University or MM5 from Pennsylvania State University). This conceptual framework of models is being used as part of the design and analyses in a State/EPA pilot project to develop a TMDL for mercury in a specified section of the Florida Everglades, as discussed in Chapter III.

The Electric Power Research Institute (EPRI) has developed and continues to develop environmental mercury cycling models (MCMs) to assess the transport and fate of atmospheric mercury (Watras and Huckabee 1994, Leonard et al. 1995, Logan 1998, Pai et al. 1999). The MCMs have been used to predict the fate of mercury in the Great Lakes (Leonard et al. 1995). The Maryland Department of Natural Resources reviewed two EPRI models, the Lake MCM (L-MCM) and the Regional MCM (R-MCM), and concluded that they had the potential for use in Maryland to investigate cycling of environmental mercury and bioaccumulation in fish (Logan 1998). The L-MCM was developed for predicting the biogeochemical behavior of mercury in the Mercury in Temperate Lakes Study of seepage lakes in Wisconsin. The L-MCM is a dynamic, mechanistic simulation model that tracks processes and changes in concentrations through time. The R-MCM is a steady-state, mechanistic simulation model.

## ***Recent Environmental Transport And Fate Modeling Results***

### **Atmospheric Exchange Over Lakes and Oceans Surfaces (AEOLOS)**

The Atmospheric Exchange Over Lakes and Oceans Surfaces (AEOLOS) project, administered through the EPA Great Lakes National Program Office and the Office of Research and Development, was designed to study atmospheric deposition in the Great Waters. Begun in 1993 by EPA and scientists from the Universities of Minnesota, Michigan, Maryland, Delaware, and the Illinois Institute of Technology, the project's objectives were to determine (1) the dry depositional fluxes of critical urban contaminants to the northern Chesapeake Bay near Baltimore and southern Lake Michigan near the Chicago urban area, (2) the contributions of urban source categories to measured atmospheric concentrations and deposition, and (3) the air-water exchange of contaminants and their partitioning into aquatic phases (U.S. EPA 1997b). The AEOLOS project proceeded under the hypothesis that emissions of HAPs into the coastal urban atmosphere enhance atmospheric depositional fluxes to the adjacent Great Waters such as Lake Michigan in the vicinity of Chicago and Gary, Indiana, and the Chesapeake Bay near Baltimore (Simcik et al. 1997). Results of some AEOLOS studies are reported in Chapter II for PAHs and PCBs as well as below.

A study under the AEOLOS project found that urban air emissions have an effect on the average coastal atmospheric concentrations of PAHs and PCBs above continental background, increasing them by factors of 12 and 4, respectively. As part of AEOLOS, air concentrations of PCBs and PAHs were measured in the urban/industrial complex of Chicago, over the southern portion of Lake Michigan, and in a non-urban location, in May and July 1994 and January 1995. Gas-phase PAH and PCB concentrations over the lake were much lower than urban air concentrations. The highest concentrations were associated with winds that first crossed-over the urban/industrial area from Evanston, Illinois to Gary, Indiana. Concentrations were near regional background for winds from any other direction. Seasonal variation of PCB occurred, with volatilization being higher during the summer (Simcik et al. 1997).

In another AEOLOS study in the Chicago area, PCB concentrations in wet precipitation collected over southern Lake Michigan ranged from two to as high as 400 times greater than the measured regional background concentration, indicating that the "urban plume" of Chicago increases atmospheric deposition of contaminants to Lake Michigan over tens of kilometers. Concentrations of PCBs in urban

precipitation were dominated by particle-bound congeners, indicating PCB enrichment in rainwater due to efficient scavenging of contaminated particulate matter in the urban atmosphere (Offenberg and Baker 1997).

Simcik et al. (1998), under the AEOLUS project, investigated gas-particle partitioning of PCBs and PAHs in the Chicago urban area and over Lake Michigan and found that PCBs and PAHs in the Chicago/Lake Michigan atmosphere were at equilibrium between the gas and particle phases. Understanding gas-particle partitioning is important because it can be used to help determine the mode of atmospheric deposition (i.e., wet deposition, dry deposition, air-water exchange).

### **Chesapeake Bay NO<sub>x</sub> Modeling with RADM**

The Regional Acid Deposition Model (RADM) has been used to develop estimates of the primary airshed of NO<sub>x</sub> emissions that are contributing nitrogen deposition to the Chesapeake Bay watershed. The RADM was originally developed to address policy and technical issues associated with acidic deposition. The model is designed to provide a scientific basis for predicting changes in deposition resulting from changes in precursor emissions, to predict the influence of sources in one region on acidic deposition in other sensitive receptor regions, and to predict the levels of acidic deposition in certain sensitive receptor regions (Dennis 1997).

In the RADM, the concentrations of gaseous and particulate species are calculated for specific fixed positions in space as a function of time. The geographic extent, or domain, of the model is 2,800 by 3,040 km and extends south from James Bay in Canada to the southern tip of Florida and westward to central Texas. This domain is partitioned into 80 km-by-80 km grid cells. The space is three-dimensional, having 15 logarithmically-spaced vertical layers, covering the distance from ground level to 16 km in altitude. The RADM has a chemistry component that consists of 140 reactions among 60 species. Chemical decomposition by solar radiation and aqueous-phase reactions that occur in clouds are both included in the model's chemistry. For each grid cell, predictions are generated at dynamically determined time steps of seconds to minutes that are output hourly by the model. The species predicted by RADM include ambient concentrations (SO<sub>2</sub>, NO, NO<sub>2</sub>, HNO<sub>3</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, NH<sub>3</sub>, PAN, HCHO, CO, and SO<sub>4</sub><sup>-</sup>), wet deposition (SO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> as HNO<sub>3</sub>, NH<sub>4</sub><sup>+</sup> as NH<sub>3</sub>, and H<sup>+</sup>), and dry deposition (SO<sub>2</sub>, SO<sub>4</sub><sup>-</sup>, HNO<sub>3</sub>, O<sub>3</sub>, and NO<sub>2</sub>). The meteorological fields that are used to determine the turbulent motion of the atmosphere, which in turn affects the transport of species by wind into and out of the grid in three dimensions, are from the Pennsylvania State University, National Center for Atmospheric Research Mesoscale Model (MM4). The MM4 is a weather model used to recreate historical meteorology.

Recent analysis with RADM shows that the range of influence of nitrogen emissions is similar to the range for sulfur emissions – on the order of 600 - 800 km. However, results suggest that the nitrogen range given is too short (Dennis 1997). This implies the range for nitrogen should be longer than that for sulfur. In other words, the RADM results and analysis used to define the airshed for the Chesapeake Bay watershed is producing an estimate of the boundary of the airshed that is conservative, that is, one that is too small.

In the original 1995 study (Dennis 1997), the extent of the Chesapeake Bay airshed was approximately 900,000 km<sup>2</sup>, or more than 5½ times larger than the watershed. The NO<sub>x</sub> emissions in the airshed account for approximately 75 percent of the anthropogenic nitrogen deposition to the Chesapeake Bay watershed. More recently, using the same methodology, Dennis conducted a more refined analysis of the subregions within the RADM domain, resulting in a revised estimate of the Chesapeake Bay airshed. This revised airshed, presented in Figure IV-2, is approximately 1,081,600 km<sup>2</sup>, making it about 6½ times larger than the watershed (see [http://www.chesapeakebay.net/data/model/mod\\_gis/air\\_dom.gif](http://www.chesapeakebay.net/data/model/mod_gis/air_dom.gif)). This larger airshed estimate results in only a slight increase (76 percent) of the amount of

NO<sub>x</sub> emissions from the airshed which are deposited to the watershed. The contribution from utility and mobile sources are roughly equal and make up the majority of the emissions which are eventually deposited. However, when model simulations are used to compare these emission sources to nitrate deposition a significant pattern emerges. Utilities, which are heavily concentrated to the west of the Bay, tend to contribute a majority of the nitrate that deposits on the western side of the watershed. Moving across the watershed from west to east, nitrate deposition from utility emissions shows a decreasing trend. In contrast, a large amount of the mobile source emissions take place in cities and heavily developed areas relatively close to the Bay. Thus, mobile emissions tend to contribute a majority of the nitrate that deposits along the Delmarva Peninsula, the Chesapeake Bay itself, and the lower portions of the western shore tidal tributaries. Nitrate deposition from mobile emissions shows a decreasing trend moving from east to west across the watershed (Dennis 1997).

**Figure IV-2**  
**Revised Principal Airshed for the Chesapeake Bay**



(Developed by R. Dennis, Atmospheric Sciences Modeling Division: ARL, NOAA, and NERL U.S. EPA)

### **Lake Michigan Mass Balance Study**

The Lake Michigan Mass Balance Study (LMMBS) was developed and is being implemented by the Great Lakes National Program Office in cooperation with five U.S. Federal agencies (i.e., Department of Energy, NOAA, U.S. Geological Survey, U.S. Fish and Wildlife Service, U.S. Army Corps of Engineers), one foreign agency (i.e., Environment Canada), two State agencies, and eight academic institutions. The LMMBS was initiated to address the objectives of the Lake Michigan Monitoring Program, as well as to assist EPA in implementing section 112(m) of the CAA by characterizing the loadings, transport, and fate of selected pollutants through monitoring and modeling. The *Second Great Waters Report to Congress* describes the project in more detail and describes the

atmospheric monitoring efforts, a system of ten stations situated around Lake Michigan. Additional information can be found at [www.epa.gov/glnpo/lmmb](http://www.epa.gov/glnpo/lmmb). The ultimate goal is to develop a predictive model that forecasts impacts on lakes based on inputs of toxics to the system from a variety of sources (sediments, atmospheric deposition, tributaries). Preliminary modeling results for mercury are presented in Chapter II. Additional results are expected in 2000 that will support, in addition to section 112(m), such efforts as the Binational Toxics Strategy and LaMPs.

The LMMBS model is constructed for a limited group of pollutants: PCBs, chlordane, total mercury, and atrazine. For mercury and atrazine, an emissions inventory either existed or could be developed, so comprehensive modeling is being conducted for these two pollutants. For PCBs and chlordane, a comprehensive modeling approach was not attempted because a comprehensive emissions inventory did not exist. In addition, monitoring data were collected for an extended suite of chemicals, including additional pesticides, PAHs, and heavy metals. Currently, a multimedia database is being developed to house all the data and quality assurance information for use by the modelers. In the future, the data will be available upon request.

Atmospheric loadings of the LMMBS pollutants are being calculated for input into the models. A major finding of the LMMBS to date is that traditional atmospheric loading estimation techniques are not adequate to describe the variability and source influence on deposition to the lake. New techniques have been developed to better characterize the impact of atmospheric deposition on large lake systems. Efforts have also been made to coordinate with ongoing fate and transport modeling activities and to support the most advanced developments. The LMMBS is contributing a major amount of resources to the CMAQ model system (page IV-11) for use in estimating emissions and transport of atrazine and mercury to Lake Michigan. In addition, this project has assisted in the development of an atrazine soil emissions model that could also be used to develop emissions inventories in other regions.

### **Recent REMSAD Applications**

The Regulatory Modeling System for Aerosols and Deposition (REMSAD) was originally developed in part to address the issue of atmospheric deposition of HAPs to the Great Waters. The REMSAD is a grid model designed for use on workstation-class computers. As currently configured, REMSAD (version 4.0) tracks the transport, transformation, and deposition (both wet and dry) of nitrogen, mercury, cadmium, dioxin, polycyclic organic matter (POM), atrazine, speciated primary and secondary fine particles, photochemical oxidants, acids, and ammonia. All of these substances are treated simultaneously for a single integrated emission inventory, so that the effects of proposed policy options on multiple pollutants with common sources may be analyzed at the same time. The model extends vertically all the way to the tropopause, so that long-range transport of pollutants in the upper troposphere can be captured.

The model is capable of nesting finer (i.e., higher resolution) grids within an overall coarse grid, which makes it possible to focus on deposition to a particular watershed within the context of a broad regional distribution of emission sources. The EPA recently sponsored the 1990 Base Case Evaluation Study (Guthrie et al. 1999a, b) in which the National Emission Trends 1990 inventory was used, along with a calendar 1990 meteorological data set produced by the Interagency Working Group on Air Quality Models (IWAQM). This model run was conducted for a full year (less 5 days) for the contiguous U.S. with adjacent portions of Canada and Mexico. The run was carried out on a coarse grid of approximately 60 km resolution, but included seven nested sub-grids at approximately 20 km resolution. These nested sub-grids focused on the eastern seaboard (especially around the Chesapeake Bay), the Lake Michigan-Lake Superior region, the northern Gulf of Mexico, Puget Sound, southern Florida, and the Houston-Galveston region of Texas.

The annual deposition pattern of total wet and dry nitrogen deposition (as nitrate) as simulated in the 1990 Base Case is very similar to that reported by Dennis (1997) for the eastern U.S., given differences in emissions. The REMSAD results indicate a significant seasonal variation, however, especially in the wet deposition fraction, as might be expected. The pattern of mercury deposition from the same model run is similar overall to that seen in the RELMAP simulations reported in the *Mercury Study Report to Congress* (U.S. EPA 1997e), but the localized “hot spots” are more prominent.

In another context, REMSAD has been used in a study to assess the most efficient combination of NO<sub>x</sub> controls designed to reach specified reduction levels in nitrogen reaching the Chesapeake Bay via atmospheric deposition. In this application, the total reduction desired is held fixed, but the combination of air quality health benefits attributable to NO<sub>x</sub> in various locations is combined with specific costs of NO<sub>x</sub> reductions in those locations. This forms the basis for both a least-net-cost analysis and for a potential emission trading approach based on spatially differentiated values for NO<sub>x</sub> emission reductions (Krupnick et al. 1998).

## ***Recent Environmental Transport and Fate Research***

### **The Fate of Mercury in the Lake Superior Basin**

This project, which began in 1998, is designed to examine mercury sources and deposition in the Lake Superior basin, particularly the contribution of a coal-fired power plant to the mercury loading of local and regional ecosystems. The research is being conducted at the Minnesota Power and Light's Clay Boswell Station and at the Wisconsin Electric Power Company's Presque Isle Power Plant and is expected to answer questions about what forms of mercury are emitted, and how much mercury from the power plant is deposited locally compared to regionally. The overall goal of the project is to determine the fate of anthropogenic mercury in the Lake Superior region, thereby allowing the prediction of the effects of mercury reduction strategies on the bioaccumulation of methylmercury in fish. The project is expected to be completed at the end of 2000.

### **Sources and Impacts of Nutrient Enrichment in the Gulf of Mexico**

Nutrient enrichment in the northern Gulf of Mexico is responsible for one of the largest zones of oxygen-deficient bottom waters in the western Atlantic Ocean. To address this problem, the White House's Committee on Environment and Natural Resources (CENR) established a multiagency scientific team to review the extent and causes (including air pollution sources) of hypoxic waters, the ecological and economic impacts of hypoxia on the gulf, and potential solutions. Specifically, the multiagency team identified six topics of study:

1. Distribution, dynamics, and causes of hypoxia in the gulf;
2. Ecological and economic consequences of hypoxia in the gulf;
3. Sources and loads of nutrients to the gulf from the Mississippi River;
4. Effects of reducing nutrient loading to the Mississippi River and the gulf;
5. Methods to reduce nutrient loads; and,
6. Social and economic costs and benefits of nutrient reduction strategies.



The scientific assessments for the above six topics of study are complete and available at [www.nos.noaa.gov/products/pubs\\_hypox.html](http://www.nos.noaa.gov/products/pubs_hypox.html). The integrated assessment, which will address all six topics together, is currently under review and will be available later in 2000. These assessments will be used by the Gulf of Mexico Program, State agencies, and other involved agencies to combat nutrient enrichment and hypoxia and measure progress toward the goal of a restored Gulf of Mexico ecosystem.

### **Pollutant Exchange Mechanisms**

Many pollutants, depending on their specific chemical and physical properties, can be transferred between environmental media. In recent years, research has focused primarily on the exchange of pollutants between air and water. The major air-water transfer processes include wet and dry atmospheric deposition, gaseous exchange, bubble stripping and bursting, and spray transfer (Gustafson and Dickhut 1997). In 1996, Hoff et al. reported on revisions to the estimates of atmospheric inputs of 11 organochlorine (OC) chemicals, five trace elements, and four PAHs to the Great Lakes based on IADN data. Calculations include the flux for wet deposition, dry deposition, and vapor transfer across each of the lakes, with highest confidence in the estimates for wet deposition and lowest confidence in the estimates for gas transfer components. Polychlorinated biphenyls, dieldrin, HCB, DDE, phenanthrene, and pyrene all showed net losses from the lakes to the atmosphere via volatilization, while p,p'-DDT was loaded into the lakes from the atmosphere. Alpha- and  $\gamma$ -HCH were near equilibrium with the waterbodies and the atmosphere, with seasonal changes for  $\beta$ -HCH. These results show that the waters of the Great Lakes are close to long-term equilibrium with the atmosphere for most of these chemicals, but that equilibrium is in a constant state of short-term seasonal displacement and adjustment (Mackay and Bentzen 1997). There is a need, however, for integrated assessments of air-water transfer (i.e., measuring both water and air simultaneously and over widely varying conditions) for each lake to obtain reliable estimates of distribution coefficients, deposition velocities, and loadings from other sources.

More recently, Gustafson and Dickhut (1997) quantified the gaseous exchange fluxes for PAHs across the air-water interface of the southern Chesapeake Bay and demonstrated that, for individual PAHs, different particle characteristics influenced particle-gas distributions at the urban and rural sites. Atmospheric PAH concentrations were measured at four sites that were characterized as rural, semi-urban, urban, and industrialized. Exponential increases in gaseous PAH concentrations with temperature were observed at the non-rural sites, which the authors suggested was volatilization from contaminated surfaces during warmer weather. The PAH gas concentrations at the rural site exhibited little seasonal variability. Aerosol particle-associated PAH levels were similar at all sites and increased in winter. This was attributed to the temperature dependence of particle-gas partitioning, including the cold condensation of gases to background aerosols as air masses were dispersed from source areas to remote regions, and also increased emissions from combustion of fossil fuel and wood for home heating during the wintertime. Indications were that either PAH partitioning is not at equilibrium or that different distribution processes were operating in rural areas of southern Chesapeake Bay.

Nelson et al. (1998) measured the dissolved- and gas-phase concentrations of nine PAHs and 46 PCB congeners at eight sites on the Chesapeake Bay at four different times of the year to estimate the diffusive exchange of gaseous PAHs and PCBs across the air-water interface. They found that PAH fluxes varied both temporally and spatially in the Chesapeake Bay. Fluxes were usually larger in the northern bay as a result of higher gaseous concentrations. Gaseous PAHs were absorbed into the bay's surface waters during the spring, and lighter compounds revolatilized in the late summer and early fall due to seasonal changes in surface water temperature and atmospheric PAH levels. On an annual basis, Nelson et al. found that the atmosphere is a net source of volatile PAHs to the bay and that gas absorption may be the largest external source of fluorene and phenanthrene, providing up to three times the combined loadings from wet and dry aerosol deposition and from the tributaries. In contrast to PAHs, PCBs volatilized from Chesapeake Bay throughout the year, with the largest fluxes occurring in

September due to high dissolved concentrations and warmer water, while the smallest fluxes occurred during stratification in June when both dissolved phase concentrations and wind speeds were low.

A study by Ridal et al. (1997) found that as much as 60 percent of the  $\alpha$ -HCH in the air above Lake Ontario was derived from the lake itself. Another study of air and water samples from the Bering and Chukchi Seas and on a transect across the polar ice cap to the Greenland Sea concluded that soils and surface waters containing HCH will be a diffuse, non-point source to the atmosphere that will likely maintain detectable atmospheric concentrations for some time into the future (Jantunen and Bidleman 1996, Li et al. 1998).

Hurley et al. (1998a) investigated partitioning and transport of total mercury and methylmercury in the lower Fox River in Wisconsin and found that resuspended sediments were the predominant source of mercury from the Fox River into the Green Bay. The researchers coupled time series data of total mercury at the river mouth with transect sampling in the Lower Fox River. The researchers reported that concentrations of unfiltered total mercury were significantly elevated compared with other large tributaries to Lake Michigan. The transect sampling revealed progressively increasing water column total mercury concentrations and total mercury particulate enrichment downstream, which the authors suggest were consistent with trends in sediment total mercury levels in the river. Despite elevated total mercury concentrations, Hurley et al. (1998a) reported that methylmercury concentrations were relatively low, suggesting limited bioavailability of total mercury associated with sediments.

The processes that take place in the water surface microlayer, particularly those related to pollutant exchange mechanisms at the air-water interface, are receiving increasing attention in the research literature as one of the most important regions of large surface waterbodies. The surface microlayer is the top 30 to 300  $\mu\text{m}$  of a waterbody where atmospheric pollutants first deposit. Hydrophobic contaminants, such as PCBs, can adsorb at the air-water interface even without previous organic accumulations present due to the lower energy state of the interface. The accumulation of organic matter in the surface microlayer also causes a lowering of surface tension values, resulting in further enrichment of the organic matter in the surface microlayer as compared to the subsurface water. As a result of its organic nature, many pollutants concentrate in the surface microlayer, especially hydrophobic organic contaminants such as PAHs, PCBs, and other pollutants that adhere to particles or exhibit increased solubility with elevated dissolved organic matter. Yet, despite its importance, the surface microlayer is possibly the least understood and poorly characterized region of the aquatic environment.

Liu and Dickhut (1997) compared PAH enrichment in the surface microlayer at an urban site (Elizabeth River) and a semiurban site (York River) in the southern Chesapeake Bay watershed and found particulate PAH concentrations in the surface microlayer of the Elizabeth River to be an order of magnitude higher than in the York River. In comparing the enrichment of PAHs in the surface microlayer relative to subsurface water, total PAH concentrations in the surface microlayer were found to be 1-4,900 times higher. The authors speculated that the difference in PAH concentrations in the surface microlayers of the two rivers was due to a greater contribution of atmospheric deposition of soot-like aerosols to the surface microlayer in the urban Elizabeth River.

Liu and Dickhut (1998) concluded that wind-driven mixing is the principal mechanism that distributes suspended particles collected at the air-water interface into the surface microlayer. The researchers found a significant relationship ( $p < 0.05$ ) between wind speed and the surface microlayer thickness at the York River site. Thicker surface microlayers result in greater enrichments of organic material. Liu and Dickhut (1998) also concluded that enrichment of suspended particles and organic carbon in the surface microlayer is related to the sources of these materials in aquatic ecosystems. In the York River, where *in situ* production of organic matter plays a greater role than runoff and atmospheric

deposition, enrichment of the surface microlayer appeared to be related to the buoyancy and density of the particle types. In contrast, in the Elizabeth River, where productivity is lower, small, dense particles presumably derived from runoff and atmospheric deposition appeared to accumulate in the surface microlayer.

## **MEASURING AND MONITORING TECHNIQUES**

### ***Ambient Mercury***

Some of the most important new developments made during the last few years of atmospheric mercury research were reliable methods developed to measure reactive (divalent) gaseous mercury species ( $\text{Hg}^{+2}$ ). The importance of developing a reliable method for measuring ambient  $\text{Hg}^{+2}$  (in the picogram per cubic meter range) was identified as the highest priority research topic at the expert panel on Mercury Atmospheric Processes convened on March 16-18, 1994 in Tampa, Florida. Researchers from the U.S. and Europe reported observing significant spatial gradients in mercury deposition around urban and industrial areas, indicating local anthropogenic influences. The panel considered improved characterization of mercury species from sources and at impacted receptor locations to be vital to elucidate source-receptor relationships.

Over the past several years, three different methods to measure ambient  $\text{Hg}^{+2}$  have been proposed, including impregnated filters (Gill et al. 1996), refluxing mist chambers (Lindberg and Stratton 1998), and thermal annular denuders (Stevens et al. 1998a). An instrument utilizing thermal denuder technology recently has been introduced by Tekran Inc. that is capable of continuously measuring both  $\text{Hg}^0$  and  $\text{Hg}^{+2}$  (Stevens et al. 1998b). Determining the applicability of this new Tekran instrument in establishing a national automated mercury monitoring network was recommended at the October 1998 Tri-lateral Commission for Environmental Cooperation meeting in Las Vegas, Nevada. The EPA's National Exposure Research Laboratory is presently evaluating the accuracy and precision of the available ambient  $\text{Hg}^{+2}$  measurement technologies in order to determine which may be better for routine monitoring purposes.

A method for collection and analysis of total particulate mercury ( $\text{Hg}_p$ ) was recently published in the EPA *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air (Method IO-5)*. Air is pulled through a pre-fired glass filter, which is subsequently microwave digested in nitric acid. The filter extract is then analyzed using cold vapor atomic fluorescence spectrometry (CVAFS). A semi-continuous method for  $\text{Hg}_p$  determination was developed by Lu et al. (1998). Ambient samples are collected onto a quartz filter housed in a quartz chamber. The quartz chamber is then heated to 900°C releasing the  $\text{Hg}_p$  as elemental  $\text{Hg}^0$ , which is quantified using CVAFS. Research is currently under way to merge the thermal quartz filter  $\text{Hg}_p$  technique with the Tekran automated mercury instrument so that the three most prevalent forms of mercury can be measured at ambient concentration levels.

### ***Source-Receptor Linkages***

A combination of certain analytical techniques with appropriate modeling approaches has been used on a number of occasions to ascertain sources contributing certain contaminants in receptor matrices. Some of these studies have been conducted in geographic locations outside the Great Waters; however, the methods may prove useful in linking sources and receptors in the Great Waters.

Using a combination of statistical and radioisotope dating techniques, Huntley et al. (1998) found that the majority of dioxin and furan loads in Newark Bay Estuary sediments were attributable to

combustion sources and sewage sludge sources. Fifty sediment cores were collected throughout Newark Bay and analyzed for dioxins and furans. In addition, the cores were dated using radioisotopic techniques. The samples were grouped into three categories based on their estimated dates of deposition, and polytopic vector analysis was performed separately on each group to determine the congener fingerprint patterns. The congener fingerprint patterns were used to identify the source of contamination.

Biegalski et al. (1998) used source-receptor modeling to attribute metal concentrations in the air at three sites near Lake Ontario to sources including oil and coal combustion units, mines, incinerators, and smelting operations. Air samples were collected at the three sites and analyzed for trace elements by neutron activation analysis. Factor analysis, elemental ratios, and enrichment factor analysis were used to determine source-receptor relationships at the three sites.

Another new technique used to trace persistent organic pollutants to their sources is the measurement of the enantiomeric ratios of chiral pollutants in the environment (Ridal et al. 1997, Jantunen and Bidleman 1996). For example, information about the enantioselective degradation organochlorine pesticides in soils (e.g., Aigner et al. 1998) could be coupled with data on the enantiomeric composition of the compounds at the point of deposition to help determine pollutant sources.

Using the technique of chemical mass balance, Su and Christensen (1997) determined that coal-fired power plants, municipal waste incinerators, and pentachlorophenol use areas were major sources of dioxins and furans in the Housatonic River (CT), Lake Huron, and the Baltic Sea. Other studies reported in recent years examining source-receptor linkages include an investigation of source-receptor relationships for mercury in South Florida (Dvonch et al. 1998) and stable isotope analysis for characterization of pollutants at high elevation alpine sites (Pichlmayer et al. 1998).

## EXPOSURE AND EFFECTS RESEARCH

### *Endocrine Disruptors*

Endocrine disruptors cause adverse effects by interfering with the normal operation of the endocrine system. These chemicals can act in a variety of ways, such as by mimicking natural hormones or by blocking natural hormones. For example, p,p'-DDE (a breakdown product of DDT) has been shown to inhibit the binding of androgen, a male hormone, to receptors (U.S. EPA 1997b). By interfering with the endocrine system, endocrine disruptors may cause changes in homeostasis, reproduction, and development. Also, since the neural and immune systems are closely linked to the endocrine systems, endocrine disruptors may also act as immunosuppressant and neurotoxins. The *Second Great Waters Report to Congress* (U.S. EPA 1997b) provides more detail about the possible mechanisms of endocrine disruption.

The *Second Report to Congress* acknowledged that a growing body of animal and human data suggests that a number of the Great Waters pollutants of concern potentially act as endocrine disruptors. The report specifically identified 11 of the 15 Great Waters pollutants of concern as possible endocrine disruptors in wildlife: chlordane, dieldrin, DDT/DDE, hexachlorobenzene, lead, lindane, mercury (in the form of dimethylmercury), PCBs, dioxins, furans, and toxaphene. These 11 chemicals, as well as polycyclic organic matter, were also listed as potentially affecting the endocrine system in humans. Since the *Second Report to Congress*, scientific research on endocrine disruptors has continued to provide evidence of their adverse effects in wildlife and humans. In addition, EPA recently developed a draft screening and testing approach for systematically identifying endocrine disruptors and quantifying their effects.



## Recent Research

Some research on endocrine disruptors is focused on the role of the endocrine system in prenatal and perinatal development (see sidebar). Development is under hormonal control, and a precise integration of multiple endocrine systems is required in all stages of development. Developmental effects traditionally have been thought of as physical birth defects; however, this view has been expanded to consider the proper functioning of the individual throughout its life cycle. Environmental pollutants that mimic, block, or modulate the chemical messengers of the endocrine system can cause a variety of functional developmental deficits (e.g., impaired learning, memory, motor skills). For example, the *Second Report to Congress* describes several findings of a study of children whose mothers ate PCB-contaminated fish from Lake Michigan. In this study, children born to mothers consuming the greatest amount of contaminated fish exhibited impaired neurobehavioral ability (e.g., reflexes and response to stimulation) as infants and impaired intellectual function (e.g., IQ, reading comprehension) at school age (U.S. EPA 1997b). The interim findings of two new epidemiology studies support the results of the Lake Michigan study. These effects are important to the Great Waters program because the endocrine disrupting pollutants found in Great Waters fish tissue may be entering the waterbody through atmospheric deposition, among other pathways.

### Workshop on Perinatal Exposure to Dioxin-like Compounds

The workshop, which was held June 13-15, 1993 in Berkeley, California, considered the effects of perinatal exposure to chemicals such as dioxins, furans, and PCBs on the reproductive, endocrine, neurodevelopmental, and immune systems. Lindström et al. (1995) concluded that many of the observed effects of these compounds suggest they act as endocrine disruptors. They further proposed that neurobehavioral effects (e.g., spatial learning/memory and motor deficits) may be caused by complex interactions between neuroendocrine and neurophysiological systems.

- C The Oswego Newborn and Infant Development Project was begun to examine the behavioral effects in human newborns, infants, and children of maternal consumption of Lake Ontario fish that were contaminated with a wide range of persistent toxic chemicals, including several Great Waters pollutants of concern such as PCBs, hexachlorobenzene, dioxins, dieldrin, lindane, chlordane, cadmium, and mercury. Interim study results indicate that newborns of women who consumed high levels of fish from Lake Ontario performed lower on tests of neurobehavioral ability (e.g., reflexes, physiologic responses to stress, and reactivity to stimulation) (Lonky et al. 1996).
- C A group of researchers in the Netherlands studied the effects of prenatal exposure to PCBs (estimated from levels in mother during pregnancy) and perinatal exposure to PCBs and dioxins (measured in breast milk) on the psychomotor and mental development of infants (Koopman-Esseboom et al. 1996). At 3 months of age, infants with higher prenatal exposure to PCBs had slightly lower psychomotor scores. At 7 months of age, psychomotor development was negatively influenced by perinatal PCB and dioxin exposure. There was no significant influence of the perinatal PCBs and dioxin exposure on mental development at 3 and 7 months of age.

## Endocrine Disruptor Screening and Testing Advisory Committee

The 1996 Food Quality Protection Act and the 1996 Safe Drinking Water Act Amendments mandated that EPA “develop a screening program, using appropriate validated test systems and other specifically relevant information, to determine whether certain substances may have an effect in humans that is similar to an effect produced by a naturally occurring estrogen, or other such endocrine effect as the Administrator may designate.” According to these mandates, EPA was required to develop this screening program by August 1998, implement the program by August 1999, and report to Congress on



the program's progress by August 2000. In response, EPA formed the Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) and charged the committee with designing a screening and testing program for endocrine disrupting chemicals. The EDSTAC was composed of representatives from EPA, other Federal agencies, State agencies, various sectors of industry, water providers, worker protection organizations, national environmental groups, environmental justice groups, public health groups, and research scientists.

The EDSTAC's final report was released in August 1998 (U.S. EPA 1998c). The report outlines a tiered approach for detecting endocrine disrupting chemicals and quantifying their effects. Under this system, chemicals may be subjected to high throughput pre-screening, tier 1 screening, tier 2 testing, and/or hazard assessment. In the report, EDSTAC recommended specific assays that would be conducted at each step; however, at present, none of the assays are fully validated. The recommended assays address the need to consider multiple species and endpoints because historic reliance on existing test species and endpoints was insufficient to appropriately screen, test, and characterize the risks from endocrine disruption.

The EDSTAC estimated that approximately 87,000 chemicals need to be considered for endocrine disruptor screening and testing, including pesticides, commodity chemicals, naturally occurring non-steroidal estrogens, food additives, cosmetics, nutritional supplements, and representative mixtures. Because simultaneous screening, testing, and evaluation of so many chemicals is far beyond the capabilities of available facilities and resources, EDSTAC suggested that the universe of chemicals undergo an initial sorting into four categories with recommended action as follows:

1. Chemicals that are unlikely to have endocrine disrupting effects would be placed on hold initially;
2. Chemicals with insufficient data would initially undergo high throughput pre-screening and tier 1 screening;
3. Chemicals with sufficient data to bypass tier 1 screening would go directly to tier 2 testing; and,
4. Chemicals with sufficient data would go directly to hazard assessment.

The EDSTAC estimated that following the sorting exercise, approximately 62,000 chemicals would still require screening and/or testing. Therefore, EDSTAC recommended these chemicals should be prioritized for further evaluation and that the Endocrine Disruptor Screening and Testing Program should be implemented in a phased manner (i.e., high priority chemicals screened and tested during Phase 1). The core priority setting process recommended by EDSTAC focuses on giving high priority to chemicals with widespread exposure at the national level. The EDSTAC also recommended a nomination process to accommodate chemicals for which exposure is disproportionately high for specific groups, communities, or ecosystems.

As noted previously, some of the Great Waters pollutants of concern (e.g., PCBs, dioxins) are already known to possess endocrine disrupting capabilities. These chemicals would most likely be categorized into group 3 or group 4 using the sorting scheme recommended by EDSTAC. Nevertheless, at this time, it is uncertain what priority would be given to individual Great Waters pollutants of concern for further evaluation under the Endocrine Disruptor Screening and Testing Program.

## ***Chesapeake Bay Toxicity Testing and Biological Community Assessments***

A recent pilot project attempted to integrate an environmental ambient toxicity testing approach with a biological community assessment approach to determine to what extent toxic pollutants affect fish populations in Chesapeake Bay. The results are presented as tributary-specific ambient toxicity testing in the framework of a toxicity risk ranking model developed specifically for contrasting complex toxicological results with biological indicators of community health. The two tools that were combined in this project include an ambient toxicity approach which provides a picture of biologically significant environmental contamination and a toxicological risk ranking method which integrates an array of toxicological data results into a site-specific “risk score” (Hartwell et al. 1995).

Four tributaries of the Chesapeake Bay were chosen as test sites for this project. Each tributary represents a watershed impacted by different land uses. The Curtis Creek watershed is dominated by urban and commercial development and was selected as an example of a polluted area. The Rock Creek watershed is dominated by urban development but does not have any major industrial areas. Fishing Bay is located in a lightly developed area and is over 70 percent forest and wetlands. This area is considered a relatively uncontaminated environment. The Wicomico River watershed is dominated by forest and agriculture and represents a clean reference area with no direct point source pollution. Fish community and water column sampling was performed between May to September 1993. For the ambient toxicity program, a ranking scheme of five components (end-point severity, response proportion, test variability, site consistency, and number of measured end-points) was developed to evaluate the toxicological results on a site-by-site basis (Hartwell et al. 1995).

The results indicate that the assays are sensitive enough to identify biologically significant contamination. Trends between the Index of Biotic Integrity (IBI) scores, which are an expression of the overall condition of the structure and function of the fish community, and the toxicological risk ranking scheme exist; however, stronger statistical associations are observed between the risk scores and specific metrics in the fish community database. As other studies advance, additional sites can be included in the analyses. As more information is included in the toxicological database, correlations with a variety of community databases will be possible (Hartwell et al. 1995).

## ***ATSDR PCB/PAH Great Lakes Sensitive Population Studies***

The Great Lakes Critical Programs Act, enacted in 1990, required EPA in consultation with the Agency for Toxic Substances and Disease Registry (ATSDR) to assess the adverse affects of water pollutants in the Great Lakes. In 1996, EPA and ATSDR published a Report to Congress that summarized existing research on the human health effects of Great Lakes pollutants. In addition, ATSDR developed a Great Lakes Health Effects Research Strategy that the agencies used to guide a suite of new epidemiological studies. In particular, EPA through ATSDR made ten grants to support research related to potential adverse human health effects from consumption of contaminated Great Lakes fish. Eight of the grants supported investigations focusing on susceptible populations (i.e., Native Americans, sports anglers, the urban poor, pregnant women, and fetuses and nursing infants of mothers who eat contaminated fish). The ninth and tenth grants supported the development of an interlaboratory quality assurance and quality control program and the development of more sensitive methods for detecting contaminants in biological samples (U.S. EPA 1999f).