



# FROM AIR TO WATER: THE CHALLENGE OF ATMOSPHERIC DEPOSITION

## A Primer for Water Quality and Air Quality Professionals

Many pollution studies and programs are media specific, dealing with water or air individually. But pollution does not always happen in such a segmented way. What starts as air pollution may end up as water pollution as dangerous compounds emitted into the air fall into surface waters. In fact, nitrogen, sulfur, and mercury compounds—pollutants of particular concern in the Northeast—make their way into water primarily through such atmospheric deposition.

To understand the challenge posed by atmospheric deposition requires an awareness of the mechanics of the phenomenon. It also requires an understanding of the relevant regulations and the monitoring and modeling techniques developed over the years. It is expected that an overall understanding of the issue will only increase support for a coordinated approach that considers both air and water pollution control strategies. Atmospheric deposition is a problem involving both air and water; the search for solutions, therefore, must be similarly integrated.

### The Pathways

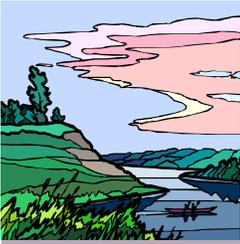
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An understanding of pollutant phase mobility is critical when considering the ecological and human health impacts of air pollution. Air can deliver pollutants great distances across political, geographic, and even international boundaries. Wind, temperature, and mixing patterns of the atmosphere can influence the distribution of pollutants. Pollutants can also volatilize out of water and back into the air, only to be re-deposited elsewhere. Air pollution deposition is a global problem; emitted pollutants can travel long distances, and deposition can occur over a large area.

Water pollution resulting from atmospheric deposition falls into the category of nonpoint source (NPS) pollution. Like other pathways of NPS pollution, such as runoff from agricultural fields and city streets, pollution caused through atmospheric deposition does not come from an isolated source, making it difficult to identify and control. It can come from the burning of fossil fuels, metal smelting operations, or even waste incinerators. The deposition of air pollutants on land or water also happens in several ways. Wet deposition occurs when air pollutants fall with rain, snow, or fog. Dry deposition is the deposition of pollutants as dry particles or gases. Pollutants can reach waterbodies by direct deposition—falling directly into the water—or through indirect deposition, in which pollutants fall onto land and wash into a waterbody as runoff.

Freshwater environments show the greatest ecological effects from atmospheric deposition. Lakes and streams become more acidic (pH value goes down) when the water and surrounding soil cannot buffer the acid deposition enough to neutralize it. Areas in the Northeast, including the Adirondacks and Catskill Mountains in New York State, contain many surface waters that are particularly sensitive to acidification. Soil-buffering capacity typically is poor in the region, and rain tends to be more acidic in the Northeast than in other regions. Some lakes in the Northeast have a pH value of less than 5, well below the normal range of 6 to 8. One of the most acidic lakes is Little Echo Pond in Franklin, N.Y., which has a pH of 4.2.

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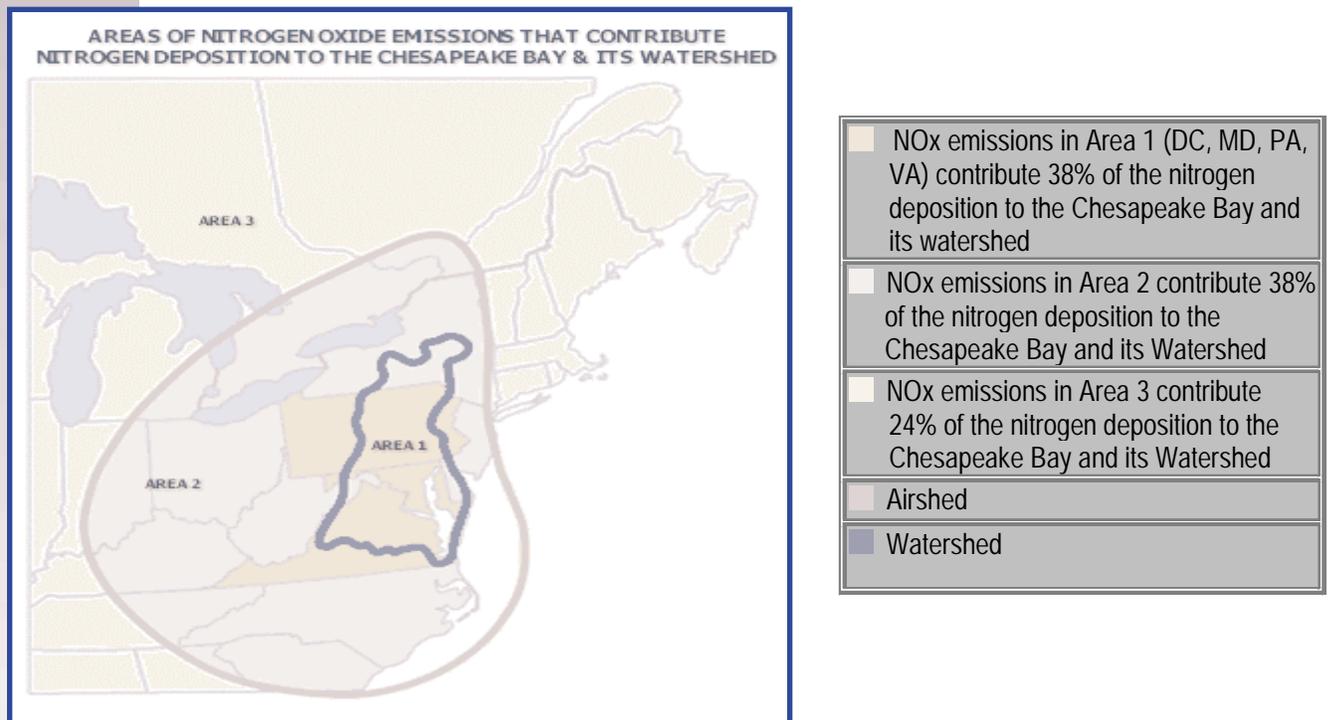


## Two Routes to a Waterbody: Watersheds and Airsheds

Watersheds define the entire drainage of a surface waterbody, such as a lake, river, stream, and wetland, and the waterbody's entire surrounding landscape. Large watersheds can contain many smaller watersheds, and because they often overlap state boundaries, a coordinated management approach is essential. Watershed-based management approaches involve integration of the strategies, priorities, and activities of all affected entities; account for interrelationships among various landscape components; and consider the effects of any changes within the watershed on the entire ecological system. The resource becomes the focal point, and environmental managers are able to gain a more complete understanding of overall conditions in an area and the stressors that affect those conditions.

An airshed is a geographical area responsible for emitting a certain percentage of air pollutants reaching a body of water. Since different pollutants behave differently in the atmosphere, the airshed of a given body of water will vary depending on the pollutant of interest. While watersheds are actual physical features of the landscape, airsheds are determined using mathematical models of atmospheric deposition. Airsheds are very useful in explaining the transportation of pollutants, and environmental managers can use them to help manage a waterbody more effectively. **Figure 1** demonstrates the concept of an airshed for the Chesapeake Bay watershed. Approximately 76 percent of nitrogen oxide emissions that end up in Chesapeake Bay and its watershed are generated within Areas 1 and 2. Clearly, airsheds—like watersheds—cross state boundaries and political jurisdictions, complicating management schemes to achieve emission reductions.

Figure 1.





## A Path to Clean Water: The Regulations

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In accordance with the Federal Clean Water Act (CWA) of 1972, states, territories, and tribes are responsible for establishing water quality standards. For each individual waterbody, the designated uses must be identified (e.g., drinking water supply, contact recreation, aquatic life support, etc.) and scientific criteria must be established to support those uses. Designated use criteria can be numeric, such as "0.38 milligrams per liter total nitrogen," or narrative, such as "no sediment loading above natural conditions." Section 303(d) of the CWA requires states to:

- Identify waters not meeting state water quality standards, and submit a list of these waters to EPA (referred to as 303(d) lists or impaired water body lists).
- Set priorities for Total Maximum Daily Load (TMDL) development.
- Develop a TMDL for each listed waterbody for each pollutant.

### What is a TMDL?

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The first step in the TMDL process is for a state to create a segment-by-segment listing of all waters that are considered threatened or impaired. This 303(d) list specifies all the water quality criteria that are violated for each segment and assigns a priority to each listed segment, which determines the order in which TMDLs will be established by a state. EPA requests that states' 303(d) lists account for all impaired waters, including those entirely or partially impaired by pollutants from atmospheric deposition.

When a waterbody cannot meet water quality standards through the use of technology-based controls, a TMDL is required. A TMDL specifies the maximum amount of a pollutant a waterbody can receive and still meet water quality standards. Furthermore, a TMDL allocates pollutant loadings among point and nonpoint sources (NPS) of pollution. The calculation must include a margin of safety to ensure that the waterbody can be used for the purposes designated by the state, and must also account for seasonal variation in water quality.

Early pollution control efforts under the CWA focused mainly on point sources of pollution, such as industrial dischargers and wastewater treatment plants, which can be regulated with discharge permits required under the National Pollutant Discharge Elimination System (NPDES) program, established by the CWA. NPS pollution is now of equal concern, but unlike pollution from single point sources, it comes from many diffuse sources, and is more difficult to control. NPS pollution is caused by rainfall or snowmelt moving over and through the ground. As the runoff travels, it picks up and carries away pollutants and sediments, finally depositing them into lakes, rivers, wetlands, coastal waters, and even underground sources of drinking water. Impervious surfaces, such as roofs, parking lots, driveways, and roads, increase the volume of runoff and the amount of NPS pollution reaching waterbodies.

Consideration of atmospheric deposition loads is important in TMDL development. The loading can usually be calculated fairly easily for lakes and estuaries by multiplying the pollutant deposition rate by the waterbody surface area. If atmospheric deposition is significant and the load is not considered in the TMDL, a waterbody may fail to meet water quality standards, despite large reductions in pollutants from water sources. Implementing a TMDL to control significant atmospheric pollutant loads can be a challenge since specific sources are difficult to identify and may be located outside a state's jurisdictional boundaries.



## A Path to Clean Water: Monitoring

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Both water quality and stream flow data are collected routinely by numerous agencies for a multitude of purposes. Stream flow, or discharge flow, is the volume of water passing a single point over time. While flow is expressed in volume, water quality parameters are usually expressed in concentrations. Often both flow and concentration need to be considered for effective water quality monitoring and management.

There are many ways to monitor water conditions. To monitor the constituents in water, sediments, and fish tissue, such as levels of dissolved oxygen, suspended sediments, nutrients, and metals, chemical measurements are taken. Physical measurements, such as temperature, flow, water color, and biological measurements, including the abundance and variety of aquatic plant and animal life and the ability of test organisms to survive in sample water, are also widely used. Monitoring can be conducted at regular sites on a continuous basis (fixed station monitoring), at selected sites to answer specific questions (intensive surveys), or on a temporary or seasonal basis. Increasingly, monitoring efforts are aimed at determining the condition of entire watersheds. This focus recognizes the impact of land-based activities on the waters that drain the land and the interconnectedness of all types of waterbodies, including those beneath the ground.

Point source monitoring involves the sampling and evaluation of discharges from facilities to assure compliance with federal or state water quality permits. The CWA prohibits discharging pollutants through a point source into a "water of the United States" in the absence of an NPDES permit. The permit will contain limits on what can be discharged and will stipulate monitoring and reporting requirements and other provisions to ensure that discharges do not harm water quality or human health.

Ambient monitoring involves sampling and assessment of the water column for contamination that is typically not attributed to specific discharges. It is performed to characterize waters and identify changes or trends in water quality over time. Ambient water quality monitoring data are also used in the process of setting permit limits for wastewater discharges at levels to maintain state and federal water quality standards and to establish criteria for receiving streams in accordance with the goals of the CWA. This is necessary to determine if standards and criteria are being achieved properly.

## Modeling

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The primary tools used in TMDL development, analyses, and implementation are watershed models, which evaluate the sources and controls of pollutant loading to receiving waters. Watershed models provide the framework for integrating data that describe the processes and land-surface characteristics that determine the amount of pollutants transported by streams. Watershed models allow the evaluation of historic and current stream conditions, enable the user to assess how changes in loads from different sources will affect stream conditions, and provide information for exploring ways to improve management practices. Models can simulate hydrology—both the land phase (water, sediment, and nutrient movement over land or through soils to waterbodies) and the water phase (the movement of water, sediment, etc. through the water channel to its outlet). Models can also simulate water quality changes based on land, atmospheric, point source, and other inputs of pollutants. Two examples of watershed models that can be useful in TMDL development in the Northeast are BASINS and the New England SPARROW model.



## A Promise of Clean Air: The Regulations

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In 1970, prior to the CWA, the United States Congress passed Amendments to the Clean Air Act (CAA) that set into motion a nationwide effort to improve the country's air quality. Since then, additional laws and regulations have been added, including the 1990 Amendments to the CAA. Although the 1990 CAA is a federal law covering the entire country, states do most of the work to implement the Act. Under the CAA, EPA establishes air quality standards to protect public health and public welfare. This ensures that all Americans have the same basic health and environmental protections.

States are required to develop state implementation plans (SIPs) that explain how they will fulfill their requirements under the CAA. A SIP is a collection of the regulations a state will use to clean up polluted areas. States must involve the public, through hearings and opportunities to comment, in the development of SIPs. Each SIP must be approved by EPA; if a SIP isn't acceptable, EPA has the authority to take over enforcing the CAA in that state. EPA assists the states by providing scientific research, expert studies, engineering designs, and funding to support clean air programs.

### Monitoring

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In order to make improvements in air quality, the amount of pollutants in the air must constantly be measured and monitored. Pollutants are typically expressed in three ways: rate of emissions, concentration of ambient air measurements, and rate of deposition. The national deposition and air monitoring networks are important resources for performing these measurements. The following are examples of such networks:

**National Atmospheric Deposition Program - National Trends Network (NADP-NTN).** The NADP was originally established in 1978 to measure acidic deposition. NADP-NTN is now considered the standard for wet deposition measurements of sulfate, nitrate, and ammonium. The network, which consists of more than 200 sites, is valuable for showing trends over space and time; the sites, however, cannot be used to identify pollutant sources.

**NADP - Mercury Deposition Network (MDN).** The MDN is a sub-network of NADP. The first sites became operational in 1995, and the network became an official part of NADP in 1996. MDN contains approximately 30 mercury deposition monitoring sites nationwide. Most of those sites monitor for total wet mercury deposition, while some also monitor for wet methyl-mercury deposition.

**NADP - Atmospheric Integrated Research and Monitoring Network (AIRMoN).** AIRMoN is sponsored by the National Oceanographic and Atmospheric Administration and run by NADP. The purpose of AIRMoN is to provide research-grade monitoring data to the NADP and data users, especially modelers. AIRMoN consists of 25 sites (15 dry and 10 wet) and measures sulfur and nitrogen compounds (dry) and several cations and anions (wet) on a daily basis.

**Clean Air Stats and Trend Network (CASTNet).** CASTNet is the nation's primary monitoring network for measuring dry acidic deposition. Used in conjunction with other national monitoring networks, CASTNet is used to determine the effectiveness of national emissions control programs. There are approximately 80 CASTNet sites nationwide.



## A Promise of Clean Air: Modeling Atmospheric Deposition

Two types of models are used to assess atmospheric deposition—deposition models and source attribution models. Each can do the following:

- Summarize current conditions to help identify management options.
- Fill in spatial or temporal holes left by a monitoring program.
- Predict future conditions due to growth or regulatory changes.
- Estimate what reductions are necessary to reach specific goals.
- Detect what changes in deposition rates will have significant impacts on to ecological or human health.

Deposition models are generally classified as Eulerian or LaGrangian. Eulerian models perform calculations based on grids. These grids are areas over which inputs are averages. For example, a model running with a 36 km grid (36 km on a side) assigns each source to be emitted in a particular grid and calculates atmospheric chemistry, transport, and deposition of those pollutants over a certain amount of time. The model then sends the pollutants to the next grids according to the results of those calculations. The key feature of this method is that atmospheric deposition is estimated for the entire grid area. Eulerian models are effective for capturing the complex nonlinear chemistry necessary to model ozone, nitrogen, sulfur, and mercury accurately. Examples of Eulerian models include:

[Regional Acid Deposition Model \(RADM\)](#), which models deposition for the eastern half of the United States for secondary particles (nitrate and sulfate) and acid deposition (nitric acid, nitrate, and sulfate).

[Regulatory Modeling System for Aerosols and Deposition \(REMSAD\)](#), a nationwide system that models wet and dry deposition for mercury, nitrogen (nitrate, nitric acid, and ammonia), and sulfate particles.

[Models3/Community Modeling for Air Quality \(CMAQ\)](#), which involves a graphical user interface, an atmospheric transport model, and a data analysis tool. CMAQ models acid precipitation (nitrate, sulfate, and nitric acid) and photochemical oxidants (NOX, VOCs, and ozone).

LaGrangian models generally work well for toxic compounds that have linear atmospheric chemistry. (This means the compound generally does not react or change from the point at which it is emitted through transport to the point of deposition.) These models track emission plumes that spread out toward some receptors, such as an estuary where deposition is taking place, based on the receptors' chemical and physical parameters and the meteorology. Examples of LaGrangian models include:

[Regional LaGrangian Model of Air Pollution \(RELMAP\)](#), which is one of the older models used for estimating atmospheric deposition rates for unreactive pollutants, such as most heavy metals and dioxin.

[California Puff Model \(CALPUFF\)](#), which is composed of a diagnostic meteorological processor and a puff dispersion model to identify the impact of sources on deposition of gases and particulates.

Some models, such as the Hybrid Single Particle LaGrangian Integration Trajectory Model (HYSPLIT), are LaGrangian models that can also be run in Eulerian mode. HYSPLIT is used to model the fate and transport of dioxin, atrazine, and mercury, and can be configured to model many other pollutants as well.



## The Need for Collaboration: Emissions of Concern

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Atmospheric deposition includes precipitation, airborne particles, or gases deposited from the atmosphere to Earth's surface. Pollutants of concern include carbon monoxide, carbon dioxide, chloroflorocarbons, lead, ozone, and particulate matter. But in the Northeast, three compounds—sulfur dioxide, nitrogen oxide, and mercury—are of particular concern. The dangers they pose only highlight the need for a collaborative approach to the problem of atmospheric deposition.

### Sulfur Dioxide

Sulfur dioxide (SO<sub>x</sub>) is the most abundant anthropogenic sulfur compound in the troposphere, and is emitted through coal and petroleum combustion, petroleum refining, and metal smelting operations. Coal burning power plants are by far the largest source of SO<sub>x</sub> emissions. Sulfate deposition, especially downwind of large SO<sub>x</sub> sources, leads to ecosystem acidification. Atmospheric deposition is the primary pathway of sulfur compounds to waters.

The ecological effects of SO<sub>x</sub> emissions are clearly seen in freshwater environments. Aquatic organisms in acidified waters often suffer from calcium deficiencies. Also, increasing acid escalates the mobility of certain trace metals like aluminum, cadmium, manganese, iron, arsenic, and mercury. Species that are sensitive to these metals, particularly fish, can suffer as a result. The effect of acidification on aluminum mobility has received the most attention because this metal is highly toxic to fish, but the negative effects of increasing levels of cadmium and mercury are becoming better known. In areas where buffering capacity is low, acid deposition also releases aluminum from soils into lakes and streams, further exacerbating acidity and toxicity problems.

### Nitrogen Oxide

Anthropogenic sources dominate the list of nitrogen emissions to the atmosphere. The largest source of NO<sub>x</sub> is the combustion of fossil fuels by automobiles and electric power plants. The adverse impact of atmospheric nitrogen deposition on waterbodies is significant; in some waterbodies, nitrogen deposited from the atmosphere is a large percentage of the total nitrogen load.

Nitrogen deposition can have devastating impacts on bays and estuaries by causing eutrophication—harmful increases in the growth of algae due to the nitrogen rich conditions. Increased algae populations consume an inordinate amount of oxygen, which can leave fish, plants, and other organisms without enough oxygen to survive. This condition, called hypoxia, occurs when the level of dissolved oxygen in the water is less than 2 parts per million. Areas of hypoxia, often called "dead zones," are present in more than half of the estuaries of the United States. Nitrogen input from the atmosphere as a percentage of total nitrogen input is about 40 percent for Maine's Casco Bay and 12 percent for Long Island Sound, which experiences severe eutrophication problems.

### Mercury

Mercury is a toxic metal released by both natural and man-made processes. It is estimated that man-made emissions have tripled mercury concentrations in the air and in the surface of the ocean since 1900. Human activities presently account for about 75 percent of worldwide mercury emissions. Man-made sources include incinerators, coal-burning facilities, and other industrial processes.

The unique chemical characteristics of mercury greatly influence its behavior in the environment and distinguish it from other metals. Aquatic biological processes can transform mercury into a very toxic compound known as methyl mercury. This compound can accumulate in the tissues of fish and shellfish to concentrations much higher than the surrounding environment. In fact, the concentration of mercury within the tissue of a fish or shellfish may be tens of thousands of times greater than the concentration of mercury in the water. Exposure to high concentrations of mercury, most often a result of eating contaminated fish, can pose a threat to the health of humans and wildlife.



## The Need for Collaboration: Signs of Progress

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Over the past 30 years, scientists have collected a large amount of data demonstrating the impacts that atmospheric deposition can have on surface water. For example, wet sulfate has acidified a number of Vermont's lakes and streams, and in Massachusetts's Waquoit Bay, atmospheric deposition accounts for 29 percent of the total nitrogen loading to the Bay, contributing to inadequate levels of dissolved oxygen. In Maine, the first New England state to issue a statewide fish consumption advisory, studies strongly suggest that atmospheric deposition is the primary source of mercury loading in a majority of the state's lakes. Managers must work together closely to solve these problems.

The control of sulfur dioxide (SO<sub>x</sub>) emissions is currently achieved using an innovative strategy called cap and trade, which assigns electrical utilities one-ton emission allowances. At the end of a given year, each utility must hold an allowance for each ton of sulfur dioxide it emitted, and may buy or sell allowances to meet its needs. Established by the CAA Amendments of 1990 and administered by EPA, the total SO<sub>x</sub> release allowed is set at a maximum of 8.95 million tons by the year 2010—approximately half of 1980 emissions. The cap and trade program has met its allowance goals since its start in 1995. Although CAA programs have had a major impact on nitrogen oxide (NO<sub>x</sub>) emissions, the emission reductions have been offset by emission increases attributable to economic growth, resulting in a relatively flat trend in NO<sub>x</sub> emissions since 1980 (23 million tons per year). EPA expects that additional NO<sub>x</sub> controls to be implemented under the CAA will slightly outpace emission increases associated with economic growth, resulting in a net decreasing trend in emissions through 2005.

EPA is taking steps to significantly reduce emissions of mercury from coal-fired power plants and other major sources. Actions include stringent regulations for municipal waste combustors, medical waste incinerators, and hazardous waste combustors. Progress is being made; EPA's new rules have already led to a drop in mercury air emissions of more than 50 percent. But even with such a dramatic reduction, the fact remains that mercury pollution is already widespread throughout New England, and is evidenced by increased fish consumption warnings by the states in the region.

## An Integrated Approach Toward Protection

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The progress that has been made so far in reducing water pollution caused by atmospheric deposition could not have been made without significant collaboration. Air and water programs are working together to address the contribution of air deposition to water quality under Total Maximum Daily Load (TMDL) determinations. Also, several state and interstate organizations have successfully worked with industry and municipalities to develop pollution prevention programs to procure banned and restricted use pesticides.

But more collaboration will be needed to take even more effective steps that will improve environmental results. With increased knowledge and better methodology, more integrated assessments can be conducted that will contribute to solving air and water problems simultaneously and will increase the effectiveness of environmental programs. A coordinated approach that emphasizes the sharing of ideas, information, and resources is the best way to confront the complex challenge of atmospheric deposition.

## Additional Sources For More Information

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New England Interstate Water Pollution Control Commission at [www.neiwpcc.org](http://www.neiwpcc.org).

Northeast States for Coordinated Air Use Management at [www.nescaum.org](http://www.nescaum.org).

United States Environmental Protection Agency Office of Air and Radiation at [www.epa.gov/oar/](http://www.epa.gov/oar/).

United States Environmental Protection Agency Office of Water at [www.epa.gov/OW/index.html](http://www.epa.gov/OW/index.html).