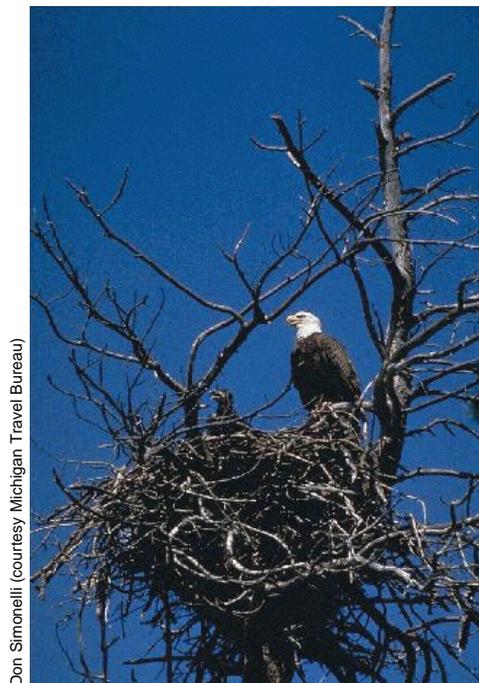


US EPA ARCHIVE DOCUMENT

CHAPTER II ENVIRONMENTAL PROGRESS

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Don Simonelli (courtesy Michigan Travel Bureau)

This chapter attempts to answer the question: *Is the problem associated with atmospheric deposition of the pollutants of concern in the Great Waters getting better or worse?* It is not intended to summarize the myriad of regulatory and nonregulatory activities and accomplishments designed to solve the problem, a discussion which is reserved for Chapter III. Likewise, this chapter is not intended to cover new scientific research or analytical tools that help improve the understanding of pieces of the problem, such as the details of pollutant behavior in the atmosphere or the ways pollutants are exchanged between air and water. This more science-oriented update is provided in Chapter IV, although some of the results of this research are included in this chapter.

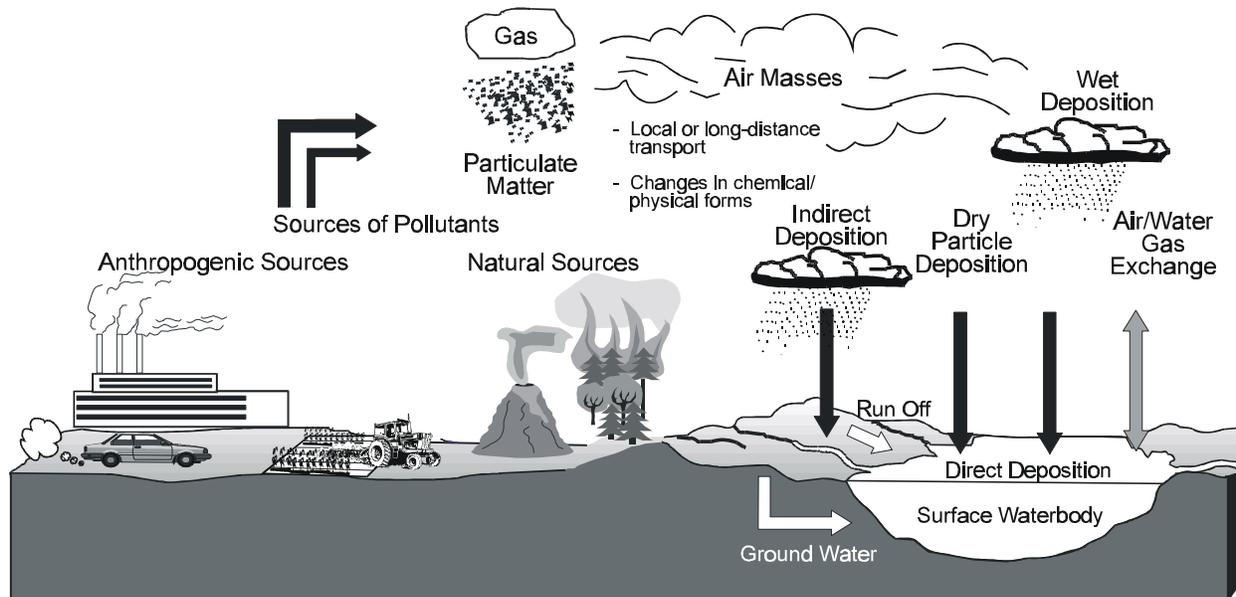
This chapter summarizes recent information on the changes in sources and emissions (including transport and transformation), loadings, and exposure and effects of pollutants of concern in the Great Waters, and is organized into two sections. The first section, organized by pollutant groups (see Chapter I), provides information for each pollutant of concern. The second section discusses trends from assessments that address multiple pollutants. These discussions reflect results of new studies published since the *Second Report to Congress*, some of which address time periods prior to the *Second Report to Congress*. They focus on the observed changes over time, including temporal and spatial changes in sources, emissions, loadings, exposure, and effects reported in new studies combined (where appropriate) with information presented in the *First* and *Second Reports to Congress*.

As background for discussing these questions, it is helpful to review the components of the atmospheric release, transport, and deposition processes (Figure II-1), as well as environmental and public health effects.

Pollutant emissions to the atmosphere can be characterized as “human-made” or “anthropogenic” (i.e., released by human activities), “natural” (i.e., releases of geologically-bound pollutants by natural processes), or “re-emitted” (i.e., the mass transfer to the atmosphere by

biologic/geologic processes for previously deposited pollutants). Examples of human-made emissions are those associated with industrial stacks, municipal waste incinerators, agricultural activities (e.g., pesticide applications, manure management), and vehicle exhaust. Examples of natural emissions include those associated with volcanic eruptions, windblown gases and particles from forest fires, windblown dust and soil particles, and sea spray. In many cases, however, it is difficult to determine if the pollutant inputs are from natural or anthropogenic sources.

Figure II-1
Atmospheric Release, Transport, and Deposition Processes



Airborne releases or emissions of pollutants can be transported away from the source to other locations. Depending on the weather conditions and the chemical and physical properties of the pollutant, air pollutants can be transported varying distances and may undergo physical, chemical, and/or biological transformations during transport (U.S. EPA 1997b). As mentioned in Chapter I, all of the Great Waters pollutants of concern are known to be subject to long-range transport.

Pollutant loadings to waterbodies can occur through many different pathways, including connecting streams and rivers, groundwater inflow, land surface runoff, rerelease of pollutants from sediments, and atmospheric deposition processes. Atmospheric inputs to waterbodies also occur through several mechanisms (Figure II-1). Pollutants that are released to the air can be deposited to land areas, tributaries, or directly to the waterbody by wet or dry deposition. The process of wet deposition refers to the removal of air pollutants from the air by a precipitation event, such as rain or snow. The process of dry deposition refers to the removal of aerosol pollutants through eddy diffusion and impaction, large particles through gravitational settling, and gaseous pollutants through direct transfer from the air to the water (i.e., gas exchange). Air pollutants can also enter the waterbody through indirect deposition which occurs when an air pollutant is deposited to a land area or tributary and is then carried into a waterbody by other routes, such as storm water runoff or inflow from tributaries. Therefore, in these mechanisms, loadings to a waterbody are both directly and indirectly affected by air pollutant emission levels.

Loadings can be expressed as the total amount of a pollutant entering a waterbody over a specified time period (e.g., kg/year) or as a loading rate (e.g., $\mu\text{g}/\text{m}^2/\text{year}$). The tendency of a specific pollutant to enter a waterbody through wet deposition, dry deposition, or gas exchange is related to the

physical and chemical properties of the pollutant as well as to current and local meteorology. Determining the relative atmospheric loading – how the loading from atmospheric deposition compares to that from other pathways, such as groundwater seepage and inflow from connecting surface waterbodies, where portions of the pollutant load may not be of atmospheric origin – is as important as determining total loading. Uncertainties exist, however, in loadings estimates because of errors inherent in sampling methodologies and the assumptions about a specific chemical's behavior that are used to develop deposition estimates. Furthermore, monitoring networks have spatial and temporal limitations, making it difficult to accurately and reliably quantify atmospheric deposition inputs.

Air pollutant loadings to the waterbody may contribute to **environmental and public health effects**, such as when **water quality and drinking water standards** are exceeded (where such standards exist). These standards provide a measure of degradation and possible exposures of plants, animals, and humans to potentially harmful levels of pollutants. The number and magnitude of water quality and drinking water standard exceedances in a waterbody may be affected, in part, by changes in pollutant loadings from the atmosphere, which in turn, are affected by changes in atmospheric emissions of those pollutants. Potential ecological and human health effects from exposures to the Great Waters pollutants of concern are not discussed comprehensively in this report because the *Second Report to Congress* focused on effects from exposures. This report focuses more on recent literature on trends, such as contaminant levels found in biota as well as fish consumption advisories. In many cases, however, information on trends in exposure levels or observed effects was not available. Therefore, surrogate measures of exposure, such as trends in concentration levels in environmental media or biota, are presented. Note that the presence of a pollutant in the environment only translates into an exposure for humans and/or biota if an exposure pathway exists.

The understanding of how the pieces of this complex puzzle fit together continues to increase, although uncertainty and gaps in information remain. This chapter reports on new information that helps to establish the links between emissions, transport and transformation, loadings, and effects. It also includes information on the various elements that contribute to establishing these links. For example, it includes inventories of emission sources, which are essential inputs to models that predict pollutant loadings to waterbodies.

POLLUTANT-SPECIFIC CHANGES

For each pollutant or pollutant group, information on sources and emissions is presented first, followed by new loadings information, and then by new information on exposure and effects. If no new information is available on one of these topics for a particular pollutant or pollutant group, that topic simply is not addressed. The second part of this section, *Cross-Pollutant Changes*, summarizes results from several EPA and other agency programs and projects that are not limited to individual pollutants, but rather provide information on many pollutants in a manner making it more appropriate to present the information as a cohesive piece as opposed to dividing the information among the pollutant groups.

Although a large amount of research has been and continues to be conducted related to the release, transport, loadings, exposure, and effects of Great Waters pollutants of concern, information gaps and uncertainties remain. In general, the information presented below consists of the highlights of the studies, and details on assumptions and uncertainties are not always presented. However, most if not all of the studies discussed below are associated with some type of uncertainty (e.g., related to the number of measurements, the time period of the study, or the lack of standard measurement methods). The original study should be consulted for these details for a better understanding of the assumptions used and resultant uncertainties. While uncertainties and information gaps continue to exist, it should be noted that research is ongoing to attempt to reduce them.

MERCURY AND COMPOUNDS

Mercury is a cationic metal – it has characteristics of both a metal and an organic compound (e.g., it is persistent in the environment, bioaccumulates in the food chain, and vaporizes at low temperatures). Mercury is an excellent conductor of electricity and is widely used in products such as batteries, electric switches, thermostats, thermometers, and barometers as well as a number of industrial processes including pharmaceutical preparations and the production of caustic soda and chlorine.

Mercury can exist in three oxidation states: Hg^0 (metallic), Hg_2^{2+} (mercurous), and Hg^{2+} (mercuric). The oxidation state strongly influences the properties and chemical behavior of mercury. For example, mercurous and mercuric mercury can form numerous inorganic and organic chemical compounds; however, mercurous mercury is rarely stable under ordinary environmental conditions. Most of the mercury encountered in water, soil, sediment, and biota is in the form of inorganic mercuric salts and organomercurics (i.e., chemical compounds with a covalent Hg-C bond, rather than inorganic mercury compounds that simply associate with organic material in the environment). The mercury compounds most likely to be found under environmental conditions include the following: the mercuric salts $HgCl_2$, $Hg(OH)_2$, and HgS ; the methylmercury compounds, methylmercuric chloride (CH_3HgCl) and methylmercuric hydroxide (CH_3HgOH); and, in small fractions, other organomercurics (i.e., dimethylmercury and phenylmercury) (U.S. EPA 1997e). The mercury compounds that are of highest concern in terms of exposure and toxicity to humans and biota are the methylated mercury compounds. The *Mercury Study Report to Congress* (U.S. EPA 1997e) provides additional background information on mercury and mercury compounds.

Sources of mercury emissions to the air in the U.S. are ubiquitous and can be broadly classified as belonging to one of three types:

1. *Re-emitted mercury* – the re-emission of mercury to the atmosphere by biologic and geologic processes from mercury that was previously deposited to the earth's surface following either anthropogenic or natural releases. For example, a large portion of the deposited mercury is the result of past human-made releases as well as releases from natural sources that previously were sequestered (e.g., arctic tundra, ice sheets, oceans and wetlands);

HIGHLIGHTS

Mercury

' **Sources.** The largest human-made sources of mercury emissions in the U.S. are coal-fired utility boilers, medical waste incinerators, and municipal waste combustors. Mercury can also be emitted from natural sources, such as volcanic activities. Mercury releases from human activities today are adding to the global reservoir of mercury cycling between land, water, and air that is the result of natural releases and past human activities. Human-made emissions of mercury have declined since 1990, due chiefly to the phase-out of mercury-containing products.

' **Loadings.** Atmospheric deposition is a principal source of mercury to several Great Waters, followed by riverine inputs. Urban areas in proximity to the Great Waters can also contribute significantly to loadings via the atmosphere and urban runoff. Deposited mercury that is buried or immobilized in soils and sediments can be transported to waterbodies by high streamflow events like storms and snowmelt. Forested watersheds retard mercury transport to the waterbody compared to agricultural or urban watersheds.

' **Human and Ecological Exposure and Effects.** Consumption of contaminated fish represents the dominant pathway for both human and wildlife exposures to methylmercury. The typical U.S. consumer of fish from restaurants and grocery stores is not believed to be at risk. Rather, consumers who eat more fish than is typical or fish that are more contaminated than typical fish may be at risk of adverse effects. Because the developing fetus is regarded as the most sensitive to the effects of methylmercury, women of childbearing age are the population of greatest concern. State and tribal fish consumption advisories have been implemented to warn people about the related risks. Measurements of mercury in loons indicate up to 30 percent of male loons in the northeastern U.S. have mercury levels sufficiently high to cause adverse effects.

2. *Natural mercury emissions* – the mobilization or release of geologically-bound mercury by natural processes; or
3. *Anthropogenic mercury emissions* – the mobilization or releases of mercury by human activities.

Atmospheric deposition of mercury occurs primarily through two processes: scavenging of particulate matter by precipitation and conversion of elemental mercury (Hg^0) to ionic mercury during rain formation. Dry deposition of reactive gaseous (Hg^{2+}) and particulate mercury is also thought to be an important process. The three dominant mercury forms act differently in the environment:

- C Hg^0 can be transported in the atmosphere for thousands of miles around the globe and deposits very inefficiently because it is insoluble in water and is less chemically reactive;
- C Hg^{2+} in the gas-phase may be removed from the atmosphere within a few ten to a few hundred miles of the source because it is highly water soluble and reactive; and,
- C Particulate-phase mercury may be deposited at intermediate distances from the source, depending on the size of the aerosol (Schroeder and Munthe 1998).

Current anthropogenic mercury emissions are only one component of the global mercury cycle. The amount of mercury in the land, water, and air at any one location is comprised of mercury from the natural global cycle, the global cycle perturbed by human activities, as well as regional sources and local anthropogenic sources. In addition to air emissions, other sources of mercury include direct water discharges or past uses of mercury, such as fungicide application to crops. Current research continues to indicate that natural sources, industrial sources, and recycled anthropogenic mercury each contribute to about one-third of the current mercury burden in the global atmosphere (Pirrone et al. 1996). However, as discussed further in Chapter IV, new measurement methods suggest that natural mercury emissions rates from mercury-rich soils and bedrocks may be larger than past estimates. It is important to understand the source of mercury and the amount of mercury contributed by each source type so that the most efficient control strategies can be devised.

Given the complexities of the global mercury cycle, much of the research in recent years focused on the environmental fate of mercury and the extent of current contamination in the environment. The state of the science at this time does not provide a complete answer to the question of whether the problem is improving. There is a general downward trend in anthropogenic mercury emissions in the U.S., although emissions from many CAA source categories are not included in this assessment. Atmospheric deposition of mercury to an adjacent waterbody is primarily a function of the amount of particulate-phase and reactive gaseous mercury emitted, the proximity of the source to the waterbody, and meteorological conditions. The National Atmospheric Deposition Program - Mercury Deposition Network (NADP-MDN) has been used to collect weekly wet deposition data for the past 4 years in some locations; however, these early data are not robust enough to discern trends. Additional monitoring data (which includes both wet and dry deposition measurements) from high quality stations over a longer period are necessary for effective trends analyses. These measurements must be performed to allow for meteorological analysis and identification of source contributions to the measured mercury. In general, the research described in this section represents an important step forward in understanding the fate of mercury in the environment and will continue to form the scientific basis for measures taken to address the problem.

Mercury Emissions

Estimates of the global contribution of mercury emissions to the atmosphere from anthropogenic sources are 2,000 to 4,000 tons per year (tpy) and from natural sources are 2,200 to 4,000 tpy, resulting in total mercury air emissions of 4,200 to 8,000 tpy (Pirrone et al. 1998). In comparison, U.S. mercury air emissions for the 1994-1995 timeframe are 158 tpy, as reported in EPA's *Mercury Study Report to Congress* (Table II-1) (U.S. EPA 1997e). Roughly 87 percent of national mercury emissions in the U.S. are from combustion sources, including waste and fossil fuel combustion.

A recently identified source of mercury to the atmosphere is emissions of elemental mercury gas (Hg^0) from soils that have been amended with municipal sewage sludge. Carpi and Lindberg (1997), using a field chamber and soil amended with sewage sludge, found that sludge application to soil increased soil Hg^0 releases by up to two orders of magnitude. The researchers estimated that land application of sewage sludge in the U.S. and European Union may account for approximately 5×10^6 g/year (5 metric tons/year) of Hg^0 released to the atmosphere based on the area of land amended each year and measured Hg^0 emission rates.

While there is a growing body of data on the total amount of mercury emitted from different source types, data on the form (or species) of mercury emitted remain a critical research need. The *Mercury Study Report to Congress* (U.S. EPA 1997e) estimated that anywhere from 0 to 73 percent of the mercury emitted from different source categories is in the form of divalent mercury (Hg^{2+}), the form that deposits and contributes the most to methylmercury concentrations in soil, water, sediment, and biota. There is, however, considerable uncertainty about the amounts of different mercury species emitted from some industrial sources.

The emission inventories provide a snapshot of recent emissions and indicate a downward trend in U.S. emissions between 1990 and 1995. This downward trend follows a general decline in domestic mercury uses and reduced emissions from waste combustion sources (including municipal waste combustors and medical waste incinerators). Industrial demand for mercury peaked in 1964 and fell 75 percent between 1988 and 1996. This decline largely reflects the phaseout of mercury in household batteries and paint. The rate of decline, however, has slowed since 1990. Future trends in mercury emissions from fossil fuel combustion sources, which currently represent a large portion of national mercury emissions, are dependent on future energy needs and fuel use. Mercury emissions from municipal waste combustors and medical waste incinerators, which also are large national sources of mercury emissions, are expected to continue to decline from 1995 through 2000 due to new regulations (see Chapter III) (U.S. EPA 1997e).

It should be noted that several uncertainties exist with the mercury emissions inventory. For example, not all source categories are included (e.g., landfills), and recent data submitted to EPA by the Chlorine Institute indicate that current emissions may be underestimated. Furthermore, mercury emissions from coal-fired electric utilities are expected to increase in future years, based on estimated changes in emissions from implementation of the acid rain program and projected trends in fuel choices and electric power demands in the year 2010 (U.S. EPA 1998p). As noted earlier in this section, the speciation of mercury emitted is important in determining its transport and fate, yet remains a key uncertainty. The EPA has worked with the Department of Energy and the American Society for Testing and Materials to develop a standard method for measuring speciated mercury from utility boilers. The EPA is also working to refine this method for other source categories, such as incinerators. The electric utility industry is currently conducting speciated mercury emission testing on a subset of coal-fired facilities, as discussed in the hazardous air pollutant section of Chapter III. Finally, in order to better understand the relative contribution of mercury to the environment from anthropogenic sources, further

research is needed into the level of natural emissions as well as the amount and original source of mercury that is re-emitted to the atmosphere after being deposited to soils, watersheds, and ocean waters. Although considerable uncertainty still exists, it has become increasingly evident that anthropogenic emissions of mercury to the air rival or exceed natural inputs (U.S. EPA 1997e).

**Table II-1
National Anthropogenic Mercury Air Emissions
(Based on 1994-1995 Inventory; U.S. EPA 1997e)**

Source Category	1994-1995 Anthropogenic Air Emissions (tons/year)	Percent Contribution to Total U.S. Anthropogenic Air Emissions
Utility boilers: coal combustion, oil, and natural gas	52	33
Municipal waste combustion	30	19
Commercial/industrial boilers: coal and oil	28	18
Medical waste incineration	16	10
Chlor-alkali production	7	4
Hazardous waste combustors	7	4
Chlor-alkali	7	4
Portland cement, excluding hazardous waste-fired	5	3
Residential boilers: oil and coal	4	2
Pulp and paper manufacturing	2	1
Others (<1percent each) ^a	3	2
Total U.S. Anthropogenic Mercury Air Emissions	158^{b,c}	100^{b,c}

^a A list of the source categories that contribute less than 1 percent to total U.S. emissions is provided in Appendix B.

^b This value represents anthropogenic mercury air emissions in the U.S. only.

^c Values do not add exactly due to rounding.

Mercury Deposition in the U.S.

Once in the air, mercury can be deposited locally or widely dispersed and transported long distances from emission sources. How far it travels and where it is deposited depends in part on the chemical and physical form of the mercury emitted. Elemental mercury may be transported in the atmosphere for relatively long periods (approximately 1 year), allowing its distribution over long distances, both regionally and globally, before being deposited to the earth. In contrast, the residence time of mercuric (Hg²⁺) compounds in the atmosphere is generally believed to be a few days or less, resulting in deposition closer to sources. Mercury also differs from other metals because it is readily re-emitted to the atmosphere following deposition and chemical transformation. In summary, principal factors that contribute to the modeled and observed patterns of mercury deposition are (1) the emission source locations and characteristics (e.g., stack height); (2) the amount of Hg²⁺ and particulate mercury

emitted; (3) atmospheric chemical and physical properties; (4) uncertainties associated with the emissions inventories, both in the magnitudes and the chemical forms emitted; (5) climate and meteorology, and (6) treatment of natural sources and re-emission within the modeling domain.

Because of the influence of the above six factors on mercury deposition, modeling of mercury transport and deposition at different spatial scales (e.g., national, regional, and local) results in slightly different information appropriate to each scale. Modeling at the local scale (i.e., approximately 100 km), can provide more specific deposition estimates for a specific waterbody, but requires meteorological modeling at the appropriate scale and up-to-date information on the amount of divalent and particulate mercury emitted from the local sources. Recent studies in the Great Lakes region and in Florida show that mercury emissions on local scales can greatly influence loadings in some locations when local sources have significant emissions of divalent and particulate forms of mercury. For example, the South Florida Atmospheric Mercury Monitoring Study (SoFAMMS) collected daily event precipitation samples at 17 sites for 1 month and, using a suite of chemical and meteorological data, was able to demonstrate that local anthropogenic sources strongly influence mercury wet deposition levels (see Section III.C for additional information on SoFAMMS) (Dvonch et al. 1998). National modeling of emissions and meteorology, on the other hand, can assist in answering some questions, but should not be applied to regional or local analyses without critical review. The various forms of mercury in emissions are all important in predicting atmospheric transport and deposition patterns, and care must be taken in estimating local deposition or longer range impacts.

For the *Mercury Study Report to Congress*, EPA used the Regional Lagrangian Model of Air Pollution (RELMAP) to model mercury emissions from the continental U.S. to estimate the amount of mercury being deposited to the U.S. The model inputs included meteorological data from 1989, the U.S. emissions inventory of 158 tons/year (U.S. EPA 1997e), and assumptions about the chemical species of mercury emitted from various source types. The results showed total deposition (i.e., wet and dry deposition of all forms of mercury) to be over 10 Fg/m² throughout most of the continental U.S. east of the Mississippi River, with values over 30 Fg/m² for the northeast corridor and other urban areas. The highest mercury deposition rates were predicted to occur in the southern Great Lakes and Ohio River valley, the Northeast, and scattered areas in the South (with highest deposition rates in the Miami and Tampa areas). Deposition of mercury is strongly influenced by the magnitude of emissions, the chemical species of the emitted mercury (ionic and particulate-bound forms of mercury being the most readily deposited), ozone and soot concentrations, and total annual precipitation.

On a national basis, the computer simulation suggested that about one-third (~ 52 tpy) of U.S. anthropogenic mercury emissions is deposited within the lower 48 States. The remaining two-thirds (~ 107 tpy) of mercury emissions are transported beyond U.S. borders. In addition, the simulation suggests that another 35 tpy of mercury from the global reservoir (which includes mercury from U.S. emissions) are deposited in the U.S., resulting in a total deposition of roughly 87 tpy. Note, however, that the results of the simulation include some uncertainty, as discussed in more detail in the following paragraph. According to the simulation, 98 percent of the deposited mercury of anthropogenic origin was emitted in the form of ionic mercury or particulate mercury. The emissions inventory and estimated chemical/speciation profiles indicate that of all combined ionic and particulate mercury emissions, 29 percent is from coal-fired electric utility boilers, 25 percent is from municipal waste combustion, 18 percent is from medical waste incineration, 16 percent is from coal-fired commercial and industrial boilers, and 12 percent is from all other modeled sources. The methods for developing these mercury emission estimates and speciation profiles are described in detail in volumes I and II of EPA's *Mercury Study Report to Congress* (U.S. EPA 1997e).

As the *Mercury Study Report to Congress* explains, there are a number of uncertainties in the RELMAP analysis, with a large degree related to the state-of-the-science on chemical and physical forms of mercury air emissions and their chemical and physical transformations in the atmosphere. The model seems most sensitive to the speciation of mercury emissions. Speciated emissions data remain a critical research need, as discussed above in the section on mercury emissions. In addition, atmospheric chemistry data are incomplete in the model. Furthermore, there is inadequate information on the atmospheric processes that affect wet and dry deposition (U.S. EPA 1997e). (Note that other sections of this report describe additional research and model development activities in these areas.)

To test the validity of the model, the wet deposition results from the RELMAP simulation were compared to limited measured data from the Mercury Deposition Network (MDN). The RELMAP estimates agreed with actual measurements within a factor of two in most cases and tended to underestimate measured wet deposition. Overall, the RELMAP model seemed to produce reasonable spatial patterns of annual wet deposition. Better spatial coverage by a long-term deposition network is needed to better evaluate the model. In addition, the high deposition rates estimated for some urban areas could not be verified because measurement data in urban areas are lacking (U.S. EPA 1997e).

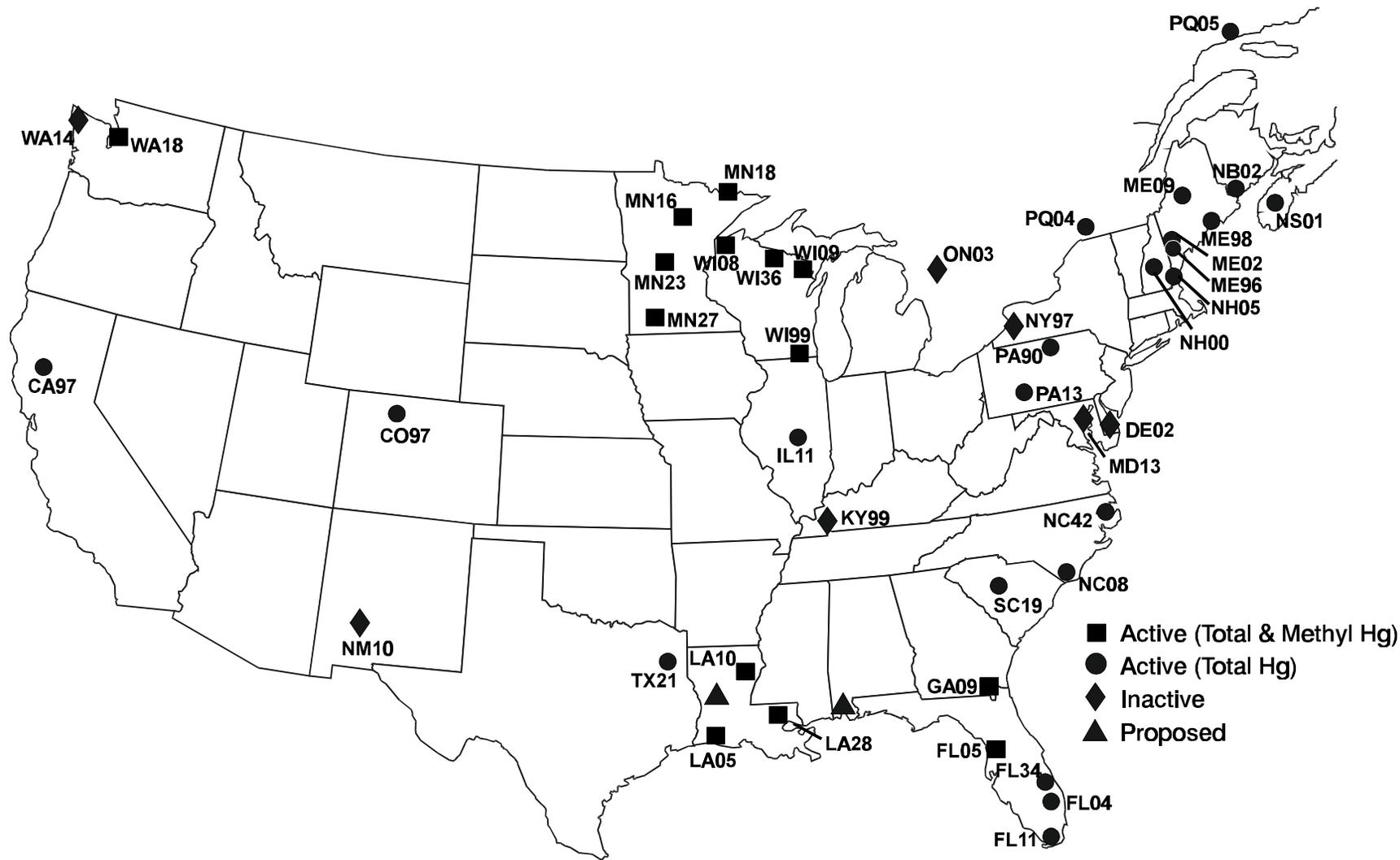
In addition to the *Mercury Study Report to Congress*, there have been a number of other recent modeling and monitoring studies of mercury deposition. For example, a regional-scale analysis, performed by the Northeast States and Eastern Canadian Provinces in collaboration with EPA, also illustrates the importance of local, regional, and global sources to mercury deposition levels (NESCAUM 1998). The purpose of this study was to determine whether deposition in the Northeast could be attributable to sources within the region or to long-range transport of mercury from upwind States. In this analysis, a RELMAP simulation suggested that approximately 47 percent of the modeled deposition in the Northeast is attributable to sources in the region, while approximately 30 percent is attributable to sources located outside the region. The remaining 23 percent was estimated to be from the global atmospheric reservoir, which includes mercury from U.S. emissions. The accompanying text box lists the source categories contributing to mercury emissions in the Northeast. As with the national EPA study, combustion sources account for more than 85 percent of the mercury emissions. Note, however, that the results of the simulation include considerable uncertainty.

Mercury Emission Inventory by Percent Contribution by Source Category for Eight Northeast States

- Municipal waste combustion -- 45 percent
- Non-utility boilers -- 18 percent
- Electric utility boilers -- 13 percent
- Manufacturing sources -- 7 percent
- Area sources -- 6 percent
- Sewage sludge incineration -- 6 percent
- Medical waste incineration -- 5 percent

The modeling predictions described above are based on average emissions over a year and as such do not provide an indication of trends over time. Two ways to assess trends in emissions and deposition are to consistently measure deposition over a wide geographic area over a long period of time, or to analyze sediment cores. Mercury monitoring of wet deposition at a number of sites began recently, and there are not enough data at present to evaluate trends over a widespread area. The Mercury Deposition Network (MDN), which began as a transition network of 17 sites in 1995, became an official subnetwork of NADP in 1996. Currently, nearly 40 sites are in operation throughout the U.S. and Canada, with sites concentrated on the east coast and in the Great Lakes basin (Figure II-2). However, the network is relatively sparse in its overall coverage, introducing uncertainty into trends analyses. The objective of the MDN is to develop a long-term database of weekly total mercury concentrations in precipitation and the annual and seasonal flux of total mercury in wet deposition. The present sites were not selected to be representative of the region and, in some cases, are highly influenced by local emission

Figure II-2
Monitoring Sites of the Mercury Deposition Network – 1999



sources. Site sponsors consist of U.S. and Canadian government agencies, State government agencies, universities, associations, and consulting firms. Currently, MDN data are available for 1996 and 1997.

Available MDN monitoring data from 1996 and 1997 indicate that the volume-weighted mean concentration of total mercury in precipitation from 22 sites ranged from 6.0 to 18.9 ng/L and annual deposition of mercury ranged from 2.1 to 25.3 $\mu\text{g}/\text{m}^2$ (or 2,100 to 25,300 ng/m^2). In 1997, average mercury concentrations in rain ranged from 6.2 to 18.3 ng/L at the 21 sites that had a full year of monitoring data and the average concentration for all sites was 10.6 ng/L. In 1996, average mercury concentrations at nine sites with a full year of data ranged from 6.0 to 14.1 ng/L with an average for all sites of 10.2 ng/L. In 1997, the annual average wet deposition of mercury for 21 sites ranged from 4.3 to 25.3 $\mu\text{g}/\text{m}^2$ (or 4,300 to 25,300 ng/m^2), whereas in 1996, the annual average wet deposition of mercury for nine sites ranged from 6.3 to 19.7 $\mu\text{g}/\text{m}^2$ (or 6,300 to 19,700 ng/m^2). In the eastern U.S., average summer mercury concentrations are more than double winter concentrations and average summer deposition values are more than three times winter values. This can be explained by higher concentrations of mercury in the rain and higher rainfall amounts during the summer. One interesting finding from the 1996 and 1997 MDN data is that several individual weeks were associated with unusually high mercury deposition amounts as a result of heavy rainfall and above average mercury concentrations. Based on National Weather Service information, the storms that contributed the precipitation in these weeks tracked along the east coast, including New Jersey, New York City, Providence, and Boston. Therefore, it is likely that emissions of mercury from these urban centers entered the air mass of the storm and were deposited at these MDN sites (Sweet et al. 1999).

While the MDN monitoring sites have not been in operation long enough to discern any temporal trends in mercury levels, one monitoring station has been in operation in the Lake Champlain basin at Underhill, Vermont since 1992. This is now the longest continuous monitoring program in the world for total mercury wet deposition, ambient particulate phase mercury, and ambient total gas phase mercury. Results do not show long-term trends in atmospheric mercury concentrations except perhaps for a downward trend for vapor phase mercury. Based on monitoring of wet deposition and modeling of dry deposition, total annual deposition of mercury in 1993 was estimated at 15.1 $\mu\text{g}/\text{m}^2$ (or 15,100 ng/m^2). However, research suggests that the dry deposition flux of mercury may be much greater and re-emission of mercury from forest ecosystems may be significant, introducing considerable uncertainty in the total wet plus dry deposition estimates (Hanson et al. 1995, Rea et al. 1998, Scherbatskoy et al. 1999, 1998, 1997).

The Underhill monitoring data collected between December 1992 and December 1997 also show seasonal variations. Deposition peaked in summer months when mercury concentrations in precipitation are highest, while the concentration of mercury vapor in the air showed only slight seasonal variation. The seasonal variations observed in mercury deposition at Underhill were similar to those observed in the Great Lakes basin (Hoyer et al. 1995, Burke et al. 1995). Concentration of particulate-associated mercury in the air in 1993-94 tended to be greatest in winter months at this site. Concurrent monitoring of mercury concentrations in stream water in a nearby forested catchment in the Lake Champlain basin showed dissolved concentrations to be fairly constant, but found that total mercury (dissolved plus particulate) was strongly correlated with flow rates. Thus, high flows may re-mobilize mercury adsorbed to sediment and organic matter. Also, maximum stream flows were often associated with spring snowmelt, which appears to be an important regulator of annual transport patterns of mercury within the Lake Champlain basin (Scherbatskoy et al. 1999, 1998, 1997, Shanley et al. 1999).

In another recent analysis, Pirrone et al. (1998) estimated atmospheric emissions and deposition of mercury in North America and compared these estimates to vertical profiles of mercury accumulation rates in sediment cores from four Great Lakes sites. The results of this analysis illustrate that

atmospheric deposition has been significant since the 1900s and still is the major contributor of mercury to the Great Lakes, although a variety of other sources (including direct discharges) also contribute to mercury inputs in the Great Lakes. Based on sediment core data and emissions estimates, Pirrone et al. calculated the atmospheric deposition flux of mercury to North America as a whole to be between 14.3 and 19.8 $\mu\text{g}/\text{m}^2/\text{yr}$ (1.43 to 1.98 $\text{ng}/\text{cm}^2/\text{yr}$), whereas in the Great Lakes region, the atmospheric deposition flux of mercury was calculated to be higher, at 135 $\mu\text{g}/\text{m}^2/\text{yr}$ (13.5 $\text{ng}/\text{cm}^2/\text{yr}$). This difference is likely due to local anthropogenic emissions and subsequent deposition of mercury in the Great Lakes region. Furthermore, mercury accumulation rates in sediment cores from the Great Lakes from pre-industrial to modern times increased from 0.7 to 235 $\text{ng}/\text{cm}^2/\text{yr}$ in Lake Ontario, from 0.8 to 65 $\text{ng}/\text{cm}^2/\text{yr}$ in Lake Michigan, and from 3 to 175 $\text{ng}/\text{cm}^2/\text{yr}$ in Lake Erie. All of these values are larger than those reported in sediment cores from small remote lakes in the northeastern U.S., indicating local and regional sources of mercury are deposited in the Great Lakes region rather than simply from the regional background in the northeastern U.S.

Engstrom and Swain (1997) analyzed sediment core data to detect recent trends in mercury emissions in the upper Midwest and found that, for a number of Minnesota lakes, mercury deposition peaked in the 1960s and 1970s and then declined. These declines were not seen in remote lakes in southeastern Alaska, indicating that deposition from the global pool had not declined. The decline in deposition inputs to Midwestern lakes can be attributed to reduced emissions from regional and local sources, which are thought to be largely due to pollution controls (particularly on waste incinerators) and a shift from coal to natural gas for residential and commercial heating.

Mass Balance Studies of Mercury

Preliminary results of the Lake Michigan Mass Balance Study (LMMBS; described in the *Second Great Waters Report to Congress*) are becoming available. Results from two studies (Hurley et al. 1998b, Landis 1998), which are discussed below, show varying results. The study by Hurley et al. (1998b) involved sampling eleven tributaries that are representative of a variety of watersheds as part of the LMMBS. For example, land-use patterns included agricultural, forest, wetland, and urban. Ten of the 11 tributaries sampled are associated with areas of concern due to past contamination. Sediment core and sediment trap analysis is still being conducted by EPA for the LMMBS samples; however, tributary sample analysis has been completed. The mean mercury concentration in the 11 tributaries was 6.9 ng/L , with the highest concentrations in the rivers running through the urban areas. The highest mean mercury concentration (36.0 ng/L) was observed on the Fox River running through Green Bay, while the lowest mean concentration (1.0 ng/L) was observed on the Muskegon River. In general, the northern rivers had lower tributary inputs than the more industrialized southern rivers.

Hurley et al. (1998b) calculated tributary loading to Lake Michigan from each river as the product of the daily average water discharge and the daily mercury concentration. The estimated annual tributary mercury flux was 230 kg/year . The total annual mercury input into Lake Michigan from the atmosphere and the tributaries during the LMMBS was estimated to be 1,419 kg/year . Atmospheric deposition was determined to be the dominant source of mercury inputs to Lake Michigan, contributing approximately 84 percent (1,189 kg/year) of the annual total.

The study by Landis (1998) involved a hybrid-modeling framework based on monitoring data in the Great Lakes region. Annual deposition estimates from Landis (1998) are provided in Table II-2. In addition, the Landis modeling effort indicated that the Chicago/Gary urban area was responsible for at least 19 percent of the total atmospheric deposition to Lake Michigan. It should be noted that reactive mercury deposition is not included in this estimate of the urban influence and, thus, likely represents an underestimate of the true impact of the Chicago/Gary urban area.

Table II-2
Preliminary Estimates of Total Atmospheric Mercury Deposition to Lake Michigan

Deposition	Annual Total (kg)	Annual Mean ($\mu\text{g}/\text{m}^2$)
Wet	614 \pm 186	10.6 \pm 3.2
Aerosol Dry	69 \pm 38	1.2 \pm 0.7
Reactive Gaseous Mercury ^a	506	8.8
Dissolved Gaseous Mercury ^b	-460	-8.0
Total	729	12.6

^a Reactive gaseous mercury (RGM) deposition values do not include error bars because they reflect a sensitivity analysis performed on a single measurement in place of direct measurements since no measurement method was available for RGM at the time of the study.

^b Dissolved gaseous mercury (DGM) deposition values do not include error bars because the values reflect a single measurement taken to establish modeling parameters.

Source: Landis 1998

In another effort, Hurley et al. (1998a) collected and analyzed field samples from the Fox River in Wisconsin, which is located in a highly industrialized area and feeds into Green Bay, and ultimately, Lake Michigan. While total mercury in this river is high relative to other tributaries feeding into Lake Michigan, most of the mercury is bound to sediments. In the Fox River, resuspended sediments appear to be the predominant source of mercury into Green Bay. However, in the Lower Fox River and Green Bay, methylmercury concentrations are relatively low, suggesting that particulate-bound mercury has limited bioavailability (Hurley et al. 1998a).

As part of the Chesapeake Bay Atmospheric Deposition Study (CBADS), mercury wet deposition, dry deposition, and gas exchange were measured at sampling sites in the Chesapeake Bay representative of regional background levels. Total atmospheric deposition of mercury to the Chesapeake Bay was estimated to be 80 kg/year. Wet deposition of mercury to the Chesapeake Bay surface waters was estimated to be 162.1 kg/year (\pm 10-20 percent). Dry deposition was estimated to be 32.4 kg/year (accurate within a factor of two or three). Gas exchange was a net output that was estimated to be -115 kg/year (\pm 40 percent). Note that to develop these estimates, it was assumed that 10 percent of the surface waters below the fall line (see Figure II-5) are impacted by urban deposition and that the loading estimates are sensitive to this assumed percentage value (Chesapeake Bay Program 1999a).

Several additional mass balance studies are ongoing in Lake Michigan, Long Island Sound, and the Chesapeake Bay to characterize mercury inputs to as well as losses from these systems (Table II-3). In Long Island Sound, Fitzgerald (1998) collected and analyzed precipitation, air, surface water, and biota samples to develop a mass balance for mercury. In the Chesapeake Bay, Mason et al. (1997) developed a mercury mass balance based on precipitation, throughfall, and stream water samples. The mass balance study of Lake Michigan by Mason and Sullivan (1997) is a smaller effort than the LMMBS and is primarily a mass-balance modeling exercise based on data extracted through a literature review.

Similarities among the various mass balance studies include the finding that atmospheric deposition is a pathway with enough relative contribution in these waters to be of consideration (e.g., from 10 to greater than 80 percent). Furthermore, several of these studies indicate that air-water exchange (through net volatilization) and sediment burial are two major loss pathways.

**Table II-3
Mercury Sources Identified in Mass Balance Studies
(by percent contribution)**

Location	Atmospheric Deposition (%)	Urban Area (%)	Riverine	Ground-water	Direct Discharge	Comments
Lake Michigan ^a	~ 80	~ 30 (Chicago)	~17	< 1	Not reported	Air-water exchange and sediment burial account for the major loss pathways from the lake, but atmospheric deposition dominates inputs
Chesapeake Bay ^b	> 50 (Wet 47-53) (Dry 9-11)	Baltimore (percent not known)	~33-49	Not reported	Not reported	Over 90 percent of the mercury entering the watershed is retained in the terrestrial system and does not reach the aquatic system
Long Island Sound ^c	~10	New York New Jersey (percent not known)	~ 52	Not reported	~ 36	Tidal exchange, sediment burial, and air-water exchange are major loss pathways. 45 percent of the mercury entering the Sound is re-emitted

^a Mason and Sullivan (1997).

^b Mason et al. (1997).

^c Fitzgerald (1998).

Factors Affecting Mercury Fate and Transport in Watersheds and Tributaries

Recent research illustrates that a number of factors influence whether mercury that is deposited to watersheds or tributaries will be transported to the lake itself. The principal factors that affect mercury loading to the aquatic ecosystem appear to be (1) the amount of annual precipitation; (2) the influence of the urban air plume (in terms of local deposition of the contaminated plume); (3) storms and other events, like snowmelt, which influence stream flow and the resuspension of particle-bound mercury in sediments; and, (4) prevailing land use (e.g., forestry, agriculture, urban). Some of these factors appear to influence the amount of mercury in throughfall (i.e., precipitation that has washed through the forest canopy) and litterfall (i.e., fallen leaves) as well as the amount of mercury that is sequestered in organic soils which prevent its transport through the watershed.

Rea et al. (1996) found that throughfall and litterfall are the dominant components of mercury deposition in forested areas of the Lake Champlain basin. Monitoring during a 6-week period in August and September 1994 produced estimates of annual throughfall and litterfall deposition of 11.7 µg/m²/yr and 13 µg/m²/yr, respectively. Thus, the total below-canopy deposition rate was estimated to be 24.7 µg/m²/yr, considerably greater than the 15.1 µg/m²/yr wet plus dry deposition estimated by Scherbatskoy

et al. (1997). In the former study, precipitation deposition accounted for just 32 percent (or 7.9 $\mu\text{g}/\text{m}^2/\text{yr}$) of this estimated below-canopy deposition.

Several recent studies related to mercury cycling in the Lake Champlain basin, which focused primarily on forested systems, suggest that urban and agricultural systems may retain less atmospheric mercury than forested systems. For example, an analysis of mercury deposition and stream export (i.e., transport of mercury out of the basin through streamflow) in an 11 hectare, deciduous forested catchment (i.e., a portion of the larger watershed) in the Lake Champlain basin based on field sampling showed net annual stream export of mercury was less than 10 percent of wet deposition. Consistent with an earlier study in the basin, stream export was strongly related to flow and dominated by mercury in particulate form (i.e., mercury complexed with organic material). In 1 year of the study, fully one-half of the total annual export occurred on the single day of peak snowmelt. A more recent stream water sampling and deposition monitoring study also showed that most of the mercury transported in stream water is in the particulate phase, with the dissolved phase contributing only about 30 percent of the annual export. Analysis of soil water mercury reported in this study suggested that the transport of dissolved mercury in shallow soil water may be the primary mechanism for mercury movement from the forest floor to streams. These studies showed that the forested catchment is a net sink for atmospheric mercury and indicated that forests in the Lake Champlain basin help reduce the movement of mercury to the lake because the mercury is bound to soil organic matter. Some portion of the mercury is mobilized, however, and undergoes three possible fates: transport to streams through groundwater and overland (flood) flow, incorporation into vegetation by root uptake, or volatilization back to the atmospheric pool (Scherbatskoy et al. 1998, 1997, Shanley et al. 1999).

Mercury Exposure and Effects

Once deposited, mercury may enter terrestrial and aquatic food chains. Mercury concentrations increase at successively higher levels in the food chain such that predators at the top of these food chains are potentially at risk from consumption of mercury in contaminated prey. Of the various forms of mercury in the environment, methylmercury has the highest potential for bioaccumulation in the food chain. In the *Mercury Study Report to Congress*, the Agency concluded that fish-eating birds and mammals are particularly at risk from mercury emissions and exposures. Ecosystems most at risk from airborne releases of mercury exhibit one or more of the following characteristics:

- C Located in areas where atmospheric deposition of mercury is high;
- C Include surface waters that are already impacted by acid deposition;
- C Possess characteristics other than low pH (e.g., high organic content, long aquatic food chains) that result in high levels of bioaccumulation; and/or,
- C Include sensitive species (U.S. EPA 1997e).

Although a large body of research exists on mercury exposure and effects, as discussed below and in previous *Great Waters Reports to Congress*, areas of uncertainty remain, particularly with respect to mercury methylation processes and their implications for exposure levels. The EPA and others are currently planning and conducting research projects to address the fate and transport of mercury compounds and subsequent exposures to methylmercury. Some examples of research under way related to methylmercury include investigations of the following:

Chapter II

Environmental Progress

- The role of a variety of biogeochemical parameters in watersheds, wetlands, and marine environments on mercury bioavailability, bioconcentration, and methylation;
- The effects of anthropogenic ecosystem changes on methylation rates, such as increased sulfate deposition, increased nutrient loads, and increased loadings of mercury due to soil disturbance;
- The role of sulfur (especially sulfide) in mercury methylation in watersheds as related to microbial activity; and
- The effects of agricultural sulfur on methylmercury in soils and wetland areas.

Effects of mercury can be two-fold. First, mercury in lower-level organisms can impact the health of those organisms. Next, these organisms become prey for higher-level organisms, resulting in higher-level organisms having higher concentrations of mercury than the lower-level organisms. Concentrations of methylmercury in fish tissue have been measured at levels one million times greater than the mercury concentration in the surrounding water column, illustrating the extent to which methylmercury can be concentrated in organisms.

Principal factors affecting the bioavailability of mercury in the waterbody include (1) whether it is bound to organic matter (which would inhibit bioavailability); and, (2) characteristics of the lake itself, such as surface area to volume ratio (with more shallow lakes having more bioavailable mercury). When conditions in a waterbody change (i.e., pH), the bioavailability of a compound can change without a change in the concentration of the compound.

Analyzing sediments for mercury concentrations can reveal the extent to which bottom dwelling organisms are exposed. Eskin et al. (1996) compiled and analyzed sediment contamination data from the Chesapeake Bay and its tributaries from 1984 to 1991. The potential for sediment contamination to impact aquatic life was evaluated by comparing median and maximum contaminant concentrations to no observed effects levels (NOELs) for aquatic biota, probable effects levels (PELs) for aquatic biota, or other aquatic health benchmarks. The NOELs are concentrations above which impacts on aquatic life are judged to be *possible*. Aquatic life impacts are considered *probable* at concentrations above the PELs. For toxic effects to occur, metals must not only be present at concentrations above aquatic life benchmarks, but must also be bioavailable.

Where data were available for comparison, sediment mercury concentrations in the Chesapeake Bay, in general, were lower in 1991 than in previous years. The median and maximum concentrations of mercury at all locations in the mainstem of Chesapeake Bay were 0.08 and 0.8 ppm, respectively, which are below the mercury PEL of 1.4 ppm for aquatic biota. However, because maximum concentrations of mercury in all segments of the bay exceeded the mercury NOEL of 0.1 ppm for aquatic biota, adverse impacts are still possible. The median and maximum mercury concentrations in tributaries were 0.1 and 4.66 ppm, respectively. Mercury concentrations were highest in the Middle River, other northwestern tributaries, and near the Sewells Point Naval Complex on the James River. Median mercury concentrations exceeded the mercury NOEL for aquatic biota in several tributaries, including the James and Potomac Rivers. The PEL concentration for mercury was exceeded only in the James River at stations near the Sewells Point Naval Complex.

Sources with episodic emissions or releases of mercury and other pollutants to the Delaware Bay influence concentrations in biota. Horseshoe crab eggs are of particular importance for monitoring efforts because they are a major food source for many species of migrating shore birds during the spring migration. While measurements of mercury levels in the eggs of horseshoe crabs from Delaware Bay,

New Jersey in 1993, 1994, and 1995 do not indicate any temporal trend, levels of mercury varied markedly among years, with the highest values in 1994 (Burger 1997). The variations in mercury levels and the peak in 1994 highlights the importance of episodic sources of pollutants to the Delaware Bay, which is situated downstream from highly industrialized areas in Trenton, New Jersey; Wilmington, Delaware; and, Philadelphia, Pennsylvania. Burger (1997) also analyzed mercury concentrations in female horseshoe crab leg muscle tissues from the Delaware Bay and found that mercury concentrations were higher in leg muscle tissues than in eggs and were indicative of few adverse effects to developing horseshoe crabs.

In an evaluation of higher level organisms, Brazner and DeVita (1998) detected mercury in yellow perch and spottail shiners from 23 sites in Green Bay, Lake Michigan. The overall distribution of mercury tissue concentrations was fairly uniform within the bay, indicating that mercury contamination originates primarily from non-point sources, including atmospheric deposition. Certain sites exhibited unusually high mercury residues in fish, however, suggesting these sites may be associated with direct discharges of mercury nearby. The mercury residue levels of 9.4 to 31.0 ng/g in yellow perch and 10.5 to 33.5 ng/g in spottail shiners were well below the International Joint Commission Aquatic Life Guideline for total mercury of 500 ng/g. Furthermore, these mercury levels were similar to or below the most recently reported (i.e., 1993, 1985) mercury levels in fish in most of the locations in the Great Lakes.

Mercury levels apparently decreased in yellow perch taken from the St. Lawrence River, which drains the Great Lakes, in 1991-1992 and were compared to results from a 1975 study (Ion et al. 1997). Mercury was detected in all yellow perch samples taken from various sites along the river. Comparison of average mercury concentrations to historical levels in St. Lawrence River fish indicates a two- to three-fold decrease since 1975. Because mercury contamination and bioaccumulation can vary considerably from site to site and species to species, additional studies of this type are needed for trends analysis of mercury levels in fish.

Fish-eating birds are of particular interest for evaluating the effects of mercury because relative to their body weight, exposures can be very high. Hughes et al. (1997) detected significant differences in mercury concentrations in both osprey eggs and chick feathers from nests at four Great Lakes study areas in Ontario (three natural lakes and one reservoir) and two Delaware Bay sites in New Jersey. Overall, eggs from the Ogoki Reservoir and chick feathers from St. Mary's River (Ontario) and the Ogoki Reservoir had significantly higher mercury concentrations than the eggs and feathers sampled from the other locations. Despite these geographic variations, mercury levels in osprey eggs, chick feathers, and adult feathers at all locations were below the levels associated with toxic reproductive effects, such as reduced number of eggs, decreased hatchability, increased hatchling mortality, and altered reproductive behavior. Fish sampled at each site also exhibited significant differences in mercury levels with a clear spatial pattern, similar to that observed for chick feathers. However, the study did not assess the relative impact of point source discharges and atmospheric deposition on spatial variation.

In a recent study that attempted to link spatial variations in mercury levels in biota with variations in atmospheric deposition of mercury, Evers et al. (1998a) found that mercury concentrations in the feathers and blood of adult and juvenile common loons from sites within five regions across North America (Canadian Maritimes, New England, Upper Great Lakes, northwestern U.S., and Alaska) increased significantly from western regions to eastern regions. Adults had average blood mercury levels which were 10 times higher than juveniles. Feather mercury levels increased significantly over a 4-year period, probably due to bioaccumulation of mercury over that time period. At some of the study locations where exposure is high (e.g., some eastern North American locations), the loon's natural mechanisms to excrete excess mercury (e.g., feathers, eggs, demethylation and storage in the liver and kidney) may not be sufficient to balance current exposure levels. The researchers note that the observed

geographical gradient agrees with EPA's Regional Environmental Monitoring and Assessment Program (R-EMAP) modeling of atmospheric deposition of mercury and predicted high impact areas (U.S. EPA 1997e) and the Northeast States and Eastern Canadian Provinces Mercury Study (NESCAUM 1998). Within the upper Great Lakes region (nine sites total), blood mercury levels were influenced the most by lake biogeochemistry and hydrology, rather than atmospheric deposition. Significantly higher concentrations from sites in north-central Wisconsin and central Ontario were detected. The authors conclude that loons breeding on low-pH lakes in the upper Great Lakes and in all lake types in northeastern North America are the most at risk from mercury contamination. A comparison of the measured blood mercury concentrations to health threshold levels determined from laboratory studies indicate that 12 to 31 percent of New England's breeding loon population exceed these levels (Evers 1998b). Based on feather mercury levels, over 30 percent of the male loons exceed threshold levels for health effects.

Like wildlife, fish consumption represents the dominant pathway for human exposure to methylmercury. Given the current scientific understanding of the environmental fate and transport of this element, it is not possible to quantify how much of the methylmercury in fish consumed by the U.S. population is contributed by U.S. emissions relative to other sources of mercury (such as natural sources and re-emissions from the global pool). As a result, it cannot be assumed that a change in total mercury emissions will be linearly related to any resulting change in methylmercury in fish, nor over what time period these changes would occur. This is an area of ongoing study.

The effects of methylmercury on humans and especially the developing fetus are well known and have been described in detail in earlier *Reports to Congress*. The critical target for methylmercury toxicity for humans is the nervous system. The factors that affect whether the mercury exposure is sufficient to cause health effects depend primarily on the species of fish consumed, the concentration of methylmercury in the fish, the quantity of fish consumed, and how frequently fish is eaten. The 1997 EPA *Mercury Study Report to Congress* includes a detailed analysis of potential public health impacts relating to fish consumption. This analysis was based on information on the mercury levels in various types of fish, dietary surveys, and EPA's current reference dose (RfD) for methylmercury. The RfD is an estimated daily ingestion level anticipated to be without adverse effect to persons, including sensitive subpopulations, over a lifetime. Note that the National Academy of Science is currently reviewing more recent mercury health effects studies and will recommend whether the EPA should revise its RfD for methylmercury. This review and recommendation is expected to be completed by mid-2000.

The *Mercury Study* report concluded that the typical U.S. consumer eating fish from restaurants and grocery stores was not in danger of consuming harmful levels of methylmercury from fish and is not advised to limit fish consumption on the basis of mercury content. However, eating more fish than is typical or eating fish that are more contaminated than typical fish can change the advice. Because the developing fetus is regarded as the most sensitive to the effects of methylmercury, women of child-bearing age are the population of greatest concern.

In addition, for cultural or economic reasons, some people in certain ethnic groups (e.g., Asians, Pacific Islanders, Native Americans) and subsistence fishers eat substantially more fish than the average consumer. Because of the higher amounts of fish in their diets, people in these groups, especially the women of child-bearing age, need to be aware of how much mercury is in the fish they consume. The *Mercury Study* report has more detailed information about amounts of mercury found in various types of fish.

The Food and Drug Administration (FDA) and State, local, and tribal agencies issue advisories that suggest limiting the consumption of contaminated fish. Mercury fish advisories in the U.S. have been

issued by 40 States and some tribes. Eleven States have Statewide advisories for mercury in freshwater lakes or rivers, and five States have Statewide advisories for mercury in coastal waters. Based on data from December 1997, 20 of 56 Great Waters are associated with mercury fish consumption advisories (U.S. EPA 1998m). The EPA is sponsoring work with the State of Wisconsin to assess current methods of communicating fish consumption advisories and to recommend improvements.

Despite this advice, a recent survey on awareness and effectiveness of fish advisories found that only half of the Great Lakes sport fish consumers were aware of health advisories related to fish consumption (Tilden et al. 1997). While one study of Lake Ontario anglers concluded that the angler subpopulation's health does not significantly differ from those experienced by the general North American population (Cole et al. 1997), a different study concluded that the consumption of contaminated fish affected time-to-pregnancy (i.e., the amount of time between when a woman plans to become pregnant and the date of pregnancy). The study also found that 42 percent of the women surveyed reported consumption of contaminated fish from Lake Ontario, despite highly publicized advisories against the consumption of fish from Lake Ontario by women of reproductive age (Buck et al. 1997).

According to Tilden et al. (1997), the most widely accepted advisory recommendation was cleaning and cooking methods. While cooking methods are effective to reduce PCB exposure, mercury concentrations will actually increase, on a per weight basis, with all cooking methods (including pan frying, deep-frying, baking, boiling, and smoking) because of the moisture and fat lost during cooking (Morgan et al. 1997). Unlike PCBs which accumulate in fatty tissue that can be removed prior to consumption, mercury accumulates in the muscle tissue or filet portion.

Studies of mercury exposure in U.S. populations are limited, particularly for the general population. However, research is being planned as part of EPA's draft Mercury Research Strategy (see Chapter III) to address this need. A number of studies have been conducted involving sport fisherman and Native peoples, which have shown high levels of fish consumption in a number of populations; but, risk of exposure is dependent, in large part, on the level of contamination in the fish (U.S. EPA 1997e). A recent study of Ojibwa tribal members from the Great Lakes region indicates that mercury concentrations in Ojibwa populations are low; however, researchers identified several individuals with elevated levels of mercury (Gerstenberger et al. 1997).

OTHER METALS (LEAD AND CADMIUM)

Sources and Emissions of Lead and Cadmium

Lead and cadmium are naturally-occurring trace metals and, therefore, are expected to be detected at some background level in the environment, depending on the location. Furthermore, because lead and cadmium are metals, they are by nature persistent compounds that may cycle between environmental compartments. Therefore, while it is possible to estimate lead and cadmium emissions from anthropogenic sources, it is difficult to determine which sources (e.g., specific human-made sources, natural sources, cycling) contribute to total and atmospheric deposition inputs to the Great Waters.

Based on a study of lead, cadmium, and other trace metals emissions and air concentrations in the Great Lakes region from 1982 to 1993, (1) sources of lead in 1993 included steel manufacturing, coal combustion, non-ferrous metal production, and waste disposal (Figure II-3), and (2) sources of cadmium

in 1993 included coal combustion, solid waste and sewage sludge incineration, iron-steel manufacturing, non-ferrous metals production, and several smaller sources (Figure II-5) (Pirrone and Keeler 1996).

A review of cadmium and lead emission sources on a national scale, based on EPA's National Toxics Inventory for the time period from 1990-1993 (1990-1993 NTI), provides a somewhat different picture compared to regional sources for the Great Lakes (Tables II-4 and II-5). The larger national-level sources of lead air emissions are mobile sources, including non-road vehicles and equipment (aircraft) and on-road vehicles. The larger national-level sources of cadmium air emissions are secondary lead smelting, primary copper smelting, and primary lead production (U.S. EPA 1999a). The NTI data for lead air emissions also indicate that there are many source categories that are emitting similar amounts of lead compounds, rather than there being a few source categories contributing the majority of the air emissions. The differences observed between the local (Figures II-3 and II-5) and national (Tables II-4 and II-5) source characterizations for these pollutants highlight the importance of examining both local sources and regional sources, as well as the need to consider the influence of urban areas on nearby waterbodies.

A study of lead emissions and air concentrations indicates that, overall, U.S. lead emissions have decreased since the 1970s, primarily due to the phaseout of leaded gas. Lead emissions in the Great Lakes region decreased steadily from 1982 to 1993 at a rate of about 6.4 percent per year. Lead emissions in the Great Lakes region in 1988 were estimated to be 4,430 tpy. Lead concentrations in ambient air also showed steady declines over the entire region between 1982 and 1993. The regional decrease in lead emissions and air concentrations is correlated to the reduction of lead in gasoline (from 0.28 g/l in 1982 to 0.026 g/l in 1989) and an increase in unleaded gasoline use in both the U.S. and Canada since 1981. Sources of lead emissions also shifted over this time period. As shown in Figures II-3 and II-4, about 80 percent of lead emissions were from leaded gasoline use in 1982 compared to 1993 when most lead emissions were from four major industrial sources in the Great Lakes region (Pirrone and Keeler 1996). Another study of lead deposition to sediments in Central Park Lake in New York City

HIGHLIGHTS
Other Metals (Lead and Cadmium)

- **Sources.** In some urban locations, local sources (versus regional sources) are primarily responsible for atmospheric deposition of lead and cadmium to the Great Lakes, whereas the opposite is true in some more remote locations. The largest national sources of lead air emissions are mobile sources, including non-road vehicles and equipment (aircraft) and on-road vehicles. Emissions and ambient air concentrations of lead have continued to decrease since the 1970s. The largest national sources of cadmium air emissions include secondary lead smelting, primary copper smelting, and primary lead production. Cadmium air emissions increased from 1982 to 1988 in the Great Lakes region and have not shown a trend since 1988.
- **Loadings.** In the Great Lakes region, lead deposition decreased from 1988 to 1994, and cadmium deposition may have decreased from 1992 to 1994. In the Chesapeake Bay, atmospheric deposition of cadmium and lead contributes no more than 5 to 7 percent, respectively, to total loadings. Total inputs from all pathways of lead and cadmium increased in the eastern section of the bay from 1966 to 1995 due to the increase in human population and industrial activities. However, trends in the relative contribution of atmospheric deposition of lead and cadmium to the Chesapeake Bay have not been discerned. In the Long Island Sound, lead inputs have been decreasing since 1980 and atmospheric deposition contributes 70-90 percent of total lead inputs.
- **Environmental Concentrations.** Sediment contamination studies in the Chesapeake Bay provide conflicting results – one study found increased lead and cadmium levels, possibly due to an increase in population, industrial activities, and agricultural activities, whereas another found decreasing levels. Lead and cadmium levels in Chesapeake Bay sediments, in general, were between the aquatic biota NOEL and PEL; however, bioavailability of these metals is low. In the Delaware Bay, lead levels decreased in horseshoe crab eggs in recent years, but cadmium levels were more variable.

using sediment cores indicates, however, that municipal solid waste incineration contributed a large portion of the lead deposited during the same time period that lead from leaded gasoline was deposited. Furthermore, lead emissions from municipal solid waste incinerators decreased beginning in 1966 due to progressive facility closures following regulations. Therefore, although it is clear that lead emissions and deposition have decreased, it is possible that solid waste incineration has been underestimated as a source of atmospheric lead in the past, particularly to urban areas (Chillrud et al. 1999).

In contrast to lead emissions and ambient air concentrations, cadmium emissions in the Great Lakes region increased from 1982 to 1988 at a rate of 5.2 percent per year, with a peak in 1988 at 150 tpy. Since 1988, emissions of cadmium have not increased or declined (Pirrone and Keeler 1996).

Deposition of Lead and Cadmium

Data collected under the Integrated Atmospheric Deposition Network (IADN), a joint U.S.-Canada program that monitors pollutant levels in air and precipitation at remote sites in the Great Lakes region, by Eisenreich and Strachan in 1992 and Hoff et al. in 1994 show that total deposition of lead decreased from 1988 to 1994 in each of the Great Lakes. Paode et al. (1998) found that measured average lead fluxes in Chicago, Illinois were 0.07 mg/m²/day, whereas over Lake Michigan, lead fluxes were 0.003 mg/m²/day, demonstrating the urban influence of Chicago on atmospheric deposition of lead onto Lake Michigan. Dry deposition of cadmium in the Great Lakes region decreased from 1992 to 1994; however, this decrease may be due to improved averages in the particulate air concentrations of the metals (Hoff et al. 1996). Sweet et al. (1998) estimated annual wet and dry deposition rates to Lake Michigan, Lake Erie, and Lake Superior using air and rain concentrations of lead and cadmium measured at three U.S. IADN sites and found that lead and cadmium deposition levels were similar at all lakes. Since the IADN sites are situated in remote locations, this finding indicates regional atmospheric deposition, rather than local emissions, is the source of lead and cadmium at the remote sites on these three lakes.

Estimates of total inputs of trace metals to the Chesapeake Bay indicate that inputs of trace metals from the non-tidal watershed are much higher than trace metal inputs to tidal waters from point source discharges, urban storm water inputs, and direct atmospheric deposition to the tidal waters. The boundary for the non-tidal and tidal waters in the Chesapeake Bay region is indicated in Figure II-6.

Inputs from the non-tidal watershed to the Chesapeake Bay consist of all point and non-point sources, including atmospheric deposition. Atmospheric deposition (measured as direct deposition to water surfaces based on monitoring data) of cadmium and lead contributes approximately 4.6 and 5.6 percent, respectively, to total inputs to the Chesapeake Bay (Table II-6). Note that these percentages may be underestimates because the monitoring site locations do not reflect the urban influences of Baltimore, Maryland on the Chesapeake Bay. However, these percentages are similar to those for other metals but are much less than percentages for polycyclic aromatic hydrocarbon (Eskin et al. 1996).

Figure II-3
1993 Lead Emissions in the Great Lakes Region
(Pirrone and Keeler 1996)

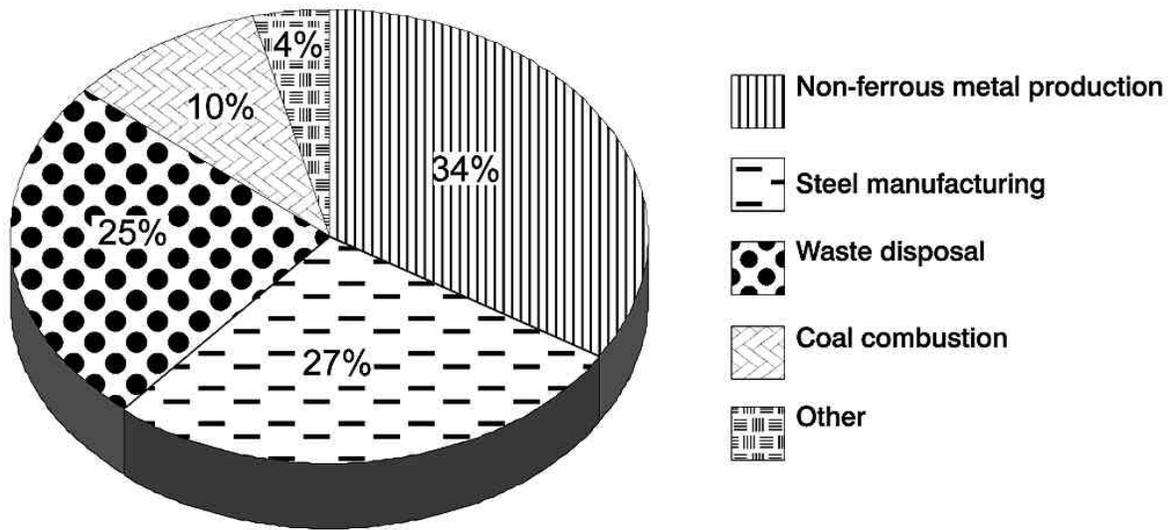


Figure II-4
1982 Lead Emissions in the Great Lakes Region
(Pirrone and Keeler 1996)

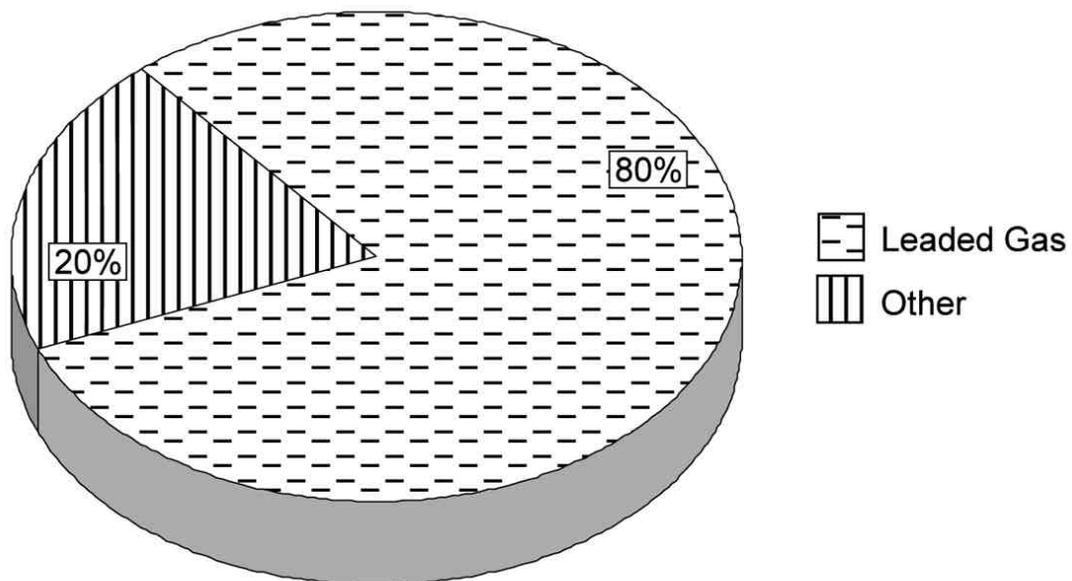


Figure II-5
1993 Cadmium Sources in the Great Lakes Region
(Pirrone and Keeler 1996)

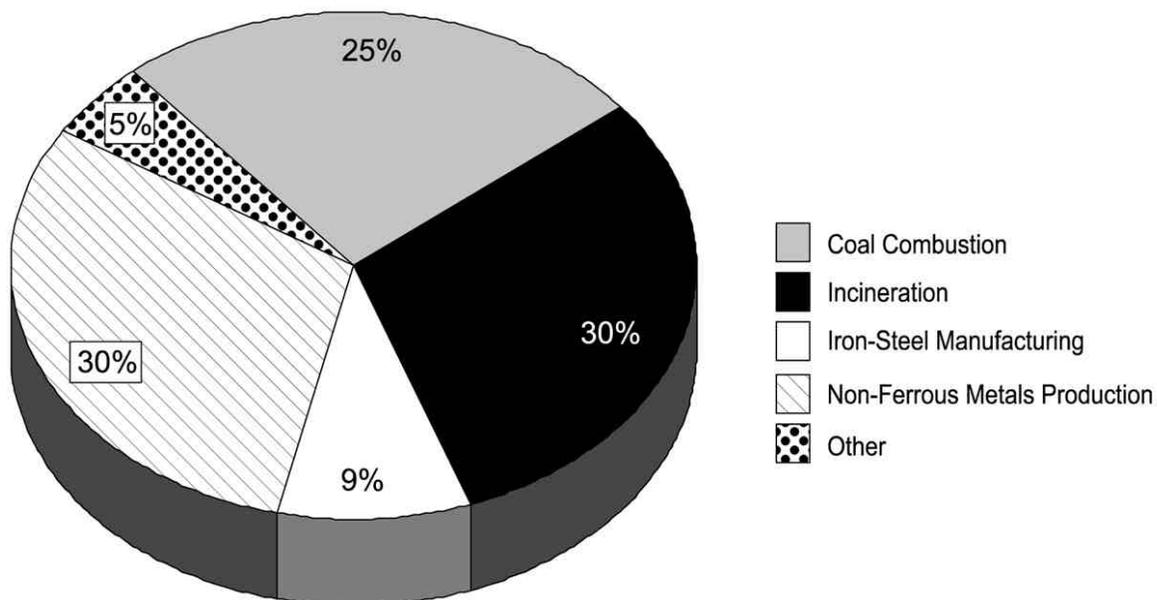


Table II-4
National Anthropogenic Lead Air Emissions
(Based on EPA's 1990-1993 National Toxics Inventory)

Source Category	Anthropogenic Air Emissions (tons/year)	Percent Contribution to Total U.S. Anthropogenic Air Emissions
Mobile sources: non-road vehicles and equipment - aircraft	619	18.7
Mobile Sources: on- road vehicles	418	12.6
Primary lead	259	7.8
Steel wire and related products manufacturing	163	4.9
Mobile sources: non-road vehicles and equipment - other	158	4.8
Primary copper smelting	152	4.6
Pulp and paper: combustion	150	4.5
Lead oxide in pigments	136	4.1
Secondary lead smelting	106	3.2

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Source Category	Anthropogenic Air Emissions (tons/year)	Percent Contribution to Total U.S. Anthropogenic Air Emissions
Municipal waste combustion	80	2.4
Non-stainless steel manufacture - EAF	79	2.4
Utility boilers: coal combustion, all types	72	2.2
Secondary copper smelting	71	2.2
Medical waste incineration	63	1.9
Hazardous waste incineration	56	1.7
Secondary nonferrous metals production	55	1.7
Pressed and blown glass and glassware manufacturing	52	1.6
Storage batteries manufacturing	51	1.5
Portland cement manufacture: hazardous waste-fired	41	1.2
Primary nonferrous metals production	40	1.2
Paint application: no spray booth	35	1.1
Others (< 1 percent each) ^a	454	13.7
Total U.S. Anthropogenic Lead Air Emissions	3,310 ^b	100 ^b

^a A list of the source categories that contribute less than 1 percent to total U.S. emissions is provided in Appendix B.

^b This value represents anthropogenic lead air emissions in the U.S. only.

Source: U.S. EPA 1999a

**Table II-5
National Anthropogenic Cadmium Air Emissions
(Based on EPA's 1990-1993 National Toxics Inventory)**

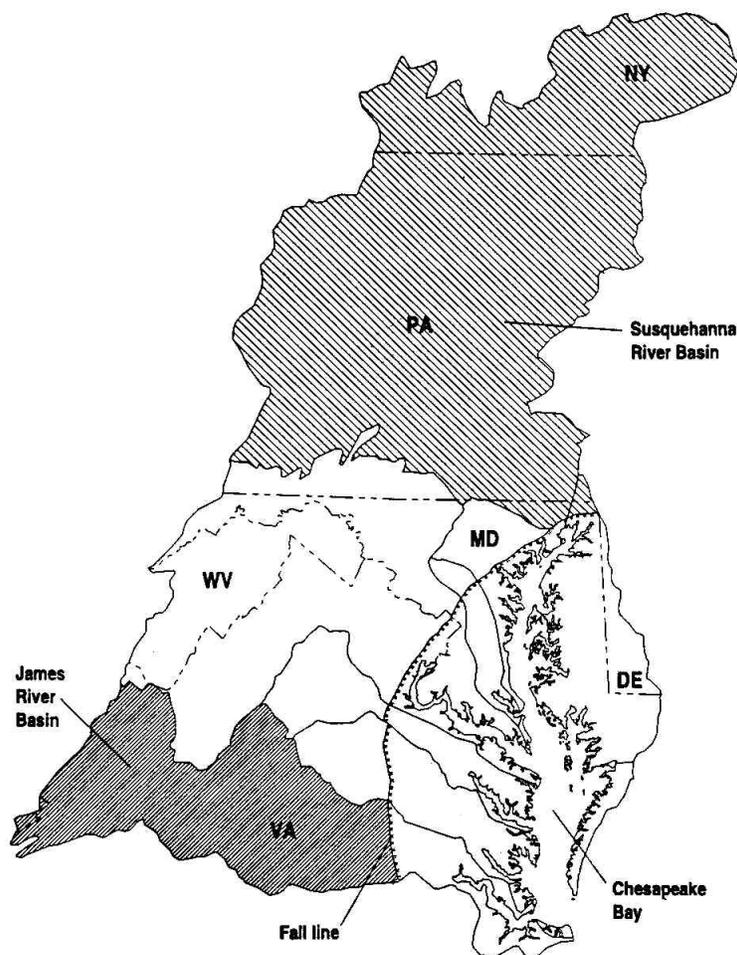
Source Category	Anthropogenic Air Emissions (tons/year)	Percent Contribution to Total U.S. Anthropogenic Air Emissions
Secondary lead smelting	84	42.2
Primary copper smelting	16	8.1
Primary lead	16	7.9
Hazardous waste incineration	9	4.3
Petroleum refining: catalytic cracking units	7	3.3
Municipal waste combustion	5	2.5
Medical waste incineration	5	2.4
Cadmium refining and cadmium oxide production	5	2.3
Secondary copper smelting	5	2.3
Industrial inorganic chemical manufacturing	4	2.2
Sewage sludge incineration	4	1.9
Cadmium stabilizers production	4	1.8
Pulp and paper: combustion	3	1.7
Portland cement manufacture: hazardous waste-fired	2	1.2
Inorganic pigments: cadmium pigments in plastics	2	1.1
Primary nonferrous metals production	2	1.0
Others (<1 percent each) ^a	28	13.8
Total U.S. Anthropogenic Cadmium Air Emissions	201^b	100^b

^a A list of the source categories that contribute less than 1 percent to total U.S. emissions is provided in Appendix B.

^b This value represents anthropogenic cadmium air emissions in the U.S. only.

Source: U.S. EPA 1999a

Figure II-6
Chesapeake Bay Tidal and Non-tidal Waters
(Tributary basins are shaded)



Note: Fall line is the upper boundary of the tidal waters of the Chesapeake Bay.
Source: Chesapeake Bay Program 1994

Table II-6
Trace Metal Inputs to the Chesapeake Bay (kg/year)

Trace Metal	Total Inputs to Chesapeake Bay ^a	Direct Atmospheric Deposition to Tidal Waters	Direct Atmospheric Deposition to Tidal Waters as Percent of Total Inputs
Cadmium	27,800	1,200	~4.6
Lead	275,300	14,500	~5.6

^a Includes inputs from the non-tidal watershed (including atmospheric deposition to the watershed), storm water inputs to the tidal waters, point source inputs to the tidal waters, and direct atmospheric deposition to the tidal waters.

Source: Eskin et al. 1996

Data collected by the Chesapeake Bay Atmospheric Deposition Study (CBADS),¹ as presented in the Chesapeake Bay Program's *1999 Toxics Loading and Release Inventory* (TLRI), result in estimates of total inputs to the Chesapeake Bay for cadmium and lead (42,600 and 254,000 kg/year, respectively) that are similar to the Eskin et al. (1996) values. Inputs of lead and cadmium via atmospheric deposition to the tidal waters of the Chesapeake Bay as a percentage of the total inputs are 7 percent and 3 percent, respectively. Inputs from the non-tidal watershed dominate for lead and cadmium (Chesapeake Bay Program 1999a, 1994).

A study on the eastern shore of the Chesapeake Bay in Maryland using sediment cores found that lead deposition rates range from 0.32 ± 0.20 to 13.60 ± 0.98 mg/m³/yr, and cadmium deposition rates range from 0.01 ± 0.01 to 0.43 ± 0.04 mg/m³/yr. Total inputs of both lead and cadmium from all pathways increased from 1966 to 1995 due to the increase in human population and industrial activities (Karuppiah and Gupta 1998).

Direct atmospheric deposition rates of lead and cadmium to the Massachusetts Bay based on monitoring data are presented in Table II-7. In general, deposition of lead and most other metals is higher at the monitoring site closer to Boston due to higher urban area emissions. However, deposition of cadmium is similar at both the urban and rural locations. While there is not a seasonal trend for trace metal deposition in general, higher dry deposition of lead has been observed in the winter (Golomb et al. 1997a).

Table II-7
Direct Atmospheric Deposition of Lead and Cadmium
to Massachusetts Bay ($\mu\text{g}/\text{m}^2/\text{yr}$)

Trace Metal	Urban	Rural
Cadmium	260	280
Lead	2,300	1,400
Total	2,560	1,680

Source: Golomb et al. 1997a

In Long Island Sound, sediment cores from salt marshes indicate that lead inputs reached a maximum between 1970 and 1980 at approximately $62 \mu\text{g}/\text{cm}^2/\text{yr}$ and have been decreasing since that time at most sites. Atmospheric deposition to the water surface of Long Island Sound contributes approximately 90 percent of total lead inputs. At sites closer to New York City, cores show that atmospheric deposition accounts for approximately 70 percent of lead inputs, suggesting that non-atmospheric sources (e.g., direct discharges, storm water runoff) play a larger role near the urban areas (Cochran et al. 1998).

¹ CBADS measurements include wet deposition, dry deposition, and gas exchange of pollutants at rural sites, with estimations for urban areas.

Lead and Cadmium Levels in the Environment

Lead and cadmium levels have been measured in a variety of environmental media and in a wide range of geographic locations in the Great Waters. The concentrations that are observed in the environment are a result of atmospheric deposition from both domestic and international sources as well as from non-atmospheric sources, including storm water runoff and direct discharges to waterbodies and tributaries.

A recent study in the Chesapeake Bay found an increase in lead and cadmium concentrations in and toxicity of the sediments and pore water (i.e., interstitial water of sediments) of two tributaries (Wicomico River and Pocomoke River) in comparing sediment cores from 1966-1975 to sediment cores from 1986-1995 (Table II-8). The authors examined the historical land use of areas adjacent to these rivers and concluded that the increases were likely due to a variety of pathways. Specifically, (1) increases in metal concentrations in Wicomico River sediments and pore water are probably due to an increase in population, industrial activities, and the volume of the sewage treatment plant influent; (2) increases in metal concentrations in Pocomoke River sediments and pore water are probably due to the increased runoff from agricultural areas, including poultry farms; and, (3) increases in lead concentrations in Wicomico River sediments and pore water are possibly due to an increase in various industrial activities, commercial facilities that use lead compounds, and atmospheric deposition (Karuppiah and Gupta 1998).

Seasonal Variation in Cadmium Concentrations

A monitoring study of the St. Lawrence River, which connects the Great Lakes with the Atlantic Ocean, emphasized the importance of seasonal variation on the concentration and distribution of metals. Quémérais and Lum (1997) collected water from sites in the river and four of its tributaries from March to November 1991 and April to June 1992 and analyzed the samples for dissolved and particulate cadmium. The mean dissolved cadmium concentration for the basin (10 ± 5 ng/L) was in the same range as that measured for rivers considered pristine environments. The mean particulate cadmium concentration (1.3 ± 1.1 $\mu\text{g/g}$) was also relatively low in comparison to other waterbodies. Dissolved cadmium concentrations exhibited a seasonal trend; concentrations increased in spring and autumn and decreased in summer. The trend was attributed to increased runoff and leaching from soil during spring snowmelt and rainfall events in autumn as well as uptake by surface water microorganisms during summer. The seasonal variation of particulate cadmium was not as apparent, probably due to the negative influence of suspended particulate matter, which is higher in spring and autumn as a result of snowmelt and rainfall patterns.

Other studies have found that sediment concentrations of lead and cadmium are declining, however. Sediment concentration data from the Chesapeake Bay Program from 1984 to 1991, for example, indicate that lead and cadmium concentrations in sediments are declining in some areas of the Chesapeake Bay (Eskin et al. 1996).

An analysis of spatial trends shows that metals concentrations in sediments of the mainstem of the bay were lowest at the head of the bay and in the extreme lower bay. The highest metals concentrations were detected in sediments of the segment of the bay closest to Baltimore, the largest urban center on the bay. Lead contamination trends were somewhat different when concentrations were normalized by the fine particle content of the sediment. In particular, normalized sediment concentrations of lead gradually declined toward the mouth of the bay, suggesting that the Susquehanna River is the primary source of lead. Lead concentrations were highest in the Middle River, other northwestern tributaries, and near the Sewells Point Naval Complex on the James River. The distribution of cadmium contamination was different from other contaminants, where the highest concentrations were located in the sediments of the James (near the Sewells Point Naval Complex) and Patuxent Rivers and in some of the southeastern tributaries (Eskin et al. 1996).

Table II-8
Temporal Changes in Metal Concentrations in Chesapeake Bay Tributaries
Based on Sediment Cores

Sediment Core Depth (cm)	Estimated Period (year)	Lead		Cadmium	
		Sediment (mg/kg)	Pore Water (mg/L)	Sediment (mg/kg)	Pore Water (mg/L)
Wicomico River					
0-7.5	1986-1995	18.01	5.12	0.49	0.026
7.5-15.0	1976-1985	7.60	0.54	0.48	0.008
15.0-23.0	1966-1975	7.43	0.42	0.37	0.007
Pocomoke River					
0-7.5	1986-1995	5.14	0.74	0.28	0.025
7.5-15.0	1976-1985	3.51	0.59	0.24	0.003
15.0-23.0	1966-1975	2.35	0.59	0.20	0.002

Source: Karuppiah and Gupta 1998

The potential for sediment contamination to impact aquatic life was evaluated by comparing median and maximum sediment contaminant concentrations to aquatic health benchmarks in both the mainstem of the Chesapeake Bay and its tributaries (Table II-9). Maximum concentrations of cadmium and lead in the mainstem of Chesapeake Bay were below PEL concentrations for aquatic biota. However, impacts must be considered possible because maximum lead and cadmium concentrations exceeded the aquatic biota NOEL in most of the upper half of the bay and at the mouth of the Potomac River (Eskin et al. 1996).

In the Chesapeake Bay tributaries, median and maximum lead concentrations in sediments were 31 and 343 parts per million (ppm), respectively. Median lead sediment concentrations exceeded the lead NOEL in northwestern tributaries, but the aquatic biota PEL for lead was exceeded only near the Sewells Point Naval Complex. The median and maximum cadmium sediment concentrations were 0.6 and 6.0 ppm, respectively. The distribution of cadmium contamination was different from other contaminants, where the highest concentrations were located in the James (near the Sewells Point Naval Complex) and Patuxent Rivers and in some of the southeastern tributaries. Median cadmium sediment concentrations in several of the western and northwestern tributaries exceeded the aquatic biota NOEL; however, the maximum concentrations did not exceed the PEL for aquatic biota (Eskin et al. 1996).

For toxic effects to be possible, metals must not only be present at concentrations above aquatic life benchmarks but must also be bioavailable (i.e., available for uptake by organisms). For instance, a portion of the lead in sediments must not be bound to the organic matter in the sediment, and the lead levels in the sediment must exceed the aquatic life benchmark in order for toxic effects to occur. Eskin et al. (1996) found low bioavailability through most of the mainstem of the bay. However, bioavailable conditions were found in a northern reach of the bay from Turkey Point to Annapolis. This reach includes the most contaminated segment of the bay, between Baltimore and Annapolis (Eskin et al. 1996).

Table II-9
Cadmium and Lead in Sediments of the Chesapeake Bay Mainstem

Contaminant	Concentration		Aquatic Life Benchmark		Location of Maximum Concentrations	Trends
	Median (ppm)	Maximum (ppm)	NOEL ^a (ppm)	PEL ^b (ppm)		
Cadmium	0.4	2.9	1.0	7.5	Baltimore region south to the Little Choptank River; mouth of Potomac River	Concentrations are declining
Lead	35	86	21	160	Baltimore region	Concentrations are declining in some areas

^a No Observed Effect Level. Level above which impacts are considered "possible."

^b Probable Effect Level. Level above which impacts are considered "probable."

Source: Eskin et al. 1996

In the Delaware Bay, one study attributed decreases in lead levels in horseshoe crab eggs to a general lowering of pollutants to the bay. Horseshoe crab eggs provide a bioindicator of pollutant levels in the Delaware Bay because they are laid beneath the sand at the bay's high tide line and are continuously inundated with water. Burger (1997) measured levels of lead and cadmium in the eggs and leg muscles of horseshoe crabs in 1993, 1994, and 1995 in the Delaware Bay and found a decrease in lead levels in horseshoe crabs from 1993 to 1995. Cadmium levels in the eggs were significantly higher in 1994 than in 1993 or 1995 (Table II-10). The variations in cadmium levels may suggest an episodic source of cadmium to the bay, which is probable given the high level of upstream industrialization in Trenton, New Jersey; Wilmington, Delaware; and, Philadelphia, Pennsylvania. Burger (1997) also analyzed lead and cadmium levels in female horseshoe crab leg muscle tissues from the Delaware Bay and found that lead and cadmium levels in leg muscle tissues were lower than in eggs and were indicative of few adverse effects.

Table II-10
Lead and Cadmium in Horseshoe Crab Eggs from Delaware Bay

Year	Lead (ppb)	Cadmium (ppb)
1993	558 (±160)	17 (±5)
1994	206 (±34)	310 (±130)
1995	87 (±8)	24 (±7)

Source: Burger 1997

COMBUSTION EMISSIONS

Dioxins and Furans

Polychlorinated dibenzo-p-dioxins (PCDDs; dioxins) and polychlorinated dibenzofurans (PCDF; furans) are compounds that are similar in structure but differ in the number and position of chlorine atoms. Much of the current research uses toxic equivalent quantities (TEQs) to express quantities of dioxins and furans. The TEQs aggregate all of the dioxin and furan congeners into a single factor that is weighted by toxicity of the individual congeners based on ratios to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and to 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). Therefore, dioxin and furan quantities are commonly expressed as dioxin TEQs and furan TEQs, respectively. This is the convention followed in this report to the extent permitted by the research results reported in the literature.

Dioxins and furans are byproducts of combustion that enter the environment primarily as a result of waste incineration and, to a lesser extent, various manufacturing processes, but also through natural combustion processes. Different sources emit different dioxin and furan compounds in certain combinations. These combinations, or source profiles, can then be used to identify the source of the emissions. One such study developed a chemical mass balance model to determine the contribution of different types of sources to sediment levels in the Housatonic River in Connecticut, Lake Huron, and the Baltic Sea. The study found that air particulate matter, coal-fired power plants, municipal incinerators, and pentachlorophenols (from manufacturing) were, in general, the largest sources of dioxins and furans in sediments. The same study reported that coal-burning was the major source of dioxins and furans prior to 1955 in the U.S. and 1970 in Europe, with municipal incinerators dominating after that time (Su and Christensen 1997). These results are similar to recent EPA estimates of national air emissions and sources of dioxin and furan TEQs which indicate that of the 0.0027 tpy of dioxin and furan TEQ air emissions, municipal waste combustion accounts for 47 percent and medical waste incineration accounts for 24.6 percent (Table II-11). A large number of smaller sources also emit dioxins and furans (U.S. EPA 1999a).

Emissions data for the U.S. and Canada were used with NOAA's hybrid single particle Lagrangian integrated trajectory (HYSPLIT)/transfer coefficient (TRANSCO) computer program to analyze dioxin and furan sources and their contributions to atmospheric deposition of dioxins and furans in the Great Lakes. For any given lake, the simulation results indicated that approximately half of the atmospheric deposition of dioxins and furans arose from sources in the immediately surrounding States and provinces, and half arose from the remainder of the U.S. and Canada. Furthermore, the relative contribution of sources by class were ranked, showing that municipal waste incineration, iron sintering, cement kilns burning hazardous waste, and medical waste incineration are responsible for at least 85 percent of the total atmospheric deposition of dioxins and furans to the Great Lakes. This study also

HIGHLIGHTS Dioxins and Furans

- ' **Sources.** The largest sources of dioxin and furan emissions in the U.S. are municipal waste combustion and medical waste incineration. By 2002, controls applied to these sources will reduce their dioxin and furan emissions by 95-99 percent (see Chapter III).
- ' **Loadings.** In the Great Lakes region, sediment accumulation rates indicate a decline in dioxin and furan inputs since the 1970s. The relative atmospheric contribution and sediment accumulation rates of dioxins and furans entering the Great Lakes differs both between and within the lakes. In some lakes, the atmospheric contribution of dioxins and furans is 100 percent, whereas in other lakes, the atmospheric contribution of dioxins and furans is less than 5 percent. In general, the pattern of industrialization around the lakes influences relative contributions and accumulation rates.
- ' **Concentrations in Biota.** In general, long-term monitoring data indicate that dioxin and furan concentrations in biota in many Great Waters have declined over time.

found that sources of dioxins as far away as central Canada may influence deposition of dioxins to the Great Lakes (Cohen et al. 1995).

Table II-11
National Anthropogenic Dioxin and Furan TEQ Air Emissions
(Based on EPA's 1990-1993 National Toxics Inventory)

Source Category	Anthropogenic Air Emissions (tons/year)	Percent Contribution to Total U.S. Anthropogenic Air Emissions
Municipal waste combustion	0.0012	47.0
Medical waste incineration	0.0007	24.6
Secondary aluminum smelting	0.0002	7.2
Utility boilers: coal combustion, all types	0.0001	4.2
Industrial boilers: wood/wood residue combustion	0.00009	3.4
Mobile sources: on-road vehicles	0.00009	3.4
Open burning: wildfires and prescribed burnings	0.00009	3.4
Portland cement, excluding hazardous waste-fired	0.00004	1.5
Residential wood/wood residue combustion	0.00004	1.5
Wood treatment/wood preserving	0.00003	1.1
Others (< 1 percent each) ^a	0.00007	2.6
Total U.S. Anthropogenic Dioxin and Furan TEQ Air Emissions	0.0027 ^b	100 ^b

^a A list of the source categories that contribute less than 1 percent to total U.S. emissions is provided in Appendix B.

^b This value represents anthropogenic dioxin and furan TEQ air emissions in the U.S. only.
Source: U.S. EPA 1999a

Sediment core studies have also been used to determine the relative atmospheric contribution of dioxins and furans. One sediment core study indicates that the relative atmospheric contribution of dioxins and furans differs by lake based on comparisons of pollutant compositions and accumulation rates among cores to estimates of atmospheric deposition (Table II-12). In the Great Lakes region, accumulation rates of dioxins and furans in sediments began to increase in the early 1940s. Maximum accumulation rates were observed in 1970 ± 10 years, and current accumulation rates are 30 to 70 percent of the maximum levels (Pearson et al. 1997a). Current accumulation rates of dioxins and furans in sediments indicate inter- and intra-lake variations. For example, the current dominant source of dioxins and furans in Lake Superior is believed to be the atmosphere because sediment accumulation rates of dioxins and furans are similar to those of lakes in which the atmosphere is the only possible source of dioxins and furans. In southern Lake Michigan near the Chicago urban area, the atmosphere contributes most of the dioxins in the lake, but 65 to 95 percent of furans entering southern Lake Michigan are estimated to be from non-atmospheric sources. In northern Lake Michigan, the analysis of sediment cores indicates that approximately 50 percent of dioxins and greater than 75 percent of furans are from non-atmospheric sources. From 65 to 95 percent of dioxins and greater than 95 percent of the furans

accumulated in Lake Ontario are estimated to be from non-atmospheric sources based on the analysis of sediment cores (Pearson et al. 1998).

Table II-12
Current Rates of Dioxins and Furans Accumulation in Great Lakes Sediments

Location	Number of Sediment Cores Analyzed	Accumulation Rates in Sediment (pg/cm ² /yr)		Percent Contribution from Atmospheric Sources	
		Dioxins ^a	Furans ^a	Dioxins ^a	Furans ^a
Lake Superior	2	7.4 - 8.0	0.8 - 0.9	100	100
Northern Lake Michigan	2	44 - 49	22 - 25	33 - 55	5 - 35
Southern Lake Michigan near Chicago Urban Area	1	17	17	100	5 - 35
Lake Ontario	3	120 - 220	130 - 230	5 - 35	<5

^a Includes the total of all dioxin homologs. Includes the total of all furan homologs.

Source: Pearson et al. 1998

To help explain and understand the inter- and intra-lake variations in loadings and accumulations of dioxins and furans, the HYSPLIT/TRANSCO computer program was used to estimate the amount of dioxin and furan emitted from identified sources to air and water that enter the five Great Lakes (Cohen et al. 1995). The model was run using 1993 source and emissions data from 1,329 identified sources in the U.S. and Canada. As shown in Table II-13, the modeled deposition flux of dioxins and furans increases from Lake Superior, Lake Huron, Lake Michigan, Lake Erie, to Lake Ontario, following the pattern of industrialization around the lakes. In addition, modeled waterborne inputs (i.e., direct discharges) of dioxins and furans to Lake Superior, Lake Michigan, and Lake Huron play a lesser role than air deposition. For Lake Michigan, these relative source findings are different from those found by Pearson et al. (1998) who used a sediment core methodology to estimate relative atmospheric contributions. In Lake Erie and Lake Ontario, the modeled waterborne inputs are uncertain because of the difficulty in quantifying discharges to and from inter-lake channels (Cohen et al. 1995).

Table II-13
Modeled Air Deposition, Depositional Flux, and Waterborne Inputs of Dioxins and Furans to the Great Lakes

Dioxins and Furans	Superior	Huron	Michigan	Erie	Ontario	Total
Atmospheric Deposition (g TEQ/yr)	5.6	8.6	13.7	7.3	6.4	42
(range)	(2-17)	(3-25)	(5-43)	(2-21)	(2-18)	(13-124)
Depositional Flux (µg/km ² /yr)	69	145	238	284	337	172
Waterborne Inputs (g TEQ/yr)	1.4	1.4	1.9	11	>3.9	>19.6
Percent Contribution from Atmospheric Sources	80	86	88	40	~62	~68

Source: Cohen et al. 1995

Biota in many Great Waters are contaminated with dioxins and furans (Firestone et al. 1996, Metcalfe et al. 1997a, 1997b, Wade et al. 1997b). Recent studies of contamination of biota in the Great Waters implicate non-atmospheric sources of dioxins (Firestone et al. 1996, Wade et al. 1997b) and furans (Wade et al. 1997b); however, the relative importance of atmospheric sources and non-atmospheric sources remains unclear. In many instances, long-term monitoring indicates that concentrations of dioxins and furans have declined over time. For example, the U.S. Food and Drug Administration monitored the presence of dioxin in the edible portions of fish and shellfish from major U.S. waterways from 1979 to 1994, and the analytical results indicate that levels in aquatic species from most waterways are declining steadily (Firestone et al. 1996). In several locations (e.g., Chesapeake Bay, Delaware Bay, Gulf of Mexico, and Galveston Bay), no dioxin was found in fish samples taken between 1987 and 1994. In addition, Huestis et al. (1997) reported that levels of dioxins and furans in Lake Ontario trout collected from 1977 to 1993 have declined substantially, although most chemical levels appear to have reached a steady state or are declining more slowly now.

Polycyclic Organic Matter

Polycyclic organic matter (POM²), like dioxins and furans, is a byproduct of fossil fuel combustion and natural combustion processes (e.g., forest fires), and consists of a group of compounds with similar chemical structures. The POM compounds are emitted in distinct patterns from various source types, allowing the identification of emission sources from emission “fingerprints” (or patterns) in contaminated sediments. Within this class of POM are the polycyclic aromatic hydrocarbons (PAHs). In most cases, human-made sources of PAHs account for the majority of PAHs released to the environment (Simcik et al. 1996). These compounds are usually the POMs of concern as many PAHs are known or suspected human carcinogens. Therefore, the discussion of POMs focuses on PAHs.

There is not one standard convention to measure and express emissions and quantities of POM. Multiple conventions have been developed because of the differences in the health effects of the variety of POM and PAH compounds. Some of the measures that are used include 16-PAH (i.e., the 16 PAH compounds that can be measured using EPA test method 610), 7-PAH (i.e., the seven PAH compounds that are probable carcinogens), or extractable organic matter (EOM) (i.e., the solvent

HIGHLIGHTS Polycyclic Organic Matter

- ' **Sources.** Nationally, the largest source of PAHs is consumer products usage, along with many smaller emission sources. Studies in the Great Lakes region also indicate that vehicular emissions, coal-fired power plants, and coke and steel production are large sources of PAH emissions. Note that multiple conventions are used to report POM and PAH quantities because of the differences in health effects of the variety of POM and PAH compounds.
- ' **Loadings.** In general, PAH deposition levels follow the pattern of population density and urbanization. In the Great Lakes region, maximum sediment accumulation levels of PAHs occurred between 1950 and 1975, after which accumulation levels declined. Data from recent years in the region, however, do not indicate a clear trend. In the Chesapeake Bay, data indicate that total loadings for several PAH compounds decreased in recent years, but data collection methodologies were altered over the same time period, making it difficult to assess the true trend.
- ' **Environmental Concentrations.** Concentrations of PAHs in the sediments of tributaries and mainstem of the Chesapeake Bay are below the aquatic biota probable effects level (PEL), but are above the no observed effect level (NOEL) for aquatic biota in the northern bay. In the tributaries, PAH sediment concentrations declined substantially between 1987 and 1991.

² The abbreviation, POM, is also used by ecologists, limnologists, and oceanographers for Particulate Organic Matter.

extractable portion of organic matter). These conventions, however, are not necessarily followed by independent researchers and thus are not always used in this report.

Based on EPA's 1990-1993 national inventory of air emissions, the dominant 16-PAH emission source is consumer products usage (e.g., metal cleaning, solvents, household cleaning products, and personal care products), along with many other smaller emission sources (Table II-14) (U.S. EPA 1999a).

Table II-14
National Anthropogenic 16-PAH Air Emissions
(Based on EPA's 1990-1993 National Toxics Inventory)

Source Category	Anthropogenic Air Emissions (tons/year)	Percent Contribution to Total U.S. Anthropogenic Air Emissions
Consumer products usage	5,733	33.2
Open burning: wildfires and prescribed burnings	2,540	14.7
Aerospace industry (surface coating)	1,697	9.8
Petroleum refining: other sources not distinctly listed	783	4.5
Primary aluminum production (from ESD)	662	3.8
Pulp and paper: kraft recovery furnaces	649	3.8
Coke ovens: charging, topside, & door leaks	538	3.1
Coke ovens: pushing, quenching, and battery stacks	517	3.0
MON - continuous processes	440	2.5
Gasoline distribution stage II	374	2.2
Gasoline distribution stage I	355	2.1
Petroleum refining: catalytic cracking units	313	1.8
Open burning: scrap tires	294	1.7
Industrial Organic chemicals manufacturing	227	1.3
Pulp and paper: lime kilns	183	1.1
Others (< 1 percent each) ^a	1,967	11.4
Total U.S. Anthropogenic 16-PAH Air Emissions	17,271^b	100^b

^a A list of the source categories that contribute less than 1 percent to total U.S. emissions is provided in Appendix B.

^b This value represents anthropogenic 16-PAH air emissions in the U.S. only.

Source: U.S. EPA 1999a

In the Great Lakes and other waterbodies, several researchers analyzed sediment cores to identify spatial and temporal trends in PAH deposition and sources, as discussed below. Researchers estimated relative contaminant contributions from specific local human-made sources (e.g., smelters, coke ovens) along with regional sources (e.g., fuel oil combustion, wood burning). In general, recent sediment core

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studies show regional deposition from oil and wood burning sources with significant contributions from local sources in industrialized areas.

In Lake Michigan sediments, PAHs originate primarily from vehicular emissions; wood, oil, and natural gas burning for home heating; coal-fired power plants; and, coke and steel production. A study by Simcik et al. (1996) that focused on the urban complex of Chicago, Illinois and Gary, Indiana concluded that the dominant source of PAHs to the entire lake from around 1900 to the present is emissions from coke and steel production. This conclusion differs from that of Karls and Christensen (1998) who found a regional historical pattern in central Lake Michigan, with a significant contribution from wood-burning and an increasing dominance of oil-burning sources (as opposed to coal-burning by coke and steel production), which is consistent with U.S. fuel consumption data. Karls and Christensen also found that PAH loadings at Green Bay, the Fox River, and the Kinnickinnic River were strongly influenced by local industrial activities, primarily coke production at the Milwaukee Solvay Coke Company which operated from 1900 to the 1970s. These differing conclusions support the finding that local urban sources of PAHs are different and often play a larger role in deposition and sediment accumulation than regional sources.

Other studies also indicate that urban sources largely influence PAH deposition. For instance, recent sediment layers in the Milwaukee Harbor area indicate that in urban areas, highway dust can be a significant source of PAHs from emissions of gasoline engine exhaust tar (Christensen et al. 1997). In a carbon particle sediment core study, the relative abundance of oil particles in sediments increased in recent years and is explained by an increase in automobile traffic (Karls and Christensen 1998). Sharma et al. (1997) found that source contributions of PAHs to the St. Mary's River (which connects Lake Superior and Lake Huron) were strongly influenced by traffic density and urban storm water runoff from impervious street surfaces.

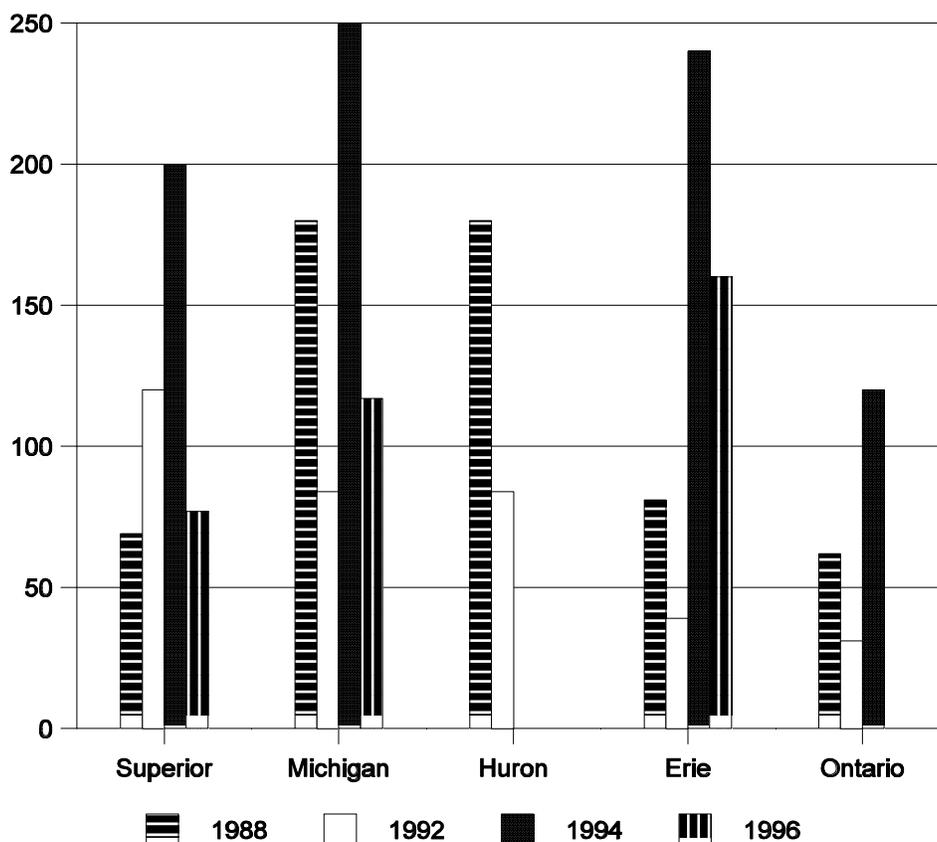
These recent findings for PAHs follow the pattern that was illustrated for several other pollutants of concern:

- C Local point sources and regional sources both play a role in the deposition of pollutants to waterbodies;
- C Urban areas play a strong role whether through the proximity of industrialized areas to waterbodies or through urban runoff; and,
- C The relative contribution to pollutant loadings by different types of emission sources shifts over time depending on industrial activities, pollution controls, and other factors such as trends in fuel use.

Lake Michigan sediment cores show that PAH accumulation began between 1880-1900, consistent with increased PAH emissions from coal combustion during industrialization. Maximum PAH accumulation occurred between 1950-1975 (Simcik et al. 1996). Karls and Christensen (1998) found similar results. Maximum accumulation rates were lower in the southern basin near the Chicago urban area (70 ng/cm²/yr) than in the northern basin (100-150 ng/cm²/yr) because of the south to north transport of sediment-bound PAHs. One study observed a slight decrease in PAH sediment accumulation rates in recent years in some cases due to a switch from coal to oil and natural gas and because of industrial emissions controls (Simcik et al. 1996). In contrast, recent deposition monitoring data from the IADN program do not indicate any clear trend in total atmospheric loadings of PAHs, as indicated by data for benzo[a]pyrene (B[a]P), to the Great Lakes from 1988 to 1996 (Figure II-7). Trends in PAH deposition

levels, in general, are difficult to discern because of (1) the degree of uncertainty in loading calculations and (2) the fluctuations in ambient air concentrations (U.S. EPA 1998l).

Figure II-7
IADN Loading Estimates of B(a)P to the Great Lakes (kg/year)
(U.S. EPA 1998i)



As part of the Lake Michigan Mass Balance Study (LMMBS) and the Atmospheric Exchange Over Lakes and Ocean Surfaces (AEOLOS) study, which examine the influence of urban air emissions on deposition to the Great Waters, Franz et al. (1998) found that dry deposition of PAHs to Lake Michigan contributes approximately 5,000 kg/year. Wet deposition estimates from previous studies are lower at approximately 1,600 kg/year. Franz et al. (1998) also found that dry deposition of PAHs is higher in Chicago than 15 km offshore and at rural sites because of (1) the greater degree of anthropogenic activity within the Chicago area, and (2) the greater atmospheric burden and subsequent deposition of large particles generated within that area. These findings are consistent with the hypothesis that larger particles are generated in urban areas and are deposited closer to the sources than smaller particles.

In the Massachusetts Bay, as in other regions, the sum of wet and dry deposition of PAHs is greater at monitoring sites in urban areas (i.e., closer to Boston and Logan Airport) than at monitoring sites in rural areas (i.e., Truro), with the exception of biphenyl and naphthalenes (Table II-15). Biphenyl and naphthalenes may be more likely to deposit at the rural site because these pollutants are more water soluble and, therefore, may be deposited as wet deposition from clouds carrying biphenyl and naphthalenes from other geographic areas. Deposition of PAHs in this region is highest in the winter, possibly due to increased use of fossil fuels during winter for residential and commercial heating and

wood burning in stoves and fireplaces, or due to the lower mixing heights in the atmosphere which occur during winter in North America (Golomb et al. 1997b).

Table II-15
Sum of Wet and Dry Deposition of PAHs onto Massachusetts Bay ($\mu\text{g}/\text{m}^2/\text{year}$)

PAH	Urban	Rural
Acenaphthene	5.0	1.8
Acenaphthylene	5.2	3.3
Anthracene	9.5	3.7
Benzo[ghi]perylene	29.2	4.1
Biphenyl	4.3	7.7
Chrysenes	98.8	9.9
Dibenzothiophenes	34.8	13.2
Fluoranthene	129.0	23.9
Fluorenes	50.0	23.0
Naphthalenes	206.6	240.0
Perylene	11.5	3.2
Phenanthrenes	215.1	41.9
Pyrenes	97.8	16.9

Source: Golomb et al. 1997b

In the Chesapeake Bay, estimates from one study of total inputs and atmospheric inputs of PAHs indicate that direct atmospheric deposition to the tidal waters of the Chesapeake Bay range from 30 percent to 56 percent (Table II-16). Estimates of the relative atmospheric contribution for benzo[a]anthracene and chrysene may be slightly high because estimates were not provided for point sources of benzo[a]anthracene and non-tidal watershed inputs for chrysene. Highest loadings occur in the West Chesapeake and Potomac regions. Intermediate loadings occur in the James and Patuxent regions, and lowest loadings occur in the Rappahannock, York, and eastern shore regions (Eskin et al. 1996). Annual net inputs (in terms of atmospheric deposition processes and the largest source of riverine inputs) of nine PAH compounds to the Chesapeake Bay are provided in Table II-17 based on sampling and analysis of surface water and air. In general, gas phase absorption (i.e., absorption of pollutants in the gas phase in the atmosphere by the water surface) of PAHs is higher than estimates of wet and dry deposition loadings; however, wet and dry deposition become more important loading factors for higher molecular weight PAHs (Nelson et al. 1998).

In contrast, the analysis of CBADS monitoring data in the Chesapeake Bay Program's 1999 *Toxics Loading Release and Inventory* (TLRI) provides additional and more recent information on total inputs and relative atmospheric deposition inputs of PAHs (including benzo[a]pyrene, chrysene, phenanthrene, and pyrene) to the tidal and non-tidal portions of the Chesapeake Bay (see Figure II-6 for the delineation of the tidal and non-tidal waters in the Chesapeake Bay watershed). Total inputs to the tidal waters of the Chesapeake Bay of benzo[a]pyrene, chrysene, phenanthrene, and pyrene are estimated to be 29,000 kg/year, 29,000 kg/year, 59,000 kg/year, and 40,000 kg/year, respectively. Total atmospheric deposition (wet, dry, and gas exchange) ranges from < 0.5 percent (35 kg/year) for

benzo[a]pyrene to 5 percent (2,900 kg/year) for phenanthrene. Inputs of PAHs from the non-tidal watershed account for less than 3 percent of the total PAH inputs to the Chesapeake Bay (Chesapeake Bay Program 1999a).

Table II-16
Estimates of PAH Inputs to the Chesapeake Bay (kg/year)

PAH	Total Inputs to Chesapeake Bay	Direct Atmospheric Deposition to Tidal Waters	Direct Atmospheric Deposition to Tidal Waters as Percent of Total Inputs
Benzo[a]anthracene	380	130	34
Benzo[a]pyrene	430	130	30
Chrysene	570	320	56
Fluoranthene	1,300	640	49
Naphthalene	1,500	NE	NE

NE = no estimate
Source: Eskin et al. 1996

Table II-17
Annual PAH Inputs to and Losses from the Chesapeake Bay

PAH	Annual Inputs and Losses (kg/year)			
	Susquehanna River ^a	Wet deposition	Dry aerosol deposition ^b	Net gas deposition (or volatilization) ^c
Fluorene	122	16	12	379
Phenanthrene	450	63	92	2875
Anthracene	NA	6	6	130
2-Methylphenanthrene	NA	NA	NA	702
1-Methylphenanthrene	NA	NA	NA	280
Fluoranthene	1130	70	120	679
Pyrenes	1030	75	109	361
Benz[a]anthracene	376	9	34	(4.6)
Chrysene	330	29	85	29

^a The Susquehanna River is the largest source of freshwater to the Chesapeake Bay.

^b Calculated from measured ambient aerosol particle contaminant concentrations and annual average dry aerosol deposition velocity of 0.49 cm/s.

^c Values in parentheses represent net volatilization from rather than net deposition to the waterbody.

Source: Nelson et al. 1998

In a study to quantify the gaseous exchange fluxes across the air-water interface at rural, semi-urban, urban, and industrialized sites of the southern Chesapeake Bay, researchers found that aerosol particle-associated PAH concentrations measured in the atmosphere were similar at the four sites and PAH gas-phase concentrations measured in the atmosphere were as much as 50 times greater at the urban site than at the rural site. Furthermore, at the rural site (Haven Beach, VA), PAH gas-phase

concentrations in the atmosphere are decreasing with time. Specifically, in 1991, the PAH gas-phase concentration was 6,203 pg/m³ whereas in 1994-1995, PAH gas-phase concentrations were only 4,550 pg/m³. This study also analyzed seasonal variations and did not find any seasonal variations in PAH gas-phase concentrations at this site. At the non-rural sites, an exponential increase in PAH gas-phase concentrations was observed with temperature increases, indicating that PAHs volatilize from contaminated surfaces near these sites in warmer weather (Gustafson and Dickhut 1997).

In a sediment contamination study of the Chesapeake Bay and its tributaries from 1984 to 1991 by Eskin et al. (1996), PAHs were most concentrated in sediments of the northern bay between Turkey Point and the mouth of the Middle River, just north of Baltimore. Maximum PAH concentrations in sediments (14,854 ppm) at all locations in the bay were below the aquatic biota PEL for total PAHs of 28,000 ppm. However, maximum concentrations exceeded the NOEL of 2,900 ppm for aquatic biota over much of the northern bay north of Annapolis. In the Chesapeake Bay tributaries, PAHs were most abundant in sediments of the western, northwestern, and northeastern tributaries. The highest concentrations were located in the Sassafraz River. However, concentrations in sediments in tributaries declined dramatically between 1987 and 1991. Median PAH sediment concentrations in tributaries rarely exceeded aquatic biota NOELs and never exceeded aquatic biota PELs. Thus, toxic effects from PAH sediment contamination are possible in the northern part of the mainstem bay, but are not likely in the tributaries.

NITROGEN AND COMPOUNDS

Nitrogen is an ubiquitous element in the natural environment and is essential to all forms of life. It is a component of protein and genetic material and plays a key role in photosynthesis. Nitrogen cycles through all terrestrial and aquatic ecosystems and in many systems is a primary factor determining the nature, diversity, and productivity of the ecosystems. Diatomic nitrogen gas (N₂), an inert, largely biologically inactive gas, comprises almost 78 percent of the earth's atmosphere. Despite the presence and essential nature of nitrogen throughout the natural environment, excessive levels of certain nitrogen compounds in the atmosphere, deposited to surface media or introduced to aquatic systems, can be detrimental to terrestrial and aquatic habitats and potentially to human health.

Nitrogen compounds are released to the atmosphere from a variety of sources, both natural and anthropogenic. Nitrogen compounds can be present in the atmosphere in a variety of inorganic and organic forms, in gaseous, liquid, or solid (particulate) states. Table II-18 identifies the most common forms of atmospheric nitrogen and summarizes their key sources and properties. As this table indicates, the most important forms of atmospheric nitrogen from the standpoint of atmospheric deposition and loadings to surface waters include the following.

- C *Nitric Oxide and Nitrogen Dioxide (NO and NO₂, or collectively NO_x)*. Nitrogen oxide compounds are the key forms of anthropogenic nitrogen released to the atmosphere and are precursors to the formation of nitrogen compounds that are ultimately deposited to the Great Waters. Most of the nitrogen emitted to the air from anthropogenic sources is in the form of NO_x primarily NO. Once released to the atmosphere, NO_x is transformed through a variety of complex photochemical reactions to oxidized nitrogen compounds and, ultimately, aerosol nitrate and nitric acid. These end products are deposited to the surface and impact surface waters. Nitrogen oxide also is a catalyst in the formation of ozone.

C *Nitric acid (HNO₃), Aerosol Nitrate (NO₃), Ammonia and Ammonium (NH₃ and NH₄⁺, or collectively NH_x), and Organic Nitrogen Compounds.* These are the nitrogen compounds that are deposited from the atmosphere to surface media and impact surface waters. Reduced nitrogen compounds (NH_x) compounds (e.g., ammonia, ammonium) also account for a significant portion of nitrogen emissions from anthropogenic (as well as biogenic) sources.

Discussions of atmospheric nitrogen emissions, deposition, and effects in this report focus on these compounds. In particular, the term “atmospheric nitrogen” hereafter refers to these compounds and excludes N₂, the inert, natural component of the earth’s atmosphere.

Nitrogen Emissions and Atmospheric Transport

In the natural environment, diatomic nitrogen gas (N₂) is converted to biologically available forms of nitrogen (e.g., NO_x, ammonium compounds) through nitrogen fixation processes such as lightning and biological fixation. Nitrogen emissions from lightning have been estimated at less than 10 million metric tons per year. Releases of fixed nitrogen from marine ecosystems are less certain and range from less than 30 to greater than 300 million metric tons per year. Nitrogen fixation in terrestrial ecosystems, prior to human influences, ranged from 90 to 140 million metric tons per year; however, these emission levels have increased due to human alterations to the nitrogen cycle (Vitousek et al. 1997).

Of the various forms of nitrogen emitted to the atmosphere through anthropogenic activities, only NO_x emissions have been quantified adequately to allow evaluation of nationwide emissions trends. Nationwide emissions of NO_x generally reflect trends in population, economic activity, and industrialization for most of this century. Nitrogen oxide emissions steadily increased in the first three decades of the century, but declined in the 1930s due to the lower economic activity during the Great Depression. With the start of World War II, NO_x emissions nationwide began a rapid upward trend that continued well into the 1970s. Between 1940 and 1970, total nationwide NO_x emissions increased by a factor of three, from 6.5 million to 19 million metric tons per year (U.S. EPA 1997f, U.S. EPA 1997h).

HIGHLIGHTS Nitrogen Compounds

' **Sources.** Sources of anthropogenic nitrogen emissions to air include on-road vehicles, fuel combustion for electricity generation, farm animal wastes, non-road vehicles and engines, fuel combustion by industry, fertilizer application, biomass burning, and miscellaneous other minor sources. Anthropogenic nitrogen oxide (NO_x) emissions rose rapidly through the late 1970s. Nitrogen oxide emissions have leveled off since around 1980, mainly due to controls under the CAA. Nationwide trends in emissions of other compounds cannot be determined with available data.

' **Loadings.** The rate of anthropogenic nitrogen compound deposition from the air to the Great Waters rose through the late 1970s, but has leveled off since around 1980. Trends in atmospheric deposition nitrogen (ADN) loading to the Great Waters are uncertain, but have probably been static for the past two decades. ADN loadings to various Great Waters along the east coast account for roughly 10 percent to 40 percent of total nitrogen loadings.

' **Human and Ecological Effects.** The effects of ADN on the Great Waters is indistinguishable from the effects of nitrogen from other sources. Anthropogenic nitrogen loads to the Great Waters are currently many times natural rates. Mechanisms for eliminating or assimilating nitrogen are overwhelmed in many waterbodies, leading to nitrogen buildup. Effects of excess nitrogen include algal blooms, eutrophication, anoxia, loss of species diversity, and fundamental changes to ecosystem structure. These effects are observed with increasing frequency and extent in many of the Great Waters of the east and Gulf coasts. In sufficient concentrations, some nitrogen compounds have toxic effects on humans. However, nitrogen compounds generally do not cause exceedances of drinking water standards in the Great Waters.

**Table II-18
Common Forms of Atmospheric Nitrogen**

Compound	Notation	Sources	State in the Atmosphere	Effects
<i>Inert Compounds</i>				
Diatomic nitrogen gas	N ₂	Comprises approximately 78 percent of the earth's atmosphere	Gaseous	Inert; no direct effects. Converted to other compounds through certain biological and physical processes
Nitrous oxide	N ₂ O	Wide variety of natural sources, fertilizer production and use, fossil fuel combustion, industrial acid production, microbial denitrification in soil and water	Gaseous	Not reactive in lower atmosphere; potent greenhouse gas, 320 times as effective as CO ₂ in trapping heat in the atmosphere
<i>Oxidized Compounds</i>				
Nitric oxide	NO	Natural soil emissions, lightning, combustion processes with temperatures greater than 2200 EC	Gaseous	Precursor in the formation of NO ₂ , nitrates, nitric acid, and ozone in the atmosphere, and to NO ₂ , nitrate, and nitric acid deposition
Nitrogen dioxide	NO ₂	Combustion processes with temperatures greater than 2200 EC, atmospheric oxidation of NO	Gaseous	Highly reactive; a variety of acute and chronic human health effects; precursor or catalyst in the formation of nitrates, nitric acid, and ozone in the atmosphere; deposits slowly to surface media; precursor to nitrate and nitric acid deposition
Aerosol nitrate	NO ₃	Photochemical oxidation of NO _x (i.e., NO and NO ₂) in the atmosphere; combustion processes. Partitioning of HNO ₃ to the aerosol phase by ammonia gas in the atmosphere; microbial oxidation of ammonium in soil and water	Fine particles, dissolved in precipitation	Possible mutagen; variety of adverse health effects associated with fine particles; deposits to surface media. Excess NO ₃ in drinking water has adverse health effects, including methyoglobinemia in infants. Potent nutrient stimulant of plant growth, contributing to eutrophication in waterbodies
Nitric acid	HNO ₃	Photochemical oxidation of NO _x in the atmosphere.	Vapor, liquid aerosol, dissolved in precipitation	Deposits quickly to surface; is the source of most oxidized nitrogen deposited to the surface; causes surface water acidification, property damage; detrimental to aquatic biota and ecological systems. Contributes to NO ₃ concentrations and related health effects in drinking water. Potent nutrient stimulant of plant growth, contributing to eutrophication in waterbodies

Compound	Notation	Sources	State in the Atmosphere	Effects
Other oxides of nitrogen	PAN, N ₂ O ₅ , others	Intermediate reservoir products in atmospheric chemical reactions forming HNO ₃ from NO _x	Gaseous	Eye irritant; possible mutagen; precursor or catalysts in formation of ozone; PAN is an important oxidant in the atmosphere and a component of photochemical smog
<i>Reduced Compounds (NH_x)</i>				
Ammonia	NH ₃	Volatilization from animal wastes; natural microbial decomposition of organic matter in oceans and soils; manufacture and application of fertilizers; hydrolysis of urea in fertilized soils; biomass and fossil fuel combustion	Gaseous, vapor, dissolved in precipitation	Highly reactive; reacts to form NH ₄ ⁺ , establishing an NH ₄ ⁺ /NH ₃ equilibrium in the atmosphere. Deposits to the surface; potent nutrient stimulant of plant growth, contributing to eutrophication in waterbodies
Ammonium	NH ₄ ⁺	Formed in the atmosphere from reaction of NH ₃ with atmospheric acids such as H ₂ SO ₄ and SO ₄ , microbial transformation of organic nitrogen, microbial fixation in soil and water	Particulate, dissolved in precipitation	Can be transported long distances; ultimately deposits to the surface; with NH ₃ contributes as much as 20-40 percent of atmospheric nitrogen deposition to coastal waters. Potent nutrient stimulant of plant growth, contributing to eutrophication in waterbodies.
<i>Organic Compounds</i>				
A wide variety of compounds of unknown composition, believed to include urea, pollen and, amino acids	Various, mostly unknown	Primarily released from biological processes; also released from anthropogenic processes and formed in the atmosphere from chemical and photochemical reactions of NO _x , hydrocarbons, and O ₃	Various	Comprises 10-30 percent of atmospheric nitrogen wet deposition to coastal waters; contributes to eutrophication in surface waters

The 1970 CAA introduced significant regulation of NO_x emissions. Various programs and rules under the CAA regulate specific sources of NO_x air emissions (a more detailed discussion of programs affecting NO_x emissions is presented in Chapter III). Nationwide NO_x emissions continued to increase and reached a peak in 1978, but declined slightly in 1979 and 1980 as more and more CAA NO_x programs began to take effect. Since 1980, the effects of increasing economic activity and the effects of increasingly comprehensive regulation of NO_x have roughly balanced out, and NO_x emissions have been relatively constant.

Figure II-8 shows the trend in national NO_x emission rates from 1985 to 1996. As this figure indicates, nationwide NO_x emissions have fluctuated around 21 to 23 million metric tons per year throughout this period. Nationwide NO_x emissions in 1996 were 21.2 million metric tons (U.S. EPA 1997g). Figure II-9 presents 1996 NO_x emissions by State (U.S. EPA 1997f).

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Figure II-10 presents relative NO_x emissions from principal anthropogenic sources in 1996 on a nationwide basis (U.S. EPA 1997f). The “all other” category includes miscellaneous minor sources such as chemical and allied product manufacturing, storage, and transport; metals processing; petroleum and related industrial processing; solvent utilization; other industrial processes; and, waste disposal and recycling.

Reduced nitrogen (ammonium) compounds are also released from anthropogenic sources at rates approaching those for NO_x in some areas. Relative contributions of various anthropogenic nitrogen sources to atmospheric nitrogen and nitrogen deposition vary from region to region depending on the predominant economic activities of each region. Both North Carolina and the Chesapeake Bay region, for example, have relatively high concentrations of animal farming operations, a key source of ammonium compound emissions. For example, Aneja et al. (1998) determined that anthropogenic emissions of ammonium compounds account for over 40 percent of anthropogenic nitrogen releases to air in North Carolina (Figure II-11). Similarly, Fisher and Oppenheimer (1991) found that ammonia and ammonium primarily released from crop and animal farming operations contributes 20 to 40 percent of total atmospheric deposition nitrogen (ADN) to the Chesapeake Bay. However, additional research is needed to better quantify ammonia and ammonium emissions to the environment. The EPA is collaborating with the U.S. Department of Agriculture (USDA) and academia to develop emission factors for various practices and to better model transport and deposition.

A recent monitoring study of wet deposition of nitrogen in the Chesapeake Bay used stable isotope analysis to identify sources. Results of the study indicate some seasonal trends. For example, in the spring, a peak in ammonium was observed as a result of agricultural emissions, including fertilizers, soil, animal excreta from the southwest and west regions of the bay. An observed peak in nitrate in the spring indicates greater soil emission rates during the spring; however, the dominant source of nitrate in the region is probably fossil fuel combustion primarily from the northwest and west regions of the bay. No seasonal trend was observed for dissolved organic nitrogen, but it is likely that it originates from sources similar to nitrate sources (Russell et al. 1998).

Once emitted to the atmosphere, nitrogen compounds (particularly NO_x) can travel great distances – 600 to 800 kilometers or farther from the point of emission to the point of deposition (Dennis 1997). The airsheds of the Great Waters for nitrogen compounds (defined as the geographic region from which atmospheric nitrogen deposited to the Great Waters originates) are, therefore, extensive and collectively encompass much of the U.S. as well as parts of neighboring countries. Using the Regional Atmospheric Deposition Model (RADM), Dennis (1997) determined that the NO_x airshed for the Chesapeake Bay watershed encompasses roughly 900,000 square kilometers, including all or part of 15 States and two Canadian provinces, extending into Indiana to the west, South Carolina to the south, and Quebec to the north. Using the same methodology, Dennis recently conducted a more refined analysis and revised the estimate of the Chesapeake Bay airshed upward to 1,081,600 square kilometers (see Figure IV-2). Thus, nitrogen emitted to the atmosphere several States away can be deposited to the watersheds of the Great Waters and to the waterbodies themselves.

Figure II-8
National NO_x Emission Trends, 1985-1996
(U.S. EPA 1997f)

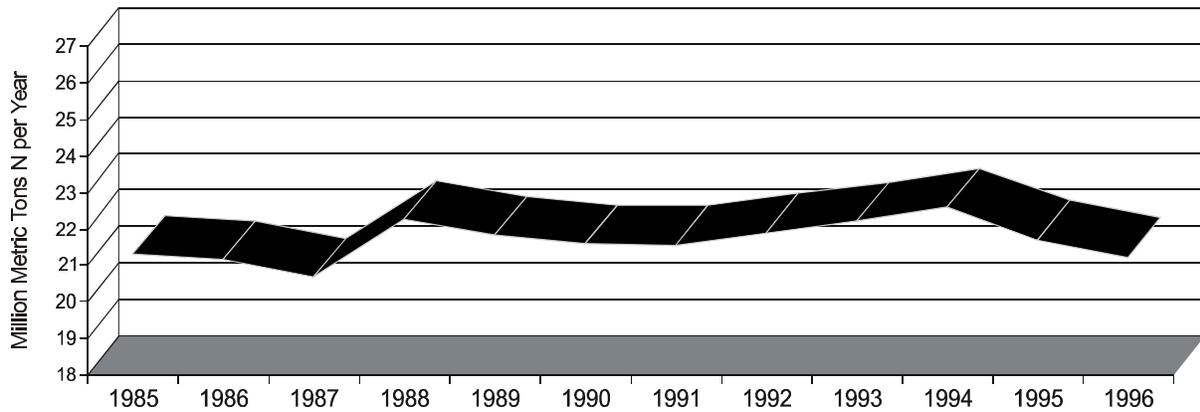


Figure II-10
1996 National Anthropogenic NO_x Emissions by Principal Source Category
(U.S. EPA 1997f)

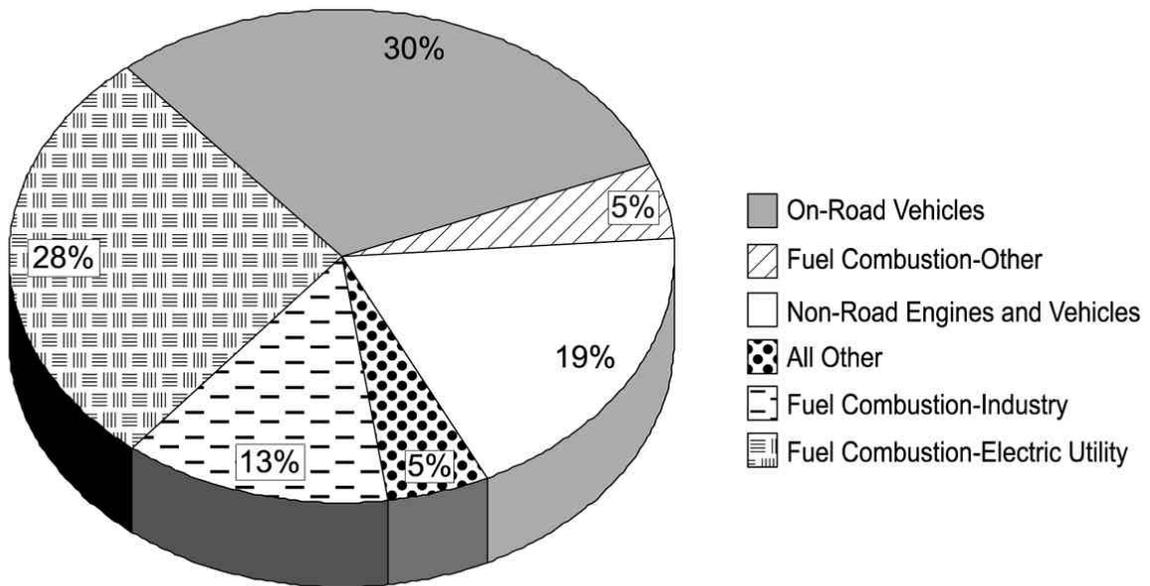
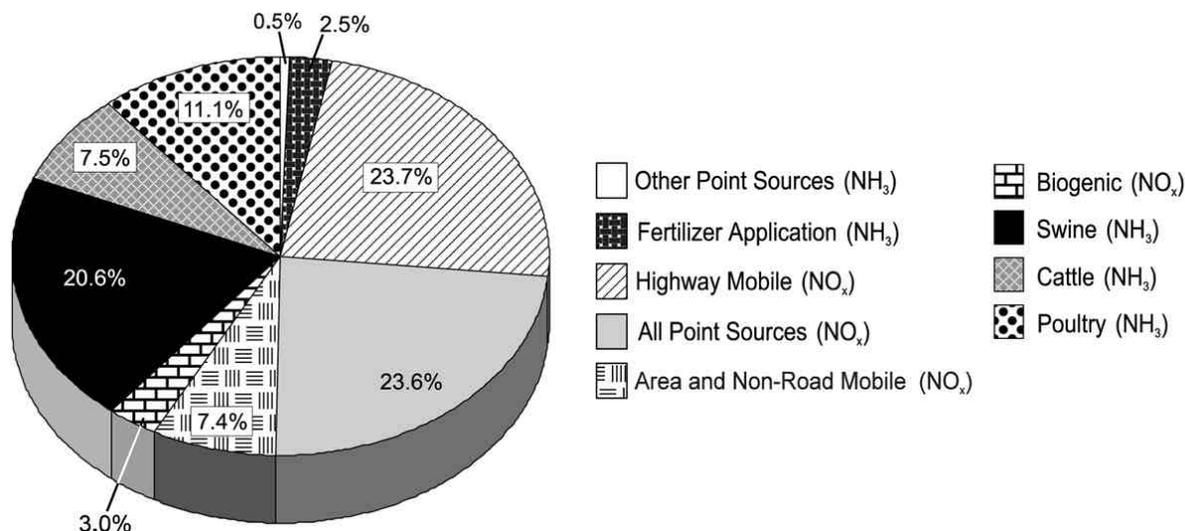


Figure II-11
Estimated Nitrogen Emissions to Air by Principal Source Category
in North Carolina – Anthropogenic and Biogenic
(Aneja et al. 1998)



Nitrogen Deposition in the U.S.

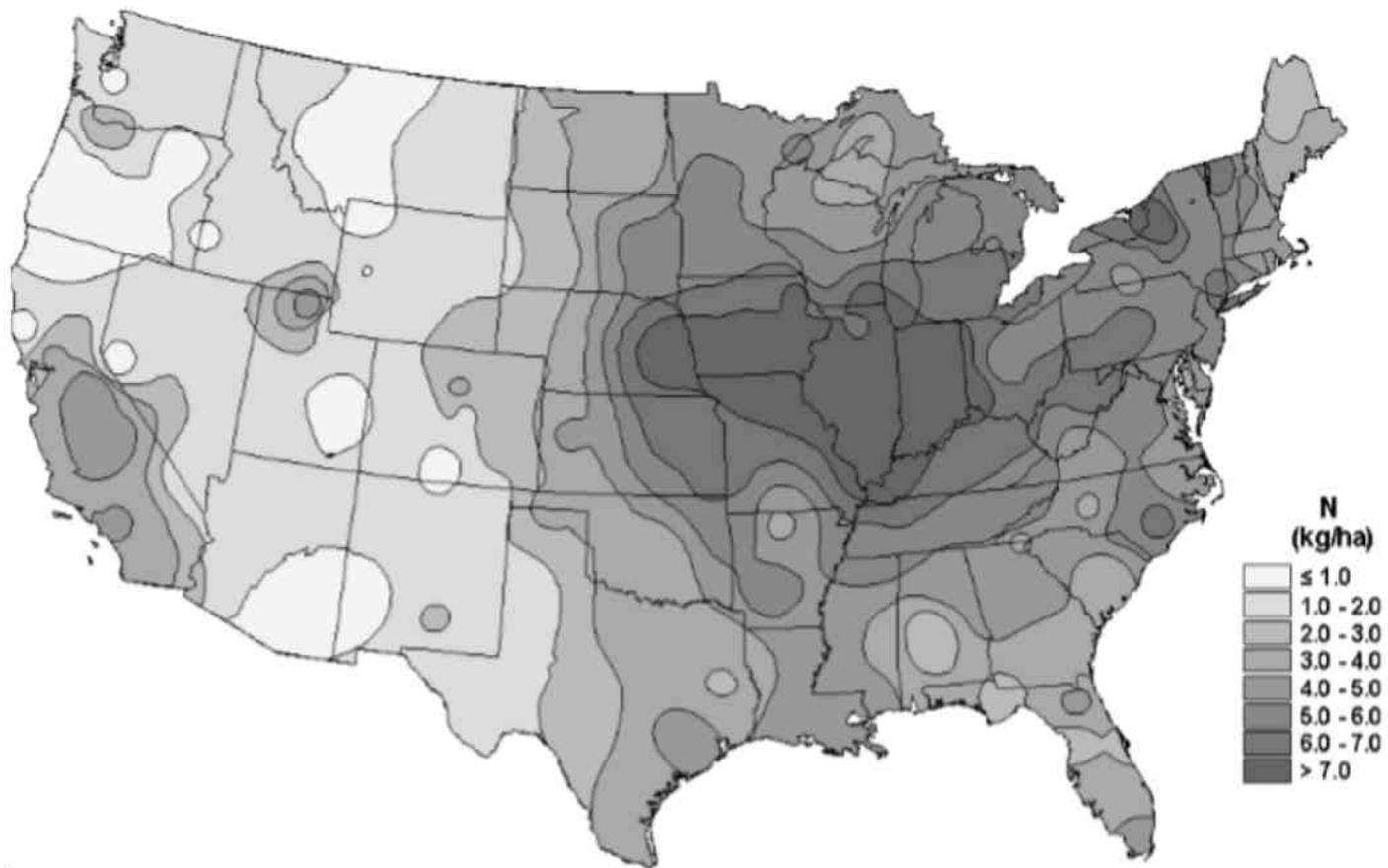
Nitrogen compounds are deposited to surface media by dry and wet deposition. Rates and trends of inorganic nitrogen wet deposition to the Great Waters can be evaluated based on data developed by the National Atmospheric Deposition Program (NADP) National Trends Network (NADP/NTN), which monitors wet deposition rates for ammonium (NH₄⁺) and nitrate (NO₃) at approximately 200 monitoring stations across the country. The network provides weekly and annual deposition rates for these two nitrogen compounds (in terms of kg/ha as the ions) and for total inorganic nitrogen (in terms of kg/ha as N).³

The NADP/NTN has monitoring sites within the watersheds of most of the Great Waters, providing measurements of nitrogen wet deposition to at least portions of the watersheds. Data from monitoring points nearest the Great Waters can be extrapolated to estimate regional nitrogen wet deposition to the Great Waters and their watersheds. While this approach involves increasing uncertainty with increasing distance between monitoring sites and waterbodies, it nevertheless is currently the best available approach for evaluating the trends in inorganic nitrogen wet deposition to the Great Waters.

Figure II-12 presents rates of inorganic nitrogen wet deposition from the atmosphere as measured at the NADP monitoring sites nationwide for 1997. Data from individual monitoring points have been extrapolated in this figure to obtain isopleths for inorganic nitrogen wet deposition rates nationwide (including the Great Waters). These data indicate that inorganic nitrogen wet deposition ranged from lows of 0.1 kg/ha/yr in Alaska and 0.2 kg/ha/yr in Oregon to a high of 9.6 kg/ha/yr in upstate New York.

³ Total inorganic N is calculated based on the sum of ammonium and nitrate nitrogen (Personal Communication with Van C. Bowersox, NADP Coordinator, 12/9/98).

Figure II-12
 Estimated Inorganic Nitrogen Wet Deposition, 1997
 (NADP/NTN 1998a)



Adapted from <http://nadp.sws.uiuc.edu>.

The NADP monitoring data suggest that the rates of inorganic nitrogen wet deposition to many of the Great Waters watersheds have been relatively constant for the past two decades. Figures II-13, II-14, and II-15 present the average rates of nitrogen wet deposition within the watersheds of three of the Great Waters, from 1980 through 1997.³ Year-to-year patterns vary among watersheds, but all three watersheds exhibit a similar trend – relatively constant rates of nitrogen wet deposition over this period. Data from other sources suggest that deposition trends vary locally, however. Deposition of NH_x has increased since 1980 in areas downwind of intensive livestock operations (Paerl 1999), and annual atmospheric deposition of NO_3 , NH_x , and total inorganic nitrogen measured at the NADP site nearest to Tampa and Sarasota Bays has increased significantly in the past decade. The increase in nitrogen atmospheric deposition near Tampa and Sarasota bays is correlated with increases in population in the region over the same time period (Dixon et al. 1996).

As with all dry deposition processes, nitrogen dry deposition is extremely difficult and expensive to monitor directly, and no programs currently do this. The lack of a reliable approach for quantifying dry deposition remains a significant gap in the understanding of nitrogen deposition processes and effects. Dry deposition can be inferred based on the nitrogen content of atmospheric gases and particles and computed deposition rates. Two networks are using this approach: NOAA's Atmospheric Integrated Research Monitoring Network (AIRMoN-dry) and the EPA-sponsored Clean Air Status and Trends Network (CASTNet). However, extrapolation of inferred nitrogen dry deposition values to surrounding areas is unreliable (Hicks 1998, Dennis 1999) and is still under investigation. In the absence of measured nitrogen dry deposition rates, many investigators have attempted to estimate dry deposition based on a ratio of dry deposition to wet deposition. A 1:1 ratio is most commonly derived (Hinga et al. 1991, Valiela et al. 1997). However, this approach also introduces considerable uncertainty, and the 1:1 ratio is applicable only for oxidized inorganic nitrogen, not ammonium compounds (Dennis 1999, Chimka et al. 1997).

Organic nitrogen is also deposited from the atmosphere to the ground and surface waters. However, measurement of dry organic nitrogen deposition is unreliable and, to date, only a limited number of measurements of organic nitrogen dry deposition rates have been made (Scudlark et al. 1998). Measurement of wet organic nitrogen is more reliable, and more and more data on wet deposition are becoming available. Based on a number of measurements of the organic nitrogen content in precipitation on the mid-Atlantic coast, Scudlark et al. (1998) found that organic nitrogen averages at least 20 percent of total dissolved nitrogen in precipitation, and can comprise as much as 64 percent of total dissolved nitrogen for single precipitation events. Based on measurements in North Carolina, Peierls and Paerl (1997) determined that roughly 30 percent of dissolved nitrogen in precipitation and rainwater deposition was organic nitrogen. Based on these results, it appears that organic nitrogen is a significant component of atmospheric deposition nitrogen (ADN) loads to surface waters, although the current understanding of the contribution of organic nitrogen to overall ADN is limited.

³ NADP data were analyzed by selecting the monitoring sites within the watersheds of the Great Waters and averaging the reported deposition rates for all monitoring sites within each watershed to obtain an average deposition rate for the watershed. Data from 9 monitoring sites were averaged for the Chesapeake Bay watershed; data from 18 monitoring sites were averaged for the Great Lakes watersheds, and data from 4 monitoring sites were averaged for the Lake Champlain watershed.

Figure II-13
Nitrogen Wet Deposition in the Chesapeake Bay Watershed
(NADP/NTN 1998b)

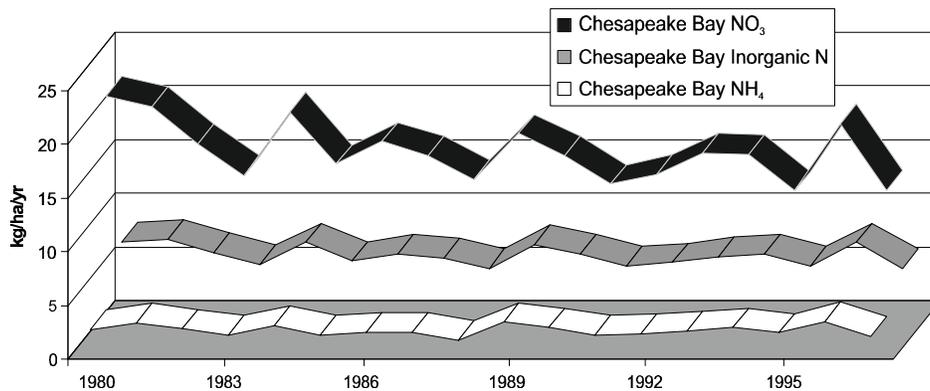


Figure II-14
Nitrogen Wet Deposition in the Great Lakes Watersheds
(NADP/NTN 1998b)

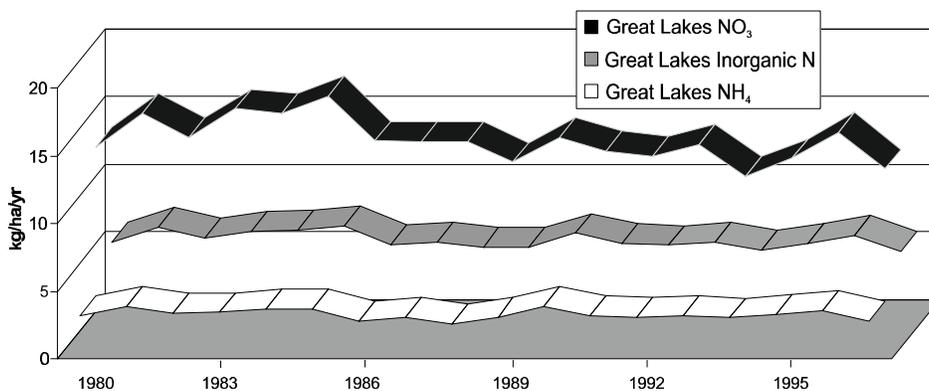
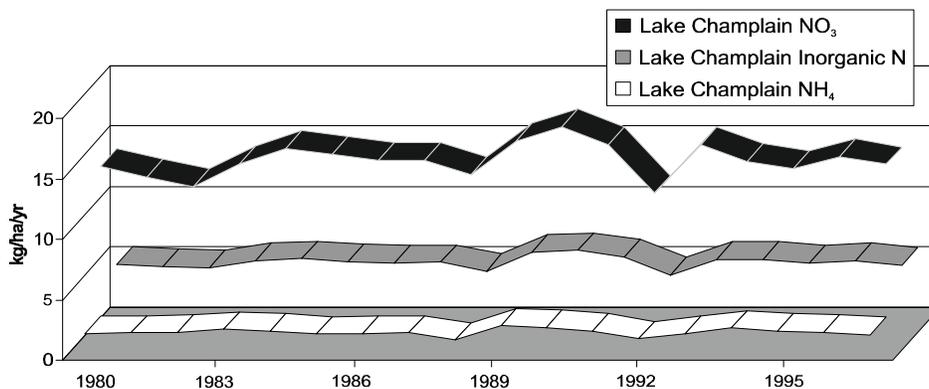


Figure II-15
Nitrogen Wet Deposition in the Lake Champlain Watershed
(NADP/NTN 1998b)



Note: Total inorganic N expressed as N; NO_3 and NH_4^+ expressed as the ions.

Atmospheric Nitrogen Loadings to the Great Waters

The total ADN load delivered to each of the Great Waters is a sum of the nitrogen deposited directly to the waters surface, plus a portion of the nitrogen deposited to the watershed. Although only a fraction of the atmospheric nitrogen deposited to watersheds ultimately reaches downstream Great Waters waterbodies, ADN transfer from watersheds is nevertheless the more important pathway for introduction of ADN to these waterbodies. This is due to the much larger areal extent of watersheds relative to the surface areas of the receiving waterbodies. The portion of ADN transferred from watersheds to downstream waterbodies is still relatively uncertain, and although several ongoing projects are attempting to quantify this, the rate of ADN transfer from watersheds to downstream waterbodies remains one of the greatest sources of uncertainty in estimating nitrogen and ADN loadings to surface waters. Transfer rates appear to vary greatly among watersheds and among areas within watersheds. For example, estimates of ADN transfer rates from various watershed areas to Great Bay Estuary, New Hampshire and to Waquoit Bay, Massachusetts are presented in Table II-19. Table II-20 presents estimated overall ADN transfer estimates for the watersheds of various coastal waterbodies (as developed by a number of researchers using a variety of techniques). The ADN transfer rates in Tables II-19 and II-20 were generally estimated based on estimated steady-state flux of nitrogen.

The ADN loads to surface waters join nitrogen loadings from a variety of other sources. Key sources of nitrogen reaching surface waters via routes other than the atmosphere (i.e., point source discharges, runoff, ground water) include (1) fertilizer from agricultural operations, recreation areas, suburban lawns; (2) manure from animal production facilities; (3) municipal and industrial treatment plant sludge and effluent and residential septic tanks; (4) crop residues (especially nitrogen-fixing crops such as legumes); and, (5) industrial wastes.

Table II-21 presents a number of estimates of the total nitrogen load, the nitrogen load attributable to ADN, and the portion of total nitrogen load represented by ADN for a number of Atlantic and Gulf coast Great Waters (developed using a variety of techniques). Based on these data, ADN contributes roughly 10 to 40 percent of total nitrogen loads reaching the bays and estuaries studied. If these values are assumed to be representative of the remaining Great Waters in the east and Gulf coast region, it is clear that ADN contributes very significantly to the total load of nitrogen reaching the Great Waters of these regions. It should be noted, however, that ADN accounts for roughly only 1 percent of nitrogen loadings in the Mississippi River basin, which has highly diverse sources of anthropogenic nitrogen (Goolsby et al. 1998, as cited by Paerl 1999). The ADN is also likely to be a relatively less important contributor to nitrogen loadings in Pacific coast Great Waters than is the case in the east and Gulf coast areas, due to the prevailing westerly winds over Pacific coastal waters and their watersheds, originating from unpolluted ocean areas.

Table II-19
Transfer of Atmospheric Deposition Nitrogen (ADN)
from Various Watershed Areas

Great Bay Estuary, New Hampshire ^a		Waquoit Bay, Massachusetts ^b	
Type of Area Receiving ADN	Percent ADN Transferred to Estuary	Type of Area Receiving ADN	Percent ADN Transferred to Bay
Urban	38	Roads, runways, commercial areas	25
Active agriculture	10	Agricultural land (other than turf and cranberry)	10
Forest	5	Natural vegetation	9
Surface water in the watershed	90	Ponds in the watershed	44
Wetlands	3	Cranberry bogs	10
Disturbed/open land	6	Turf	10

^a Talbot and Mosher 1998

^b Valiela et al. 1997

Table II-20
Transfer of Atmospheric Deposition Nitrogen (ADN)
from Watersheds to Several Bays and Estuaries

Watershed	Percent of ADN Transferred to Bay/Estuary	Reference
Albemarle-Pamlico Sounds	15	Paerl and Fogel 1994, as cited in Valigura et al. 1997
Chesapeake Bay	15	Linker 1998
Delaware Bay	9.4	Scudlark and Church, 1993, as cited in Valigura et al. 1997
Long Island Sound	15	Long Island Sound Study, as cited in Valigura et al. 1997
Narragansett Bay	7	Hinga et al. 1991, as cited in Valigura et al. 1997
New York Bight	12	Hinga et al. 1991, as cited in Valigura et al. 1997
Waquoit Bay	11	Valiela et al. 1997

Table II-21
Atmospheric Nitrogen Loads Relative to Total Nitrogen Loads
in Selected Great Waters*

Waterbody	Total Nitrogen Load (million kg/yr)	Atmospheric Nitrogen Load (million kg/yr)	Percent Load From the Atmosphere
Albemarle-Pamlico Sounds ^a	23	9	38
Chesapeake Bay ^b	170	36	21
Delaware Bay ^c	54	8	15
Long Island Sound ^d	60	12	20
Narragansett Bay ^e	5	0.6	12
New York Bight ^e	164	62	38
<i>Based on ADN loads from the watershed only (excluding direct nitrogen deposition to the bay surface):</i>			
Waquoit Bay, MA ^f	.022	.0065	29
<i>Based on atmospheric N deposition directly to the Waterbody (excluding ADN loads from the watershed):</i>			
Delaware inland bays ^g	1.3	.28	21
Flanders Bay, NY ^h	.36	.027	7
Guadalupe Estuary, TX ⁱ	4.2 - 15.9	.31	2 - 8
Massachusetts Bays ^j	22 - 30	1.6 - 6	5 - 27
Narragansett Bay ^k	9	.4	4
Newport River Coastal Waters, NC ^a	.27 - .85	.095 - .68	>35
Potomac River MD ^l	35.5	1.9	5
Sarasota Bay, FL ^m	.6	.16	26
Tampa Bay, FL ⁿ	3.8	1.1	28

*As cited in Valigura et al. 1997: ^aPaerl and Fogel 1994, ^bLinker 1998, ^cScudlark and Church 1993, ^dLong Island Sound Study 1996, ^eHinga et al. 1991, ^fValiela et al. 1996, ^gDelaware Bays NEP, ^hPeconic Bay NEP, ⁱBrock et al. 1995, ^jMassachusetts Bays NEP 1996, ^kNixon et al. 1995, ^lBoynton et al. 1995, ^mSarasota Bay NEP 1995, ⁿTampa Bay NEP, Zarbock et al. 1994

Effects of Nitrogen Loadings on the Great Waters

While ADN contributes significantly to the overall adverse effects associated with excessive nitrogen loadings to the Great Waters, the effects of atmospherically-derived nitrogen on the Great Waters is very difficult to distinguish from the effects of nitrogen loadings from other sources. The effects of atmospheric nitrogen deposition to the Great Waters and associated trends can only be reviewed in terms of the effects of overall nitrogen loadings to these waters and the associated trends.

Although historical data for total aquatic nitrogen concentrations in the Great Waters are not available, nitrate concentrations have been monitored in many rivers and drinking water supplies in the U.S. for decades. Nitrate (NO₃) concentrations in surface water are directly related to anthropogenic nitrogen loadings to watersheds and surface waters (Vitousek et al. 1997). Aerosol nitrate is the most mobile form of nitrogen in watersheds and aquatic systems, and other forms of anthropogenic nitrogen, notably NH_x and organic nitrogen, are partly oxidized to NO₃ in the environment (Hessen et al. 1997). Surface water NO₃ concentration trends, although only part of the picture, provide some insight on the trends in anthropogenic nitrogen loadings and their effects on the Great Waters.

Available data indicate a significant increasing trend in the fluxes of nitrates in major surface waters in the U.S., including the Great Waters and their tributaries.

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- C Nitrate has more than doubled in the Mississippi River since 1965 (Vitousek et al. 1997). Note, however, that ADN accounts for roughly only 1 percent of nitrogen loadings in the Mississippi River basin (Goolsby et al. 1998, as cited by Paerl 1999).
- C Nitrate fluxes in 10 major rivers feeding coastal waters in the northeastern U.S. have increased by factors of three to eight since 1900 (Jaworski et al. 1997). This increase is correlated with a three- to five-fold increase in NO_x emissions in the watersheds of these same rivers and more than a four-fold increase in atmospheric nitrogen deposition rates to northeastern coastal watersheds over the same time period (Vitousek et al. 1997).
- C Increases in surface water nitrogen concentrations of 10 to 25 percent have been observed in Long Island Sound, portions of the Potomac River, and the Chesapeake Bay, the Neuse River, and portions of Biscayne Bay over the past 2 to 15 years (NOAA 1996, NOAA 1997a, as cited in U.S. EPA 1997f).

The long-term upward trend in nitrogen fluxes and nitrogen concentrations in many surface waters reflects similar upward trends in atmospheric emissions of nitrogen, in fertilizer use, and in municipal wastewater discharges in the initial seven decades of this century. Some evidence suggests, however, that nitrogen fluxes attributable to atmospheric deposition may have leveled off in more recent years in at least some waterbodies.

- C Based on historical watershed data, Jaworski et al. (1997) found that nitrogen fluxes (total and attributable to ADN) for a number of northeastern U.S. coastal waters rose rapidly until about 1970, but have been more or less constant since then.
- C Stoddard et al. (1998) found that the nitrate concentrations in higher elevation lakes and streams in the northeastern U.S. have either remained relatively constant or shown no discernable trend since the early 1980s. Atmospheric deposition nitrogen is the principal and, in some cases, the only source of anthropogenic nitrogen loadings to these lakes, which feed tributaries of the Great Waters.

Fluxes of ADN and total nitrogen to some of the Great Waters may, therefore, have leveled off in recent years. For many of the Great Waters, however, these fluxes remain many times greater than natural levels that occurred prior to human activity in the watersheds and airsheds (Vitousek et al. 1997). Human loadings of nitrogen to the land can overwhelm the capacities of watersheds to assimilate nitrogen, meaning that greater and greater percentages of the nitrogen deposited to watersheds are transferred directly to downstream waterbodies. Thus, constant rates of nitrogen deposition to watersheds can result in increasing nitrogen loadings to downstream waterbodies. Loadings of nitrogen to waterbodies can similarly overwhelm the capacity of waterbodies to assimilate or eliminate nitrogen, leading to a significant buildup of nitrogen concentrations and, in some cases, nitrogen saturation and related ecosystem degradation (Vitousek et al. 1997, Moffat 1998). These factors are believed to contribute to significant increases in concentrations of nitrogen in some of the Great Waters and rivers feeding the Great Waters, specifically the Mississippi River and a number of major rivers in the northeastern U.S. (Vitousek et al. 1997).

The “natural” or ecologically ideal concentration of nitrogen in the water column varies considerably among waterbodies. As one example, the Chesapeake Bay Program (1992, as cited in U.S. EPA 1998b) has determined that the most desirable concentration of dissolved inorganic nitrogen in the Chesapeake Bay (i.e., the concentration necessary to promote continued survival of submerged aquatic vegetation) is <0.15 mg/L.

Recent NOAA Estuarine Eutrophication Surveys (NOAA 1996, 1997a, b, c, as summarized in U.S. EPA 1998t) indicate elevated nitrogen concentrations in many of the Great Waters coastal estuaries on the Atlantic and Gulf coasts. These surveys found the following:

- C High aquatic nitrogen concentrations (> 1 mg/L) in two of 18 estuaries on the U.S. north Atlantic coast, 14 of 22 mid-Atlantic estuaries, 11 of 21 south Atlantic estuaries, and 18 of 37 Gulf of Mexico estuaries; and,
- C Moderate to moderately elevated aquatic nitrogen concentrations (0.1 - 0.9 mg/L) in 13 of 18 north Atlantic estuaries, five of 22 mid-Atlantic estuaries, seven of 21 south Atlantic estuaries, and 19 of 37 Gulf of Mexico estuaries.

Excess nitrogen loadings in the Great Waters can have a range of effects on the ecological structure and processes of these waters and, ultimately, on human use of the waters. Effects of excess nitrogen loadings can be considered in three broad categories (U.S. EPA 1997a).

1. Dramatic increases in plant productivity and algal blooms in systems where algal growth was previously nitrogen-limited. This can in turn cause fish kills, loss of submerged aquatic vegetation due to reduced sunlight penetration, loss of recreational use of waterbodies, and ultimately hypoxic (low oxygen) or anoxic (no oxygen) conditions as algal blooms die and decomposition processes consume the available oxygen – a condition referred to as eutrophication. Hypoxic and anoxic conditions can lead to loss of aquatic biodiversity as species requiring higher oxygen concentrations are lost, can affect the biogeochemical cycling of nutrients and toxic compounds, and can affect the bioavailability of toxic compounds. In addition to these consequences associated with normal algal blooms, excess nitrogen loadings are also linked to harmful or toxic algal blooms, often referred to as red or brown tides, involving algae species that are toxic to other aquatic biota or humans, often causing fish kills and human illness or mortality (Paerl et al. 1999, 1998, Paerl 1997a, Pelley 1998, Tibbets 1998, Rabalais et al. 1996).
2. Changes in the ecological balance brought on by fundamental changes at the base of the food web (i.e., the loss of aquatic grasses and other vegetation and the dominance of a relatively few algal species) and loss of biological diversity throughout the system as fundamental aquatic ecological parameters such as oxygen level, sunlight penetration, diversity and abundance of food species, and habitat availability change.
3. Direct toxicity of some nitrogen compounds to aquatic organisms. Toxicity of nitrogen compounds to aquatic organisms is not well understood, but mounting evidence suggests that these compounds can affect the ability of some species to adapt to other stresses (Linton et al. 1998). Dissolved ammonia at concentrations above 0.2 mg/L can be toxic to aquatic organisms (Paerl 1997a, as cited by U.S. EPA 1997a).

Many of these adverse effects have been observed by researchers in the Great Waters. Examples are provided below.

- C McClelland and Valiela (1998) and Short and Burdick (1996) found that increased loads of anthropogenic nitrogen to Waquoit Bay, Massachusetts have a significant effect on the pathways by which nitrogen enters the food web. The diets of primary consumers in the bay are influenced by the dominant forms of food material available. Eelgrass is an important dietary component of primary consumers in areas of the bay receiving lower anthropogenic nitrogen loadings.

Laboratory studies by Short and Burdick (1996) indicated that excessive nitrogen loadings stimulated growth of algal competitors that shade and stress eelgrass. These laboratory results were borne out in field observations in Waquoit Bay, where domination by algal competitors was observed in areas of significant eelgrass decline. McClelland and Valiela (1998) found that eelgrass is lost and is largely replaced by algae in areas of the bay receiving higher anthropogenic nitrogen loadings. Thus, an important pathway for nitrogen entry to the food web may be altered. McClelland and Valiela conclude that this change in the nitrogen pathway probably affects the rate and manner in which nitrogen is cycled within the bay ecosystem and may reduce the stability of shallow estuarine ecosystems in the bay. Loss of eelgrass also results in loss of habitat for shellfish and other small fish, further affecting the ecological structure and function of the bay.

- C Allen and Hershey (1996) demonstrated that the immediate effects of atmospheric deposition of nitrogen can vary seasonally for some waterbodies. In a north shore river tributary to Lake Superior, availability of nitrogen was found to alternate with availability of phosphorus and other factors as the limiting factor controlling algal biomass growth. Introduction of additional nitrogen resulted in increased algal biomass during early summer and late summer, but not during other seasons. Introduction of additional phosphorus caused increased algal growth in spring, but not in other seasons. Algal growth was not affected by additional nitrogen or additional phosphorus during the fall season, suggesting limitation by factors other than nitrogen or phosphorus availability. The dissolved inorganic nitrogen to soluble reactive phosphorus (DIN/SRP) ratio was not a reliable predictor of nutrient limitation in the studied river.
- C Linton et al. (1998) found that the combination of global warming and increased ammonia loadings from atmospheric and other sources could have a greater impact on aquatic species in Lake Superior than either factor alone. These researchers studied rainbow trout reactions to elevated aquatic ammonia concentrations in conditions simulating Lake Ontario under a global warming scenario (2 EC above natural water fluctuating water temperature cycle). Their results indicate that elevated ammonia concentrations could reduce the ability of rainbow trout to adapt to long-term, small temperature increases such as could be caused by global warming.
- C The disappearance of the economically important scallop from Tampa Bay waters is attributed to algal blooms and associated changes in ecological conditions in the bay, which in turn is attributed to excess nitrogen loadings (U.S. EPA 1997a).
- C Hypoxia attributed to nitrogen-induced eutrophication is now a common and recurring condition in many bays along the Atlantic and Gulf coasts, notably Long Island Sound, New York-New Jersey Harbor, Chesapeake Bay, Albemarle-Pamlico Sound, and the Mississippi Delta region (U.S. EPA 1997a).
- C Major algal blooms attributed to increases in aquatic nitrogen concentrations have occurred in several Atlantic and Gulf coast waters in recent years. These blooms have been accompanied by deleterious visual and odor effects and fish kills (U.S. EPA 1997a).
- The number of U.S. coastal areas experiencing major, recurring harmful or toxic algal blooms, linked to increases in aquatic nitrogen availability, have doubled since 1972 and include areas on the Atlantic, Gulf of Mexico, and Pacific coasts (Pelley 1998, Tibbetts 1998).

The NOAA Estuarine Eutrophication Surveys (NOAA 1996, 1997a, b, c, as summarized in U.S. EPA 1998t) indicate that the adverse effects of excess nitrogen concentrations are currently evident to

greater or lesser degrees in approximately 89 percent of the U.S. coastal estuary Great Waters. These surveys report the following:

- C Anoxic or hypoxic conditions (oxygen content 0 - 2 mg/L) in portions of four of 18 north Atlantic estuaries, 13 of 22 mid-Atlantic estuaries, 13 of 21 south Atlantic estuaries, and 26 of 37 Gulf of Mexico estuaries; and,
- C Biologically stressful levels of oxygen (2 - 5 mg/L) in at least portions of nine of 18 north Atlantic estuaries, 21 of 22 mid-Atlantic estuaries, seven of 21 south Atlantic estuaries, and 35 of 37 Gulf of Mexico estuaries.

Human Health Effects of Nitrogen in the Great Waters

Under the Safe Drinking Water Act, EPA set maximum contaminant levels (MCLs) for nitrate and nitrite in drinking water to protect human health. These levels are established at 10 mg/L of nitrate and 1 mg/L of nitrite. The primary adverse human health effect associated with exposure to nitrate or nitrite is methemoglobinemia, a dangerous condition in which nitrite in the blood stream prevents oxygen transport, potentially leading to brain damage or death. This condition is rare in adults, but is a significant danger for infants because microbes present in the stomachs of infants can convert large amounts of nitrate to nitrite. The National Research Council concluded, in 1995, that results from epidemiological studies are inadequate to support an association between nitrate or nitrite exposure from drinking water in the U.S. and increased cancer rates in humans. However, an epidemiological study led by a researcher from the National Research Council, published in 1996, of rural populations using community water supplies in Nebraska concluded that long-term exposure to elevated nitrate levels in drinking water may contribute to the risk for non-Hodgkin's Lymphoma. Research is continuing in this area (U.S. EPA 1997h, Ward et al. 1996).

Data indicate that most of the Great Lakes nearshore waters can be used as a source of drinking water with normal treatment, meeting the nitrate and nitrite levels (U.S. EPA 1998n). Similarly, Lake Champlain was not associated with any violations of standards in place for drinking water supplies due to Great Waters pollutants of concern from 1986 to 1995 (Lake Champlain Basin Program 1999). Further reductions in pollutant concentrations may reduce the cost of drinking water treatment in some areas.

Excess nutrients in coastal waters have also been implicated in the increased incidence of harmful or toxic algal blooms in the coastal waters of nearly every U.S. coastal State. These blooms have been linked to health effects among exposed human populations ranging from shortness of breath to dizziness, diarrhea, disorientation, permanent memory loss, and occasion death (Pelley 1998, Tibbetts 1998). To the extent that ADN contributes to elevated nitrogen content in coastal waters, ADN also contributes to human health risks associated with harmful and toxic algal blooms. No evidence exists to date suggesting negative human health effects attributable directly to atmospherically-derived nitrogen in the Great Waters.

BANNED AND RESTRICTED USE SUBSTANCES

Polychlorinated Biphenyls (PCBs)

Manufacture of PCBs in the U.S. was voluntarily stopped in the late 1970s, and the use of PCBs was restricted under the Toxic Substances Control Act (TSCA) in 1979. Therefore, sources of PCBs in the U.S. are limited. However, PCBs are still present in older commercial and industrial equipment (e.g., electrical transformers and capacitors) and are released from non-point and non-regulated sources including Superfund sites. In addition, despite reductions in use, PCBs are released during some combustion processes, such as the incomplete burning of PCB-containing wastes during incineration. New research is also indicating that PCBs are actually being formed during certain combustion processes, similar to the way in which dioxins and furans are formed (Lemieux et al. 1999).

The number and magnitude of sources of PCBs have decreased 20-fold in the last 20 years, and sources of PCBs generally are limited to atmospheric deposition and localized point source discharges (Froese et al. 1997). Some studies detected PCBs in

smallmouth bass from Fumee Lake, a remote lake in Michigan (Henry et al. 1998), and in the blubber of Beluga whales from Alaska's north coast (Wade et al. 1997a), indicating long range transport and atmospheric deposition as a major source in these areas. Many recent studies in the Great Waters, however, implicate non-atmospheric sources of PCBs (e.g., Brazner and DeVita 1998, Metcalfe et al. 1997a). The relative importance of atmospheric inputs and non-atmospheric sources remains unclear. Nevertheless, the largest stationary source of PCB air emissions on a national basis, as indicated by EPA's 1990-1993 NTI, is hazardous waste incineration at dedicated hazardous waste incinerators, along with several other smaller sources (Table II-22) (U.S. EPA 1999a). The EPA is pursuing additional research to determine the extent of PCB releases during incomplete combustion in these and other facilities as well as the effects on emissions and loadings of PCBs.

In Lake Superior, specifically, approximately 52 kg/year of PCBs are from point source inputs, 15 kg/year are from runoff (including pollutants in rainfall plus pollutants that are transported from land areas), and 85-156 kg/year are from wet and dry deposition (Hoff et al. 1996). Similarly, water samples collected during an investigation of the source of PCBs in the Detroit River (which feeds Lake Erie) indicate that the dominant sources of PCBs in this location are surface runoff from urban areas during rainfall and resuspension of in-place deposits of PCBs in the sediments of the river and bays due to high flow events in the rivers and due to severe wind conditions in the lakes (Froese et al. 1997).

HIGHLIGHTS Polychlorinated Biphenyls

• **Sources.** In general, the number and magnitude of PCB sources have decreased 20-fold in the past 20 years. PCB sources generally are limited to atmospheric deposition and localized stationary sources. The largest national-level stationary air emission source of PCBs is hazardous waste incineration, along with several smaller sources. Sources to surface waters include atmospheric deposition, urban runoff, resuspension of contaminated sediments, and recycling through volatilization followed by deposition.

• **Loadings.** In the Great Lakes, studies show that deposition of PCBs has decreased and that PCBs in surface waters may be in equilibrium with the atmosphere (i.e., no net loadings). Deposition rates are higher near the Chicago urban area when compared to offshore and rural locations. In the Chesapeake Bay, a net loss of PCBs from the water surface has been observed.

• **Environmental Concentrations and Exposure.** PCB contamination levels in biota from the Great Lakes have declined; however, certain human subpopulations continue to be exposed to PCBs through fish consumption. In the Chesapeake Bay, maximum PCB sediment concentrations are below the PEL and NOEL for aquatic biota, with the exception of one location on the James River.

Table II-22
National Anthropogenic PCB Air Emissions
(Based on EPA's 1990-1993 National Toxics Inventory)

Source Category	Anthropogenic Air Emissions (tons/year)	Percent Contribution to Total U.S. Anthropogenic Air Emissions
Hazardous waste incineration	0.03	56.0
Sewage sludge incineration	0.005	10.3
Fabricated metal products, nec	0.005	10.1
Industrial boilers: natural gas combustion	0.004	7.7
Portland cement manufacture: all fuels	0.004	7.3
Scrap and waste materials	0.001	2.7
Scrap tire combustion	0.001	2.1
Refuse systems	0.0006	1.2
Fabricated rubber products, nec	0.0005	1.0
Others (< 1 percent) ^a	0.0008	1.7
Total U.S. Anthropogenic PCB Air Emissions	0.052^b	100^b

^a A list of the source categories that contribute less than 1 percent to total U.S. emissions is provided in Appendix B.

^b This value represents anthropogenic PCB air emissions in the U.S. only.

Source: U.S. EPA 1999a

Research based on deposition monitoring under the Atmospheric Exchange Over Lakes and Ocean Surfaces (AEOLOS) project found that the “urban plume” of Chicago increases the deposition of PCBs to Lake Michigan and is a major source of atmospheric PCBs to coastal Lake Michigan. Total ambient air PCB concentrations on the lakeshore near Chicago are two to three times higher than background levels and the values collected under IADN, which monitors remote locations on the Great Lakes (Offenberg and Baker 1997). Franz et al. (1998) found similar results using dry deposition monitoring data from AEOLOS and the Lake Michigan Mass Balance Study where fluxes of particulate PCBs were higher in Chicago than less than 15 km offshore and at rural sites. The higher urban fluxes are due to increased anthropogenic activity and the greater atmospheric burden of large particles that are generated in the urban area and deposited closer to their sources. Franz et al. (1998) estimated dry deposition of PCBs to Lake Michigan to be approximately 1,100 kg/year, which is at least an order of magnitude greater than some previously reported values. Other studies report inputs of PCBs through air/water exchange at approximately 880 kg/year and wet deposition at 50 - 250 kg/year (Franz et al. 1998). In contrast, Offenberg and Baker (1997) found that the amount of yearly wet deposition plays a major role in determining the annual deposition of PCBs to Lake Michigan, and IADN monitoring results indicate that gas absorption is a dominant deposition process for delivering PCBs to lake surfaces (U.S./Canada IADN Scientific Steering Committee 1998). The observed differences from these studies illustrate the importance of considering local meteorology and the location of monitoring stations (rural versus urban) when interpreting deposition data.

In addition to depositing PCBs released to the atmosphere from emission sources, atmospheric deposition processes play a strong role in PCB recycling in Lakes Superior, Michigan, and Huron, but

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less of a role in Lakes Erie and Ontario. Volatilization of PCBs from the water, however, is the dominant mechanism for exchange of PCBs between the lakes and the atmosphere. According to IADN monitoring data from 1988 to 1996, wet and dry deposition of PCBs to each of the Great Lakes decreased (Hoff et al. 1996) (Table II-23). In the Detroit River, which is a heavily industrialized and urbanized area and is a primary transport route of PCBs to Lake Erie and Lake Ontario, the mass of PCBs transported through the Trenton Channel to the western basin of Lake Erie in 1995 was estimated at 600 kg/yr, constituting a potential decrease from 1986 estimates of approximately 1,500 kg/year. (Note, however, that different sampling methodologies were employed in the different years and may be responsible for a portion of the change (Froese et al. 1997)). Other monitoring studies show a net loss of PCBs to the atmosphere, particularly from Lake Superior and Lake Michigan (Offenberg and Baker 1997, U.S. EPA 1998m). For example, PCBs are being purged from Lake Superior at 21 percent per year of its annual burden (Hoff et al. 1996). Another monitoring data analysis indicates that gas transfer of PCBs out of the lakes is counteracted by net deposition, meaning PCBs are in equilibrium with the water surface and the atmosphere (Hillery et al. 1997).

Table II-23
IADN Loading Estimates of PCBs (wet and dry) for the Great Lakes (kg/year)

Year	Superior	Michigan	Huron	Erie	Ontario
1988	550	400	400	180	140
1992	160	110	110	53	42
1994	85	69	180	37	64
1996	50	42	N/A	34	N/A

Source: U.S. EPA 1998l

Studies using surface water and air sampling indicate that Chesapeake Bay waters have higher relative concentrations than the overlying atmosphere, and volatilization is the dominant loss process for PCBs from the bay. Polychlorinated biphenyls are volatilizing to the atmosphere at an average rate of 35 $\mu\text{g}/\text{m}^2/\text{yr}$, with a range of 31 to 112 $\mu\text{g}/\text{m}^2/\text{yr}$. Annual loss of PCBs from the bay from net volatilization (403 kg/yr) is 10 times greater than inputs from wet and dry deposition of 37 kg/yr and is more than two times greater than the loadings from the Susquehanna River of 165 kg/yr (Nelson et al. 1998). The Chesapeake Bay Program's *1999 Toxics Loading and Release Inventory* (TLRI) provides information on the total inputs and relative atmospheric inputs of PCBs to the tidal and non-tidal waters of the Chesapeake Bay based on monitoring data. Total PCB inputs to the Chesapeake Bay, without point source estimates, are similar for both inputs from the non-tidal watershed (254 kg/year) and inputs from wet and dry atmospheric deposition to the tidal waters (245 kg/year) (Chesapeake Bay Program 1999a).

The comparison of current contamination levels to historical values provides evidence that concentrations of PCBs in biota have declined in the Great Lakes. For example, Dykstra et al. (1998) measured PCB concentrations in nestling blood (1989-1994) and addled eggs (1986-1993) of bald eagles in Lake Superior and inland Wisconsin sites. A comparison to published and unpublished historical data of PCBs in addled bald eagle eggs on Lake Superior indicates that PCB levels declined significantly between 1969 and 1993; however, PCBs may still be at levels high enough to affect reproductive success. Similarly, Ion et al. (1997) measured the concentration of PCBs in yellow perch from the St. Lawrence River between 1975 and 1991-1992. Comparison of average PCB concentrations detected to historical levels in St. Lawrence River fish indicates that levels have decreased by a factor of 30 since 1975. The concentration of PCBs in all fish sampled by Ion et al. (1997) were below the International Joint

Commission guideline of 100 ng/g in whole fish, which is protective of aquatic life and consumers of fish.

A study by Eby et al. (1997) shed doubt on findings reported in the *Second Great Waters Report to Congress* that concluded that PCB concentrations in Great Lakes have leveled off or even increased slightly in the last 10 years (U.S. EPA 1997b). In those earlier studies, scientists hypothesized that the trend in PCB contamination could be due to changes in the composition of the food web. Eby et al. (1997) demonstrate, however, that sampling methodology may have influenced the apparent PCB concentration trends rather than changes in fish diet. As part of a long-term PCB monitoring survey, the USGS collects and analyzes bloaters (*Coregonus hoyi*) from the same site in Lake Michigan every year. Because fish size is used to predict fish age, similar size fish are collected each year. However, since the early 1980s, bloater populations experienced a decline in growth rate due to a shift in diet, which placed older, more contaminated bloaters in the size range sampled. This resulted in an apparent trend of steady state or increasing PCB levels. In contrast, Eby et al. (1997) modeled an increase in the amount of the most contaminated prey in the bloater diet and found that this shift in diet had little effect on PCB contamination levels in bloaters.

A recent study by Haffner et al. (1997) found that total PCB concentrations in herring gull eggs decreased significantly between 1981 and 1992 in Lake Ontario and Lake Erie, although the decrease in lake Erie was not of the same magnitude. The PCB concentrations detected during this study are not expected to affect reproduction in herring gull populations. In addition, Haffner et al. (1997) found that total PCB concentrations in double-crested cormorant eggs did not decrease in Lake Ontario but decreased slightly in Lake Erie between 1981 and 1992. The PCB concentrations detected in this study may be high enough to cause toxicological stress on the cormorant population (e.g., egg mortality, infertility, deformity).

Although some studies indicate that PCB levels in fish have decreased or reached a steady state in recent years, consumption of contaminated fish from the Great Lakes remains a concern. Several recent studies examined the relationship between increased health risks in certain subpopulations and the consumption of fish from the Great Lakes contaminated with PCBs, concluding that certain subpopulations continue to be exposed to PCBs through fish consumption despite declines in contamination levels and despite continued fish consumption advisories. Study results include the following.

- C Pellettieri et al. (1996) determined that the estimated PCB intake for sport fisherman in the Chicago area exceeded the level recommended by the Great Lakes Advisory Task Force of no more than one meal of fish per week (assuming the average meal of fish is composed of 227 g of uncooked fish and that the intake of PCBs is reduced by half due to skinning, trimming, and cooking).
- C A study of Ojibwa tribal members from the Great Lakes region indicated that PCB concentrations in Ojibwa populations were low with a maximum value of 9.6 ppb in blood serum; however, a significant association was found between serum PCB concentration and age (Gerstenberger et al. 1997). This is important because PCBs are persistent and bioaccumulate in the food chain.
- C According to a 1997 survey (Tilden et al. 1997) of Great Lakes States' residents, the most widely accepted fish consumption advisory recommendation was cleaning and cooking methods. A study of six cooking methods determined that choice of cooking method greatly impacted the loss of PCBs during the cooking process, with smoking and microwave baking as the most

effective methods. Smoking reduced PCB levels by 65 percent, and microwave baking reduced PCB levels by 60 percent (Salama et al. 1998).

In a sediment contamination study of the Chesapeake Bay and its tributaries from 1984 to 1991 by Eskin et al. (1996) under the Chesapeake Bay Program, PCBs were detected at low levels in sediments throughout the bay and its tributaries, indicating that aquatic life impacts (based on the aquatic biota NOEL and PEL) from PCBs in the bay are not widespread. The highest concentrations were detected in sediments in the northern bay near the Baltimore area and on the James River. Maximum PCB concentrations were below aquatic biota NOEL and PEL concentrations in sediments at all locations, with the exception of one location on the James River.

Despite observed declines in some organisms, a study of PCB levels (as serum concentrations) in male and female juvenile American alligators in Lake Apopka, Florida indicated that 23 of 28 PCB congeners were present in juvenile alligators. The mean total PCB concentration in the serum was 1.54 ± 0.12 (SE) ng/mL. Alligators in Lake Apopka have been reported to have a number reproductive and endocrine system abnormalities which may be due to embryonic exposure to these and other compounds (Guillette et al. 1999).

Pesticides

Table I-1 presents the uses and sources of Great Waters pesticides and indicates that many of these pesticides are banned or use restricted; however, many of these pesticides may still be used in other countries. Therefore, long-range transport of emissions from other countries may contribute to current levels in Great Waters along with other current sources, such as use of existing stocks of pesticides, and releases from contaminated sites (e.g., Superfund sites) and from soils upon which pesticides were applied in the past. Because most of these pesticides are persistent and bioaccumulative, pesticides that were used or unintentionally released previously can cycle between environmental compartments (e.g., air, water, soil, sediment, biota). Therefore, some of these pesticides can be re-released to the atmosphere, transported short or long distances, and redeposited to surface waters.

Given these possible sources of banned and restricted use pesticides, efforts to reduce releases focus primarily on promoting (1) international agreements to reduce or eliminate the manufacture and use of these pesticides, and (2) pesticide collection programs (i.e., Clean Sweeps as described on page III-56). Additional future reductions may result from the clean up of existing stockpiles and contaminated sites. Research continues at EPA and other institutions on soil remediation methods that will reduce emissions of these pollutants from contaminated sites. In addition, efforts to limit the exposure of human and ecological populations to these pesticides include EPA and other agency monitoring programs and continued outreach activities to make the public aware of contaminated fish and waterbodies. Some

HIGHLIGHTS **Pesticides**

- **Sources.** Because most of the Great Waters pesticides of concern are banned or restricted use substances, the major sources include long range transport from other countries, use of existing pesticide stocks, and releases from contaminated sites and soils.
- **Loadings.** Since many of these pesticides are persistent and bioaccumulative, they are cycling between environmental compartments. In general, deposition of these substances remained constant or declined in recent years.
- **Environmental Concentrations.** DDT and its metabolites have, in general, declined to levels below which adverse environmental effects of concern are expected. In Chesapeake Bay sediments, chlordane and dieldrin concentrations were between the level expected to show widespread effects and the level expected to show limited effects.

recent studies of these pesticides focus on the role of atmospheric transport, both historic and current, in the contamination of waterbodies and biota of the Great Waters.

Atmospheric transport and deposition of these pesticides remains a principal source in the Great Waters, as shown by studies of both regional and global transport. For most pesticides, however, the relative contribution of atmospheric deposition versus other sources (e.g., runoff from contaminated soils, groundwater contamination) to total loadings is not yet known. It is expected that with the development of mass balance models and better sources and emissions estimates, it will be possible to determine relative contributions of different sources of pesticides and other pollutants to the Great Waters waterbodies. Furthermore, the contamination of biota in remote waterbodies that receive no point source inputs emphasizes the role of atmospheric transport and deposition of pesticides. For example, DDT/DDE, toxaphene, chlordane, dieldrin, and hexachlorobenzene were detected in smallmouth bass from Fumee Lake, which is in the Upper Peninsula of Michigan. The remote location of Fumee Lake suggests atmospheric loading is the source of pesticide contamination. Concentrations of these pesticides (except toxaphene which is associated with elevated levels in Lake Superior because of point source inputs) were similar to those found in fish from Lake Superior, where atmospheric inputs are thought to be the primary source of contaminants. All pesticide concentrations were less than those reported in Lake Michigan, which typically receives contaminants by direct input from point sources as well as atmospheric deposition (Henry et al. 1998). The detection of toxaphene, DDT/DDE, and chlordane in the blubber of Beluga whales from Alaska's north coast (Wade et al. 1997a) demonstrates the global scale of atmospheric transport. Toxaphene, chlordane, lindane, γ -HCH, hexachlorobenzene, dieldrin, and DDE also were detected in a variety of organisms at multiple trophic levels in Lake Superior (Kucklick and Baker 1998).

Banning and restricting uses of these pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) in the past 25 years have proven to be the most effective methods of removing these compounds from the environment, as would be expected. Because these substances are no longer intentionally released in the U.S. and the goal was to remove them from the environment, a group of researchers investigated how long these pesticides would persist in the atmosphere above the Great Lakes. Cortes et al. (1998) calculated atmospheric half-lives (i.e., the amount of time required for the concentration in the air to decrease by 50 percent) and used measured atmospheric concentrations to estimate minimum virtual elimination dates (i.e., when the contaminant levels are below the detection limits of the measurement equipment) in the Great Lakes regional atmosphere for DDT, DDE, dieldrin, chlordane, lindane (γ -HCH), and hexachlorobenzene (HCB) (Figure II-16). Based on these dates, DDT and DDE will be the first compounds to be reduced to concentrations below current detection limits in the Great Lakes atmosphere, followed by dieldrin and chlordane between 2010 and 2030, γ -HCH by 2030, and HCB by 2060. These estimates assume current rates of long-range transport of these pollutants into the region. Because of their persistence, it should be noted that elimination of these pollutants in the atmosphere does not mean that concentrations would be eliminated in deposited media by these dates. However, these estimates indicate that reduction strategies in the Great Lakes, along with the original bans or restrictions on the use of these substances, are having the intended effect.

DDT/DDD/DDE. In general, several studies indicate declines in atmospheric deposition of DDT and its metabolites as well as declines in concentrations in different environmental media. According to deposition monitoring data collected under IADN, wet and dry deposition of DDT to Lakes Superior, Michigan, and Erie in 1996 was less than values from 1994, 1992, and 1988 (Table II-24) (U.S. EPA 1998). The IADN data from 1993-1994 indicate that the net flux of total DDT is into Lake Superior and Lake Erie, possibly due to the high levels of wet deposition during 1993-1994. In Lake Huron, there is a net loss of total DDT to the atmosphere, and total DDT is in equilibrium between the surface water and the atmosphere in Lake Ontario. These data indicate a reversal from net volatilization of total DDT from

Figure II-16
Expected Year that Great Waters Pesticides will be Below Current Detection Limits in the Great Lakes Atmosphere (Cortes et al. 1998)

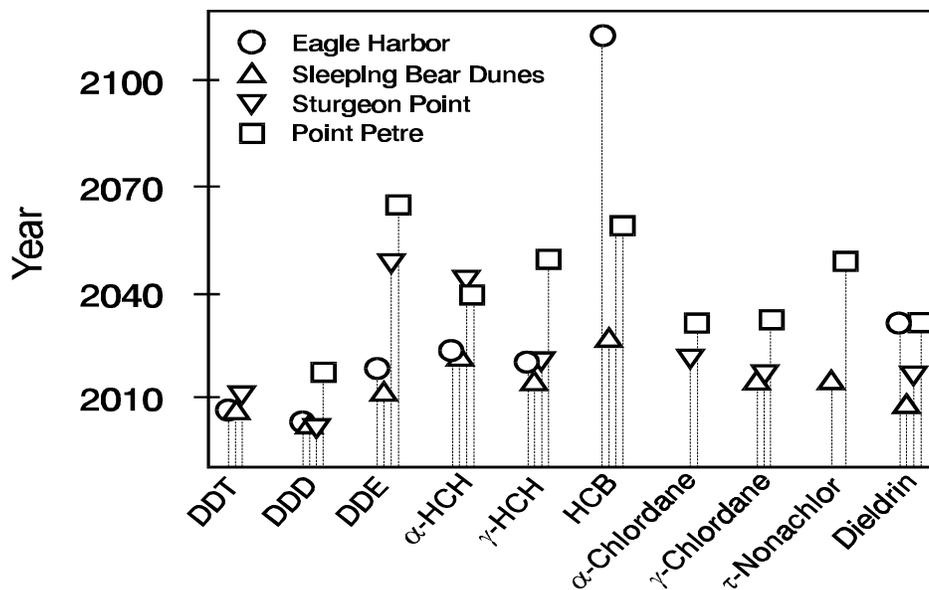


Table II-24
IADN Loading Estimates of DDT (wet and dry) to the Great Lakes (kg/year)

Year	Superior	Michigan	Huron	Erie	Ontario
1988	90	64	65	33	26
1992	34	25	25	12	10
1994	17	32	37	46	16
1996	4	12	N/A	2	N/A

Source: U.S. EPA 1998l

some of the lakes to net deposition to those lakes (U.S./Canada IADN Scientific Steering Committee 1998).

Current data indicate that elevated air concentrations of DDT and its metabolites in the South Haven, Michigan area are due to volatilization from the soil where the pesticide was placed during historical applications (Michigan Department of Environmental Quality 1998). The Great Lakes National Program Office (GLNPO; see page III-35) is funding a study to evaluate the source of the DDT and its metabolites in the air near a large fruit-growing area in South Haven where, historically, a number of researchers detected elevated levels of DDT and its metabolites. These levels are about 20 times greater than concentrations detected elsewhere in the Great Lakes basin. Recent studies that reported on DDT and DDE levels at a Canadian IADN site in Egbert, Ontario found that while increased levels in Egbert were not as pronounced as those in southwest Michigan (i.e., less than half), back trajectory analysis indicated that air parcels with elevated DDT and DDE levels usually had passed through South

Haven, Michigan. South Haven is located in an area which is primarily devoted to fruit and vegetable production where the historic application of DDT could have been extensive. However, another potential source of DDT and its metabolites could be the current use of dicofol (1,1-bis(4'-chlorophenyl)2,2,2-trichloroethanol). It has been postulated that agricultural practices and air-soil diffusion affect DDT volatilization rates from soil. Therefore, a study by the Michigan Department of Environmental Quality is under way to determine impacts of tillage practices on ambient DDT levels in southwest Michigan and to assess any possible long-range transport effects (Michigan Department of Environmental Quality 1998).

Brazner and DeVita (1998) detected DDE in yellow perch and spottail shiners from 23 sites in Green Bay, Lake Michigan. Because the overall distribution of DDE tissue concentrations was fairly uniform within the bay, DDE contamination probably originates primarily from non-point sources, including atmospheric deposition. The few sites that exhibited unusually high DDE residues in fish may have point sources of DDE in nearby rivers.

1,1'-(dichloroethenylidene)bis(4-chlorobenzene), or DDE, has been detected in a variety of organisms at multiple trophic levels in Lake Superior (Kucklick and Baker 1998). For example, Dykstra et al. (1998) measured DDE concentrations in nestling blood (1989-1994) and addled eggs (1986-1993) of bald eagles in Lake Superior and inland Wisconsin sites. A comparison to published and unpublished historical data indicated that DDE levels declined significantly between 1969 and 1993, with current levels below those known to result in reproductive impairment.

In a study of juvenile American alligators in Lake Apopka, Florida, p,p'-DDE was detected in female serum at 17.98 ± 5.3 (SEM) ng/mL and in male serum at 7.35 ± 2.4 (SEM) ng/mL. Serum concentrations were significantly higher in females than males. Both male and female alligators in this area have been associated with abnormal reproductive and endocrine functions (Guillette et al. 1999).

In a sediment contamination study of the Chesapeake Bay and its tributaries from 1984 to 1991 by Eskin et al. (1996) under the Chesapeake Bay Program, concentrations of DDT and its metabolites tended to decline from the head to the mouth of the mainstem bay. Highest concentrations (0.0016 ppm DDT and 0.0023 ppm DDE) were detected in sediments in the upper half of the bay and near the mouths of the York and Potomac Rivers. Elsewhere in the lower half of the bay, concentrations were generally below detection limits. All DDT sediment concentrations were below the aquatic biota PEL of 0.270 ppm and the aquatic biota NOEL of 0.0045 ppm. DDE sediment concentrations were below the aquatic biota PEL of 0.130 ppm at all locations, but maximum concentrations exceeded the DDE NOEL of 0.0017 ppm for aquatic biota in some locations in the upper bay. In the tributaries, concentrations were generally below the PELs for aquatic biota.

Dieldrin. Recent monitoring data from IADN indicate that dieldrin is being transferred out of the Great Lakes with volatilization from Lake Superior, Lake Erie, and Lake Ontario at 5.9, 6.7, and 6.6 times the loadings in 1994 (Hoff et al. 1996). In general, concentrations of dieldrin in precipitation decreased from 1986 to 1994, but concentrations were three to four times higher at the Lake Erie site than at the other sites due to higher usage rates in the surrounding agricultural areas. Higher wet deposition levels were also observed over Lake Michigan due to the greater degree of urbanization surrounding that lake (U.S. EPA 1998). In Chesapeake Bay sediments between 1984 and 1991, dieldrin was detected at one site at levels between the aquatic biota PEL and NOEL (Eskin et al. 1996).

Chlordane. Chlordane, which was restricted in 1973 to use as a termiticide and was banned in 1988, was used primarily as a pesticide for corn crops (Aigner et al. 1998). Gas phase concentrations of chlordane in the air over Lake Superior do not currently exhibit a decreasing trend, as has been seen with

several other banned pesticides. In Chesapeake Bay sediments between 1984 and 1991, maximum chlordane concentrations were detected at levels between the aquatic biota PEL and NOEL (Eskin et al. 1996).

Toxaphene. In general, historical toxaphene concentration profiles in sediment cores across the Great Lakes indicate that the onset of contamination was between 1940 and 1950. Maximum levels occurred in the early 1970s to early 1980s, and accumulation rates in Lake Superior and Lake Michigan largely declined from historical peaks, as shown by comparing maximum historical rates to present rates (Table II-25). In addition, Lake Ontario and Lake Superior may have received toxaphene from non-atmospheric sources in the past (Pearson et al. 1997b). A back trajectory analysis using IADN monitoring data indicates that the Great Lakes receive toxaphene via atmospheric deposition from sources outside of the Great Lakes basin (U.S./Canada IADN Scientific Steering Committee 1998). Pearson et al. (1997b) investigated the history of toxaphene concentrations and accumulation in dated sediment cores from Lakes Superior, Ontario, and Michigan and two control lakes near Lake Superior that receive toxaphene only via atmospheric deposition. Concentrations at the surface of the cores, which represent current contamination levels, were similar among all samples with the exception of two samples from northern Lake Michigan. The similar toxaphene concentrations among the Great Lakes cores and control lakes suggest atmospheric input is the dominant source of toxaphene to the Great Lakes. The higher concentrations in the surface of the two northern Lake Michigan cores indicates that this area may be receiving current inputs (as great as 30-50 percent) from non-atmospheric sources.

Table II-25
Current and Maximum Rates of Toxaphene Accumulation in Great Lakes Sediments ^a

Location	Number of Sediment Cores Analyzed	Accumulation Rates in Sediment (ng/cm ² /yr)	
		Present	Maximum Historical
Lake Superior	3	0.097 - 0.14	0.25
Northern Lake Michigan	3	0.52 - 1.01	1.07
Southern Lake Michigan near Chicago Urban Area	1	0.24	0.32
Lake Ontario	3	0.39 - 0.60	1.4

^a All accumulations are focus-corrected.
 Source: Pearson et al. 1997b

Hexachlorocyclohexanes. The α -HCH and γ -HCH isomers are Great Waters pollutants of concern, whereas β -HCH (i.e., another of the eight HCH isomers) is not. Both α -HCH and γ -HCH can be transformed into β -HCH, which is a more toxic and bioaccumulative HCH isomer. Monitoring data indicate that air concentrations of HCH are decreasing, but the atmosphere continues to be a large source of HCHs to the Great Lakes. Since the 1980s, α -HCH and lindane (δ -HCH) precipitation concentrations declined; however, between 1991 and 1994, lindane concentrations increased at Lakes Superior and Ontario, possibly simply due to data variability. Although dry deposition inputs of HCH are relatively small (e.g., ranging from 0.2 to 1.5 kg/yr in all but Lake Ontario), the 1994 estimates of dry deposition are three to 10 times higher than 1992 estimates. Wet deposition, which is generally uniform across the lakes, ranges from 46 to 170 kg/yr and is between 0.25 and 1.2 times 1992 estimates, indicating a general downward trend in wet deposition. A gradient of α -HCH exists, with higher loadings in the lower lakes than in Lakes Superior and Michigan. Lindane has the highest wet deposition inputs over Lake Huron, possibly due to a source in upper Michigan (U.S. EPA 1998).

The net gas flux of HCH ranges from -140 to +1200 kg/yr (where positive values indicate volatilization out of the lake) based on monitoring studies. Both Lake Michigan and Lake Ontario are saturated with ¹⁴C-HCH (Hoff et al. 1996). For example, the mass of ¹⁴C-HCH lost through air-water gas exchange in Lake Ontario is similar to major input and loss factors such as wet deposition and advection (i.e., transport of the pollutant out of the lake) (Ridal et al. 1997). The IADN monitoring data also indicate that total HCHs are in equilibrium with the surface water and the atmosphere in the Great Lakes (Hillery et al. 1997).

Hexachlorobenzene. In general, levels of atmospheric deposition of HCB has remained constant over the past few years. Cohen et al. (1995) used the HYSPLIT/TRANSCO computer program to determine the amount of HCB emitted from sources to air and water media that is deposited in the five Great Lakes. The model was run using 1993 source and emissions data from 1,329 identified sources in the U.S. and Canada. Table II-26 provides modeled air deposition estimates, average depositional flux, and water effluent inputs for the five Great Lakes. The results indicate the following.

- C The depositional flux of HCB to the lakes increases from Lake Superior, Lake Michigan, Lake Huron, Lake Erie, to Lake Ontario, following the trend in industrialization around the lakes.
- C Hexachlorobenzene inputs from air deposition are greater than water discharge inputs for Lake Superior, Lake Michigan, and Lake Huron. In Lake Ontario and Lake Erie, the opposite is true; however, the estimates for air deposition and waterborne inputs are uncertain for HCB because sources outside the U.S. and Canada were not considered in the model and because estimates represent the amount of HCB that would be deposited if the lakes were uncontaminated with HCB (Cohen et al. 1995).

Table II-26
Modeled Air Deposition, Depositional Flux, and Waterborne Inputs
of HCB to the Great Lakes

HCB	Superior	Michigan	Huron	Erie	Ontario	Total
Total Deposition (kg/yr)	11	15	16	15	23	79
(range)	(4-49)	(5-73)	(6-74)	(6-65)	(9-101)	(30-362)
Depositional Flux (g/km ² /yr)	0.13	0.26	0.27	0.58	1.19	0.32
Waterborne Inputs (kg/yr)	0.1	0.8	0.6	<72	35	<108.5

Source: Cohen et al. 1995

In general, based on IADN monitoring data, wet and dry deposition of hexachlorobenzene (HCB) to the Great Lakes did not change from 1992 to 1994. In Lake Ontario, however, wet deposition of HCB increased six times in 1994 over the 1992 estimate. Hexachlorobenzene is in near equilibrium with the atmosphere and surface water, but is slightly loading Lake Superior and Lake Michigan and slightly volatilizing from Lake Erie and Lake Ontario (Hoff et al. 1996).

CROSS-POLLUTANT TRENDS

The EPA and other groups have initiated programs and projects to collect and compile information to assess current sources, emissions, loadings, exposure, and effects of pollutants in the Great Waters. Because many of these programs and projects address multiple pollutants of concern and

present cross-pollutant results, it is more appropriate to present the pollutant-specific information together with the program background rather than to split the information between pollutant categories. Therefore, background information on these various programs or projects along with information on their results is presented below by program or project. Note that most of these programs and projects are designed to assess contamination levels in certain media or specific waterbodies. While each program or project discussed below addresses a Great Waters waterbody and pollutants of concern, these programs generally do not directly assess atmospheric deposition. Instead, they address general pollution from many sources, one of which may be the atmosphere. Other programs and initiatives that portray how EPA and other agencies are working together to address the remaining issues related to atmospheric deposition of pollutants to the Great Waters are discussed in Chapter III.

FISH CONSUMPTION ADVISORIES

Fish consumption advisories are means of limiting human exposure when fish taken from a particular waterbody contain levels of pollutants that exceed recommended intake levels. National and regional trends in fish advisories can be estimated using EPA's database which contains information such as date of advisory, waterbody name and location, pollutant, fish or other wildlife species and range, advisory type, advisory status (e.g., active), and a contact name and telephone number (U.S. EPA 1998k). Note that different sampling methodologies and different approaches among States and years makes comparisons among States and years difficult. In addition, the amount of monitoring can vary widely from State to State.

In 1997, the number of waterbodies under advisory represented 16.5 percent of the Nation's total lake acreage and 8.2 percent of the Nation's river miles. In addition, 100 percent of the Great Lakes surface waters and their connecting waters, and a large portion of the Nation's coastal waters, are under advisory for one or more Great Waters pollutants of concern. According to the Listing of Fish and Wildlife Advisories in December 1997, 39 of 56 Great Waters were associated with fish advisories for pollutants of concern (see Appendix C for details on fish advisories in the Great Waters). The number of advisories in effect for U.S. waterbodies in 1997 increased 5 percent over the number reported in 1996 and 80 percent over the number reported in 1993 (U.S. EPA 1998k). This increase does not necessarily reflect actual increases of these pollutants in the environment. Rather, the increase is attributed to an increase in the number of assessments of contamination levels in fish and wildlife tissues as well as the use of more rigorous EPA risk assessment procedures by some States to set advisories.

Although advisories in the U.S. have been issued for a total of 46 pollutants, five Great Waters pollutants – mercury, PCBs, chlordane, dioxins, and DDT – comprised 95 percent of the advisories in 1997 (U.S. EPA 1998k). The number of advisories in the U.S. increased for three of these major pollutants and decreased for one, specifically:

Types of Fish Advisories

States, including the four U.S. Territories and tribal governments, issue advisories for waterbodies in an effort to reduce health risks associated with exposure to pollutants in certain freshwater fish and shellfish species:

- [*Advisories to limit consumption* – advisories to either the general population or subpopulations potentially at greater risk (e.g., children, pregnant or nursing women) to restrict their consumption of specific species of fish and other wildlife.
- [*Commercial fishing bans* – advisories that prohibit the commercial harvest and sale of fish, shellfish, and/or wildlife species from a designated water body (U.S. EPA 1998k).

- C Mercury advisories increased 6 percent (1,677 to 1,782) from 1996 to 1997 and 98 percent from 1993 to 1997 (899 to 1,782). This increase is primarily because of new mercury advisories in 11 States, particularly in Minnesota, Ohio, and Louisiana.
- C Advisories for DDT and dioxin rose slightly from 1996 to 1997. Advisories for DDT rose 3 percent (32 to 33), and dioxin advisories rose 8 percent (60 to 65), after a decline in the number of dioxin advisories in 1996. Dioxin advisories were rescinded in some States, in part, because many pulp and paper mills changed their processes. However, in Michigan, according to the 1999 Michigan Fish Advisory from the Michigan Department of Community Health, dioxin fish advisories were expanded to include Lake Huron, Lake Michigan, and Lake Superior.
- C The number of PCB advisories rose 84 percent from 1993 to 1997. In the last year of this period, however, advisories decreased 5 percent (617 to 588), due primarily to rescinding and readjusting some previously issued advisories. Despite this recent decline, 30 new advisories were issued in 1997 -- mostly by Ohio, Maine, Alabama, Connecticut, Minnesota, Nebraska, and New York -- making it difficult to discern trends from these advisories alone.

WATER QUALITY ASSESSMENTS

Surface waters and ground waters throughout the U.S. are monitored regularly to ensure that they are meeting the water quality standards appropriate to the intended uses. Pollutant concentration levels are measured to ensure that freshwater sources, including the Great Lakes and Lake Champlain, that are intended to be used for drinking water do not exceed the maximum contaminant level (MCL) guidelines for drinking water sources. In other surface waters, including all Great Waters, monitoring is conducted to ensure that ambient water quality criteria and other relevant guidelines are not exceeded and that the waterbodies meet the designated uses (e.g., fishing, swimming, boating). The current status of the Great Waters in terms of water quality criteria is described below.

Drinking Water

Of the Great Waters, only the Great Lakes and Lake Champlain are fresh waters that can be used as drinking water sources. Data indicate that both of these water systems provide safe drinking water, particularly as related to the Great Waters pollutants of concern. Based on data from 1994 and 1995 collected in support of section 305(b) of the Clean Water Act (CWA) by States, tribes, and other jurisdictions, most of the Great Lakes nearshore waters can be used as a source of drinking water with normal treatment (U.S. EPA 1998n). Similarly, the Lake Champlain Basin Program reported that from 1986 to 1995, only nine violations of EPA drinking water standards were reported -- all of which were for coliform contamination in Vermont (Lake Champlain Basin Program 1999).

Other Water Uses

Data on water quality conditions of the Nation's waters, including the Great Lakes in particular, are collected and reported by States, tribes, and other jurisdictions to EPA every 2 years as required under section 305(b) of the CWA. These assessments are based on water quality data that are compared to water quality standards, such as designated beneficial uses, numeric and narrative criteria for supporting each use, and an antidegradation statement to protect existing uses and to protect waterbodies from deteriorating in quality. Data from 1994 and 1995 indicate that approximately 40 percent of the Nation's surveyed rivers, lakes, and estuaries are too polluted to support basic uses, such as fishing and swimming. Nutrients and metals are the most widespread pollutants impacting lakes and rivers with

agriculture as the most common sources of pollutants; however, atmospheric deposition was also identified as a source of pollutants. In estuaries, nutrients are the most widespread pollutants with industrial point sources, urban runoff, and storm sewers as the most common sources of pollutants (U.S. EPA 1998n).

Most of the Great Lakes, in contrast, are safe for swimming and other recreational activities. However, approximately 97 percent of the surveyed shoreline area shows unfavorable conditions for supporting aquatic life and is impacted by toxic organic chemicals that appear in fish tissue samples at much higher concentrations than in water samples. These impacts are partially due to persistent toxic pollutant burdens, such as PCBs, in the food web. Several of the Great Lakes States identified air pollution, discontinued discharges from industrial facilities that are no longer in use, urban runoff and storm sewers, contaminated sediments, land disposal of wastes, and unspecified non-point sources as pollutant sources contributing to water quality problems (U.S. EPA 1998n).

NOAA'S NATIONAL STATUS AND TRENDS PROGRAM

Since 1984, NOAA's National Status and Trends (NS&T) Program has conducted annual monitoring of chemical contamination and biological responses to contamination to document current conditions and long-term trends in the environmental quality of U.S. near shore waters and sediments. The Mussel Watch Project is a major component of this monitoring program. Initiated in 1986, the Mussel Watch Project is designed to provide long-term trends and large-scale monitoring of pollutant distributions, with an emphasis on temporal rather than spatial trends. The project tracks trends in pollutant concentrations in mollusks at 287 coastal and estuarine sites on the Atlantic, Pacific, and Gulf coasts (including Great Waters). Eighty-three of these sites were recently added, including several sites from the Great Lakes region. Mussels and oysters are useful for monitoring changes in pollutant levels because they are sedentary organisms and concentrations in their tissues generally reflect changes in the concentrations in the surrounding water. Trends were examined in the Mussel Watch Project for the following Great Waters pollutants of concern: DDT, chlordane, dieldrin, PCBs, PAHs, cadmium, lead, and mercury (O'Connor 1999).

Florida NS&T Sites

A recent monitoring study suggests general decreasing trends in contaminant levels in South Florida (Cantillo et al. 1997), based on concentrations of PAH, PCB, DDT, lindane, hexachlorobenzene, chlordane, lead, mercury, and cadmium in bivalves from seven South Florida sites monitored by the NS&T Program during the period 1986 to 1994. Contaminant levels in South Florida were generally lower than nationwide. Nevertheless, a recent sediment quality assessment indicates that resident benthic communities may be adversely impacted by contaminants at a number of locations in Tampa Bay (Carr et al. 1996). For instance, up to 73 percent of the sediment pore water samples were toxic to sediment biota in at least one of the toxicity tests. In addition, sediment concentrations of several metals and PAHs were correlated with sediment toxicity, and concentrations of lead, PAHs, PCBs, and DDT equaled or exceeded sediment quality guidelines in several locations.

Also as part of the Mussel Watch and Benthic Surveillance Projects, NOAA conducts sediment toxicity assessment studies to determine the extent and severity of sediment toxicity in U.S. coastal regions. Sediment toxicity studies are conducted based on the following considerations: (1) a high level of contamination in oysters or mussels sampled in the NS&T Program; (2) the likelihood of adverse biological effects of contamination based on State and local data; and (3) possible collaboration with other Federal, State, and local agencies. Since 1991 when NOAA began conducting these studies, 23 coastal bays and estuaries covering approximately 4,000 km² have been the subject of studies (see text box). Study sites range in size from 0.3 km² to 1,350 km². Sediment toxicity surveys include three different toxicity tests which measure different biological endpoints leading to different results: (1) the

amphipod survival test using whole sediment; (2) the sea urchin fertilization test using sediment porewater; and (3) the Microtox test which measures decreased light production by a luminescent marine bacterium, *Vibrio fischeri*, using an organic extract of the sediment. The concentration of approximately 80 chemical contaminants, including mercury, lead, cadmium, PAHs, chlorinated dioxins and dibenzofurans, DDT and its metabolites, dieldrin, chlordane, lindane, HCH, and HCB, are measured in sampled sediments. Results of these studies are discussed below (NOAA 1999).

National Trends

Data collected between 1986 and 1996 from the Mussel Watch Project indicate that concentrations of most of the Great Waters pollutants of concerns in mussel and oyster tissues are decreasing at some sites. Specifically, decreasing trends of DDT, chlordane, dieldrin, PCBs, and cadmium were evident. Concentrations of cadmium declined despite the fact that other trace metals, including mercury and lead, exhibited no overall trend during this period. Data for PAHs also indicated no overall trend. Lindane and hexachlorobenzene were so infrequently detected that no trend determinations could be made. Another study found a decreasing trend for cadmium and lead, and no overall trend for PAHs (Lauenstein and Daskalakis 1999, O'Connor 1999, NOAA 1998).

The NOAA analyzed spatial trends in sediment contamination based on data collected for the Benthic Surveillance Project and the Mussel Watch Project (NOAA 1998), and found that both trace metal and organic contamination are associated with urban areas. Sites with “high” levels of contamination were located in urbanized areas of the Northeast, San Diego, Los Angeles, and Seattle.⁴ The cut-off levels that indicated “high” concentrations for DDT, PCBs, chlordane, dieldrin, PAHs, mercury, cadmium, and lead are 140 ppb, 430 ppb, 34, ppb, 9.1 ppb, 1100 ppb, 0.23 ppm, 6.2 ppm, and 4.8 ppm (mussels) and 0.84 ppm (oysters), respectively. “High” concentrations were rare in the southeast and along the Gulf of Mexico. Most sites with “high” contaminant concentrations can be linked to anthropogenic sources. Tissue concentration data can be misleading, however, because in some areas natural background levels and characteristics of chemicals can result in higher tissue concentrations. For example, high concentrations of cadmium and other trace metals in zebra mussels of the Great Lakes may be due to greater bioavailability of those metals in fresh water (NOAA 1998).

The sediment toxicity surveys, on a national level, indicate that 7 percent of the sediment in all of the study area was toxic based on the amphipod survival test; 39 percent was toxic based on the sea urchin fertilization test; and 66 percent was toxic based on the Microtox luminescence test. In general, larger estuaries and bays (areas greater than or equal to 250 km² or 100 mi²) had a lower average spatial extent of sediment toxicity (i.e., 6 percent) as compared to smaller estuaries and bays (i.e., 10 percent). However, sediment toxicity varies considerably among study areas in terms of spatial extent and severity of toxicity. Furthermore, based on amphipod survival tests, NOAA found that the spatial extent of toxicity was about 35 percent in small urbanized estuaries in the Northeast and southern California and was only 3 percent in southeastern estuaries, which border coastlines, farms, forests, wetlands, and fewer industrialized areas (NOAA 1999).

⁴ Areas with “high” concentrations were identified based on concentration distributions. “High” concentrations were defined as those with logarithmic values greater than the mean logarithmic value for all concentrations plus one standard deviation. Therefore, about 15 percent of all concentrations were “high.”

Trends in Great Waters

Pollutant trends based on mussel and oyster tissue data collected for the Mussel Watch Project from 1986 to 1996 at several Great Waters sites are shown in Table II-27 (NOAA 1998). Similar trends were also reported in the *Second Report to Congress* (U.S. EPA 1997b). Decreasing trends are statistically significant (confidence level of 95 percent); however, quantitative information regarding the changes in pollutant levels was not provided. Therefore, the magnitudes of the increases or decreases cannot be compared between sites.

Table II-27
Trends of Pollutant Concentrations in Mussel Watch Project (1986-1996)

Waterbodies (number of sites examined)	Contaminant Trend (number of sites affected) ^a							
	Mercury	Lead	Cadmium	PCB	DDT	PAH	Chlordane	Dieldrin
Chesapeake Bay (6 sites)	∅ (6)	∅ (5) " (1)	∅ (5) " (1)	" (4) ∅ (2)	∅ (3) " (3)	∅ (6)	" (5) ∅ (1)	∅ (3) " (3)
Delaware Bay (6 sites)	∅ (6)	∅ (6)	∅ (5) " (1)	∅ (5) " (1)	∅ (6)	∅ (6)	∅ (4) " (2)	∅ (5) " (1)
Long Island Sound (9 sites)	∅ (9)	∅ (8) " (1)	" (5) ∅ (4)	" (5) ∅ (4)	∅ (5) " (4)	∅ (9)	" (6) ∅ (3)	∅ (9)
Narragansett Bay (3 sites)	∅ (3)	∅ (2) " (1)	∅ (3)	∅ (3)	∅ (3)	∅ (3)	∅ (3)	∅ (3)
Tampa Bay (6 sites)	∅ (6)	∅ (5) £ (1)	∅ (6)	∅ (6)	∅ (4) " (2)	∅ (6)	∅ (3) " (3)	∅ (6)
Galveston Bay (6 sites)	∅ (6)	∅ (6)	∅ (6)	∅ (6)	∅ (6)	∅ (6)	∅ (4) " (2)	∅ (4) " (2)

^a Sites were sampled in at least 6 of 10 years; trend indicated by arrow (i.e., " = decreasing trend; £ = increasing trend; ∅ = no trend). Number of sites showing trend within each waterbody is indicated in parentheses. Source: NOAA 1998

In Tampa Bay, specifically, NS&T chemical contamination data for sediments, bivalves, and fish through 1991 indicate that there is not a bay-wide pattern of increasing or decreasing concentrations over recent years. However, increases and decreases were observed in some sample locations. Local geographic contamination trends indicate that sediment toxicity is highest in regions of northern Hillsborough Bay and moderate in regions of western Old Tampa Bay, along the western shore of Middle Tampa Bay, and in lower Boca Ciega Bay. The least toxic or nontoxic samples were taken from portions of Old Tampa Bay, and Middle and Lower Tampa Bay. Relatively high concentrations of petroleum hydrocarbons, chlorinated pesticides, other chlorinated hydrocarbons, ammonia, and trace metals were detected in the most toxic samples (Long and Greening 1999).

In the Chesapeake Bay, NS&T Program data from 186 sites from 1986 through 1995 generally indicate no trend in contamination levels in mollusks for each chemical analyzed. However, when trends were detected, decreases greatly outnumbered increases. Specifically, contamination levels decreased for chlordane, DDT, and dieldrin (Cantillo et al. 1998).

Consistent with trends on a national level, most of the Great Waters sites do not exhibit a statistically significant trend or change in pollutant levels in mollusk tissues during the 10-year period. Trends, when present, were mainly decreasing since 1986 (i.e., for cadmium, PCBs, DDT, PAHs,

chlordane, and dieldrin). According to O'Connor (1999) and NOAA (1998), decreases in levels of these chemicals are probably the result of bans on the use of chlorinated hydrocarbons (e.g., chlordane, DDT, PCBs) and the reduced use of certain chemicals.

NATIONAL SEDIMENT QUALITY SURVEY

The National Sediment Quality Survey (NSQS) describes the accumulation of chemical contaminants in the Nation's rivers, lakes, estuaries, and coastal waters. The NSQS is the first of three volumes of the first biennial *Report to Congress on the Incidence and Severity of Sediment Contamination in the United States* (U.S. EPA 1997i). The NSQS includes a screening-level assessment comparing human and ecological health benchmarks (e.g., draft sediment quality criteria, EPA cancer and noncancer human health risk levels) to concentrations of contaminants in sediment or, for human health only, to actual or estimated fish tissue concentrations. Results indicate the following.

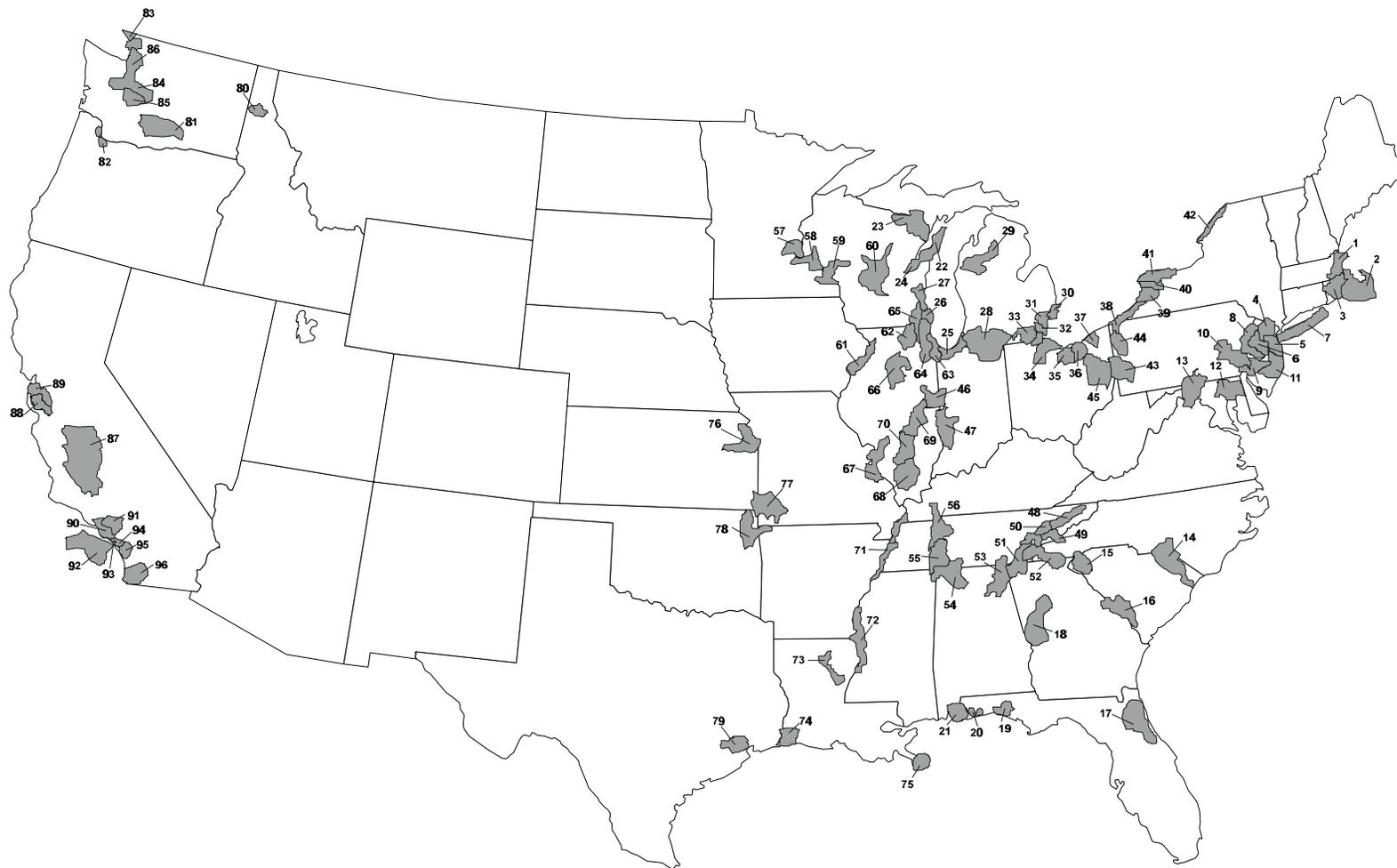
- C About 5 percent (i.e., 96) of the Nation's watersheds include APCs (Figure II-17, Appendix D includes the names of the numbered sites). The watersheds of the Great Lakes, Chesapeake Bay, and at least 17 NEP and NERRS sites are associated with APCs. An additional 39 percent of watersheds include at least one sampling station where contamination levels suggest probable adverse effects. Among that 39 percent are the watersheds of the Great Lakes, Chesapeake Bay, Lake Champlain, and some coastal waters. Only about 6 percent of watersheds did not indicate potential adverse effects on aquatic life or human health. Although there were no contaminant data for 35 percent of the watersheds, the data used were from monitoring programs targeted to areas with known or suspected contamination.
- C Probable aquatic life impacts were observed 41 percent more frequently than probable human health impacts. Specifically, of the 21,096 sites sampled, 3,287 had probable aquatic life impacts and 2,327 had probable human health impacts.
- C The contaminants detected most frequently at levels indicating probable adverse effects include PCBs, mercury, pesticides, and PAHs. Polychlorinated biphenyls were the sole or among the responsible indicators at 58 percent of the most contaminated (i.e., probable effects) sampling stations. Non-mercury metals were solely responsible for about 6 percent of the most contaminated sampling stations and 28 percent of the moderately contaminated (i.e., possible effects) sampling stations.

CHESAPEAKE BAY PROGRAM

As part of the Chesapeake Bay Program and in support of the goals and commitments of the Chesapeake Bay Agreement, information has been collected to assess the progress that has been made in reaching those goals.

- C A recent analysis of 10 years of monitoring data indicates that the water quality of major rivers and freshwater portions of the bay has improved, probably due to reduced runoff from agricultural lands, the phosphate detergent ban, and point source reductions in phosphorous and nitrogen releases (e.g., at wastewater treatment facilities) (Chesapeake Bay Program 1998d).
- The amount and extent of submerged aquatic vegetation (SAV) is a good indicator of water quality in the Chesapeake Bay. Although the areal coverage of bay grasses, or SAV, increased by 9 percent to 69,238 acres in 1997, in 1998 the acreage had decreased by 8 percent to 63,496

Figure II-17
Locations of Areas of Probable Concern Within Watersheds



See Appendix D for names of numbered sites.
Source: U.S. EPA 1997i

acres. The reasons for the 1998 decrease are unclear, but higher-than-average flow conditions in 1998 are a likely factor. Even so, the total acreage of SAV in 1998 still represents a 70 percent increase over the 1984 low point and 56 percent of the goal to restore 114,000 acres of SAV by 2005 (Chesapeake Bay Program 1999b).

- C National Toxics Release Inventory (TRI) data from 1988 to 1997 indicate a 67 percent reduction in chemical releases and transfers from industrial facilities to the bay. Releases of eight of the Chesapeake Bay Program Toxics of Concern (several of which are Great Waters program pollutants of concern), however, increased sharply in 1995, mostly due to the activities of a few facilities that were responsible for almost half of the releases (Chesapeake Bay Program 1998c).
- C From 1985 to 1997, total nitrogen concentrations decreased in the Susquehanna River, which provides over 50 percent of the fresh water to the bay. Nitrogen concentrations decreased in six of the major rivers to the bay (i.e., Susquehanna, Patuxent, Rappahannock, Mattaponi, James, Appomattox) and remained unchanged in two other rivers (i.e., Potomac, Pamunkey (a tributary to the York)). In contrast, total nitrogen concentrations increased in the upper central portion of the bay (i.e., the region around the Patapsco and Chester rivers) (Chesapeake Bay Program 1998b).

LAKE CHAMPLAIN SEDIMENT TOXICS ASSESSMENT PROGRAM

Phase II of the Lake Champlain Sediment Toxics Assessment Program investigated the three most contaminated areas of the lake: Cumberland Bay, Burlington Harbor, and Malletts Bay (McIntosh et al. 1997). Sediments of Cumberland Bay at Plattsburgh, New York are contaminated with PCBs from local historical sources and a possible source entering from the Saranac River. Water column concentrations in Cumberland Bay generally range from 0.3 to 2.1 ng/L, approximately an order of magnitude higher than in the main portion of the lake which has concentrations similar to present day levels in the Great Lakes. Water column concentrations of PCBs decreased dramatically with distance from the PCB “hot spot” near Wilcox Dock. Maximum concentrations near Wilcox Dock are up to 41 ng/L or 100 times greater than levels in the main body of the lake (McIntosh et al. 1997). The New York State Department of Environmental Protection recently completed a cleanup plan for Cumberland Bay, which will remove the most contaminated sediment near Wilcox Dock.

Surface sediment analyses at Burlington Harbor reveal that cadmium, copper, chromium, lead, and zinc display no clear spatial distribution, suggesting non-point sources (e.g., storm water, atmospheric deposition) for these metals. Bioavailability of metals appears to vary seasonally. Organic contaminants in Burlington Harbor (including PCBs, PAHs, and selected pesticides) generally exceeded the low estimate of sediment contamination levels at which adverse effects are predicted to occur among sensitive species or sensitive life stages. The PAHs and DDE exceeded the estimate of the sediment concentration levels at which toxic effects are predicted to occur among most species. Toxicity tests and benthic community analyses in Burlington Harbor showed chronic toxicity for a limited number of species, but the harbor does not appear to exhibit widespread hazardous conditions for aquatic life. In outer Malletts Bay, sediments frequently exceeded severe effects levels for some metals; however, mercury, lead, and cadmium were not the responsible contaminants (McIntosh et al. 1997).

SAN FRANCISCO ESTUARY REGIONAL MONITORING PROGRAM FOR TRACE SUBSTANCES

The San Francisco Estuary Regional Monitoring Program for Trace Substances began in 1993, and results are available from monitoring through 1996. This program collects data on water, sediment, and tissue contamination levels for a variety of pollutants, including some Great Waters pollutants of concern. Analyses of water column concentrations indicate that PCBs, PAHs, certain chlorinated pesticides, and mercury exceed water quality criteria (Table II-28). In sediments, mercury, total DDTs, and dieldrin frequently exceed levels at which adverse ecological effects are possible. An analysis of contaminant bioaccumulation by bivalves indicates that PCBs and PAHs are above the maximum tissue residue levels (MTRs, relatively recently developed, science-based guidelines). Polychlorinated biphenyls, dioxin, mercury, dieldrin, DDT, and chlordane concentrations in fish tissue exceed EPA screening values for human consumption. Lead levels are usually below water and sediment quality guidelines and have not shown evidence of bioaccumulation or biological effects. In comparing data over several years, concentrations of mercury, lead, and chlordane are decreasing in tissues. Overall, the condition of the San Francisco estuary seems to be improving over time. Additional trends analyses will be conducted as additional data are collected (San Francisco Estuary Institute 1997).

Table II-28
Percentages of 1996 Samples that Exceeded Guidelines
in the San Francisco Estuary

Pollutant	Water (Dissolved)	Water (Total)	Sediment	Bivalve Tissue
Cadmium	0	0	0	--
Mercury	0	19	81	0
Lead	0	6	6	--
PCBs	NA	93	6	100
PAHs	NA	0	38	100
Chlordane	NA	12	31	89
Dieldrin	NA	8	68	78
p,p'-DDE	NA	16	71	15

-- = no consistent guidelines

Source: San Francisco Estuary Institute 1997