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Impacts of Atmospheric Pollution on Aquatic Ecosystems
**Impacts of Atmospheric Pollutants on Aquatic Ecosystems**

**SUMMARY**

Considerable progress has been made in reducing the discharge of atmospheric pollutants from point sources such as effluent pipes. A more difficult challenge involves identifying and controlling environmental contaminants generated by dispersed or nonpoint sources such as automobile exhaust, pesticide applications, and myriad commercial and industrial processes. Nonpoint pollutants can travel far from their sources when they are discharged into rivers or enter the atmosphere. While waterborne contaminants have received growing attention, little recognition has so far been given to the far-ranging environmental consequences of toxic substances and nutrients that are transported via the air.

This report reviews three categories of airborne pollutants that we consider of greatest concern, both for their ecological effects and their impacts on the health of fish, wildlife, and humans:

- **Organic compounds**: These include long-recognized persistent organic pollutants and a vastly larger group of chemicals such as brominated flame retardants, water-repellent coatings, and synthetic fragrances that remain largely unmonitored and unregulated.
- **Mercury**: Oxidized forms of mercury readily rain from the air onto terrestrial and aquatic ecosystems. In sediments, they can be transformed into monomethyl mercury, the form most toxic to fish and the wildlife and humans that consume fish.
- **Nutrients**: Atmospheric transport is a significant and increasing source of plant nutrients to freshwater and marine ecosystems and can accelerate eutrophication of these waters.

A review of the available scientific information indicates that:

- The pollutants that are most likely to present ecological risks are those that are (1) highly bioaccumulative, building up to high levels in animal tissues even when concentrations in the water remain relatively low, and (2) highly toxic, so that they cause harm at comparatively low doses.
- Atmosphere-water interactions that control the input and outgassing of persistent organic pollutants in aquatic systems are critically important in determining the cycling and residence times of these compounds and the extent of contamination of food webs.
- Although the effects of various types of pollutants are usually evaluated independently, many regions are subject to multiple pollutants, and their fate and impacts are intertwined. The effects of nutrient deposition on coastal waters, for instance, can alter how various organic contaminants and mercury are processed and bioaccumulated, and ultimately, how they affect aquatic organisms.
- For many organic pollutants, even long-banned chemicals such as PCBs and other organochlorines, non-atmospheric sources have been well controlled while atmospheric sources have either been neglected or ignored.
- Ecological effects of airborne organochlorines are a particular concern at high latitudes and altitudes. Even though concentrations of organochlorines in air masses and snow from northern and alpine regions are generally low, the food web dynamics, physiologies, and life cycles of cold region animals allow these contaminants to be biomagnified to extraordinary degrees in food chains.

Atmospherically deposited contaminants are generated largely by human activities, and reducing the extent and impacts of this increasingly significant source of environmental pollution will require greater recognition, monitoring, and ultimately, regulation.

**Cover Photo**: Fog over Lonesome Point on Lake Superior, Grand Marais, MI (courtesy the U.S. Environmental Protection Agency and U.S. Fish and Wildlife Service).
INTRODUCTION

Over the past several decades, the United States has made considerable progress in reducing the amount of pollutants discharged from identifiable point sources such as municipal effluent pipes. A more difficult challenge has been to identify and control environmental contaminants generated by dispersed or nonpoint sources such as automobile exhaust, livestock wastes, fertilizer and pesticide applications, and myriad commercial and industrial processes. These nonpoint pollutants can travel far from their sources when they seep or flow into rivers or enter the air. In particular, volatile chemicals – those that evaporate readily – can be carried through the atmosphere and fall on parts of the world far removed from their origins. They can either be deposited directly onto terrestrial and aquatic ecosystems (“direct” deposition) or deposited onto land surfaces and subsequently run off and be transferred into downstream waters (“indirect” deposition). Deposition of these pollutants can occur via wet or dry forms. Wet deposition includes rain, snow, sleet, hail, clouds, or fog, while dry deposition includes gases, dust, and minute particulate matter. Rates of wet deposition are most influenced by how readily the chemicals dissolve in water, while rates of dry deposition are very sensitive to the form (gas or particle) of the chemicals and the “stickiness” of the surface upon which they are being deposited. Chemicals deposited to aquatic ecosystems can re-volatilize and thus be redistributed via the atmosphere. During atmospheric transport, pollutants also can be transformed into other chemicals, some of which are of greater concern than those originally released to the atmosphere. Pollutants may also be transformed into other chemicals once they are deposited on and travel through watersheds. Until recently, however, little recognition has been given to the environmental consequences of toxic substances and nutrients that fall from the air as wet and dry deposition onto land-based and aquatic ecosystems.

Since air moves rapidly, atmospheric pollutants can travel long distances quickly and be deposited on distant watersheds. The “airshed” for a particular body of water can encompass hundreds of miles. An airshed defines the geographic area that contains the emissions sources that contribute 75 percent of the pollutants deposited in a particular watershed (Figure 1). Airsheds differ for each form of every pollutant and are determined by modeling atmospheric deposition of each chemical. They are useful theoretical tools for explaining atmospheric transport and for illustrating the need to control emission sources far removed from the ecosystem of concern.

This report reviews three categories of atmospheric pollutants that we consider of greatest concern, both for their ecological effects and their impacts on the health of a wide range of biota, including lower levels of the food web (algae, macrophytes, and invertebrates), fish, wildlife, and humans. These categories include organic compounds, mercury, and inorganic nutrients.

First, semi-volatile organic contaminants often have properties that allow them to persist in the environment for very long periods, to bioaccumulate (that is, build up in animal tissues), and to be toxic to aquatic organisms at lower levels of the food web, as well as to fish and to the wildlife and humans that eat fish. These persistent organic pollutants include a wide range of chemicals from pesticides and poly-chlorinated biphenyls (PCBs) to brominated flame-retardants, water- and stain-repellent coatings, and synthetic fragrances.

Second, the metal mercury can be transported in the atmosphere and fall onto terrestrial and aquatic ecosystems as precipitation or dry deposition. In aquatic systems, mercury may eventually be transformed into monomethyl mercury, a form that is bioaccumulative and can harm fish, wildlife, and humans.

Finally, the significance of inorganic forms of nutrients as atmospheric pollutants has been gaining increased attention. Nutrient-laden runoff from the land has long been acknowledged as a culprit in the over-enrichment and eutrophication of coastal ecosystems.
waters. Now, atmospheric nitrogen deposited in coastal and estuarine waters has been shown to be a major nutrient source in some coastal regions. The result can be excessive algal (phytoplankton) growth, oxygen depletion, degradation of marine habitats, and loss of both biodiversity and commercially valuable fish and shellfish species.

The properties that determine whether or not a chemical is likely to become a “problem” in aquatic ecosystems include its intrinsic toxicity, how long it can persist in air without decomposing (or without transforming to a chemical of greater concern), whether it bioaccumulates, how it interacts with other chemicals, whether it re-volatilizes, and how it is transformed once deposited in water.

Usually, the emission, airborne transport, fate, and ecological impacts of these three classes of pollutants are considered independently. However, while these contaminants may be generated by different sources, their impacts on the environment cannot be evaluated separately. Many coastal regions are subject to pollution from multiple sources, and the atmospheric deposition of nutrients often occurs in concert with deposition of mercury and one or more organic contaminants. Thus, the effects of nutrients on coastal ecosystems and their food webs can alter how various organic contaminants and mercury are processed, how they build up in the food web, and ultimately, how these toxic chemicals affect fish, wildlife, and humans.

The first section of this report examines these three classes of pollutants, their characteristics, and sources. The second section explores atmosphere-water interactions that determine the fate and persistence of airborne pollutants in freshwater and marine ecosystems. The third discusses the factors that determine whether atmospherically delivered pollutants present a risk to fish, wildlife, and humans. The fourth section looks at the relationship between nutrient deposition and the fate and impact of organic pollutants. The fifth and final section outlines priorities for regulation and monitoring of atmospheric pollutants.

**POLLUTANTS OF CONCERN**

**Organic Compounds**

The organic compounds that merit concern as atmospheric pollutants have diverse chemical structures, sources, and uses. They can generally be categorized either as deliberately produced substances such as pesticides, industrial compounds, and their persistent degradation products, or as byproducts of fossil fuel combustion or impurities in the synthesis of other chemicals. Although diverse structurally, the organic chemicals that are transported atmospherically, deposited into remote environments, and build up to levels that can affect wildlife and human health, have a relatively narrow range of physical and chemical properties (see Box 1). These are properties that (1) allow them to move in measurable quantities from land and water surfaces to the atmosphere, (2) give them sufficient stability (in the form of resistance to degradation by ultraviolet light and oxidation by hydroxyl radicals) to be transported long distances, and (3) impart a relatively high affinity for fatty tissues and resistance to breakdown in the body and thus allow them to accumulate in organisms and biomagnify (increase in concentration as they move up) in food chains.

Most atmospherically-transported chemicals that also bioaccumulate, such as PCBs and chlorobenzenes, are known as “multimedia chemicals” because they can be distributed through air, water, and soil rather than a single medium. Virtually all of the persistent organic pollutants listed under the Stockholm Convention — aldrin, chlordane, dieldrin, dichlorodiphenylchloroethane (DDT), endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) — are multimedia chemicals. A few highly chlorinated PCDD/F and PCB congeners are solid phase chemicals that concentrate solely in soils and sediments. (Congeners are members of a family of chemicals that have the same basic structure but have different amounts of chlorine.)

Persistent organic pollutants, as defined by the Stockholm Convention, are now scheduled for either global bans (chlorinated pesticides) or emission reductions (by-products such as PCDD/Fs). Nevertheless, the risk they present to the environment will persist because of their extraordinary resistance to degradation and because contaminated sources such as agricultural soils or PCB-containing building materials continue to re-supply the atmosphere. In addition, the Priority Substances List in the European Water Framework Directive includes many of these same chemicals, as well as polybrominated diphenyl ethers (PBDEs) used as fire retardants and chlorinated alkanes.

Chemicals that accumulate largely in one environmental medium (air, water, or soil) are generally not a concern for ecosystems impacted primarily by atmospheric pollution. For example, the herbicide atrazine is known to be very persistent in nutrient-poor waters, but little of it volatilizes to the atmosphere. Because of this, its impacts are largely of concern locally, for example in agricultural streams and wetlands near fields where atrazine is applied. Similarly, alkyl phenols and acid pharmaceuticals present an exposure risk to aquatic life in receiving waters near municipal waste treatment plants. Substantial concentrations of alkyl phenols are also observed in the atmosphere above estuaries receiving wastewater effluents, but these chemicals adhere efficiently to atmospheric aerosols and are soon removed by rainfall. Thus they travel only short distances in the atmosphere and are generally not a concern for remote aquatic environments where atmospheric deposition is the predominant source of pollution.

It is more difficult to classify the atmospheric pollution potential of the many semi-volatile chemicals that have multimedia characteristics but are rapidly degraded either in the atmosphere or in the biosphere. Examples of this group are the 2, 3 and 4-ring polyaromatic hydrocarbons (PAHs), organophosphorus pesticides, and mono-, di- and trichlorobenzenes. Under some circumstances, concentrations of these chemicals could build up even in remote environments if rates of atmospheric and water degradation are low — for example, in cold climate regions. This might lead to exposure of some aquatic or terrestrial organisms, but these compounds would likely be broken down during metabolism by vertebrates and thus would generally not be expected to build up in food webs. This generality needs to be
The combination of physical properties that give rise to environmentally mobile and bioaccumulative substances is best viewed by a two-dimensional plot of the key partition coefficients (Figure 2). Partition coefficients describe how much of a contaminant will be in one medium (e.g. air) compared to another medium (e.g. water) at equilibrium. For example, if a chemical has an air-water partition coefficient of 2, then there will be twice as much of the chemical in air than in water when expressed in equivalent concentrations. The octanol-water partition coefficient (Kow) is commonly used as an index of toxicity because solubility in octanol mimics solubility in biological lipid tissues and indicates the potential for bioaccumulation. Van de Meent et al. proposed classifying chemicals as either (A) gas phase chemicals that partition into the gas phase regardless of their mode of entry into the environment, (B) aqueous phase chemicals that partition into the aqueous environment regardless of mode of entry, (C) solid phase chemicals that partition into soils and sediments, and (D) multimedia chemicals that partition into more than one environmental medium. To visualize these categories, a global scale multimedia model (similar to GloboPOP) was applied that assumed no degradation except in air (class A), water (class B), and soil (class C). The shaded areas in Figure 2 reflect substances with a wide range of air-water and octanol-water partition coefficients, which indicate their relative affinity for air vs. water or for the lipid tissues of organisms vs. water, respectively.
Among the new organic contaminants of greatest concern are synthetic musk fragrances, PBDE flame retardants, and fluorinated surfactants.

**Synthetic Fragrances.** Synthetic musk fragrances are semi-volatile and lipophilic (literally “fat-loving” because they are attracted to fatty tissues) compounds that are added to a wide range of personal care products, including perfumes, cosmetics, soaps, and shampoos as well as laundry detergents. These synthetic fragrances are on the U. S. HPVC list but have only recently been studied as contaminants in any natural system in this country. The most common synthetic fragrances used are two nitro musks called musk xylene and musk ketone and two polycyclic musks known as HHCB (hexahydro-hexamethylcyclopentabenzopyran) and AHTN (hexamethyl-tetraline). In Europe, approximately 6,500 metric tons of these four synthetic compounds were produced in 1999 for use as consumer product additives.16

In the early 1980s, concentrations of synthetic musk fragrances were discovered in animal tissues for the first time. Since then, there has been an increasing awareness of the ubiquitous distribution and possible toxicological effects of these compounds. Recent measurements of these compounds in wastewater effluent and in air and water in the Great Lakes region, for instance, have illustrated that ecological exposures are chronic and likely to be increasing.17 This is cause for concern because both HHCB and AHTN have been shown to exhibit hormonal disruption in fish.18 (Hormonally active substances are chemicals that mimic or interfere with hormone function and can distort normal reproductive development, alter behavior, and impair disease resistance in wildlife and humans.) Several studies with cell cultures indicate that musk xylene, musk ketone, p-amino-musk xylene (a major breakdown product of musk xylene), and the polycyclic musk fragrance AHTN all demonstrate estrogenic activity in laboratory tests. In Europe, musk ketone and musk xylene were effectively banned from use as fragrances in 2002 because of their reported toxicities.19

Although HHCB and AHTN are both on the U. S. HPVC list, their use in personal care and household products is privileged information in the United States, and companies that use them do not have to report how much they use or manufacture. They also do not have to report any estimates on how much synthetic fragrance may ultimately be discharged into the environment. Because of this, ecological impacts of these compounds can only be identified through field and toxicological studies conducted long after exposures have begun. Fortunately, thanks to the intense interest in the fate and impacts of these compounds in Europe, analytical methods have been developed and standards are available for these fragrances.

For the vast majority of high production volume chemicals identified as potentially bioaccumulative and persistent, however, there are no trace analytical methods available for tracking their fate and impacts.20 Many of the recently initiated measurements of organic chemicals have been made using advances in analytical methodology, especially in the case of fluorinated organics.

**Flame retardants.** Among the newly emerging chemical contaminants of aquatic environments, the PBDE flame retardants and the perfluorinated surfactants discussed below have generated the greatest concern. PBDEs are used in thousands of consumer products from fire-resistant textiles and upholstered furniture to computers and televisions. Global demand for these additives increased from 40,000 tons in 1992 to 67,125 tons in 1999.21 The tetra- and pentaBDEs (TeBDE and PeBDE) are of greatest concern, and their concentrations are increasing in humans and wildlife.22 TeBDE and PeBDE are multimedia chemicals with physical properties similar to those of some PCBs. A higher brominated product, decabromodiphenyl ether (DecaBDE), is a solid phase chemical, but it may degrade in sunlight and in the tissues of fish to these lower brominated multimedia forms. Researchers measured a nine-fold increase in PBDEs in the tissues of ringed seals from the western Canadian Arctic over the period of 1981 to 2000.23

**Fluorinated surfactants.** Scientists have recently documented widespread contamination of wildlife and the general human population with perfluorinated acids.25 “Perfluorinated” is a term used to describe organic molecules that are fully fluorinated, meaning fluorine atoms have replaced all hydrogen atoms in the carbon-hydrogen bonds. The most widely known perfluorinated acids are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA); however, similar compounds having longer or shorter perfluorinated chains are also produced or exist as impurities within manufactured formulations. These important industrial chemicals fall into the category of surfactants because they are surface-active agents that repel water and oil or resist heat or other chemicals. The major use of PFOS is in treating fabric surfaces for stain resistance. The existing database describing physical properties of perfluorinated acids, including PFOS and PFOA, is severely limited because of their anomalous physical and chemical behavior. The properties of PFOS and PFOA suggest that they are poor candidates for long-range airborne transport, yet they have been discovered throughout the global environment. Worldwide dissemination of perfluorinated acids must therefore occur by way of an airborne neutral derivative that yields the free acid when it degrades.26 Widespread detection of precursors of PFOS and PFOA in the air in North America is providing increasing evidence that this is indeed the means by which these nonvolatile compounds have become such widespread contaminants.27

Over the past decade, researchers have found PFOS in birds, fish, and marine and land mammals around the world. For example, PFOS has been detected in the blood of ringed seals from the northern Baltic Sea, the eastern Canadian arctic, and Svalbard; the blood and liver of northern fur seals from Alaska; and the livers of polar bears from northern Alaska.28 PFOS concentrations in polar bear livers range from 1 to 5 micrograms per gram of tissue (wet weight), making it the most prominent organohalogen contaminant in these mammals.29

**Mercury**

Mercury is a metallic element (Hg) that has been extracted for centuries from sulfide ore or cinnabar (HgS). It has become a global pollutant and can be mobilized into the atmosphere from many human activities, including municipal trash incineration, burning of high sulfur coal (which contains cinnabar) in coal-fired power plants, metal smelting, chlorine-alkali plants, cement
making, and gold extraction, as well as from use of mercury-based fungicides in latex paints and the paper and pulp industry. Mercury in its elemental state has low reactivity and a long atmospheric residence time, thus allowing it to be mixed in the atmosphere on a global scale, while the oxidized forms are removed by wet and dry deposition. Oxidized reactive gaseous mercury (RGM), for example, is very soluble in water and is effectively deposited on land and water by snow and rainfall. Particulate forms of mercury fall as dry deposition.

The total mass of mercury in the atmosphere has been estimated at 5,000 to 6,000 metric tons, and approximately half of that was generated by human activities. Atmospheric concentrations of mercury peaked in the 1960s and 1970s and have been declining since then. It has been estimated that human activities contribute 70 to 80 percent of the total annual mercury emissions to the atmosphere and that more than 95 percent of mercury vapor in the atmosphere exists as elemental mercury (Hg). The remaining balance of the mercury exists as RGM, as particulate complexes of divalent mercury, and in the organic form as monomethyl mercury.

Although atmospheric concentrations have been declining for several decades, mass balance calculations that relate net mercury accumulation in the atmosphere with net loss indicate that human inputs of mercury to the atmosphere have increased threefold since the beginning of the industrial age. This estimate has been supported by data from several field-based studies of dated sediment cores from lakes and wetlands. The mass balance calculations also suggest that a legacy of mercury inputs is stored in terrestrial landscapes since only 5 percent of the atmospheric mercury deposited on the land is carried to the oceans via runoff. Refinement of mass balance calculations has led some researchers to conclude that dry deposition of RGM from the atmosphere can represent up to 35 percent of the total mercury input to the ocean.

Table 1 - Natural and anthropogenic sources of atmospheric nitrogen compounds (the major chemical forms of atmospheric nitrogen compounds are the reduced, oxidized and organic forms).

<table>
<thead>
<tr>
<th>Chemical Form</th>
<th>Sources (in approximate order of importance)</th>
</tr>
</thead>
</table>
| **Reduced Nitrogen**           | **Agricultural**  
Livestock waste (volatilized NH₃)  
Chemical fertilizers (volatilized NH₃)  
Biomass burning  
Dust from deforestation & land clearing  
**Urban & Rural (non-agricultural)**  
Wastewater treatment (volatilized NH₃)  
Fossil fuel combustion (from automobile catalytic converters)  
**Natural**  
Biomass burning (forest and grass fires)  
Decomposition of organic matter  
Dust and aerosols  
Volcanism  
**Urban & Rural (non-agricultural)**  
Fossil fuel combustion  
Mobile & stationary engines  
powerplants & industrial  
**Natural**  
Biomass burning  
Lightning  
Photolysis of N₂O (air, land, water)  
Dust and aerosols generated by storms  
Microbially-mediated volatilization |
| **Oxidized Nitrogen**          | **Agricultural**  
Dust and volatilization of wastes??  
**Urban & Rural (non-agricultural)**  
Dust/aerosols??  
**Natural**  
Atmospheric photochemical and lightning  
Biological production in oceans?? |
| **Organic Nitrogen**           | ?? = possible, but little known about, sources                                                                 |
| (Dissolved and Particulate)    |                                                                                                             |
While the mass balance has identified the magnitude of the various fluxes and pools of mercury and possible pathways for contamination of land and water, it does not provide information on the true partitioning of various forms of mercury in the atmosphere. This information is vital for predictive modeling of global mercury cycling and the effectiveness of mercury reduction strategies, and it continues to be an active topic of research. The potential for atmospheric deposition of mercury, for example, depends upon the distribution of various forms of mercury in emissions and plumes. Both particulate mercury and RGM are likely be deposited closer to their local or regional sources, while gaseous mercury is expected to be transported long range and have a one to two year residence time in the atmosphere. Current instrumentation allows for real-time measurement of atmospheric mercury as RGM, particulate mercury, and gaseous mercury at the picogram or sub-picogram level. The simultaneous measurement of these various atmospheric forms has allowed for analysis of phase distribution of mercury near point sources, at offshore oceanic stations, and in remote areas.

### Nutrients

A significant and increasing source of nutrients to freshwater and marine ecosystems is atmospheric deposition, either as rain or snow or as dry deposition of particles and gases. The nutrients that have received most attention are those that are essential for plant growth (primary production) because their concentrations control the growth of algae, which form the base of aquatic food webs. These nutrients include nitrogen, phosphorus, iron, and trace elements such as zinc, manganese, copper, cobalt, molybdenum, boron, and selenium. By far, the greatest attention has been focused on nitrogen because it is the most common limiting nutrient in marine, estuarine, and a few freshwater systems. Nitrogen is also a highly significant component of atmospheric deposition. In the marine environment, iron has been the subject of increasing interest because recent studies have shown that this metal limits primary production in some open ocean waters. Iron can also act synergistically with nitrogen to enhance algal production in coastal and ocean waters. Both nitrogen and phosphorus have received attention in freshwater ecosystems, which are most often phosphorus limited.

Early studies on human-generated contaminants delivered to ecosystems via the atmosphere identified nitrogen as a major nutrient constituent of both rain- and dry-fall. Atmospherically deposited nitrogen provides aquatic systems with a variety of biologically available nitrogen compounds, reflecting a diverse array of human activities and, to a lesser extent, natural processes (Table 1). These compounds include inorganic reduced forms (ammonia, ammonium), inorganic oxidized forms (nitrogen oxides, nitrate, nitrite), and organic forms (urea, amino acids, and unknown compounds). During the past century, atmospherically deposited nitrogen has increased tenfold, driven by trends in urbanization, industrial expansion, and agricultural intensification. Nitrogen deposition ranges from 400 to more than 1,200 kilograms per hectare each year and represents from 10 to more than 40 percent of the “new” nitrogen coming into North American and European inland and coastal waters (Table 2). On a larger scale, nitrogen flux to the North Atlantic Ocean basin is approximately 11.2 teragrams (trillion grams) per year and accounts for 46 to 57 percent of its “new” nitrogen input. This is comparable to the “new” nitrogen inputs delivered to the ocean by rivers. Indeed, in the waters of the North American continental shelf, nitrogen inputs via the atmosphere exceed those arriving by rivers.

### Table 2 - Estimated contributions of atmospheric deposition of nitrogen to “new” nitrogen inputs in diverse estuarine, coastal and open ocean waters.

<table>
<thead>
<tr>
<th>RECEIVING WATERS</th>
<th>PERCENT OF “NEW” NITROGEN THAT IS ATMOSPHERICALLY DEPOSITED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baltic Sea (Proper)</td>
<td>~ 30 W + D, I</td>
</tr>
<tr>
<td>Kiel Bight (Baltic)</td>
<td>40% W, I</td>
</tr>
<tr>
<td>North Sea (Coastal)</td>
<td>20-40% W + D, I</td>
</tr>
<tr>
<td>Eastern Mediterranean Sea</td>
<td>60% W, I</td>
</tr>
<tr>
<td>Waquoit Bay, MA, USA</td>
<td>29% W, I + O</td>
</tr>
<tr>
<td>Narragansett Bay, USA</td>
<td>12% W, I + O</td>
</tr>
<tr>
<td>Long Island Sound, USA</td>
<td>20% W, I + O</td>
</tr>
<tr>
<td>New York Bight, USA</td>
<td>38% W, I + O</td>
</tr>
<tr>
<td>Barnegat Bay, USA</td>
<td>40% W, I + O</td>
</tr>
<tr>
<td>Chesapeake Bay, USA</td>
<td>27% W, I + O</td>
</tr>
<tr>
<td>Rhode River, MD, USA</td>
<td>40% W, I + O</td>
</tr>
<tr>
<td>Neuse River Estuary, NC, USA</td>
<td>35% W, I + O</td>
</tr>
<tr>
<td>Pamlico Sound, NC, USA</td>
<td>~ 40% W + D, I</td>
</tr>
<tr>
<td>Sarasota/Tampa Bay, FL, USA</td>
<td>30% W + D, I</td>
</tr>
<tr>
<td>Mississipi River Plume, USA</td>
<td>2.5% W + D, I</td>
</tr>
</tbody>
</table>

Excessive nitrogen loading to estuarine and coastal waters is the key cause of accelerating eutrophication and the associated environmental consequences, including algal blooms, decreases in water clarity, toxicity, hypoxia or anoxia (oxygen-depleted or “dead zones”), fish kills, declines in submerged aquatic vegetation, and associated habitat loss.

As a significant source of “new” nitrogen, atmospheric deposition is both a local and regional issue because emission sources may be situated either within or far outside affected watersheds. Nitrogen oxides, mostly generated by fossil fuel combustion, account for 50 to 75 percent of nitrogen pollution in the United States, with reduced nitrogen and organic nitrogen making up the rest. Rapidly expanding livestock (swine, cattle and poultry) operations in the Midwest and Mid-Atlantic regions have accelerated the generation of nitrogen-enriched wastes and manures, and 30 to 70 percent or more of this may be emitted as ammonia (NH₃) gas. This has led to local and regional increases in ammonium (NH₄⁺) deposition, which can be seen in a two-decade analysis of atmospheric nitrogen deposition at the National Acid Deposition Program network site in Duplin County, North Carolina, a location that has experienced a rapid rise in animal operations during this period (Figure 3).

In Western Europe, where animal operations have dominated agricultural production for the
better part of the past century, ammonium is the most abundant form of atmospherically deposited nitrogen.\(^{67}\)

Phosphorus is a component of atmospheric deposition, but it typically occurs at concentrations less than a few percent those of nitrogen.\(^{68}\) This is especially true in regions where wet exceeds dry deposition, since phosphorus is usually bound to particles such as dust and windblown soils. Accordingly, in agricultural regions where phosphorus is applied as a fertilizer, or in arid regions where soils are readily transported by wind, atmospheric deposition tends to be most highly enriched with phosphorus.\(^{69}\) Even in these situations, phosphorus inputs rarely exceed nitrogen inputs.

From an ecological perspective, however, phosphorus may be of considerable importance since far less phosphorus than nitrogen is required for balanced plant growth.\(^{70}\) Therefore, in phosphorus-limited lakes, rivers, reservoirs, and even some marine systems such as the eastern Mediterranean Sea, atmospheric phosphorus inputs can be a significant nutrient source. For example, in Mid-western lakes, including the Great Lakes, atmospheric deposition of phosphorus contributes from 5 to 15 percent of the externally supplied phosphorus.\(^{71}\) In a recent study of the Mid-Atlantic coastal region, concentrations of total dissolved phosphorus in rainfall ranged from 4 to 15 micrograms per liter at nine sites, and total wet deposition ranged from 3.9 to 14 milligrams per square meter per year across the region.\(^{72}\) Annual total phosphorus leading to Lake Michigan in 1976 was 1.7 million kilograms per year, representing about 16 percent of the whole lake’s phosphorus budget.\(^{73}\) In alpine Lake Tahoe on the California-Nevada border, atmospherically deposited phosphorus accounts for approximately 25 percent of annual phosphorus inputs, while in the phosphorus-limited eastern Mediterranean Sea, atmospheric deliveries represent about 10 percent of the “new” phosphorus. Overall, it appears that airborne phosphorus typically accounts for 10 to 20 percent of total phosphorus loadings to water bodies from all sources. It remains unknown whether phosphorus transported into aquatic systems by river or air differs in its availability for stimulating plant growth.

Atmospheric deposition of both nitrogen and phosphorus varies with the seasons. For example, during the dry summer months when plant nutrient demands are highest, phosphorus inputs from surface runoff are minimal. At the same time, dry and windy conditions tend to favor transport of dust. Since phosphorus is often bound to dust particles, it is possible that atmospherically deposited phosphorus assumes a more important role as a source of “new” phosphorus during these crucial growth periods. Further investigation and quantification are needed of absolute and seasonal atmospheric deposition rates in various geographic regions relative to other phosphorus input sources. In the case of nitrogen, emissions from agricultural, urban, and industrial sources are generally highest in summer.

In the case of iron and other metals, atmospheric deposition, mainly in the form of dust, is a major source of “new” supplies of these nutrients to coastal and open ocean waters.\(^{74}\) Iron can be transported over great distances, as demonstrated by the iron-enriched Saharan dust storms that travel thousands of kilometers over the subtropical North Atlantic to “fertilize” iron-deficient and nutrient-poor waters as far away as the Caribbean Sea and the Eastern Seaboard of the United States.\(^{75}\) Iron and trace metals are also generated by volcanic emissions and by various continental pollution sources, including power plant, automotive, and industrial emissions.\(^{76}\) While there is uncertainty about the chemical forms and behavior of atmospherically deposited iron that enters the ocean, there is little doubt that it represents an important source of “new” iron in an environment that is otherwise free of external iron inputs.\(^{77}\)

**EMISSION, DEPOSITION, AND FATE PROCESSES AND SCALES**

The three major atmospheric pathways by which persistent organic pollutants enter water bodies such as the Great Lakes, Chesapeake Bay, other coastal estuaries, and the coastal and open sea are as (1) wet deposition via rain, snow, and fog, (2) dry deposition of particles, and (3) gaseous exchange between the air and water (Figure 4). Many urban industrial centers are located on or near coastal estuaries and the Great Lakes. Emissions of pollutants into the urban atmosphere are reflected in elevated local and regional pollutant concentrations and also in areas of intense localized atmospheric deposition that are over and above
the regional signal. For example, the southern basin of Lake Michigan and northern Chesapeake Bay are subject to contamination by air pollutants (PCBs, polyaromatic hydrocarbons (PAHs), mercury, and trace metals) because of their proximity to industrialized and urbanized Chicago and Baltimore, respectively. Concentrations of PCBs and PAHs are significantly elevated in Chicago and coastal Lake Michigan and in the air over Chesapeake Bay near Baltimore compared to the regional signal. Higher atmospheric concentrations of pollutants are ultimately reflected in increased precipitation and dry particle inputs of contaminants to the lake or to estuarine waters, as well as enhanced air-water exchange of organic compounds such as PCBs and PAHs. Of course, the relative importance of these atmospheric pathways to overall water pollution must be evaluated in terms of other inputs, including discharges from wastewater treatment facilities, pollution from upstream river flow, and mobilization of pollutants from sediments.

All three atmospheric pathways deliver pollutants directly to the water surface. This is especially significant for water bodies that have large surface areas compared to the area of the watershed that supplies their runoff. The Great Lakes and coastal seas are two examples. In turn, polluted water bodies may become sources of contaminants to the local and regional atmosphere as gases are lost from the water column to the air. This has been demonstrated for PCBs in the Great Lakes regions of southern Lake Michigan and Green Bay for PCBs, PAHs, polychlorinated dibenzo-p-dioxins and -dibenzofurans (PCDD/Fs), and nonylphenols in the New York-New Jersey Harbor Estuary, and for PCBs and PAHs in the Chesapeake Bay.

In contrast, many aquatic systems have large watershed-to-water area ratios. In these systems, deposits of atmospheric pollutants onto forests, grasslands, crops, paved areas, and other land surfaces in the watershed serve as important sources of runoff contamination to downstream lakes and estuaries. This is true of most lakes and estuaries in the Mid-Atlantic States, for example.

The relative importance of atmospheric deposition versus other sources of contamination is best demonstrated by chemical mass balances (Figures 5 and 6). Lake Superior, the largest and most pristine of the Great Lakes, is a prime example of an aquatic system in which the atmosphere must play a dominant role in inputs and losses of persistent organic pollutants. That is because the lake is cold, nutrient poor, has a large surface area that covers most of its watershed, and the urban and industrial density in the area is low. Cold water and a large surface area enhance the lake’s sensitivity to atmospheric inputs and air-water exchange through outgassing or volatilization. During the 1980s, for instance, the PCB burden in Lake Superior decreased exponentially at about 20 percent a year, primarily because of outgassing losses to the air. Although some PCBs bind to organic particles and sink to the lake bottom, this sedimentation process does not provide permanent removal of these contaminants from the water column. Thus, water-air exchange is the dominant loss mechanism. PCBs in the water column today are in approximate equilibrium with atmospheric concentrations.

The two-to-five fold higher concentration of toxaphene (an insecticide banned in the United States since 1990) than PCBs in Lake Superior has been attributed to a lower sedimentation rate and colder water temperatures relative to the other Great Lakes. Outgassing is an important loss mechanism for toxaphene, just as it is for PCBs, but on a longer time scale. The half-life for PCB decline in Lake Superior waters is 3.5 years compared to 12 years for toxaphene. Clearance of toxaphene by volatilization would be faster were it not for the higher atmospheric concentrations generated by continued outgassing of toxaphene from agricultural soils in the southern states upwind from Lake Superior.

The pesticide atrazine provides a counter example to PCBs and toxaphene since it is delivered to water bodies mainly by riverine transport of agricultural runoff, and the role of atmospheric delivery is believed to be minimal. Although atrazine has a 30- to 90-day half-life in soils, transport into rivers and lakes significantly extends its half-life. Lake Michigan and other large aquatic systems are most sensitive to tributary inputs of atrazine, but the long-term impacts on the lake environment are controlled by the long residence times in water and the slow rates at which the compound is transformed. Only about 1 percent of the atrazine applied to crop fields is lost by runoff to rivers and lakes and another 1 percent to aerial transport. Nevertheless, the large quantities of this pesticide that are applied combine with efficient transport, slow transformation rates, and long residence times in water to cause significant accumulation of atrazine in aquatic systems. The atmosphere plays little or no role in the re-
as well as large lakes and the global oceans. Recent studies of remote freshwater ecosystems and their food webs, especially the aquatic food chain. This is the dominant process for contamination of persistent organic pollutants into the aquatic food web and water-algal exchange may promote the introduction of contaminants from the water column as algae die and sink to the bottom. Conditions lead to faster algal uptake and removal of contaminants from the water column as algae die and sink to the bottom.

That is, atmospheric deposition in general, and air-water exchange specifically, dominates total inputs. Moreover, air-water exchange is the likely mode of contaminant entry into the food chain where inputs from surface runoff are minimal, and even in some cases where local surface loadings are significant. The nutrient status of water bodies and the cycling of organic material through the food web also play critical roles in determining the fate and impact of persistent organic pollutants in aquatic ecosystems.

ECOLOGICAL RESPONSES

The environmental factors discussed above determine whether aquatic life will be exposed to atmospherically transported chemicals. Several additional factors, however, determine whether these contaminants will harm aquatic organisms or the animals and humans that consume them. Essentially, all chemicals can be toxic to aquatic life if the exposure concentrations are sufficiently high. Conversely, most chemicals also have threshold concentrations below which no appreciable adverse effects on aquatic life are expected. From the perspective of identifying inputs from surface runoff are minimal, and even in some cases where local surface loadings are significant. The nutrient status of water bodies and the cycling of organic material through the food web also play critical roles in determining the fate and impact of persistent organic pollutants in aquatic ecosystems.

In summary, atmosphere-water interactions are critically important in the cycling and residence times of persistent organic pollutants and the contamination of food webs in lakes, estuaries, coastal waters and the global ocean. In remote aquatic systems or those with large surface areas, atmospheric deposition in general, and air-water exchange specifically, dominates total inputs. Moreover, air-water exchange is the likely mode of contaminant entry into the food chain where inputs from surface runoff are minimal, and even in some cases where local surface loadings are significant. The nutrient status of water bodies and the cycling of organic material through the food web also play critical roles in determining the fate and impact of persistent organic pollutants in aquatic ecosystems.

As shown in Figure 4, the processes of air-water and water-algal exchange may promote the introduction of persistent organic pollutants into the aquatic food chain. This is the dominant process for contamination of remote freshwater ecosystems and their food webs, as well as large lakes and the global oceans. Recent data even suggest that estuarine food chains dominated by surface runoff of pollutants may also experience food chain contamination from air-water exchange, especially where local and regional emissions create high atmospheric concentrations of pollutants. A key consideration is that air-water exchange delivers organic pollutants to the water column in the form of 100 percent bioavailable dissolved gases, whereas contaminants from riverine sources and in stirred and resuspended sediments may not be readily available for use by organisms.

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Organisms whose food chains are heavily connected to sediments or atmospheric transport might experience greater bioaccumulation and biomagnification. Sediments may far exceed those in the water column. Thus, reduction in recent years, concentrations of DDT in the atmospheric transport of DDT began many decades ago and where a chemical is found in the ecosystem. For example, because of the high potency of the chemical. By comparison, airborne contaminants with lower bioaccumulation or lower toxicity would be much less likely to cause ecological risk, unless the mass of atmospherically deposited chemicals was much greater.

A second common feature of chemicals that tend to cause ecological effects following airborne transport is that they often have relatively high toxicity; that is, they cause toxic effects at comparatively low exposure levels. Combining this with bioaccumulation builds a typical scenario: Low environmental concentrations of atmospherically transported chemicals are transformed into much higher doses in animal tissues via bioaccumulation, and the accumulated dose creates toxic effects because of the high potency of the chemical. By comparison, airborne contaminants with lower bioaccumulation or lower toxicity would be much less likely to cause ecological risk, unless the mass of atmospherically deposited chemicals was much greater.

Several other factors also affect bioaccumulation. Some chemicals biomagnify as they pass up the food chain. Because the chemical concentration increases with each step up the food chain, organisms that are part of long food chains with multiple links can be more susceptible to bioaccumulative chemicals. For example, a lake trout might feed on relatively large fish, which eat smaller fish, which in turn eat zooplankton, which feed on algae. Thus a lake trout would be expected to acquire greater doses of contaminants than a fish feeding primarily on zooplankton. Another factor is the structure of the food chain in relation to where a chemical is found in the ecosystem. For example, because the atmospheric transport of DDT began many decades ago and has been reduced in recent years, concentrations of DDT in sediments may far exceed those in the water column. Thus, organisms whose food chains are heavily connected to sediments –systems where fish feed on bottom-dwelling insect larvae, for instance — may experience greater bioaccumulation than organisms in food chains based on algae living in the water column. Also, as mentioned previously, eutrophic systems with high levels and turnover of algal biomass have the capacity to remove greater contaminant loads from the water column and sequester it in deep sediments where it is less available to the rest of the aquatic food chain than oligotrophic systems.

With regard to toxicity, many problem chemicals have such a high degree of biological activity in the body that they can disrupt normal physiology at comparatively low concentrations. In this sense, it should not be surprising that many pesticides are highly toxic because they are specifically designed to interact with biological systems. In other cases, however, high toxicity appears to be an unfortunate coincidence. Such is the case with methyl mercury, the organic form of mercury that is readily absorbed by fish and for which fish and other animals have evolved no specific detoxification mechanism. Chlorinated dioxins/furans and PCBs interact in the body with a specific cell receptor called the aryl-hydrocarbon (Ah) receptor. Depending on their molecular geometry, some congeners bind very tightly to this receptor and thereby cause a high degree of toxicity. While the mechanism by which a chemical causes toxicity is generally similar across a wide range of animal species, the absolute sensitivity that is, the dose required to cause an adverse effect — can vary substantially across species, often by factors of 100-fold or more. This obviously places some species at greater risk than others.

Considering past and present environmental problems associated with toxic chemicals, it becomes clear how various factors can interact to produce ecological risks. For example, the scenario of risks to lake trout in Lake Ontario from dioxin/furan and PCB exposure combines highly toxic multimedia chemicals with an organism that has a relatively long food chain and a high toxicological sensitivity to Ah-active chemicals. Loons may be particularly sensitive to mercury because they have a diet high in fish, which indicates a long food chain, and live comparatively long lives. Marine mammals are also long lived, eat aquatic life, and are often used as an indicator of exposure to bioaccumulative chemicals.

Organochlorine Chemicals, a Legacy of the Past

In general, the management response to many organochlorine pollutants — including PCBs, dioxins, furans, and chlorinated pesticides such as DDT, DDE, PCBs, toxaphene, HCHs, dieldrin, mirex, and chlordane — has become an ecological success story in recent decades. Following the recognition in the 1960s and 1970s that widespread use and airborne transport of several
For many organic pollutants that are persistent, bioaccumulative, and toxic, non-atmospheric sources have been well controlled while atmospheric sources have been either neglected or ignored. PCBs are a good example of this phenomenon. PCBs were used in a wide variety of industrial applications and contaminated many industrial and municipal effluent discharges during the period of their use from 1930 to the 1970s. Significant inputs to ecological systems occurred through direct discharge to surface waters or to wastewater treatment plants. Currently, these sources have been diverted, eliminated, or significantly reduced. The entire state of Illinois, for example, discharges no municipal effluent to Lake Michigan, preventing significant input of residual PCBs to the lake. However, atmospheric sources have not received the same attention, probably because few measurements of atmospheric concentrations of PCBs in any urban area were available prior to the mid-1990s. Even now, Chicago is one of the very few urban areas for which substantial atmospheric measurements are available, and concentrations of PCBs are very high in the Chicago area. As a result, deposition of gas-phase PCBs from Chicago to Lake Michigan is probably the most important current source of these chemicals to the lake. In fact, if the prevailing winds drive the Chicago source away from the lake, Lake Michigan will degas PCBs at a faster rate than it is absorbing them from the air. When the Chicago plume is pushed over the lake by southwest winds, the area of deposition can range from several kilometers to three-quarters of the entire lake (Figure 8). Other urban areas with similar industrial histories are also likely to remain major sources of long-banned organic pollutants, at least until the importance of atmospheric sources is recognized and decisions are made for their control.

Concerns remain about ecological effects of airborne organochlorines at high latitudes and altitudes. The semi-volatile nature of many organochlorines allows them to be re-emitted from contaminated ecosystems during warm weather, and to be carried in air masses and re-deposited where temperatures are cooler. This so-called "cold condensation" effect has allowed the gradual atmospheric migration of persistent compounds from tropical and temperate regions to arctic and alpine sites. Circumpolar movement in air masses has also allowed some of the chemicals to migrate from areas of Asia where they are still in use to be deposited in arctic and alpine regions of North America and Europe. As a result, deposition of many chemicals in northern and alpine regions continued to increase for 10 to 30 years after the chemicals were banned in North America, as shown from profiles in dated sediments and glaciers. Concentrations in some areas of the arctic are still high enough to cause reproductive failure and eggshell thinning in predatory birds such as peregrine falcons and sea eagles. Liver enzyme induction, which is strongly affected by PCBs and other organochlorines, has been observed in beluga whales, seals, and polar bears.

While concentrations of organochlorines in air masses and precipitation from northern and alpine regions are generally low, the food web dynamics, physiologies, and life cycles of cold region organisms allow these chemicals to be biomagnified to extraordinary degrees in food chains. Most organochlorines are lipophilic, and animals in cold regions generally store large amounts of lipids to allow their survival during long winters. Many of the organisms also grow slowly and have long life spans, characteristics that promote biomagnification. As a result, many pollutants are biomagnified by a million-fold and more in arctic food chains. Concentrations are high enough to be of considerable concern for predators of marine mammals, including native people and polar bears. For example, Inuit women in northern Quebec who rely heavily on fish and marine mammals for food have concentrations of many pollutants in their breast milk and notocord blood that are many times higher than in urban Caucasian women.
from that province. Concentrations of many of the compounds greatly exceed World Health Organization recommendations, and they also exceed concentrations that have caused detectable reproductive effects in women from contaminated temperate regions. So far, no published studies have documented health effects in northern human populations, but such studies are only in preliminary stages and epidemiologically significant results are difficult to obtain from small populations.

Some northern inland areas where predatory freshwater fish grow slowly and live long can also have concentrations of organochlorines high enough to be of concern. One example is Lake Laberge, Yukon, where lake trout were found to have elevated concentrations of toxaphene, DDT, and PCBs. Toxaphene concentrations were high enough to cause Health Canada to issue a consumption advisory to aboriginal populations who used fish from the lake as an important part of their diets. The main reason for high values in Laberge appears to be that its food chain is effectively one step longer than in other area lakes, thus enhancing biomagnification of these pollutants.

Unusually high concentrations of these same organo-chlorines were noted in some lake trout populations in the national parks of the Canadian Rocky Mountains, a region generally regarded as near pristine. A detailed study of Bow Lake, where some of the highest concentrations were found, indicated that in this case the contamination levels resulted not from biomagnification but largely from increased deposition at high altitude as well as from the melting of glacial strata from the mid twentieth century when high concentrations of the substances were deposited in glaciers before their use was banned in North America. Biomagnification in food chains is low in the lake, and high concentrations of organochlorines in fish appear to result from high inputs and direct absorption of the compounds by small crustaceans on which the fish feed. No consumption advisories were issued for Bow Lake because there are no human populations who rely on the lake for subsistence. Similarly, high concentrations of organochlorines have been measured in the sediments and fishes of alpine lakes in Europe, the result of high atmospheric inputs. Unlike in western Canada, however, the source areas for the compounds appear to be regional rather than trans-Pacific.

Another example of northern concerns involves polar bears (Figure 9). A study in the Svalbard region of Norway found no reproductive effects in polar bears that were attributable to high PCBs. Yet researchers did observe high mortalities of young bears, and two of the bears had deformed genitalia. One hypothesis is that these effects might be the result of high body burdens of organochlorines. For polar bears and many other arctic species, concentrations of organochlorines exceed the No-Observed-Adverse-Effect Level (NOAEL) and Low-Observed-Adverse-Effect Level (LOAEL) that have been determined for southern species.

There is also concern about additive or synergistic effects of many organochlorines. For example, it is now known that dioxins, furans, and some mono-ortho PCBs all bind to the Ah receptor. Effects appear to be additive, but different compounds have different potencies. In recognition of this, a combined toxic equivalency factor (TEF) scheme has been developed which allows concentrations of many dioxins, furans, and PCBs to be converted to an equivalent concentration of the most potent of these, the dioxin 2,3,7,8-TCDD. The TEF scheme is now widely used, whereas 10 years ago, the effects of various organo-clorines were considered in isolation.

New Chemicals of Concern

While older organo-chlorines appear to have been controlled before they caused extinctions of predatory bird species or severe global reproductive effects, there are concerns about new organic pollutants that are persistent, toxic, and biomagnify in food chains. Atrazine, melalachlor, and endosulfan pesticides continue to be used, although they are reasonably persistent and toxic. Complex chemicals containing other halogens than chlorine (such as bromine and fluorine) have also emerged as potential environmental toxins. Flame retardants, for example, recent studies have shown that levels of flame retardants (PBDEs) are increasing rapidly in the Great Lakes, with doubling times on the order of 3.5 years. These contaminants are also found in northern and arctic sites. PBDEs are persistent and biomagnify in aquatic food chains.

Reviews of chemicals detected in high-latitude snow indicate that dozens or even hundreds of industrial organic chemicals that are not used in the region are present, indicating long-range atmospheric transport. In most cases, little is known of the biogeochemistry or toxicity of these contaminants.
Mercury

Once removed from the atmosphere, much deposited mercury ends up in aquatic systems, either by direct deposit or in surface runoff.\textsuperscript{122} The effects of mercury on fish, as well as birds and mammals that eat contaminated fish, are of significant concern, and those concerns stem from exposure to the methylated (organic) form, monomethyl mercury (MMHg).\textsuperscript{123} In anaerobic environments such as lake or wetland sediments, mercury is transformed to MMHg by microbial action, most notably by sulfur-reducing bacteria. The MMHg diffuses into the water column where it can be taken up by fish, accumulating in their muscle tissue by binding to organic compounds known as thiol groups or mercaptans. MMHg is the most toxic form of mercury. Reproductive effects have been documented in fish, fish-eating wildlife, and humans.\textsuperscript{124} MMHg causes neurological, liver, and kidney damage, as well as neurodevelopmental effects in children.\textsuperscript{125}

In the United States, 48 states advise the public against unlimited consumption of freshwater fish due to their MMHg levels. In addition, the U.S. Environmental Protection Agency (EPA) has issued a mercury-based national fish consumption advisory for five species of oceanic fish. The EPA considers the maximum allowable no-effects dose of mercury to be 0.1 micrograms per kilogram of body weight per day, and this guideline was recently supported in an independent study by the National Academy of Sciences.\textsuperscript{126}

Arctic ecosystems and their associated human communities are particularly susceptible to mercury contamination. When mercury reaches the Arctic, it is transformed such that it is deposited on the snow at the start of the arctic sunrise (the first appearance of the sun after the long arctic winter). A significant amount of this mercury enters the ecosystem and the rest re-enters the atmosphere where it can be again transported and deposited in other locations.

Nutrients

Nitrogen over-enrichment has been blamed for a wide array of impacts on aquatic ecosystems, including changes in the function and composition of the algal community, changes in the food web, and declines in water quality and fisheries habitat. Increases in nitrogen and changes in nitrogen sources can influence competitive interactions and succession among algal groups, as well as dominance by certain undesirable groups such as red tide dinoflagellates and toxic cyanobacteria (formerly blue-green algae).\textsuperscript{127} The ability of some algal groups to utilize organic nitrogen, which can be plentiful in atmospheric deposition, can also provide a competitive advantage.\textsuperscript{128} Iron, which is largely atmospherically derived, may interact synergistically with nitrogen to enhance coastal and oceanic primary production.\textsuperscript{129} These effects of atmospherically transported nitrogen and other nutrient sources may be promoting the major biological changes that are now apparent in coastal and oceanic waters, including the proliferation of harmful algal blooms and declines in water quality and fisheries. Because of its potentially large contribution to total "new" nitrogen loading to nitrogen-sensitive waters, atmospheric deposition requires attention from those responsible for local and regional air and watershed nutrient management.

In estuarine and coastal marine settings, sediments represent relatively rich sources of phosphorus that are readily cycled between the sediments and the water column. In these waters, atmospherically deposited phosphorus has not been shown to be widely significant, although it may be significant in specific locales. An example is in Florida coastal waters where local airborne phosphorus inputs may be high at times. A few researchers have suggested that primary production in some oceanic regions is limited by low phosphorus levels;\textsuperscript{130} however, this is a controversial notion and the overwhelming evidence continues to point to nitrogen and/or iron as the limiting nutrients in these waters.\textsuperscript{131} Although only a few measurements have been made, oceanic regions tend to exhibit extremely low levels of atmospherically deposited phosphorus.\textsuperscript{122} This is not surprising since the open oceans are far removed from continental sources of dust and windblown soils. Volcanic eruptions and large-scale dust storms may be a source of "new" airborne phosphorus inputs in some parts of the world, but the biogeochemical and ecological importance of these inputs remains unknown.

Iron deposited from the atmosphere appears to play a critical role in sustaining and stimulating productivity in iron-deprived coastal and oceanic waters.\textsuperscript{133} Atmospheric sources of iron have been proposed as key stimulants of marine algal and red tide blooms.\textsuperscript{134}

The ecological roles and effects of airborne deposits of trace elements — copper, zinc, manganese, cobalt, molybdenum, and boron — are far less clear.\textsuperscript{135} The impacts could include stimulation or inhibition of primary and secondary production or synergistic or antagonistic interactions with other nutrient effects. Far more mechanistic research (using response bioassays with natural microbial and plant communities as well as test species) is needed to help elucidate basic ecological and biogeochemical roles of
these trace nutrients. It is also conceivable that complex co-
limitations exist between trace elements and the major nutrients
such as nitrogen, phosphorus, and iron in freshwater and marine
environments. And it is possible that atmospheric deposition
provides unique nutrient combinations that together have a more
potent effect than individual nutrient constituents.

**NITROGEN DEPOSITION AND
THE FATE OF ORGANIC POLLUTANTS**

Atmospheric deposition contains a mixture of biologically
available nitrogen compounds, both organic and inorganic.
Bioassay studies in nitrogen-limited waters have demonstrated
that organisms respond differently to various nitrogen sources.
This provides a mechanism whereby nitrogen deposition can
influence the structure and makeup of aquatic communities.
Differential uptake and growth in response to ammonium versus
nitrate have been attributed to contrasts in energy required to
assimilate these compounds. Under light-limited conditions
encountered in turbid waters, organisms may prefer ammonium
because the energy requirements for using this reduced nitrogen
source are less than those for using nitrate. In light-limited
waters, motile algal groups such as dinoflagellates and
cryptomonads are capable of migrating to near-surface depths to
ensure access to the light energy needed to reduce nitrate to
ammonium, which is a critical step for incorporating this oxidized
form of nitrogen into biosynthetic pathways and growth. In
contrast, non-motile organisms must cope with deeper, lower-
irradiance waters, possibly limiting their nitrate uptake and thus
ammonium uptake. Intrinsic physiological differences in nitrogen
uptake among different algal taxa also exist, and these may lead
to contrasting responses to different nitrogen sources. Under
conditions of restricted nitrogen availability, which are characteristic
of many estuaries, such differences can lead to intense competition
for ammonium, nitrate, or organic nitrogen.

Bioassay experiments on the Neuse River Estuary in North
Carolina have shown that major algal taxonomic groups — diatoms,
dinoflagellates, cryptomonads, cyanobacteria, and chlorophytes
— may exhibit different growth responses to varying nitrogen
sources and mixtures of sources. However, these differential
responses are not consistent in time and space. Other complex
environmental factors, including light availability, water column
mixing depth, water residence time, salinity, and temperature,
also exert control over the dynamics of nitrogen uptake and growth
rates among the algal community. Atmospherically derived
dissolved organic nitrogen has also been shown to stimulate
bacterial and algal growth. This organic nitrogen may selectively
stimulate growth of facultative heterotrophic algae such as
dinoflagellates and cyanobacteria. (Facultative heterotrophic
organisms can make their own food or derive their nutrition by
consuming organic molecules.)

Responses to specific nitrogen inputs that alter the algal
community may in turn spur changes all the way up the food
chain, at the zooplankton, herbivorous fish, invertebrate, and
higher consumer levels. Shifts in algal community composition
may also alter the flux of carbon, nitrogen, phosphorus, and other
nutrients and impact oxygen dynamics in the estuary.

The fact that different sources of atmospherically derived
nitrogen may influence the structure and growth dynamics of
the algal community is also important to the fate of persistent
organic pollutants in aquatic food webs. Algae, with their high
lipid content, readily bioaccumulate these pollutants, but the
rate of uptake of these compounds is heavily influenced by
the growth rate of the community. The more productive the
system, the less bioaccumulation occurs due to the difference
in the rate of uptake compared to the rate of growth. In
addition, the more productive the system, the more the fate of
these contaminants is dominated by sedimentation of senescent
and dead algae. In oligotrophic systems, algal biomass is usually
low, but uptake of nutrients and other contaminants is quite
efficient. In these systems, effective grazing by zooplankton
ensures that these contaminants are readily passed to higher
levels of the food web.

A second reason that the source of atmospherically derived
nitrogen can influence the fate of persistent organic pollutants is
related to the changes in community structure that can occur. It
has recently been shown that the microbial loop may be an
important vector in organic pollutant transfer in food webs, and
its importance increases in systems that are less productive. The
microbial loop is an aquatic micro-food chain in which microscopic
bacteria and pico-plankton feed on dissolved organic material,
then these organisms are grazed on by flagellates and ciliates,
and these are consumed by tiny crustaceans called copepods.
Because the microbial loop consists of ciliates preying on flagellates
preying on bacteria, and the flagellate/ciliate component can be
influenced by atmospherically derived nitrogen, this new nitrogen
source may indirectly influence the food web dynamics controlling
pollutant bioaccumulation.

**PRIORITIES FOR REGULATION AND MONITORING**

Above we have identified a number of challenges that
atmospheric pollutants present to aquatic ecosystems and to
the human communities that rely on them. In this section, we
suggest some priorities for regulation and monitoring of
atmospherically transported chemicals. Effective regulations
must be based on a solid understanding of the problem
developed through research and monitoring. Actions should
be focused on chemicals that are toxic, bioaccumulate or
biomagnify, move in measurable quantities into and via the
atmosphere, are sufficiently stable to be transported long
distances, and interact with other chemicals to have negative
impacts on organisms and ecosystems. The actions suggested
below allow researchers and managers to identify with some
certainty how atmospheric deposition affects aquatic ecosystems
and to pinpoint likely sources and consequences.

- Develop a comprehensive strategy for reducing impacts
  and problems caused by airborne organic contaminants.
  - Use quantitative structure activity relationships (QSAR)
    to predict whether new chemicals that are proposed
    for commercial use will likely be persistent,
    bioaccumulative, and/or toxic to organisms, and use
    this information in decision-making and regulation.
Develop a comprehensive strategy for reducing the nitrogen problem.

- Develop more effective and broadly applied controls on nitrogen oxide emissions from internal combustion engines in automobiles, boats (i.e. outboard motors), personal watercraft and all terrain vehicles, lawnmowers, chain saws, and other fossil fuel-powered tools and machines.

- Minimize open-air storage of animal wastes and other reduced nitrogen products and sources and improve treatment of animal wastes using on-site "treatment plants" and engineered wetlands. Use recycled water in animal operations to minimize the generation and storage of liquid animal waste.

- Recycle accumulated solid waste into commercial fertilizers. Apply nitrate, ammonium and urea-based fertilizers at agronomic rates.

- Use "controlled" burns to minimize atmospheric "fertilization" of downwind nitrogen-sensitive waters with either nitrogen oxides or ammonia/ammonium.

Develop less expensive and more accurate methods to measure atmospheric deposition and to monitor and model how atmospherically deposited pollutants travel through a watershed. This should include establishing monitoring programs in critically vulnerable ecosystems, such as monitoring for organic pollutants in alpine and arctic ecosystems and for nutrients in estuaries.

Strengthen understanding of the linkages between atmospheric deposition and ecological effects, particularly for new chemicals of interest and interactions of nutrients and toxic compounds. Exposure risk must be analyzed for sensitive habitats and sensitive life stages as well as general populations.

Develop quantitative estimates of atmospheric pollutant deposition loads through monitoring and measurements. This should be done in conjunction with identifying sources of atmospheric contaminants and how much comes from local, regional, and long-range sources. Quantitative measurements will also help in identifying the role that atmospheric deposition plays in a watershed’s overall pollutant load.

Build proactive cooperation between air pollution agencies, water pollution agencies, and the public. Agencies monitoring and regulating air quality and those monitoring and regulating water quality will need to cooperate to address this issue. Now that the public is beginning to embrace the concept of watersheds, it is important to increase their understanding of the links between airsheds and watersheds.

CONCLUSION

In recent decades, much progress has been made in reducing the input of toxic chemicals and nutrients into the environment from point sources. However, atmospheric sources of toxic substances and nutrients are just now starting to be recognized for the role they play in contaminating the environment.

Organic chemicals that volatilize easily can be transported and deposited in other regions of the world, exposing aquatic ecosystems to chemicals not used in those regions. In some cases, little is known of their biogeochemistry or toxicity. Often, however, these chemicals have properties that make them environmentally mobile, persistent in the ecosystem, and bioaccumulative in living tissue. Many are toxic to aquatic organisms, fish, and fish-eating wildlife and humans.

Mercury is also a global pollutant that is mobile in the atmosphere, and its effects on fish, and on the birds and mammals that eat contaminated fish, are of significant concern. In some aquatic systems, mercury is transformed by microbial action into its methylated form, which can cause neurological, liver, and kidney damage as well as reproductive effects and neurodevelopmental problems.

Atmospheric deposition is also a significant and potent source of nutrients that can accelerate eutrophication and its associated environmental consequences in freshwater, estuarine, and coastal ecosystems. Aquatic ecosystems are often impacted by atmospheric deposition of both nutrients and toxic chemicals. The effects of nutrient deposition on food web structure and ecological function influence how other toxic substances are processed by the ecosystem, how they bioaccumulate, and ultimately how they impact fish, wildlife, and humans.

Considering that these atmospherically deposited contaminants are generated largely by human activities, it is clear that solutions must involve greater recognition, monitoring, and ultimately, regulation of this increasingly significant source of environmental pollution.

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REFERENCES AND SUGGESTED READINGS


2 Airsheds developed by R. Dennis, Atmospheric Science Modeling Division, NOAA Air Resources Laboratory and USEPA National...
Exposure Research Laboratory. Presented in USEPA 2001 (see 1); courtesy of the U.S. Environmental Protection Agency.


21 SCCNFP (Scientific Committee on Cosmetic Products and Non-Food Products). 2002. On the basis of the International Fragrance Association (IFRA) Code of Practice, the SCCNFP has listed 36 chemical substances, including musk ketone and musk xylene that must not form part of fragrance compounds used in cosmetic products. European Community Legislation Official Journal L 102 45:19 (18 Apr 2002).


28 Ikonomou et al. 2002 (see 22).


30 Kanna, K., J.K. Hansen, T.L. Wade, and J.P. Giesy. 2002c. Perfluorooctane sulfonate in oysters, Crassostrea virginica, from the Gulf of Mexico and the Chesapeake Bay, USA. Arch Environ Contam Toxicol 42: 313-318.


48 Takeda et al. 1995 (see 40).

49 Paerl, H.W., J.D. Willey, M. Go, B.L. Peierls, J.L. Pinckney and M.L. Fogel. 1999. Rainfall stimulation of primary production in...

Likens et al. 1974 (see 39).


Howarth et al. 1996 (see 43).

Paerl et al. 2002 (see 39).

Table adapted from Paerl et al. 2002 (see 39).


Paerl and Fogel 1994 (see 45).


Nixon 1995 (see 54).


Paerl 1997 (see 64).

Whittall and Paerl 2001 (see 60).


Duce 1986 (see 39).


Herut et al. 1999 (see 52.)
Kay et al. 2000 (see 53.)
Kay et al. 2000 (see 53.)
Totten et al. 2001 (see 82).
Totten et al. 2003 (see 81).
Gigliotti et al. 2002 (see 82).
Lohmann et al. 2002 (see 82).
Swackhammer et al. 1999 (see 85).
MacDonald et al. 2000 (see 88).
Dachs et al. 1999 (see 89).
Dachs et al. 1999 (see 89)
Dachs et al. 1999 (see 89).
Dachs et al. 2000 (see 88).
AMAP 1998 (see 99).
Cook, P., J.A. Robbins, D.D. Endicott, K.B. Lodge, P.D. Guiney,
MacDonald et al., 2000 (see 88).
Hesslein. 1995. High concentrations of toxaphene in fishes from a
Cook, P., J.A. Robbins, D.D. Endicott, K.B. Lodge, P.D. Guiney,
aryl hydrocarbon receptor-mediated early life stage toxicity on
lake trout populations in Lake Ontario during the 20th Century.
Contaminant trends in Lake Trout and Walleye from the Laurentian
Blais, J.M., D.W. Schindler, M. Sharp, E. Braekevelt, M. Lafreniere, 
Assessment report: Arctic Pollution Issues. Oslo.
AMAP 1998 (see 99).
Muir, B. Rosenberg, A. Sole and D.W. Schindler. 1999. Delayed 
deposition of organochlorine pesticides at a temperate glacier. 
Deposition of Polychlorinated-Biphenyls in Urban Areas. Environ 
Cotham, W. E., and T. F. Bidleman. 1995. Polycyclic Aromatic-Hydrocarbons and Polychlorinated-Biphenyls in air at an urban and a 
Offenberg. 1999. Evidence for increased gaseous PCB fluxes to 
Green et al. 2000 (see 78).
Offenberg, J. H., and J. E. Baker. 2000. PCBs and PAHs in southern 
Miller, S. M., M. L. Green, J. V. Depinto, and K. C. Hornbuckle. 
2001. Results from the Lake Michigan mass balance study: 
Hsu, Y. K., T. M. Holsen, and P. K. Hopke. 2003. Locating and 
quantifying PCB sources in Chicago: Receptor modeling and field 
in pesticide and PCB concentrations in air near the Great Lakes. 
Environ Sci Technol 38:414-422.
condensation of low volatility organo-chlorine compounds in polar 
Muir, D.C.G., Wagemann, R., Hargrave, B.T., Thomas, D.J., Peakall, 
polar bears from eastern Russia, North America, Greenland, and 
Svalbard: biomonitoring of Arctic pollution. Arch Environ Contam 
B. Rosenberg. 1998. Accumulation of persistent organochlorine 
Carrera, G., P. Fernández, J.O. Grimalt, M. Ventura, L. Camarero, 
Sci Technol 36:2587.
AMAP 1998 (see 99).
Donald et al. 1999 (see 101).
AMAP 1998 (see 99).
The effects of ecosystem characteristics on contaminant distribution 
AMAP 1998 (see 99).
Muir et al. 1992 (see 104).
Dewailly, E., P. Ayotte, S. Bruneau, C. Lalibert, D. Muir, and R. 
Norstrom. 1993. Inuit exposure to organochloride through the 
aquatic food chain in arctic Quebec, Environ Health Persp 101:618- 
20.
AMAP 1998 (see 99).
Jacobson J.L. and S.W. Jacobson. 1996. Intellectual impairment in 
children exposed to polychlorinated biphenyls in utero. N Engl J 
Med 335:783-789.
Kidd et al. 1995 (see 95).
Modified from Hornbuckle, K. C., and M. L. Green. 2003. The 
impact of an urban-industrial region on the magnitude and 
variability of persistent organic pollutant deposition to Lake 
Donald, D., R. Bailey, R. Crosley, D. Muir, P. Shaw and J. Syrgiannis. 
1993. Polychlorinated biphenyls and organochlorine pesticides in 
the aquatic environment along the continental divide region of 
Alberta and British Columbia, Inland Waters Directorate, Regina, 
Sask.
Blais et al. 1998 (see 104).
Donald et al. 1999 (see 101).
Agbeti. 2000. Assessment of recent eutrophication histories in 
Lake Ste. Anne and Lake Isle, Alberta, Canada, using 
paleolimnological methods. Lake and Reservoir Management 16: 
292-304.
Campbell, L.M., D.W. Schindler, D.C.G. Muir, D.B. Donald, and 
K.A. Kidd. 2000. Organochlorine transfer in the food web of
Blais et al. 2000 (see 113)
AMAP 1998 (see 99).
D. Muir, pers. comm
Ikonomou et al. 2002 (see 22).
Norstrom R.J., M. Simon, J. Moisey, B. Wakeford, and D.V. C. Muir, pers. comm
Takeda et al. 1995 (see 40).
Scudlark and Church 1997 (see 74).
Stolte et al. 1994 (see 127).
Prospero et al. 1996 (see 68).
Takeda et al. 1995 (see 40).
Eelmgren and Larsson 2001 (see 44).
Duce 1986 (see 39).
GESAMP 1989 (see 51).
Herut et al. 1999 (see 69).
Martin et al. 1994 (see 40).
Takeda et al. 1995 (see 40).
Scudlark and Church 1997 (see 74).
Takeda et al. 1995 (see 40).
Stolte et al. 1994 (see 127).
Eppley et al. 1969 (see 138).
Stolte et al. 1994 (see 127).


Peirls and Paerl 1997 (see 128).

Antia et al. 1991 (see 128).


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