RELATIVE ATMOSPHERIC LOADINGS OF TOXIC

CONTAMINANTS AND NITROGEN TO THE GREAT WATERS

A report prepared for:

Melissa McCullough
Great Waters Program Coordinator
Pollution Assessment Branch, ESD (MD-13)
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

by:

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DISCLAIMER

This document was prepared by researchers in Great Waters-related scientific disciplines, and a draft of this report was reviewed by an expanded group of scientists at a workshop held in November 1992 in Chapel Hill, North Carolina. Other workshop participants included representatives from the U.S. Environmental Protection Agency, the National Oceanic and Atmospheric Administration, the International Joint Commission, and the affected States.

This report has been reviewed by the Office of Air Quality Planning and Standards, Pollutant Assessment Branch, U.S. Environmental Protection Agency, and has been approved for distribution as received from the team of authors. Approval does not signify that the contents reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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A. EXECUTIVE SUMMARY

A.1 OVERVIEW

The 1990 Amendments to the Clean Air Act (CAA) recognize a geochemical paradigm which has been evolving during the past 30 years. Pollutants emitted into the atmosphere are transported for various distances and may later deposit in aquatic systems far removed from their original sources. This atmospheric deposition may seriously degrade water quality. Linkages between the atmosphere and surface waters operate on several scales, ranging from trace metal contamination of ponds adjacent to smelting operations to regional episodes of acidic deposition to global dispersion of organochlorine insecticides and greenhouse gases. As increasingly stringent controls are applied to conventional (*i.e.*, point) sources of pollutants to surface waters, the relative importance of diffuse, non-point sources of contamination, including loadings from the atmosphere is increasing. This fact requires a fundamental reevaluation of our approach to controlling air and water quality, as it has become increasingly evident that one cannot achieve water quality objectives if corresponding air quality goals are neglected.

Section 112(m) of the 1990 CAA Amendments requires the U.S. Environmental Protection Agency and the National Oceanic and Atmospheric Administration to estimate the importance of atmospheric deposition of hazardous air pollutants to the Great Lakes, Lake Champlain, the Chesapeake Bay, and other coastal waters (collectively dubbed the Great Waters). This Section requires not only that *gross* atmospheric contaminant loadings to each water body be documented, but, more importantly, that the *relative* importance of those loadings compared to those from all other possible sources be quantified. Further, the agencies are required to determine whether atmospherically-derived contamination results in exceedences of water quality standards, and to estimate the fraction of contaminants accumulating in biota which are derived from the atmosphere. Simply stated, Section 112(m) requires the agencies to construct quantitative chemical mass balances for relevant contaminants in each of the Great Waters. This is clearly a tall order.

In this paper, we first summarize the current understanding of atmospheric depositional processes for trace elements, mercury, nitrogen, and synthetic and combustion-derived organic contaminants. After addressing the question of whether gross contaminant loadings from the atmosphere can be estimated, we address whether both the conceptual understanding and the necessary data to construct defensible mass balances of these chemicals in the Great Waters are available. Specifically, we address the following questions:

1. What is the consensus view of our current understanding of the fundamental processes resulting in atmospheric deposition?

    During the past three decades, the scientific community has recognized the importance of atmospheric deposition as a source of contaminants to surface waters and has developed and refined relatively simplistic models describing the fundamental physical and chemical processes responsible for atmospheric deposition. At the present time, our

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knowledge of processes in the atmosphere and in surface waters are insufficient to adequately predict the magnitude and impact of atmospheric deposition to the Great Waters

2. Do we have the tools to determine atmospheric deposition rates with the accuracy and precision required to make the regulatory decisions required by the Great Waters Program?

   Methodologies of suitable accuracy and precision exist to determine the rate of atmospheric deposition of many chemical species to specific locations in the Great Waters. Specifically, deposition of trace elements and some organic contaminants during rainfall can be adequately measured. Conversely, deposition of aerosol-bound contaminants and exchange of gaseous contaminants across the air-water interface can only be estimated by indirect methods, and is, at present, poorly known.

3. Do we have the conceptual understanding required to estimate the *relative* atmospheric loadings of contaminants to the Great Waters?

   The mass balance paradigm, in which all contaminant loadings to and sinks from a water body are identified and quantified, provides an appropriate conceptual framework in which to estimate the importance of atmospheric deposition as a source of contaminants relative to all other sources to the Great Waters. While some of these sources and sinks are difficult to quantify and require new research initiatives, development of the mass balance framework is straightforward.

4. Do we currently have data of sufficient accuracy and precision to estimate *relative* atmospheric loadings of contaminants to the Great Waters?

   In order to estimate the importance of atmospheric deposition relative to all other sources of contaminants to the Great Waters, it is necessary to construct mass balances for each contaminant. With very few exceptions, this has not been possible due to a lack of consistent, coherent, and coincident measurements of all loadings to a water body. While technically possible, such measurements require a significant, long-term commitment in order to generate adequate information to construct scientifically-credible mass balances.

5. What specific studies are required to improve our ability to address the relative loadings questions of the Great Waters Program?

   Our current understanding of many processes is inadequate to make the evaluations required within Section 112(m). Specific studies of aerosol behavior and deposition, of absorption of gases and volatilization of dissolved contaminants, and of the reactivity and bioavailability of deposited contaminants are needed. Coordinated studies in the atmosphere and within the Great Waters are required in order to fully understand the

linkages between these two media. Improvements and validations of predictive, integrated atmospheric emission, transport, and deposition models are required in order to provide the predictive ability required by the Agency.

To address these questions, we first review the current understanding of atmospheric deposition processes, and then apply this understanding by constructing mass balances for the trace elements cobalt and cadmium and the nutrient nitrogen in the Delaware Bay, for mercury in a Wisconsin seepage lake, and for polychlorinated biphenyls (PCBs) in Lake Superior.

A.2 CASE STUDY MASS BALANCES

The framework for interpreting the *relative* inputs of chemicals into a body of water is a mass balance or input-output budget. The boundaries are often defined as the water column of the water body, and mass exchanges across the air-water, sediment-water, and land-water interfaces are inputs and outputs. Considering the case of a fresh water body as a chemical reactor (Figure 1), contaminants may enter by riverine flow (dissolved and particulate matter), groundwater flow (dissolved matter), atmospheric deposition (in the form of gas and particle scavenging by rain and snow, dry particle deposition, and gas absorption at the air-water interface), sediment and benthic layer exchange (dissolved and particulate), and *in situ* production. Chemical outputs from the lake volume include volatilization, riverine and connecting channel outflow (dissolved and particulate), chemical and biological degradation, sedimentation and burial of particles, and groundwater output (dissolved). Chemical species entering the water column may undergo turbulent and diffusive mixing and reactions which result in a change of speciation (*e.g.*, dissolved to particulate; oxidation or reduction; hydrolysis and complexation).

The components of a mass balance model of estuarine ecosystems such as the Chesapeake Bay and the Delaware Bay differ from those of lakes because of the importance of tidal exchange of water, solutes, and particles, and because of the frequently higher productivity of coastal marshes and waters (Figure 2). Over the period of several days to weeks, tidal flow flushes material into and out of the estuary and exerts a significant control on estuarine water quality. Therefore, the water residence times in estuaries are often significantly less than those in large lakes. However, estuaries are also efficient traps of particulate matter, leading to longer residence times of particle-reactive chemicals. For example, the hydraulic residence time of the Chesapeake Bay is less than one year, while the water column residence time of particles is significantly longer. For estuaries, the time rate of change in chemical concentration in the water column is similar to that of a fresh water system, with the inclusion of a tidal component.
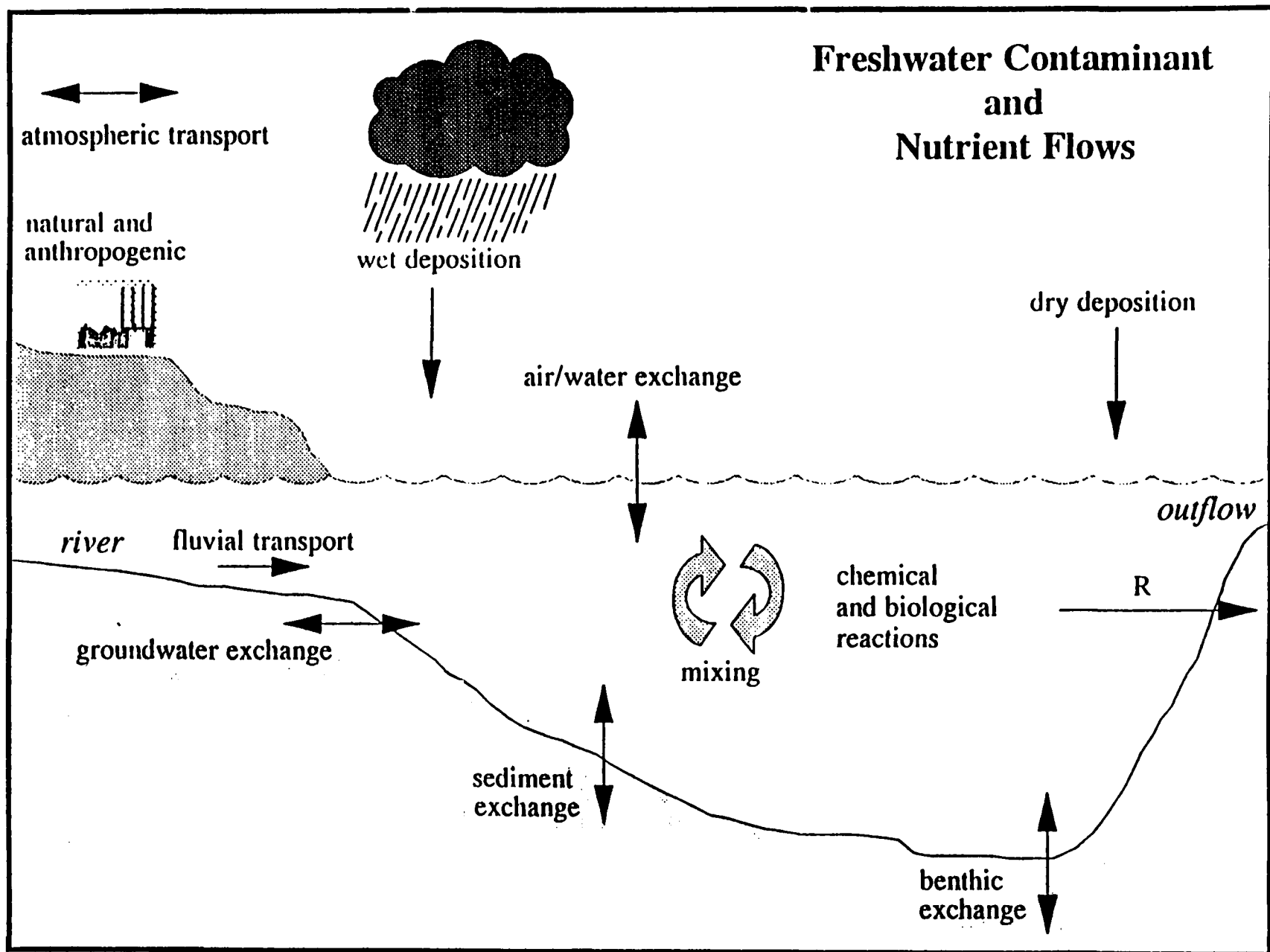
Figure 1. Mass balance paradigm in lakes
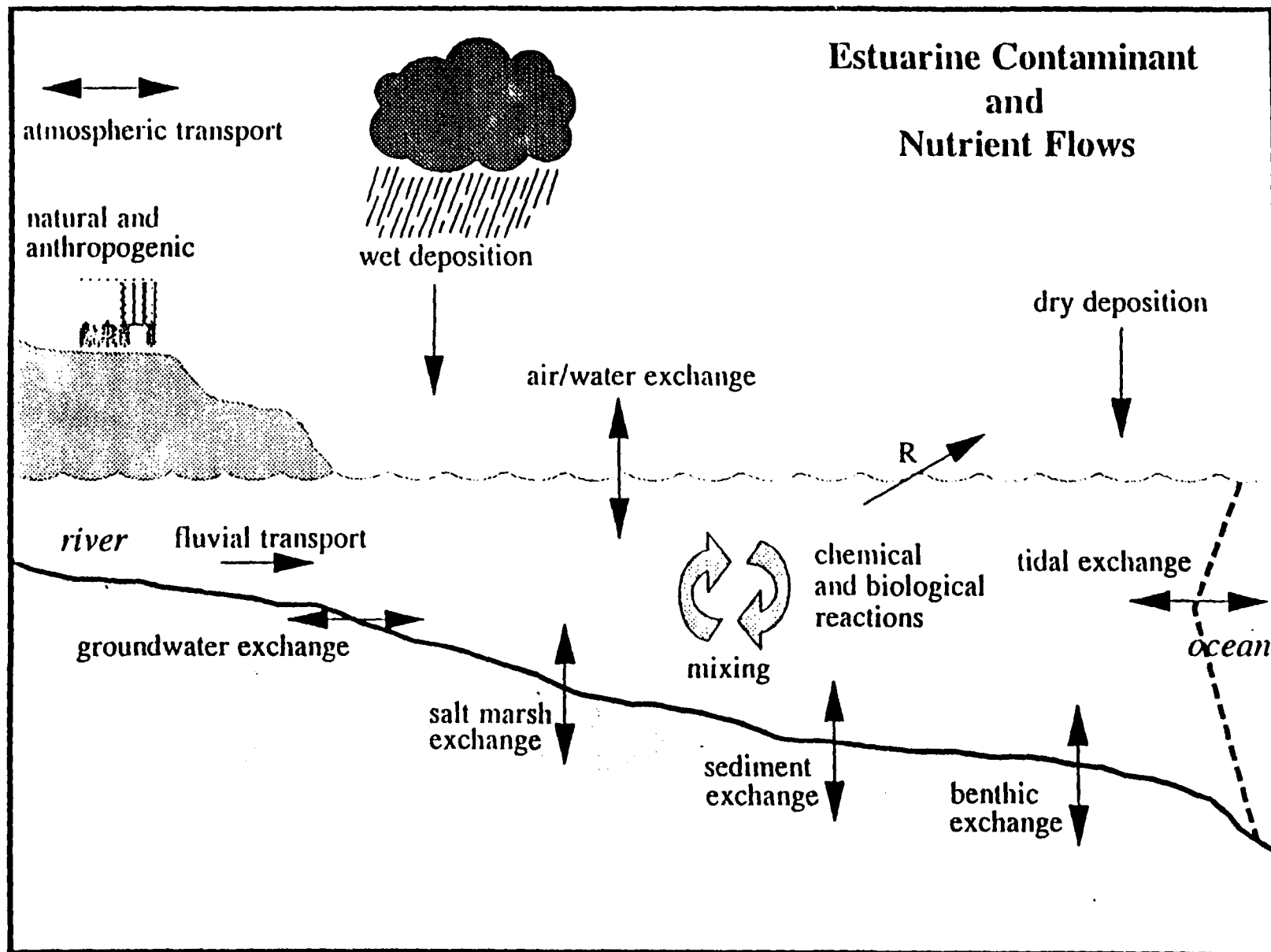
Figure 2. Mass balance paradigm in estuaries

A.2.1 Trace Elements

Mass balances of several trace elements in the Delaware estuary were estimated by Church *et al.* (1986). The primary fluvial fluxes were calculated as the seasonally averaged concentrations at the zero salinity end member times the riverine discharge. In this sense, any ground water fluxes downstream of this point were ignored. Some unknown quantity of the fluvial flux is comprised of atmospheric fallout onto the watershed. The secondary source of trace elements from the surrounding salt marshes were estimated by multiplying the non-conservative maximum concentration in a representative tidal creek times the net exchange volume of the tidal wedge integrated over the tidal cycle. The primary components of this flux come from atmospheric fallout into the marsh watershed and from the diagenetic release of sedimentary components. Trace elements can enter the salt marsh with both upstream terrestrial and downstream marine particulate matter. The oceanic tidal inputs to the bay are difficult to quantify, but have been attempted using a two layer model and salt balance (Church *et al.* 1986). Using such an approach, one can close the balance between the trace element sources (rivers and salt marshes) and the sinks (sediment burial and oceanic export) from the Delaware estuary within a factor two. It is thought that the major unknown source in this balance may be those trace elements which enter from ungauged groundwater. These groundwater fluxes may be as great as those in the gauged fluvial sources.

Two examples of trace element budgets for Delaware Bay are shown in Figures 3 and 4. These budgets are notable in that they are among the few that are rather complete and realistic balances as they consider both fluvial and atmospheric fluxes, a multitude of exchanges (including tidal, intertidal, benthic), and output as well as input terms to the estuarine loading. As the benthic fluxes are determined from incubated box cores taken in softer sediments, the magnitude of the flux may not be representative of the whole bay. The direction of the benthic flux measured by this method is a likely indication of the bay-wide benthic flux, however. The first example is cobalt, an element which although toxic has a behavior much like those of the more abundant non-toxic crustal trace elements, such as iron and aluminum. Fluvial transport is half the total input and is dominated by particulate loading (Figure 3). Surprisingly, the salt marsh input of cobalt is equivalent to the river loading, and is dominated by dissolved cobalt. This is a consequence of the diagenetic remobilization of redox trace elements by acidic sulfide reoxidation, which dissolves oxides in surface sediments. As these particles are originally carried into the salt marsh by tidal waters from the bay, this input may be considered secondary to the fluvial term. The atmospheric input of cobalt to the Delaware Bay is comparatively small, and from limited studies probably occurs in equal amounts of wet and dry deposition. As a particle-reactive element, the majority (87%) of the cobalt loading in Delaware is buried in the bottom sediments of the estuary and not exported to coastal waters. Benthic flux measurements suggest that cobalt diffuses into the sediments, which indicate the diagenetic capacity of the sediments to assimilate dissolved cobalt is at least equivalent to the rate of particulate cobalt burial.

A cadmium mass balance for the Delaware Bay is shown in Figure 4. Cadmium is both
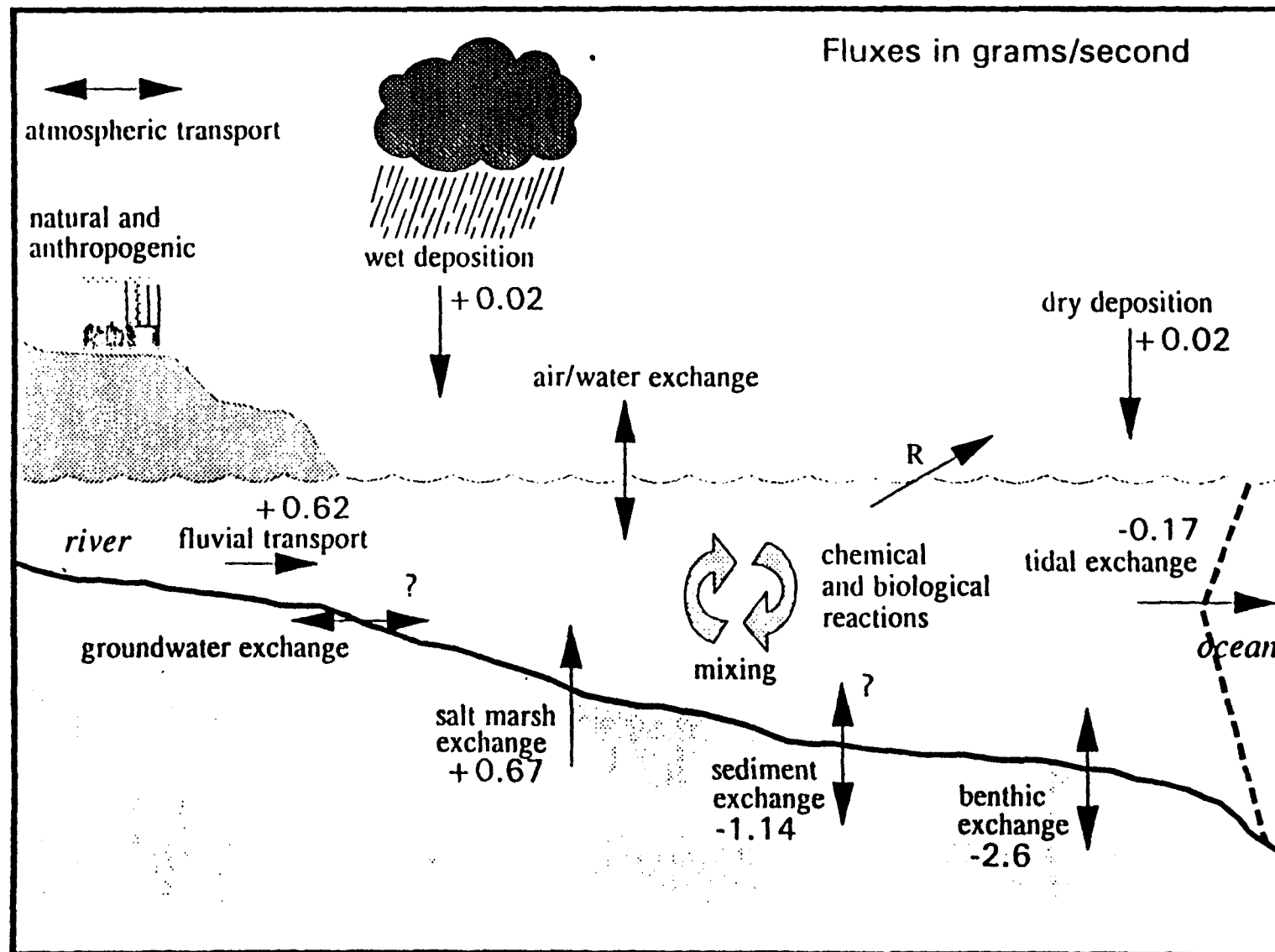
Figure 3. Cobalt mass balance for the Delaware Bay (Church, 1986).
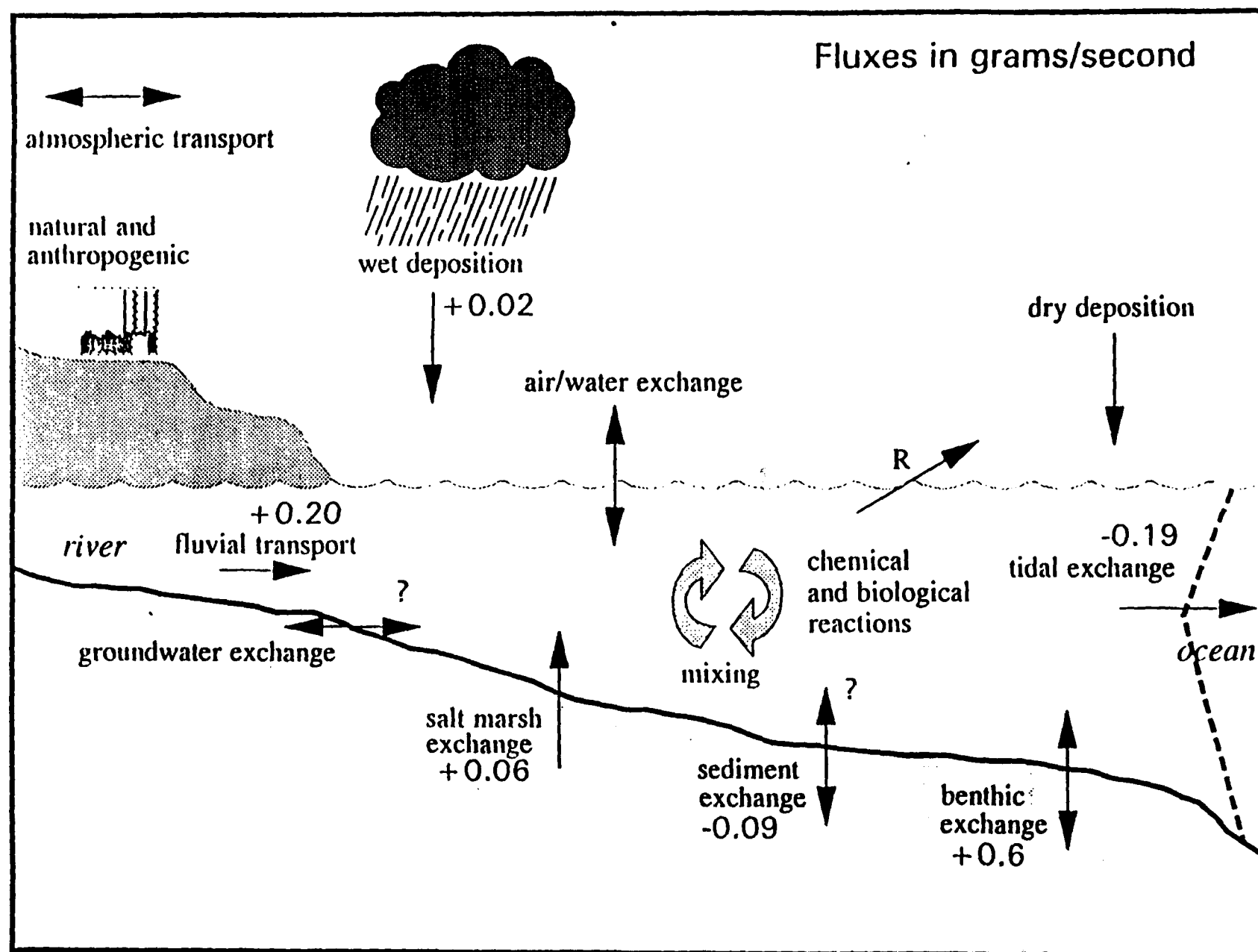
Figure 4. Cadmium mass balance for the Delaware Bay (Church, 1986).

very toxic and displays strong nutrient-like geochemistry. Again, the fluvial input dominates the cadmium loading to the Delaware Bay, but, unlike cobalt, the salt marsh input is only 10%. This is because the diagenetic processes in the sediments produce insoluble authigenic cadmium sulfide precipitates which are more immune to the redox processes of recycling. The atmospheric input of cadmium is at least 10% of the total input, and in other less urbanized estuaries would probably be more. This is the consequence of high atmospheric loadings for cadmium from upwind combustion sources. Most of the estuarine cadmium loading (68%) is exported to coastal waters, most likely due to strong organic complexing which decreases reactivity to removal reactions, and to nutrient-like regeneration during bioassimilation. The measured benthic flux of cadmium out of the sediments is seven times larger than the cadmium burial rate, and exceeds both the net input and export fluxes. This reflects the large extent of cadmium benthic recycling and demonstrates the potential effects of activities such as dredging which could disrupt this cyclic balance.

A.2.2 Semivolatile Organic Contaminants

Of the potential hydrophobic organic chemicals for which a mass balance can be demonstrated, polychlorinated biphenyls (PCBs) have been studied the most because of their bioaccumulation, persistence, ubiquitous distribution in the environment, and alleged toxicity. Eisenreich and co-workers (e.g., Eisenreich, 1987; Baker and Eisenreich, 1990; Baker et al., 1991; Jeremiason et al. 1993) have accumulated sufficient information on the inventories and cycling of PCBs in Lake Superior that a PCB budget may be constructed (Figure 5). Lake Superior is the second largest lake on earth after Lake Baikal, is the largest of the Great Lakes possessing >50% of its water volume and approximately 20% of the surface freshwater on earth, has a large lake area to watershed ratio, has a long water residence time of ~ 170 years, is oligotrophic, and is driven primarily by atmospheric interactions. Inputs to the lake include riverine flows (including municipal/industrial discharges) and atmospheric deposition. PCBs may be lost from the lake by riverine flow through the St. Mary's River, by sedimentation, by chemical or biological degradation, and by volatilization.

The inventories of PCBs in the Lake Superior ecosystem are:

atmosphere:	~ 200 kg (~ 1.2 ng/m^3)
water column:	~ 7200 kg (~ 0.6 ng/L)
sediment:	~ 5000 kg (~ 6 ng/cm^2)

Riverine inflow and outflow are estimated to contribute 20 to 50 kg/yr and 40 kg/yr, respectively, to the mass balance (Table 1). Eisenreich and Strachan (1992) estimate that atmospheric deposition of PCBs in the late 1980's was ~ 167 kg/yr, 125 kg/yr in wet deposition, and 32 kg/yr in dry particle deposition. The burial of PCBs in bottom sediments is ~ 10 to 50 kg/yr based on detailed analysis of ^{210}Pb-dated sediment cores over the whole lake (Eisenreich, 1987; Baker et al., 1991; Jeremiason et al., 1993). The assumption is made that chemical and biological degradation reactions are negligible in the mass balance.

PCB BUDGET FOR LAKE SUPERIOR 1986

Atmosphere
200 kg

Atmospheric Deposition
Wet   125
Dry   32

Total 167 kg/yr

Volatilization
1 ~ 600-4200 kg/yr
2 ~ 670-750 kg/yr
3 ~ 720   kg/ yr

Water Column
~7200 kg

Rivers

~20-50 kg/yr

Outflow

~40 kg/yr

Particle Settling
~3000 kg/yr

Recycling
~2950 kg/yr

Burial
10-50 kg/yr

Sediment
~5000 kg
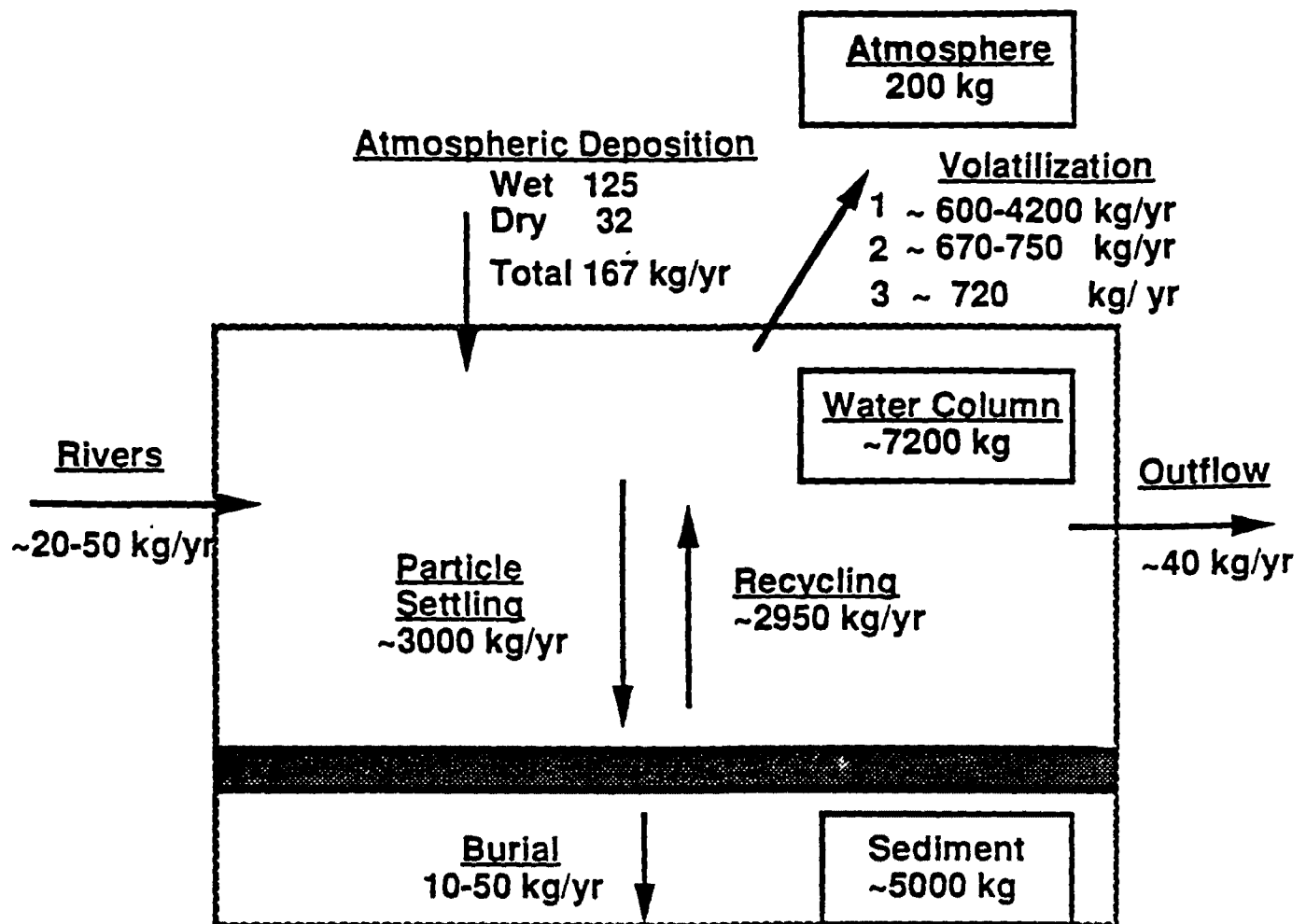
*Water Column - 1980   ~ 12000 kg
           - 1986   ~ 7200 kg
           - 1992   ~ 2200 kg
*Linear Water Column Loss Rate
  1980 to 1986:   ~ 800 kg/yr
  1986 to 1988:   ~ 790 kg/yr
*1st Order Loss Rate
  1986:   ~ 500 kg/yr

1 Baker and Eisenreich (1990)
2 Mass Balance
3 Swackhamer et al. (1988)

Figure 5.   Mass balance of PCBs in Lake Superior

TABLE 1

A PCB BUDGET FOR LAKE SUPERIOR - 1986

Inputs (kg/yr):		Outputs (kg/yr):	
Rivers:	20 to 50	St. Mary's River	40
Atmosphere:		Sedimentation:	10-50
Wet	125	Reaction:	?
Dry	32	Volatilization	600-4200
Total	167		
		Linear Water Column Loss:	800
TOTAL	187-217	TOTAL	840-890

PCBs are lost from the lake by volatilization at a rate of about 600 to 4200 kg/yr (Baker and Eisenreich 1990) based on air-water gradients and estimated mass transfer coefficients. Swackhamer *et al.* (1988) estimated PCB volatilization from Siskiwit Lake on Isle Royale in Lake Superior to be at a rate comparable to an annual loss from Lake Superior of about 720 kg/yr. Measurements of water column PCBs since 1978 suggest a linear loss rate of ~800 kg/yr (1.3 ng/L in 1978 to 0.18 ng/L in 1992). Using the decrease of PCB concentrations in the water column in the mass balance suggests volatilization is about 670 to 750 kg/yr.

According to this mass balance calculation, atmospheric deposition contributed 77% to 89% of the total inputs of PCBs to Lake Superior in 1986, similar to the earlier calculations of Strachan and Eisenreich (1988). Annual atmospheric loadings to the Great Lakes are similar to those to the Chesapeake Bay, reflecting rapid atmospheric mixing and transport over North America (Figure 6). PCB losses from the lake occur primarily by volatilization which represents nearly 90% of total losses, while burial in bottom sediments represents only about 5% of total PCB losses. This finding is consistent with the earlier calculations of Strachan and Eisenreich (1988), is near the lower end of that estimated by Baker and Eisenreich (1990), and about equal to the estimate of Swackhamer *et al.* (1988) based on their Siskiwit Lake studies. Given the magnitude and uncertainty of the field measured volatilization rates, this process represents a critical need in the relative loading paradigm.

The estimated first order residence time of PCBs in the water column of Lake Superior based on the decrease in concentrations over the last 10 to 15 years is 5 to 6 years (Jeremiason *et al.*, 1993). The majority of the decrease in water column concentrations is attributed to volatilization, the rate of which will decrease with decreasing water concentrations. Based on an ecosystem loss rate of 850 kg/yr and an ecosystem inventory of 12,400 kg, a steady state residence time is about 15 years. The system is, of course, not at steady state and the overall system response can only be correctly calculated using dynamic models showing changes in inputs, outputs, and inventories with time.
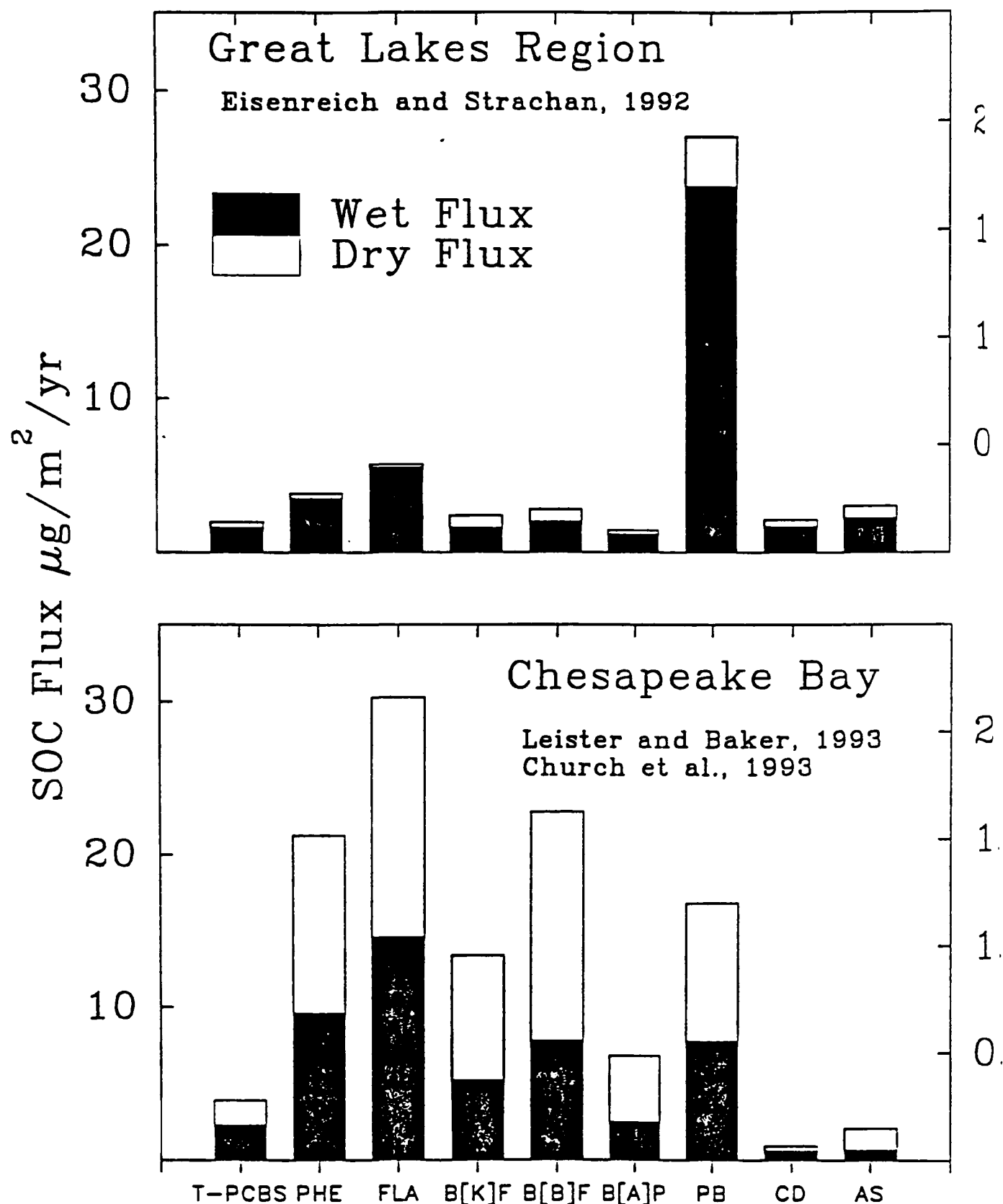
Figure 6. Atmospheric depositional fluxes to the Great Lake and to the Chesapeake Bay (Strachan and Eisienreich. 1988; Baker and Eisenreich. 1993; Church et al.. 1993).

The mass balance paradigm is a necessary framework to estimate relative loadings of chemical constituents to lakes and estuaries. To correctly do so requires the measurement of concentrations, inventories, and fluxes over time in a precise and accurate manner to statistically demonstrate differences in absolute and relative loadings.

A.2.3 Mercury

The prominence of atmospheric mobilization and depositional processes in the global biogeochemical cycling of mercury is well known. Atmospheric mercury emissions associated with contemporary human endeavors are comparable to natural emissions, and atmospheric deposition is, in general, the principal input of mercury to natural waters. Current international human-health and environmental concerns associated with elevated levels of monomethylmercury (MMHg) in freshwater and marine piscivorous fish have focused attention on mercury as a pollutant, and on its atmospheric cycle. Most of the mercury species in the troposphere are in the vapor phase, and consist almost entirely of elemental mercury (Hg^0). Yet, recent studies point to particulate mercury cycle and scavenging of particle associated mercury as the principal source of mercury in deposition. Much information is needed about sources, chemical composition, physical state, and direct impact of mercury compounds to the Great Waters. Additionally, we must investigate processes associated with the post-depositional *in situ* bacterial conversion of mercury species to more toxic forms, especially MMHg, which is the principal form of mercury in fish. Human exposure to methylmercury compounds comes almost exclusively from the consumption of fish and fish products.

Environmental mercury research is improving. There is a heightened awareness of the need for accurate and broader measurements of mercury in the environment, and for the incorporation of ultra trace-metal clean sampling and analytical protocols into mercury research. Recent analytical developments and trace-metal-free methodologies allow for the determination of total mercury (Hg_T), reactive mercury (Hg_R), inorganic mercury [Hg(II)], elemental mercury (Hg^0) and alkylated mercury species [monomethyl mercury (MMHg); dimethyl mercury (DMHg)] at the picomolar to femtomolar level in air, water, and precipitation.

The importance of atmospheric mercury deposition in the aquatic biogeochemistry of mercury in the Great Waters has been demonstrated in two major mercury investigations: 1) for seepage lakes as part of The Mercury in Temperate Lakes (MTL) Program in Wisconsin, and 2) for drainage lakes as part of the broadly based investigation, Mercury in Swedish Environment. Both studies indicate that small increases in atmospheric depositional fluxes of mercury could yield enhanced mercury concentrations in fish. These two investigations provide a framework for assessing the quality of the available information for the atmospheric cycling of mercury, and identifying the parts of the cycle where information is needed, especially as it relates to the impact of atmospheric mercury deposition to the Great Waters.

For a model temperate seepage system, Little Rock Lake (summarized in Figure 7) total atmospheric mercury deposition (Hg_T) of ca. 10 μg m^{-2} y^{-1} (ca. 66% wet and 33% dry

Total Mercury: Little Rock Lake (Treatment Basin)

Atmosphere

Gaseous	Particulate
1.6 ± 0.4 ng/m^3	0.02 ± 0.02 ng/m^3

Wet
6.8 ± 2 μg/m^2/y
0.7 g/y

0.07 g/y
0.7 ± 0.3 μg/m^2/y
Evasion

Dry
3.5 ± 3.0 μg/m^2/y
0.4 g/y

Lake

Fish	Dissolved	Seston
156 ± 4 ng/g	1 ± 0.02 ng/L	25 ± 8 ng/g
0.15 gram	0.3 gram	0.1 gram

Sedimentation
10 μg/m^2/y
1 g/y

Sediment

Sediment
8.9 ± 1.3 ng/g
1 gram/mm
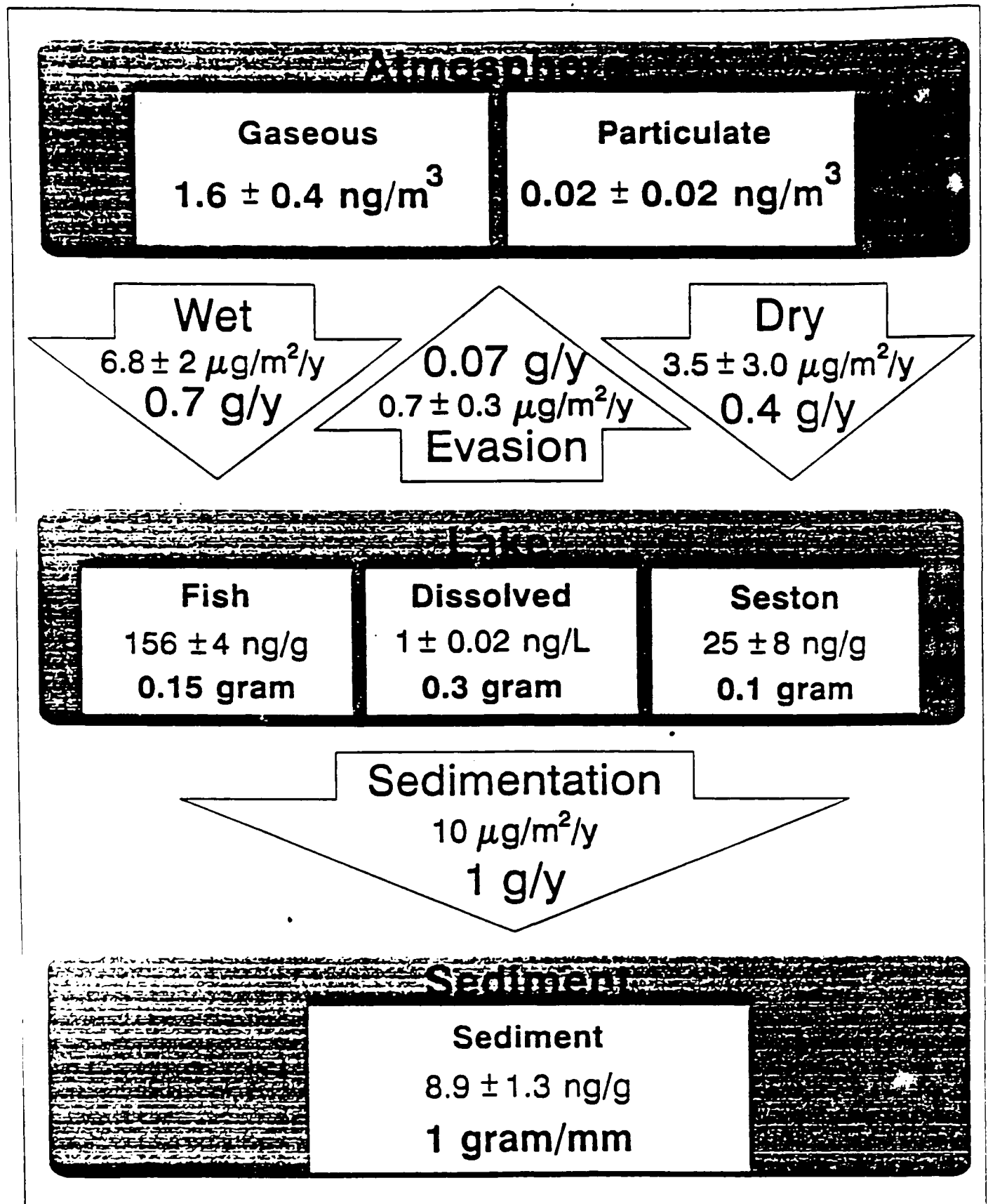
Figure 7. Mass balance model for Hg in the treatment basin of Little Rock Lake, Wisconsin (adapted from Fitzgerald et al., 1991 and based on work and preliminary budgets appearing in Wiener et al., 1990, Fitzgerald and Watras, 1989, and to appear in Watras et al., 1992).

deposition) readily accounts for the total mass of mercury in fish, water and accumulating in the sediments. The ecosystem appears delicately poised with respect to atmospheric inputs, since a relatively small fraction of the input ($<10\%$) can supply the estimated accumulation of mercury in fish. This suggests that modest increases in atmospheric mercury loading could lead directly to elevated levels in the fish stock. As summarized in Figure 8, atmospheric deposition of MMHg is insufficient to account for the amounts of MMHg observed in biota, thereby indicating the need for in-lake synthesis. Chemical and physical speciation measurements of particulate matter and precipitation point to scavenging of atmospheric particulate mercury as the source of mercury in rain. Gaseous mercury in lake water is principally Hg°, and the evasional fluxes of Hg° are significant. Moreover, the in-situ production and efflux of Hg° could provide a potential buffering and/or amelioration role in aqueous systems.

The depositional results for mercury as established by the Little Rock Lake budget are placed in larger regional and geographic perspective. There is broad agreement among the Swedish work, the Nordic countries precipitation network, complementary whole lake depositional experiments in Wisconsin and Minnesota, and the results from the MTL program in Wisconsin. For example, simulation of the mercury flows into and out of a typical Swedish lake in the southern half of Sweden (Figure 9) clearly demonstrates that: 1) atmospheric mercury deposition is the preeminent source of mercury to a drainage lake, and 2) evasional fluxes of Hg° are significant, though the estimates require refinement. One striking difference between the drainage and seepage lake modelling is the significant portion of the mercury input that is stored in forest soils of the catchment. On average, present atmospheric deposition is greater than the output of mercury in run-off waters by about a factor of 10. Thus, even if anthropogenic mercury inputs were to cease, modern mercury deposition that has accumulated in the soil would continue to be released to the lakes from the forest soils. Indeed, 70 to 80% of the mercury in the catchment is anthropogenic, and as a consequence, the watershed transport of mercury to the lakes will remain elevated for long periods of time, perhaps several centuries.

Atmospheric deposition dominates the flux of mercury to lacustrine systems and the open ocean, and it appears that modest increases in atmospheric mercury loading could lead directly to enhanced levels of mercury in biota. The U.S. and Scandinavian studies of current and historical mercury deposition show broad agreement. Mid-latitudinal preindustrial depositional fluxes of total mercury were ca. 4 μg m^{-2} yr^{-1}, while present day annual fluxes may vary between ca. 10 μg m^{-2} yr^{-1} in rural semi-remote regions to > ca. 25 μg m^{-2} yr^{-1} in places where the presence of local/regional mercury sources is pronounced. The influence of anthropogenic activities on the total mercury cycling is evident, and site specific research must be conducted to assess the impact of human-related interferences in particular localities. However, the more important and subtle concerns are associated with the physical and chemical speciation of mercury deposition. For example, the presence of a significant regional particulate mercury cycle is found in specific chemical analysis of mercury in atmospheric particulate matter and precipitation. A portion of the Hg_T observed in precipitation at Little Rock Lake and in Scandinavian regions, is in a particulate form which is not derived from the oxidation of Hg° in the atmosphere. Moreover, significant differences are evident in the deposition of Hg_R, and differences in Hg_R inputs may have profound effects on the Hg° and MMHg cycle in natural

Methylmercury: Little Rock Lake (Treatment Basin)

Atmospheric

Gaseous

< 0.005 ng/m^3

Wet

0.1 ± 0.03 μg/m^2/y

0.01 g/y

Fish	Dissolved	Seston
156 ± 4 ng/g	0.06 ± 0.03 ng/L	5.0 ± 3.0 ng/g
0.15 gram	**0.02 gram**	**0.02 gram**

Sedimentation

< 0.08 μg/m^2/y

< 0.008 g/y

Sediment

Sediment

< 0.1 ng/g

< 0.008 gram/mm
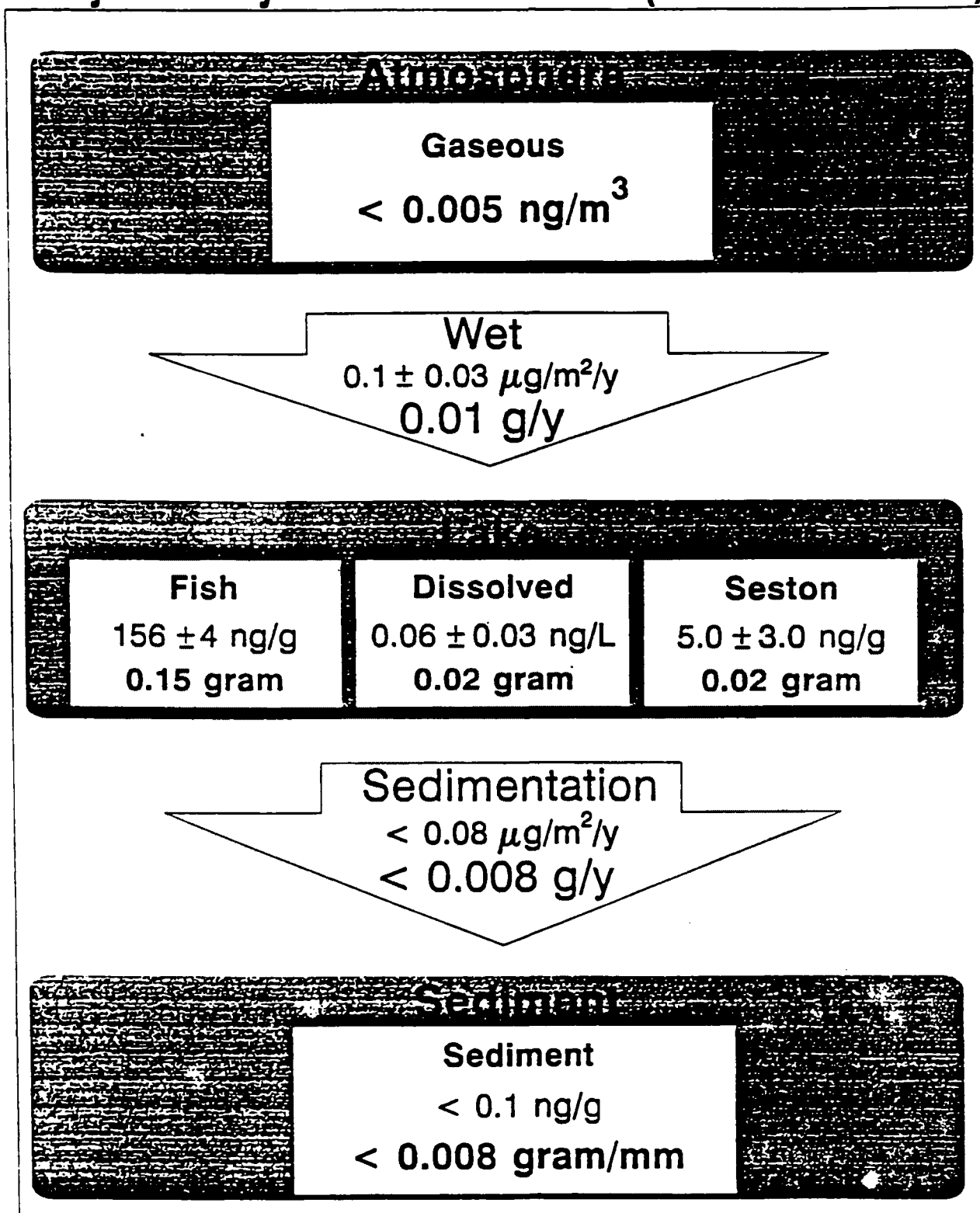
Figure 8. Mass balance model for monomethyl Hg in the treatment basin of Little Rock Wisconsin (adapted and based on work from Fitzgerald et al., 1991; Wiener e 1990; Hurley et al., 1991; Bloom et al., 1991, and Watras, et al., 1992).
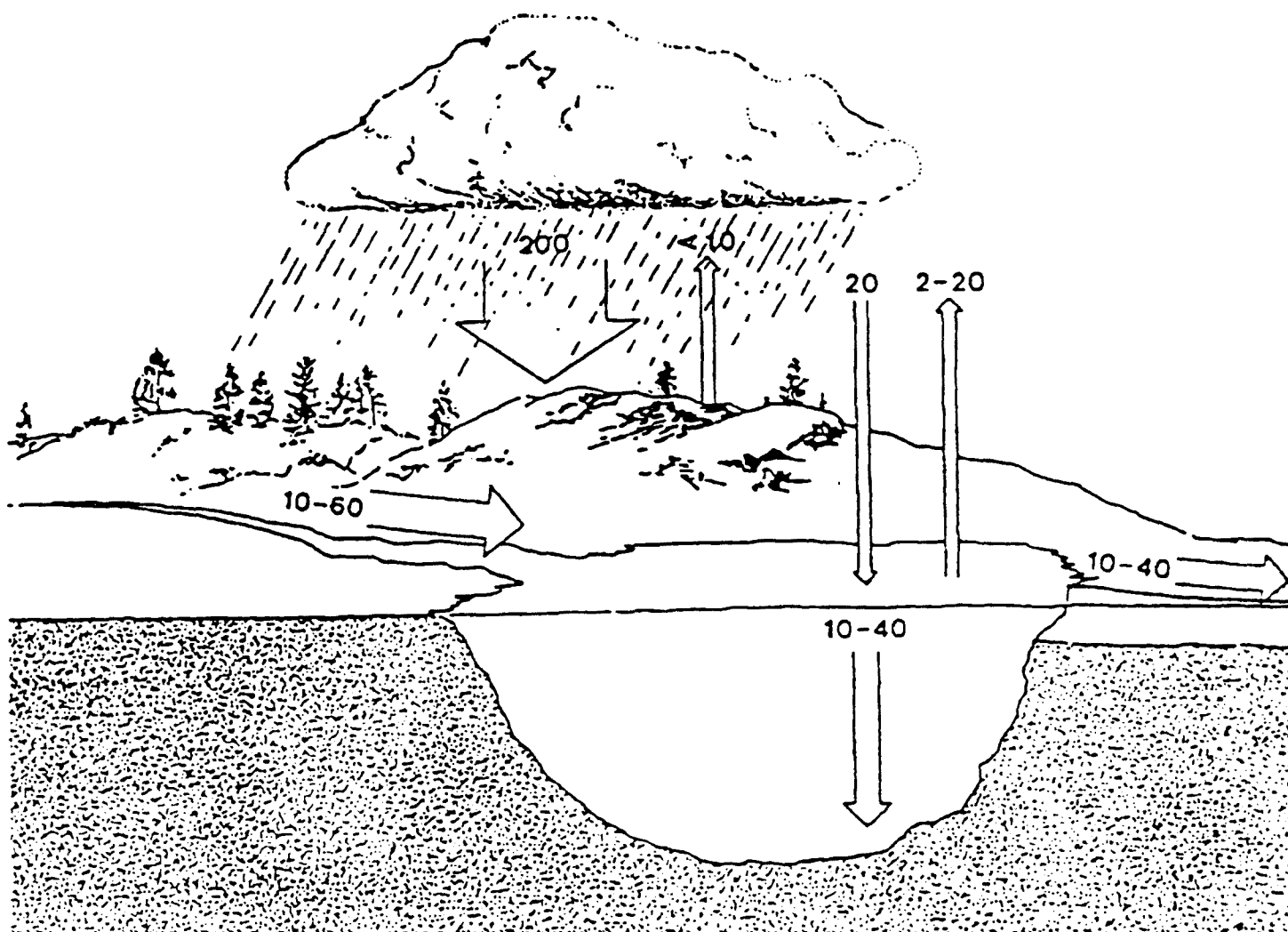
Figure 9. Flows of Hg in g yr^{-1} for a typical southern Swedish lake with an area of 1 km^2 and a drainage area of 10 km^2. Atmospheric depositional fluxes of Hg are for precipitation and do not include dry deposition. Adapted from Johansson, et al. 1991, and Lindqvist et al., 1984.

waters.

The production and evasion of Hg° in natural waters is a major feature of the aquatic biogeochemical cycling of mercury. Significant effluxes of Hg° have been observed in seepage lakes in Wisconsin as well as in a diverse range of fresh and ocean waters. Thus, Great Waters with aquatic conditions favoring Hg° production would be less likely to have elevated levels of mercury in fish. Although, such conditions are poorly known, Hg° production appears to correlate with the availability and supply of Hg_R (the Hg(II) substrate) whether it is atmospherically derived as in seepage lakes or supplied principally through upwelling as in the equatorial Pacific. The evidence suggests that Hg_R found in precipitation and atmospheric particulate matter is derived from the atmospheric oxidation products of Hg° in the atmosphere. This form of Hg is labile and highly reactive in aqueous systems and readily available, for example, to participate in competitive reactions associated with methylation, reduction to Hg°, uptake by biota, and sequestering with humics. The other fraction of the Hg_T in deposition is the operationally defined strongly bound mercury portion ("unreactive" mercury) and its environmentally activity is not known. This fraction is probably associated with soot and may be strongly bound or sequestered in some type of sulfur-carbon association. However, unreactive mercury species could be solubilized under anoxic and/or sulfitic conditions in natural waters and sediments to yield a species such as $Hg(HS)_2°$ which can be bacterially methylated.

Much study is needed since very few details of the processes affecting production and destruction of Hg° in the atmosphere and natural waters are known. There are many questions concerning short-time scale spatial and temporal variability as well as the importance of photoreduction reactions and redox boundaries (*i.e.*, oxic/anoxic transition zones) in the production of Hg°. In addition, the relationships among phytoplankton productivity, microbial populations (*e.g.*, bacterial reduction) on the activity of Hg° should be evaluated. Broadly based Hg° investigations are required, particularly those including atmospheric speciation research, ancillary biological studies and concurrent methylation investigations. Seasonal and spatial data for atmospheric Hg deposition and the evasion of Hg° are limited. This points toward a need to refine input to and efflux estimates from lake and coastal waters and to assess, quantitatively, their influences on the overall cycling of Hg in Great Waters.

The strongly bound Hg components in the atmosphere are likely to have different geographic origins than the Hg_R species. Soot associated Hg particles, for example, will probably have an anthropogenic source and a local/regional origin and tropospheric residence times should range from days to weeks. At present, little is known about this part of the atmospheric Hg cycle. The Hg_R fraction, as suggested, is most probably derived from the oxidation of Hg°. As a consequence, Hg_R will be coupled to the global mobilization of Hg° and its anthropogenic and natural sources.

These observations illustrate the value of the chemical speciation approach to our developing understanding of the cycling of Hg in nature. Indeed, they force us ask and address the following general question: How do such speciation changes in the depositional fluxes of Hg affect the cycling of Hg in aquatic systems, and what causes the variation in the Hg_T and Hg_R

composition found in deposition? At present, there are no unequivocal answers to questions concerning the sources and variability of the atmospheric Hg species. The significant aspects of physico-chemical speciation and partitioning in the atmospheric cycling of Hg, and their influences on deposition, water-air exchange and the biogeochemical behavior and fate of mercury in aqueous systems have been identified. The present level of knowledge has been evaluated and summarized. The precision limits for measurements are given, their relative importance estimated and a research priority delineated.

A.2.4 Nitrogen

It is increasingly apparent that atmospheric deposition provides an important external source of readily-available nitrogen to coastal waters. A major shortcoming common to most recent atmospheric nitrogen deposition studies is that deposition has been evaluated relative to external sources only. The failure to evaluate atmospheric deposition in the context of a balanced estuarine nitrogen budget has been largely dictated by the reality that our basic knowledge of the nitrogen cycle in coastal waters is often less than quantitative. However, to accurately assess the ecological response of atmospheric nitrogen deposition, the overall nutrient dynamics may·be as important as gauging the relative atmospheric loading. A system-oriented approach would consider nitrogen sinks, retention, export, internal cycling and rates of transformation. For example, while the overall nitrogen loading in the Delaware Bay estuary is estimated to be ten times that in the nearby Chesapeake Bay (Nixon et al., 1986), it does not experience the eutrophication problems encountered in the Chesapeake. The seasonality in atmospheric deposition is also an important consideration in coastal nitrogen dynamics. For example, while most first order studies to date have examined atmospheric nitrogen inputs on an annual basis, eutrophication is not a serious problem in the Chesapeake Bay during the fall and winter. Thus, an examination of atmospheric nitrogen loading during the spring and summer is probably more pertinent, although the feasibility of seasonally-based nitrogen emission control policies is debatable from a management perspective.

To illustrate the current state of our understanding, a annual budget for dissolved inorganic nitrogen (NO_3^- + NH_4^+) in the Delaware Estuary can be examined (Figure 10). This budget does not include organic nitrogen, or dissolved/particulate partitioning. The Delaware Bay was chosen for this case study for several reasons. First, marine systems tend to be nitrogen limited while freshwater systems are phosphorus limited. Second, in contrast to the Chesapeake Bay, Delaware Bay is a more simple system to examine in terms of hydrology and nutrient inputs from large population centers. The freshwater boundary for the nitrogen mass balance in Figure 10 is the fall line at Trenton, New Jersey, above the heavily urbanized and industrialized Philadelphia-Camden-Wilmington corridor. The marine boundary for the mass balance extends between Cape May, New Jersey and Cape Henlopen, Delaware. The specific details of the derivation of each flux term can be found in Scudlark and Church (1993).

The primary nitrogen inputs to the Delaware Bay estuary are provided by point discharges and fluvial transport, the assessment of which appears to be fairly well constrained. Contrary to the traditional "outwelling" theory describing salt marsh nutrient dynamics,
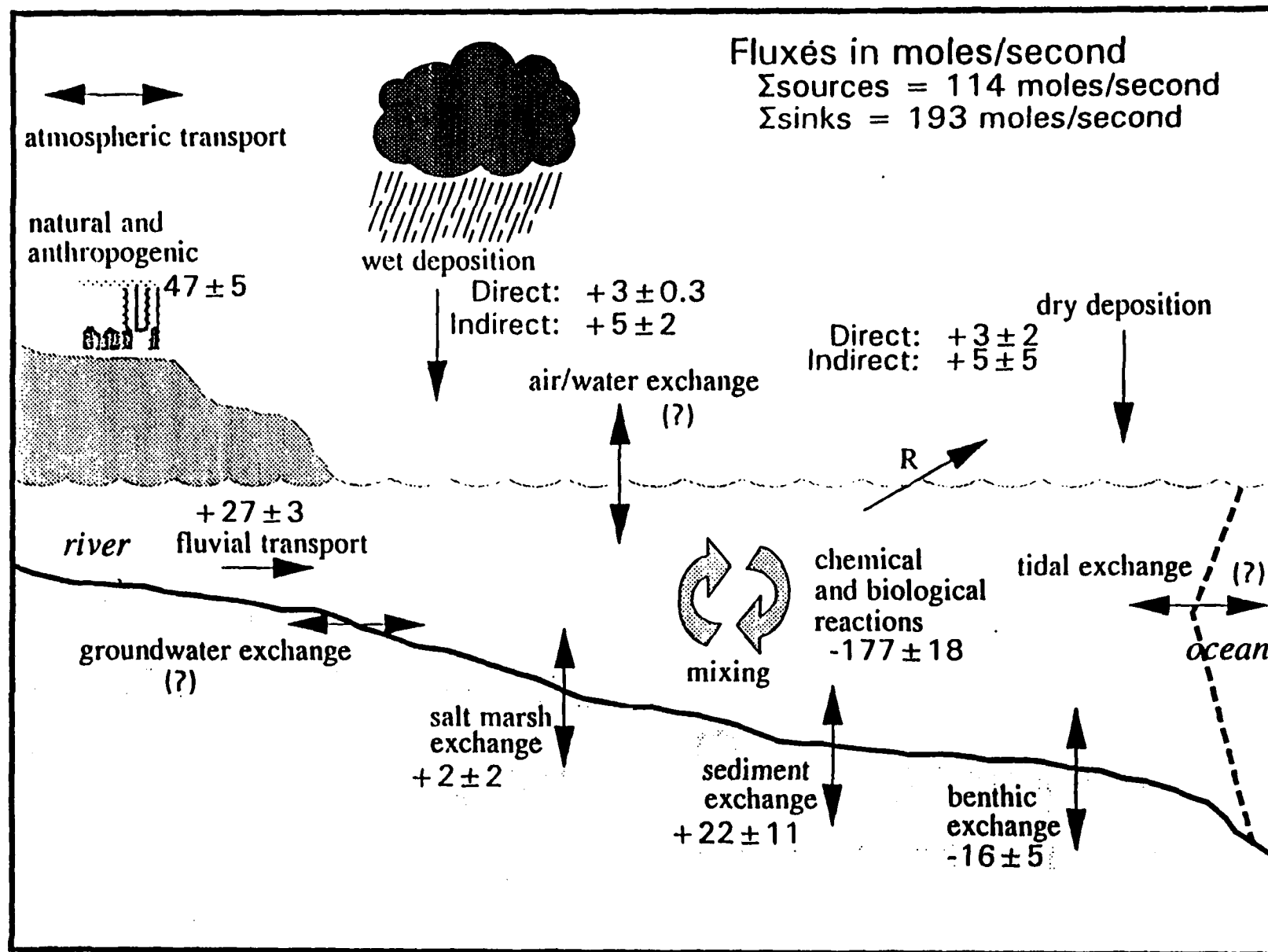
Figure 10. An annual nitrogen loading budget for the Delaware Bay

pervasive coastal wetlands do not appear to provide a significant source of inorganic nitrogen to the Delaware Bay. The "sediment exchange" term in Figure 10 represents the benthic flux of recycled nitrogen (primarily NH_4^+) and has been estimated from several independent studies. Nitrogen fixation is thought to be relatively minor in marine systems, while the relative importance of the direct absorption of gaseous ammonia from the atmosphere is unknown. Shelf exchange, a unique feature of coastal waters, is discussed in Section 8.4.1. Direct wet deposition of nitrogen from the atmosphere has been estimated based on five monitoring sites in the Delaware Bay watershed, and is assumed to comprise 50% of the total (wet+dry) atmospheric loading. Indirect atmospheric input *via* watershed export was estimated based upon a transmission factor of 0.1 (*i.e.*, 90% of the nitrogen deposited on the drainage basin is retained within the landscape or is lost in feeder tributaries prior to entering the bay proper.

Phytoplankton uptake provides a dominant, though arguably temporary, sink of nitrogen from the water column. The "benthic exchange" term in Figure 10 refers to sedimentary denitrification, which results in a net loss of gaseous end products (N_2, N_2O) from the system. It is clear from Figure 10 that the nitrogen sinks, primarily phytoplankton uptake ($\Sigma = 193$ moles/s), are not nearly balanced by the sources ($\Sigma = 114$ moles/s). In this context, atmospheric inputs provide less than 10% of the primary production requirements. Potentially important non-quantified source terms which would help close this deficit include water column remineralization, ungauged groundwater input, and tidal exchange.

The primary uncertainties associated with atmospheric nitrogen deposition to coastal waters are related to (1) estimation of dry depositional fluxes, and (2) gauging watershed retention. Estimation of dry deposition by inferential means is currently limited by our basic ability to accurately measure atmospheric NO_3^- concentrations. Other potentially important research needs, for which less is known are (3) accurately assessing the concentration and deposition of organic nitrogen in precipitation and aerosols, and (4) quantifying the gas/water mass transfer of NH_3 and HNO_3 to surface waters. In recognition of the increased focus on deposition in the coastal zone, wet and dry deposition monitoring networks should make a greater effort to include coastal sites. Process-oriented studies addressing the effects of urban plumes are also warranted.

A.3 CURRENT UNCERTAINTIES IN GREAT WATERS MASS BALANCES

There has been tremendous improvements in our understanding to the role of atmospheric deposition in supplying trace elements, mercury, nitrogen, and organic contaminants to surface waters. Many advances have been made in the basic sampling and analytical tools required to make reliable field measurements of atmospheric inventories and wet depositional fluxes. Such measurements require extreme care and are, therefore, not necessarily suitable for large, routine monitoring networks. Nonetheless, during the past ten years it has become possible to accurately measure atmospheric concentrations, speciation, and wet depositional fluxes of many chemicals, and excellent records are evolving at several locations (e.g., Lewes, DE; Chesapeake Bay, Great Lakes region). Due to the inherent variability in atmospheric processes, long-term records, on the scale of decades, will be required to assess changes in atmospheric deposition loadings to the Great Waters. It is left up to the responsible agencies to develop and maintain these long-term programs.

To prioritize future research efforts, the authors of this report have estimated the current uncertainties in the fundamental atmospheric depositional processes and assessed their relative importance (Tables 2-5). It is important to note that the "achievable uncertainty" refers to the optimal precision obtainable for a measured parameter at a single site. As such, these estimates should be viewed as goals rather than an accurate assessment of the quality of currently available data from the Great Waters. In general, more reliable measurements of wet deposition are available compared to either dry aerosol deposition or gaseous exchange. While wet deposition can be measured in the field, our ability to predict (e.g., model) contaminant scavenging from the atmosphere by precipitation is highly uncertain, perhaps no better than to within one to two orders of magnitude. Specific studies of wet depositional processes, especially those employing novel geochemical tracers and airborne sampling, are required. While it is important to continue and expand wet deposition measurements and research, much of the research effort must be placed in improving our ability to measure and model dry deposition. In particular, our estimates of dry aerosol deposition are hindered both by a lack of aerosol size distribution information and by our generally poor understanding of the micrometeorological environment above water surfaces. The potentially large contaminant fluxes resulting from the rapid settling of supermicron particles near emission sources (Holsen et al., 1991) as well as the possible elevated fluxes during short-term, intensive meteorological events deserve further study.

Mass balance calculations and measurements of concentration gradients in the field strongly suggest that many organic contaminant are degassing from the Great Lakes, especially during warm summer months. Chemicals such as PCBs, which are no longer produced, may be leaving the Great Lakes back into the atmosphere to be transported and deposited to the world's oceans and to the polar ice pack. The processes by which the Great Waters give these chemicals back to the atmosphere clearly need to be understood, both to predict contaminant levels in these water bodies and to characterize the global redistribution of these persistent chemicals.

In summary, the significant progress made during the past two decades has provided many of the tools required to answered the questions posed by Section 112(m) of the 1990 Amendments to the Clean Air Act. While much remains to be done, the regulatory community will be well served to continue to adopt the geochemical mass balance, emphasizing processes and fluxes of materials, as a rational framework for future endeavors

TABLE 2

CURRENT UNCERTAINITIES IN ESTIMATING THE ROLE OF ATMOSPHERIC DEPOSITION IN TRACE ELEMENT MASS BALANCES TO THE GREAT WATER (1993)
(+ = low, ++ = medium, +++ = high)

	Minimum Technical Uncertainity[*]	Importance to Loading Calculations	Research Priority
Wet Deposition			
Precipitation volume	+	+++	+
Precipitation concentration	+	+++	++
Diss./part. distribution	++	++	++
Speciation	+++	++	+++
Dry Deposition			
Aerosol concentration	+	++	+
Aerosol deposition velocity	+++	+++	+++
Aerosol size distribution	++	++	++
Surface microlayer reflux	+++	+	+
Episodic events/turbulence	+++	++	++
Gaseous exchange	+++	+	++
Overall Loadings Estimates[#]			
Wet Loading	++	+++	
Dry Loading	+++	+++	

[*]In the authors' judgement, this is the highest precision which could be obtained when suitably qualified personnel use the best current methods for an adequate period of time. The actual uncertainity in many of these parameters for specific locations are much greater due to a lack of quality information.

[#]The parameters listed above are site- and time-specific. Additional uncertainity is introduced in the extrapolation of these parameters to estimate spatially- and temporally-integrated contaminant loading rates.

TABLE 3

CURRENT UNCERTAINTIES IN ESTIMATING THE ROLE OF ATMOSPHERIC
DEPOSITION IN SEMIVOLATILE ORGANIC CONTAMINANT MASS
BALANCES TO THE GREAT WATERS (1993)
(+ = low, + + = medium, + + + = high)

	Minimum Technical Uncertainity[*]	Importance to Loading Calculations	Research Priority
Wet Deposition			
Precipitation volume	+	+ + +	+
Total atmospheric concentration	+	+ +	+ +
Gas/aerosol distribution			
$p° > 10^{-5}$ torr	+ +	+ + +	+ +
10^{-8} torr $> p° > 10^{-5}$ torr	+ + +	+ + +	+ + +
$p^0 < 10^{-8}$ torr	+ +	+ + +	+ +
Total precipitation concentration	+ +	+ + +	+ +
Aerosol scavenging coefficient	+ + +	+ + +	+ + +
Gas scavenging coefficient	+ +	+ + +	+ +
Dry Deposition			
SOC aerosol size distribution	+ + +	+ +	+ +
Aerosol deposition velocity	+ + +	+ + +	+ + +
Gas Exchange			
mass transfer coefficient	+ +	+ + +	+ +
total SOC concentration in water	+	+ + +	+ +
SOC speciation in water	+ +	+ + +	+ + +
Henry's Law constant = $f(T)$	+ +	+ + +	+ +
Overall Loadings Estimates[+]			
Wet Loading	+ +	+ + +	
Dry Loading	+	+ + +	

[*]In the authors' judgement, this is the highest precision which could be obtained when suitably qualified personnel use the best current methods for an adequate period of time. The actual uncertainity in many of these parameters for specific locations are much greater due to a lack of quality information.

[+]The parameters listed above are site- and time-specific. Additional uncertainity is introduced in the extrapolation of these parameters to estimate spatially- and temporally-integrated contaminant loading rates.

TABLE 4

CURRENT UNCERTAINTIES IN ESTIMATING THE ROLE OF ATMOSPHERIC
DEPOSITION IN MERCURY MASS BALANCES TO THE GREAT WATERS (1993)
(+ = low, + + = medium, + + + = high)

	Minimum Technical Uncertainity*	Importance to Loading Calculations	Research Priority
Wet Deposition			
Precipitation volume	+	+ + +	+
Gas scavenging (Hg°)	+ + +	+ +	+ +
Aerosol scavenging	+ + +	+ +	+ +
Atmospheric concentrations	+ +	+ +	+ +
Diss./part. distribution	+ +	+ +	+ +
Speciation	+ +	+ + +	+ + +
Dry Deposition			
Aerosol concentration	+ +	+ +	+ +
Aerosol size distribution	+ + +	+ +	+ +
Aerosol composition	+ + +	+ +	+ +
Aerosol reactivity	+ + +	+ + +	+ + +
Mercury Vapor Exchange			
Chemical speciation	+	+	+
Atmospheric oxidation	+ + +	+ + +	+
Gas exchange (flux)	+ + +	+ + +	+ + +
Overall Loadings Estimates⁺			
Wet Loading	+ +	+ + +	
Dry Loading	+ + +	+ + +	

*In the authors' judgement, this is the highest precision which could be obtained when suitably qualified personnel use the best current methods for an adequate period of time. The actual uncertainity in many of the parameters for specific locations are much greater due to a lack of quality information.

⁺The parameters listed above are site- and time-specific. Additional uncertainity is introduced in the extrapolation of these parameters to estimate spatially- and temporally-integrated contaminant loading rates.

TABLE 5

CURRENT UNCERTAINTIES IN ESTIMATING THE ROLE OF ATMOSPHERIC DEPOSITION IN NITROGEN MASS BALANCES TO THE GREAT WATERS (1993)
(+ = low, + + = medium, + + + = high)

Parameter	Minimum Technical Uncertainity[*]	Importance to Loading Calculations	Research Priority
Wet Deposition			
Precipitation volume	+	+ + +	+
Atmospheric concentration and speciation	(NH_4^+, NO_3^-) + (DON) + + +	+ + + + +	+ + + +
Dry Deposition			
NO_2 aerosol conc.	+ + +	+ +	+ +
DON aerosol conc.	+ + +	+ +	+ + +
NH_4^+ aerosol conc.	+	+ + +	+ +
NO_3^- aerosol conc.	+ +	+ + +	+ +
Aerosol size distribution	+ ·	+	+
Gas/water partitioning	+ + +	+ +	+ + +
Overall Loadings Estimates[#]			
Wet Loading	+	+ + +	
Dry Loading	+ +	+ + +	
Watershed transmission	+ + +	+ + +	

[*] In the authors' judgement, this is the highest precision which could be obtained when suitably qualified personnel use the best current methods for an adequate period of time. The actual uncertainity in many of these parameters for specific locations are much greater due to a lack of quality information.

[#] The parameters listed above are site- and time-specific. Additional uncertainity is introduced in the extrapolation of these parameters to estimate spatially- and temporally-integrated contaminant loading rates.

1.0   INTRODUCTION AND SCOPE OF THIS REPORT

The 1990 Amendments to the Clean Air Act (CAA) recognize a geochemical paradigm which has been evolving during the past 30 years. Pollutants emitted into the atmosphere are transported at various distances and may later deposit in aquatic systems far removed from their original sources. This atmospheric deposition may seriously degrade water quality. Linkages between the atmosphere and surface waters operate on several scales, ranging from trace metal contamination of ponds adjacent to smelting operations to regional episodes of acidic deposition to global dispersion of organochlorine insecticides and greenhouse gases. As increasingly stringent controls are applied to conventional (*i.e.*, point) sources of pollutants to surface waters, the relative importance of diffuse, non-point sources of contamination, including loadings from the atmosphere is increasing. This fact requires a fundamental reevaluation of our approach to controlling air and water quality, as it has become increasingly evident that one cannot achieve water quality objectives if corresponding air quality goals are neglected.

Section 112(m) of the 1990 CAA Amendments requires the U.S. Environmental Protection Agency and the National Oceanic and Atmospheric Administration to estimate the importance of atmospheric deposition of hazardous air pollutants to the Great Lakes, Lake Champlain, the Chesapeake Bay, and other coastal waters (collectively dubbed the Great Waters). This section requires not only that *gross* atmospheric contaminant loadings to each water body be documented, but, more importantly, that the *relative* importance of those loadings compared to all those from all other possible sources be quantified. Further, the agencies are required to determine whether atmospherically-derived contamination results in exceedences of water quality standards, and to estimate the fraction of contaminants accumulating in biota which are derived from the atmosphere. Simply stated, Section 112(m) requires the agencies to construct quantitative chemical mass balances for relevant contaminants in each of the Great Waters. This is clearly a tall order.

In this paper, we first summarize the current understanding of atmospheric depositional processes for trace elements, mercury, nitrogen, and synthetic and combustion-derived organic contaminants. After addressing the question of whether gross contaminant loadings from the atmosphere can be estimated, we address whether both the conceptual understanding and the necessary data to construct defensible mass balances of these chemicals in the Great Waters are available. Specifically, we address the following questions:

1.   What is the consensus view of our current understanding of the fundamental processes resulting in atmospheric deposition?

2.   Do we have the tools to determine atmospheric deposition rates with the accuracy and precision required to make the regulatory decisions required by the Great Waters Program?

3.   Do we have the conceptual understanding required to estimate the *relative* atmospheric loadings of contaminants to the Great Waters?

4.   Do we currently have data of sufficient accuracy and precision to estimate *relative* atmospheric loadings of contaminants to the Great Waters? and,

5.   What specific studies are required to improve our ability to address the relative loadings questions of the Great Waters Program?

2.0   RELATIVE LOADINGS: THE MASS BALANCE PARADIGM

The framework for interpreting the *relative* inputs of chemicals into a body of water is a mass balance or input-output budget. The boundaries are often defined as the water column of the water body, and mass exchanges across the air-water, sediment-water, and land-water interfaces are inputs and outputs. Considering the case of a fresh water body as a chemical reactor (Figure 1), contaminants may enter by riverine flow (dissolved and particulate matter), groundwater flow (dissolved matter), atmospheric deposition (in the form of gas and particle scavenging by rain and snow, dry particle deposition, and gas absorption at the air-water interface), sediment and benthic layer exchange (dissolved and particulate), and *in situ* production. Chemical outputs from the lake volume include dissolved gas volatilization, riverine and connecting channel outflow (dissolved and particulate), chemical and biological degradation, sedimentation and burial of particles, and groundwater output (dissolved). Chemical species entering the water column may undergo turbulent and diffusive mixing and reactions which result in a change of speciation (*e.g.*, dissolved to particulate; oxidation or reduction; hydrolysis and complexation). In a general sense, the time rate of change in chemical concentration in the water column is:

$$V \, dc/dt = \Sigma Q_i C_i \; - \; \Sigma Q_o C_{T,H2O} \; - \; k_s A C_{p,H2O} \; + \; k_r A C_{sed} \; \pm \; k_{rxn} V C_{d,H2O} \qquad [1]$$

$$\underset{\text{Inflow}}{\hphantom{V}} \quad \underset{\text{Outflow}}{\hphantom{V}} \quad \underset{\text{Sedimentation}}{\hphantom{V}} \quad \underset{\text{Resuspension}}{\hphantom{V}} \quad \underset{\text{Reactions}}{\hphantom{V}}$$

$$+ \; C_{t,rain} J A \; - \; A K_{0L} \, (C_{d,H2O} - p/H) \; + \; A V_d C_{p,air}$$

$$\underset{\text{Wet Deposition}}{\hphantom{V}} \quad \underset{\text{Air-Water Exchange}}{\hphantom{V}} \quad \underset{\text{Dry Particle Deposition}}{\hphantom{V}}$$

Where $V\dfrac{dc}{dt}$ represents the time rate of change in total chemical mass in the well-mixed water column (mols/yr), V = lake volume (m^3); A = lake surface area (m^2); $C_{T,H2O}$, $C_{P,H2O}$, $C_{d,H2O}$, C_{sed} = total, particulate, dissolved and surface sediment concentrations of chemical (mols/m^3); $C_{T,rain}$ = total rain concentrations (mol/m^3); J = annual precipitation amount (m/yr); Q_i and Q_o = volumetric hydraulic inflow and outflow rates (m^3/yr), respectively; p atmospheric partial pressure of the gas (Pa); H = Henry's Law constant [(Pa.m^3)/mol]; k_s, k_r, and k_{rxn} = rate coefficients (yr^1) describing sedimentation, resuspension, and other reactions acting on the chemical (*i.e.*, photolysis, hydrolysis, biodegradation); V_d = dry particle deposition velocity

(m/yr); and $C_{p,air}$ = the concentration of chemical in the atmospheric particle phase. If the rate of chemical input equals the rate of chemical output (i.e., no net change in water column inventory with time), the residence time (τ) is then [M_T/Σ(fluxes in or out)], where M_T is the total mass of the chemical. The residence time is a measure of the average time it takes for a molecule of a chemical entering the water column to leave via the sum of all loss processes. For example, the water residence times in Lake Superior and Lake Michigan are about 170 years and 100 years, respectively, while the residence time for non-conservative species such as PCBs and lead are only 1 to 5 years.

The components of a mass balance model of estuarine ecosystems such as the Chesapeake Bay and the Delaware Bay differ from those of lakes because of the importance of tidal exchange of water, solutes, and particles, and because of the frequently higher productivity of coastal marshes and waters (Figure 2). Over the period of several days to weeks, tidal flow flushes material of the estuary and exerts a significant control on estuarine water quality. Therefore, the water residence times in estuaries are often significantly less than large lakes. However, estuaries are also efficient traps of particulate matter, leading to longer residence times of particle-reactive chemicals. For example, the hydraulic residence time of the Chesapeake Bay is less than one year, while the water column residence time of particles are significantly longer. For estuaries, the equation describing the time rate of change in chemical concentration in the water column is similar to that of a fresh water system, with the inclusion of a tidal component.

The construction of a chemical mass balance of a lake or estuary demands that chemical inputs, outputs and internal losses and gains be quantified. For the Great Lakes, mass budgets have been attempted for semivolatile organic contaminants (SOCs) such as polychlorinated biphenyls (PCBs) (Eisenreich 1987; Swackhamer and Armstrong 1986, Swackhamer et al. 1988; Strachan and Eisenreich 1988; DePinto et al. 1992); and PAHs (McVeety and Hites 1988, Strachan and Eisenreich 1988). Inputs usually quantified are atmospheric deposition, riverine inflow and outflow, air-water exchange, and sedimentation. Processes often ignored or poorly quantified are chemical and biological degradation, groundwater flows, benthic exchange, and, in the case of estuaries, tidal exchange. Quantification of riverine inputs and outputs must recognize the inherent seasonal variability of flows, and, therefore, loadings. Likewise, air-water exchange of SOCs is a strong function of water temperature and wind conditions, necessitating seasonally dependent studies. Mass budget studies incorporating losses of chemical to sedimentation must obtain a sufficient number of spatially-representative sediment accumulation rates, a condition normally not encountered in mass balance studies. Contaminated sedimentary deposits may release nutrients, metals, and organic contaminants by diffusive and advective processes on a continuous or seasonal cycle, or in catastrophic episodes such as hurricanes, all contributing to the mass budget of the water column.

Until recently, atmospheric deposition of toxic chemicals to the Great Waters was a complete mystery. Now, reasonable estimates of wet deposition of trace elements and SOCs are being generated, but dry particle deposition is still very uncertain. Air-water exchange is only

3

now becoming recognized as an important process (*e.g.*, Achman *et al*. 1993a,b; McConnell *et al*. 1993; Atlas *et al*. 1986; Strachan and Eisenreich 1988).

The mass balance paradigm is a logical framework to establish the *relative* loadings of chemicals to the Great Waters. The first question is what is the magnitude of atmospheric deposition of target nutrients, trace metals, and organic chemicals to the Great Waters. Nex:, one must ask what is the magnitude of input of these target species from all other sources. Only then can the relative importance of each source be determined. This report details the processes by which trace elements, mercury, nitrogen, and organic chemicals are removed from the atmosphere and are loaded to the Great Waters, reports on the magnitude of chemical input from the atmosphere, and present case studies where the mass balance paradigm has been used to determine the *relative* importance of the atmosphere as a source of contamination to the Great Waters.

3.0 EVIDENCE OF ATMOSPHERIC DEPOSITION TO THE GREAT WATERS

3.1 TRACE ELEMENTS - Evidence of Deposition

Trace elements are those in rarer geochemical abundance compared to major crustal elements. These elements generally pass more rapidly through global reservoirs due to their reactivity in terms of abiotic hydrolysis reactions or biotic uptake as nutrients or toxics. In the atmosphere, trace elements are generally the result of global biogeochemical processes that include weathering, emissions, and transport. Aeolian transport can provide substantial trace element inputs to water bodies adjacent or downwind to major atmospheric sources or those characterized by a low ratios of watershed-to-surface area.

The atmosphere receives and processes trace elements from both natural and anthropogenic sources (Nriagu 1989, 1992; Nriagu and Pacyna 1988). Natural sources include both geochemical and biochemical processes and industrial sources include burning of fossil fuel and metalliferous production (Table 6). Natural and anthropogenic processes suspend fugitive dusts during dry weather and agricultural tilling (Table 7). Likewise, volatilization results from either low temperature emissions (such as evapo-transpiration or surface evaporation), or high temperature combustion (such as volcanoes, forest fires, and combustion of fossil fuels; Tables 6 and 7). Dry deposition is largely responsible for the removal of fugitive aerosols greater than a micron or in mass median diameter from the atmosphere. However, sub-micron aerosols or combustion condensates of trace metals are subjected to long atmospheric residence times and subsequent transport of days to weeks over the continents and eventually over inland or coastal water bodies. Wet deposition in the form of precipitation becomes an important means of atmospheric trace metal scavenging from the troposphere for these sub-micron aerosols (Junge

TABLE 6

EMISSIONS OF TRACE METALS FROM NATURAL SOURCES TO THE ATMOSPHERE ($\times 10^6$ kg/yr, FROM NRIAGU 1989)

Element	Soil-Derived Dust	Seasalt Sprays	Volcanoes	Forest Fires	Biogenic Sources	Total
As	2.6	1.7	3.8	0.19	3.9	12
Cd	0.21	0.06	0.82	0.11	0.24	1.4
Cr	27	0.07	15	0.09	1.1	43
Co	4.1	0.07	0.96	0.31	0.66	6.1
Cu	8.0	3.6	9.4	3.8	3.3	28
Hg	0.05	0.02	1.0	0.02	1.4	2.5
Mn	221	0.86	42	23	30	317
Mo	1.3	0.22	0.40	0.57	0.54	3.0
Ni	11	1.3	14	2.3	0.73	29
Pb	3.9	1.4	3.3	1.9	1.7	12
Sb	0.78	0.56	0.71	0.22	0.29	2.6
Se	0.18	0.55	0.95	0.26	8.4	10
V	16	3.1	5.6	1.8	1.2	45
Zn	19	0.44	9.6	7.6	8.1	45

TABLE 7

WORLDWIDE EMISSIONS OF TRACE METALS FROM INDUSTRIAL SOURCES.
UNITS: $\times 10^6$ kg/yr (FROM NRIAGU AND PACYNA, 1988)

Process	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Se	Sn	V	Zn	Ti
Energy Production	2.2	.79	13.	8.0	2.3	12.	42.	13.	1.3	3.8	3.3.	84.	17.	1.1
Mining	.06	-	-	.42	-	.62	.80	2.6	.10	.16	-	-	.46	-
Smelting and Refining	12.	5.4	-	23.	.13	2.6	4.0	46.	1.4	2.2	1.1	.06	72.	-
Manufacturing Processes	-	.60	17.	2.0	-	15.	4.5	16.	-	-	-	.74	33.	4.0
Commercial Applications	2.0	-	-	-	-	-	-	4.5	-	-	-	-	3.2	-
Waste Incineration	.31	.75	.84	1.6	1.2	8.3	.35	2.4	.67	.11	.81	1.2	5.9	-
Transportation	-	-	-	-	-	-	-	248	-	-	-	-	-	-
TOTAL	19.	7.6	3.1	35.	3.6	38.	52.	332	3.5	6.3	5.1	.86.	132	5.1

1977). Non-crustal metals are typically enriched in sub-micron aerosols over the remote areas. As such, the atmosphere can act as a powerful agent directly transporting and rapidly depositing continental materials to adjacent water bodies and their watersheds. In doing so, atmospheric deposition may largely determine the trace element input, composition, and biological exposure in certain water bodies.

Due to the typically low concentrations encountered and high potential for extraneous contamination, the accurate sampling and analysis of trace elements in the atmosphere and in wet deposition requires special equipment, rigorous procedures, and sensitive analytical equipment. This has largely limited the extent and quality of previous studies which attempted to evaluate the importance of atmospheric trace element deposition to inland and coastal waters (Galloway *et al.* 1982, Barrie *et al.* 1987). What follows is a critical review of these studies to date recognizing that mercury is treated separately from trace elements in this report.

The first successful attempts to measure trace elements in the atmosphere were done over the ocean. The Sea Air Exchange Program (SEAREX) of the NSF sampled trace elements in aerosol and in precipitation over the Atlantic (Duce *et al.* 1976) and in aerosols over the Pacific (Arimoto *et al.* 1985, 1987, 1990). Initial SEAREX results from over the Atlantic drew early attention to the hypothesis that atmospheric deposition is an important, if not dominant, source of trace elements to oceanic surface waters. French scientists supported this hypothesis in the sub-tropical Atlantic by showing the similarity of trace element enrichments in oceanic aerosols compared with those in oceanic particulates (Buat-Menard and Chesselet 1979). Atmospheric deposition of trace elements to the Sargasso Sea (Jickells *et al.* 1984, Church *et al.* 1984) dominates the inputs to and flux from the ocean water column (Jickells *et al.* 1987). These results are likely to extrapolate into the more northern Atlantic, where the continental sources are well defined (Church *et al.* 1990), the concentrations comparable (Church *et al.* 1991), and the transport in and scavenging from the upper troposphere is more efficient (Church *et al.* 1992). In the Pacific, seasonally (spring) large amounts of aeolian dust and associated trace elements are transported from southeast Asia over distances of tens of thousands of kilometers (Duce *et al.* 1980). The corrosive redox conditions of this dust during transport and wet scavenging can lead to the extraordinary large concentrations of iron (Zhuang *et al.* 1992) and other trace elements (Maring *et al.* 1989) in precipitation. Nevertheless, during similar Saharan dust transport over the sub-tropical Atlantic, much of the crustal trace elements remain as insoluble particles in the precipitation (Lim and Jickells 1990). Geochemical budgeting which demonstrates the important role of atmospheric deposition to the ocean has subsequently been tested and confirmed for a number of inland ocean water bodies such as the Baltic, Mediterranean, and North Seas (Jickells *et al.* 1989), and even on a global basis (Duce *et al.* 1991). Atmospheric deposition exceeds riverine inputs to the world oceans for many trace elements (Table 8, Nriagu 1992).

Atmospheric trace element deposition is important to coastal and inland waters (Patterson and Settle 1987, Nriagu 1992). The sources and transport of aerosol trace elements has been

TABLE 8

ATMOSPHERIC VERSUS RIVERINE INPUTS OF TRACE METALS IN THE OCEAN (FROM NRIAGU 1992)

Element	Dissolved in Rivers (ng/L)[1]	River Input $(x10^9 \ g/yr)$[2]	Atmospheric Input $(x10^9 \ g/yr)$[3]
As	47	1.6	5.8
Cd	2.1	0.07	3.2
Cr	172	5.8	-
Cu	115	4.0	34
Hg	0.82	0.03	1.7
Mo	12	0.41	-
Ni	135	4.6	25
Pb	8.5	0.29	88
Sb	14	0.48	-
Se	35	1.2	-
Zn	165	5.6	136

[1]Based on published data obtained using the ultra-clean laboratory procedures.
[2]Assuming total discharge of water by rivers to be 3.4×10^{16} L yr^{-1}.
[3]From GESAMP 1989.

evaluated in the Northeast United States (Rahn and Lowenthal 1984, 1985), and the record of their recent input have been inferred from profiles recorded in salt marshes (McCaffrey and Turekian 1980, Bricker-Orso and Nixon 1989), lake sediments (Norton and Kahl 1992, Flegal *et al.* 1989), and forest soils (Friedland 1992). The longest current trace elements deposition record to coastal waters has been made at Lewes, Delaware by the University of Delaware at an atmospheric research site near Cape Henlopen on the mid-Atlantic coast. Wet deposition has been collected on an event basis for trace metals and analyzed since 1982 (Church *et al.* 1984, Church and Scudlark 1992). The success of this record has come from the development of suitably clean protocols and sufficiently accurate and precise analytical techniques developed specifically for trace elements in precipitation (Tramontano *et al.* 1987, Scudlark *et al.* 1992). The data from Lewes, Delaware (Church and Scudlark 1992), show that the concentrations of trace elements in rural precipitation far exceed those of most surface waters and are in excess of natural crustal or sea water sources. Trajectory analyses of air masses associated with precipitation events reveal that the excess sources of trace elements are similar to those for acid precipitation, namely emissions from the combustion of fossil fuels or metal refining. Wet depositional fluxes of many trace elements at the Lewes, Delaware site are relatively constant over the past eight years, with the notable exception of lead. Concentrations of lead in precipitation and wet depositional fluxes decline from the de-leading of automobile gasoline (Figure 11). This same decreasing trend of lead deposition has been confirmed as well in the northern Great Lakes area of Minnesota (Eisenreich *et al.* 1986).

The magnitude of trace element deposition at the Lewes, Delaware site is compared to other coastal inputs in Table 9. Although the atmospheric depositional flux of trace elements into the watershed can dominate that which crosses the fall line (Church *et al.* 1988), the amount falling directly into the open estuarine waters of Delaware Bay appear to be minor (Church. 1987). However, the amount of atmospheric input for metals such as Cd, Pb, and Zn appear to dominate the riverine/estuarine inputs into coastal waters of the mid-Atlantic bight (Church 1987, 1992). However, there are several problems in deconvoluting the fraction of trace metals entering the estuary directly from weathering versus indirectly from the run-off of trace elements previously deposited from the atmosphere. Part of the problem involves complex trace element-watershed interactions (Lindberg and Turner 1988).

Other studies which document the atmospheric deposition of trace elements to coastal waters such Puget Sound (EPA 1991) are limited in length of record, location of sampling points, and analytical procedures. The Great Lakes Atmospheric Deposition (GLAD) Network has measured wet deposition of trace elements to the Great Lakes (Klappenbach 1992). Most recently, the Chesapeake Bay Atmospheric Deposition Study (CBADS) also documented dry and wet deposition of trace elements (Baker *et al.* 1992). The relatively uniform atmospheric fluxes between the CBADS and Lewes sites (Figure 12) suggest the importance of rather distant sources being transported to this important estuarine system (Wu *et al.* 1993). A comparison of the wet depositional fluxes (Figure 12) between the various aquatic systems suggest regional uniformity in the Eastern United States. Greater fluxes in the past are not supported by the

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TABLE 9

ATMOSPHERIC INPUTS OF TRACE METALS TO MID-ATLANTIC COASTAL MARINE SYSTEMS (FROM CHURCH *et al.*, 1988)

Element	Atmospheric Component (%)		
	Del. Watershed	Del. Estuary	Mid-Atlantic Bight
Al	--	--	--
Cd	--	--	--
Cr	--	--	--
Cu	41	4	18
Fe	64	2	--
Mn	-58	--	4
Ni	43	2	30
Pb	--	--	96
Zn	32	4	64
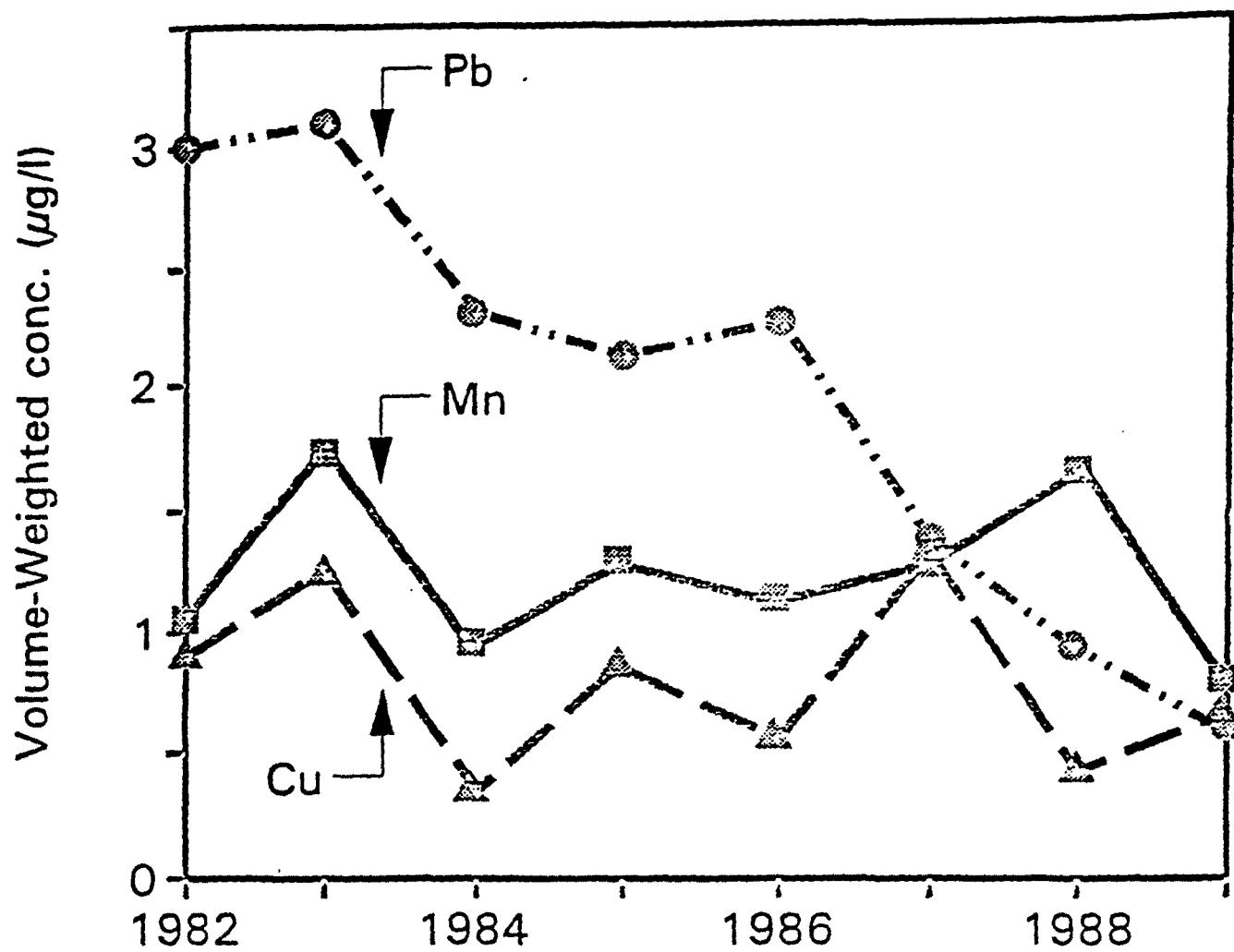
Figure 11. Inter-annual trends in precipitation trace element
concentrations, Lewes, DE

Lewes record, and it is possible that these earlier measurements are biased by poor analytical protocols. The high trace element fluxes reported for Commencement Bay, Puget Should may reflect the proximity to local emissions or bias resulting from bulk deposition sampling (EPA 1991).

3.2   SEMIVOLATILE ORGANIC CONTAMINANTS - Evidence of Deposition

Organic chemicals emitted into the atmosphere by anthropogenic activities may be transported long distances, chemically converted, and deposited at sites distant from their emission sources. The presence of persistent semivolatile organic compounds (SOC) in the Arctic snowpack and food chain (Gregor and Gummer 1989, Hargrave *et al.* 1988, Welch *et al.* 1991, Hinckley *et al.* 1990, 1991, Patton *et al.*, 1989, Cotham and Bidleman 1992) and in the Antarctic (Tanabe *et al.* 1983) is ample evidence that long range atmospheric transport and subsequent deposition is an important global pathway for these chemicals. The occurrence of current-use agrichemicals on non-target crops adjacent to treated fields (*i.e.*, Seiber and McChesney 1991) is further evidence of the importance of atmospheric transport and deposition over shorter spatial scales. The role which atmospheric transport and deposition plays in delivering SOCs to urban areas has been seldom studied and is consequently poorly understood. While it may seem intuitive that atmospheric fluxes pale in comparison to easily identified and measured point sources in urban areas, persistently high SOC levels in urban areas and enhanced depositional processes may result in significant loadings to near by water bodies. Recent studies in Chicago (Holsen *et al.* 1991) measured extremely large depositional fluxes of polychlorinated biphenyls (PCBs) from the atmosphere, which were attributed to settling of large, PCB-laden aerosols.

In the upper Great Lakes region, atmospheric deposition is believed to be the major source of SOCs (Eisenreich *et al.* 1981, Strachan and Eisenreich, 1988). For example, atmospheric deposition supplies 90%, 63%, and 58% of the PCB loading to Lakes Superior, Huron, and Michigan, respectively (Table 10). The atmosphere is also the dominant source of lead to the Great Lakes, exceeding 95% of estimated external sources to lakes Superior, Michigan, and Huron (Strachan and Eisenreich 1988). Although regulatory bans on the production and use of PCBs and other persistent SOCs (*i.e.*, dieldrin) have resulted in decreased levels of these compounds in the Great Lakes fisheries, this decrease has been tempered by the continuing deposition from the atmosphere and from internal SOC recycling. Interestingly, atmospheric inventories of these SOCs over the upper Great Lakes have not changed appreciably since the late 1970's, suggesting a dynamic exchange between the atmosphere and the much larger terrestrial reservoir (Baker and Eisenreich 1990, Manchester-Neesvig and Andren 1989). Such recycling will likely result in continued atmospheric deposition of SOCs to remote environments for some time into the future.

TABLE 10

INPUT-OUTPUT CALCULATIONS FOR PCBs and BENZO[a]PYRENE
TO THE GREAT LAKES
(STRACHAN AND EISENREICH, 1988)

Lake	Input(kg/yr)	% Atmospheric	Output (kg/yr)	% Volatilization
PCBs				
Superior	606	90	2190	86
Michigan	685	58	7550	68
Huron	636	63	2760	75
Erie	2520	20	2390	46
Ontario	2540	13	1320	53
Benzo[a]pyrene				
Superior	72	96	314	19
Michigan	208	86	6250	6
Huron	290	80	1370	31
Erir	122	79	3720	15
Ontario	155	72	1290	33

Recently, atmospheric depositional fluxes of SOCs (Leister and Baker 1993) and trace elements (Wu *et al.* 1992,1993, Scudlark *et al.* 1993) to the Chesapeake Bay were measured. In general, fluxes of SOCs to the Chesapeake Bay are larger than those to relatively remote regions of the Great Lakes (Figure 6), but smaller than those measured in urban areas (*e.g.*, Ligocki *et al.* 1985a and 1985b, Holsen *et al.* 1991), reflecting the various types of air masses travelling over the Chesapeake Bay (*i.e.*, marine *versus* urban). It is difficult to place these loadings in perspective because estimates of contaminant loadings from other sources to the Chesapeake Bay are highly uncertain. Nonetheless, Leister and Baker (1993) estimate that the atmospheric loadings of PCBs and PAHs directly to the surface of the Chesapeake Bay may be comparable to those discharged from the Susquehanna River, the dominant tributary supplying 60% of the bay's freshwater.

Atmospheric loadings to Commencement Bay and Puget Sound have been estimated using bulk deposition collectors (EPA, 1991). Loadings of PAHs and trace elements are significantly greater than those measured either to the Great Lakes or to the Chesapeake Bay, often by more than two orders of magnitude (Figure 12). These elevated loadings may reflect proximity of the sampling sites to the many emission sources around Commencement Bay, or may have resulted from oversampling by the bulk deposition samplers. In either case, it is unclear how to extrapolate these high, perhaps localized, loadings to larger geographic areas (*e.g.* the entire Puget Sound).

Sources and loadings of contaminants to the Massachusetts Bay system was studied by Werme and Menzie (1991). Based largely upon a compilation of monitoring data and literature values, they conclude that the atmosphere can be an importance source of PAHs and PCBs to these urban waters, although the Merrmack River, North Shore, and Boston Harbor drainage areas are the dominant source of trace metals and synthetic organics. The authors emphasize the considerable uncertainty inherent in developing contaminant loadings inventories using data from disparate sources.

3.3 MERCURY - Evidence of Deposition

3.3.1 The Global Mercury Cycle

To paraphrase Einstein, "Nature is not malicious, but subtle", and environmental pollutants cycle in elusive ways. Mercury for example, has proved to be one of the most challenging and insidious contaminants measured in the environment. There is widespread evidence in the United States, Canada and Europe of tissue concentrations of mercury in fish (even in pristine regions) that exceed local, national and international public health guidelines. This situation represents a serious human health concern as well as a significant economic threat to commercial and sport fishing industries. Anthropogenic mercury is derived principally from coal combustion, smelting and waste incineration. Most mercury is "invisibly" transferred

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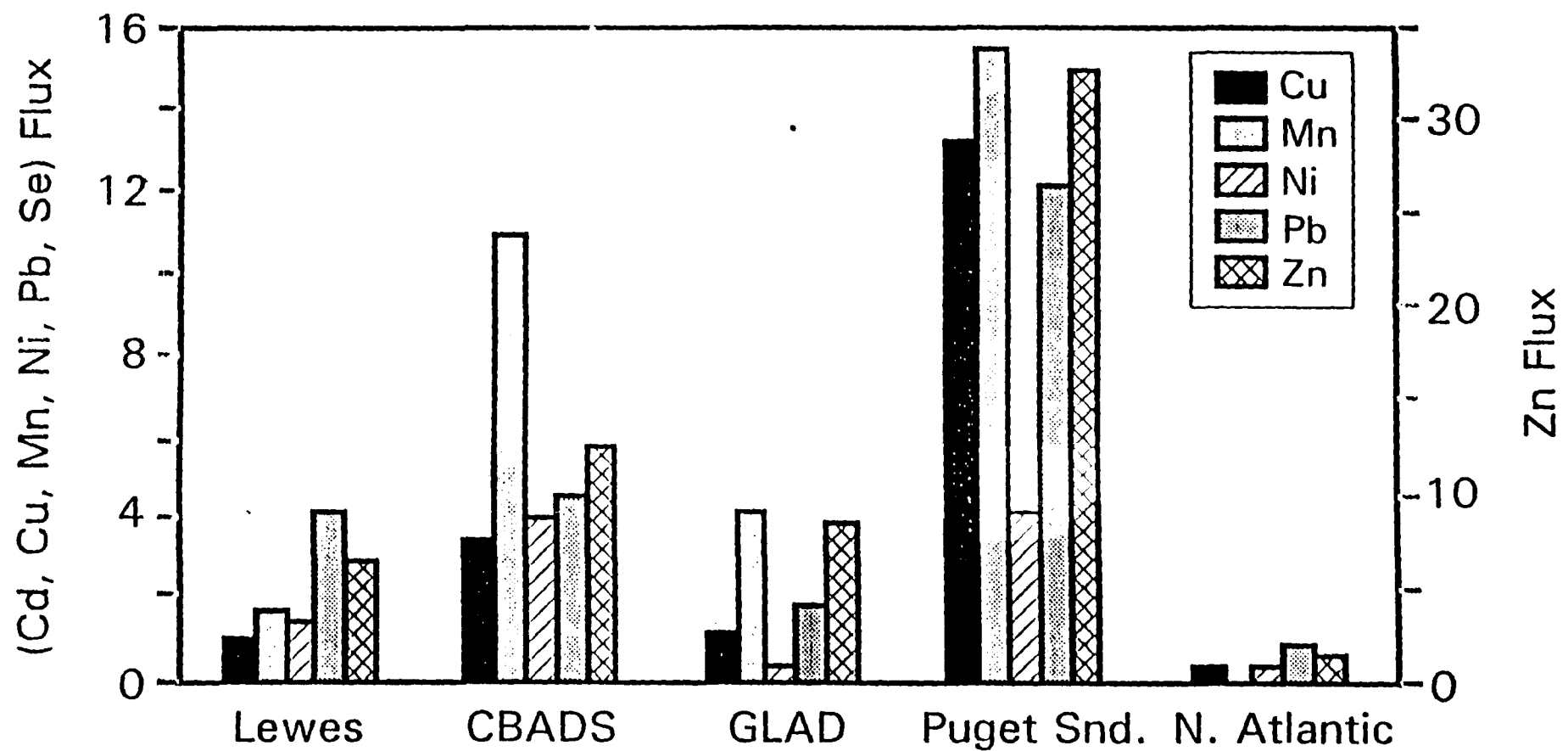
Figure 12. Trace element fluxes at various locations in North America (mg/m2-year)

through the atmosphere as a gas, Hg°, which is eventually oxidized, scavenged, and deposited with precipitation. Our understanding of the environmental cycling of Hg°, though improving, is quite limited. There is also a correspondingly important but poorly understood atmospheric mobilization of mercury associated with particles. The atmospheric particulate mercury cycle may be more significant than that of Hg° in its potential to adversely affect aquatic systems on local and regional scales. In natural waters, and as shown in Fig. 14, atmospherically derived Hg is transformed by bacteria to a very toxic organic form, monomethyl mercury, which is biologically amplified and concentrated in fish muscle tissue. While game fish filets (*e.g.*, swordfish, tuna, mako shark, and walleye pike) often show monomethyl mercury levels greater than 1 part per million, the concentrations in water are commonly less than 1 part per trillion. An amplification of more than a million times has occurred. The amounts of mercury in the air and water are extraordinarily minute such that, regardless of the highly sophisticated nature of the equipment, the study of mercury and other metals in the atmosphere and in aqueous systems requires ultra-clean and rigorous trace metal analytical protocols. Environmental scientists and engineers have been slow to incorporate clean laboratory expertise into their trace metal studies.

The prominence of atmospheric mobilization and depositional processes in the global biogeochemical cycling of mercury is well recognized and described in a variety of mass balance formulations of the global mercury cycle (*e.g.*, Wollast *et al.* 1975, NAS 1978; Slemr *et al.* 1981, Lindqvist and Rodhe 1985, Fitzgerald 1986, Nriagu 1989; Fitzgerald and Clarkson 1991, Lindqvist *et al.* 1991). Although the significance of the atmosphere was evident in early models, environmental assessments of source strengths for natural and anthropogenic processes were often in error because they lacked accurate information about critical aspects of the mercury cycle. Current international human-health and environmental concerns associated with elevated levels of monomethyl mercury in freshwater and marine piscivorous fish have focused attention on mercury as a pollutant. Consequently, there has been an expansion in Hg research, a heightened awareness of the need for an accurate and broader environmental data base for Hg in the environment, and the incorporation of ultra trace-metal clean sampling and analytical protocols into Hg research (see Evaluation of Current Sampling and Analytical Procedures Section for further details). In addition, new information is being communicated effectively. Two international meetings dealing with mercury in the environment have taken place recently, with a third meeting planned for 1994. The geochemical view of the global mercury cycle has improved significantly, and present estimates for mercury fluxes to the earth's surface and for the mercury content of active reservoirs are converging. The agreement among recently published budgets for the atmospheric cycling of mercury is quite satisfactory, given the uncertainties associated with global scale estimates (Fitzgerald 1986, Nriagu 1989, Fitzgerald and Clarkson 1991, Lindqvist *et al.*, 1991).

Elemental mercury concentrations in the marine boundary layer decrease between the northern and southern hemisphere over the Atlantic and Pacific Oceans (see Figure 13, for Pacific data). This interhemispheric distributional pattern characterizes a trace atmospheric gas whose primary sources, on a unit area basis, are continental and likely anthropogenic. Trace
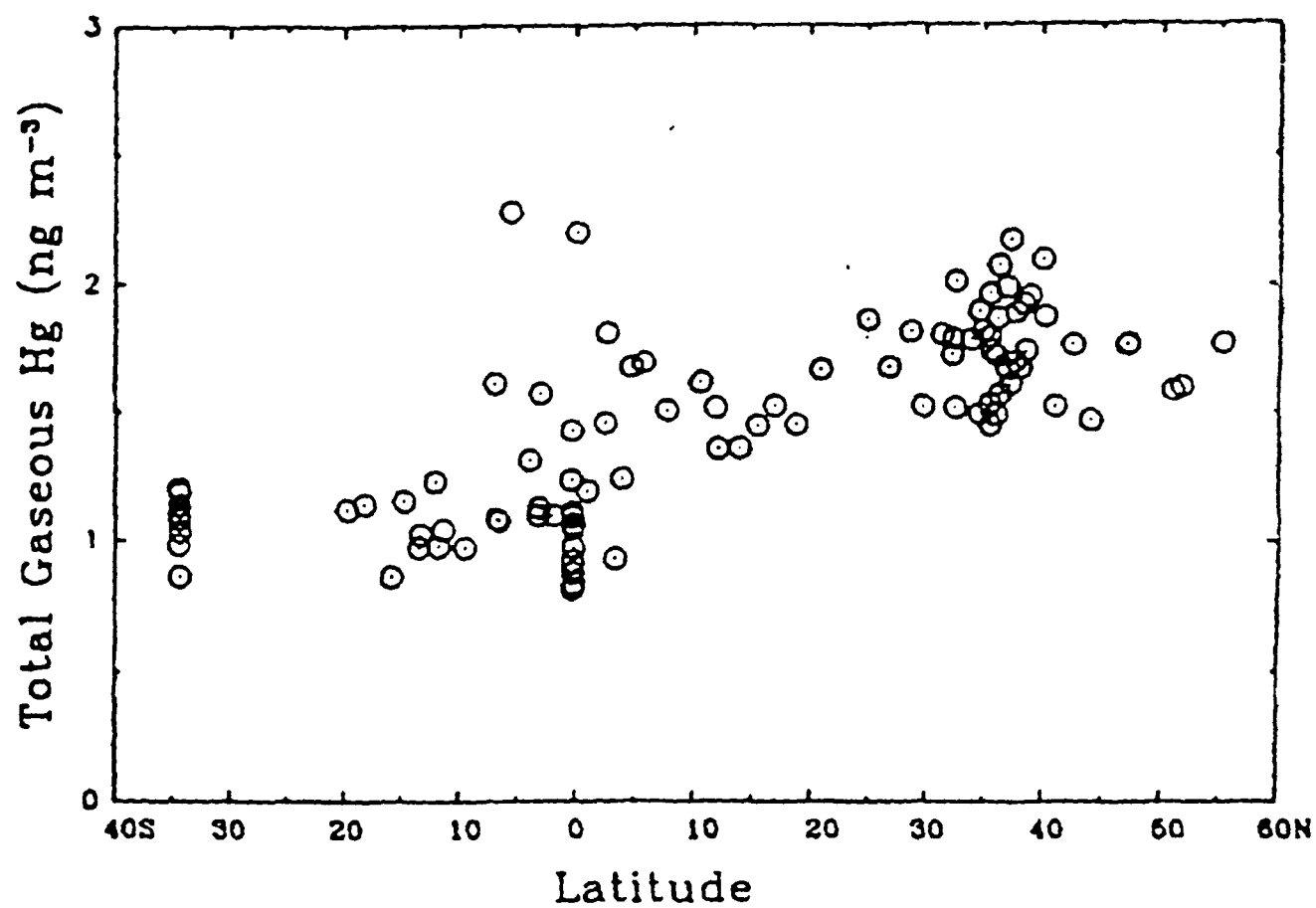
Figure 13. Latitudinal distribution of total gaseous Hg (TGM; ng m^{-3}) over the Pacific Ocean between 1980 and 1986. Adapted from Fitzgerald (1989).

RUNOFF ⇧ EXCHANGE   ⬍ DEPOSITION   ⬍ DEPOSITION   ⬍ DEPOSITION

SEEPAGE

Hg^0

$Hg(o)$

B,P

$Hg^{\circ\circ}$ ⇌ $Hg^{\circ}:L$
⇅ $Hg^{\circ}:Part$
$Hg(OH)_2$
⇅
$HgCl_2$

$Hg(II)$

B.P
A

CH_3Hg^+ ⇌ $CH_3Hg:L$
≠ $CH_3Hg:Part$
CH_3MgOH
⇅
CH_3HgCl

CH_3Mg

Hg
(Unreactive)

Hg
Unreactive

Epili

SETTLING

Hg^{II} STORAGE
CH_3Hg STORAGE

PHYTOPLANKTON

GRAZING

Hg^{II} STORAGE
CH_3Hg STORAGE

ZOOPLANKTON

FEEDING

Hg^{II} STORAGE
CH_3Hg STORAGE

SMALL FISH

FEEDING
MATURATION

Hg^{II} STORAGE
CH_3Hg STORAGE

LARGE FISH

SEEPAGE

AS ABOVE — $Hg(o)$ — $Hg(II)$ — CH_3Hg — Hg Unreactive

Hyp

KEY
REACTION MEDIATION:
P - Phytoplankton
B - Bacteria
A - Abiotic
⇨ Rate limited process
⇌ Equilibrium process

$HgS(s)$ ⇌ Hg^{II} dissolved ⇌ CH_3Hg dissolved
A   B
⇅   ⇅
Hg^{II} adsorbed CH_3Hg adsorbed   Hg (Unreactive) particulate

S

BURIAL

Hg CYCLING: MCM MODEL

Figure 14.   The major species, fluxes, and reservoirs for the physical and biogeoche:
             cycling of Hg in the atmosphere and within lakes (adapted from Hudson e:
             1992).

gas modeling of mercury yields an average tropospheric residence time of total gaseous mercury, assumed to be Hg°, of about 1-year (Fitzgerald *et al.*, 1981). Confirmation of this relatively long average residence time is provided from estimates of annual mercury deposition to the earth's surface using a steady state model for the global mercury cycle (Fitzgerald 1986, Table 11). Thus, Hg° from both natural and anthropogenic sources can be readily mixed intrahemispherically. Interhemispheric mixing allows northern hemispheric emissions of Hg° to be transported to the atmosphere of the southern hemisphere. While the broad dispersion of mercury has reduced some localized impact from human related emissions of mercury, it may have led to the geographically large problem of elevated mercury concentrations in fresh water and marine fish that are far removed from local sources.

The major fluxes associated with the global atmospheric Hg cycle are summarized in a mass balance format in Table 11. The major species, fluxes, and reservoirs for the physical and biogeochemical cycling of Hg in the atmosphere and within lakes is shown in Figure 14, which has been adapted from the MCM Lake mercury model developed by Hudson *et al.* (1992). Estimates of the total annual emission of mercury to the atmosphere range from 5 to 7.5 x 10^9 g/year. Fitzgerald (1986) noted that this estimate is much smaller than even values for "preindustrial fluxes" used in many models. Further, and as summarized in Table 11, atmospheric Hg emissions associated with contemporary human endeavors are comparable to those from natural sources. Estimates for annual anthropogenic Hg emissions are between 2 and 4.5 x 10^9 g/year, which represents about 30 to 90% of the total annual mercury input to the atmosphere. Elemental mercury evasion from the oceans and other natural waters is a significant source of atmospheric mercury, and may account for 25% to 40% of the annual fluxes of mercury. Marine studies demonstrate that *in situ* synthesis of volatile Hg, which is principally Hg° in the mixed layer (Kim and Fitzgerald 1986, Mason and Fitzgerald 1990, 1991, 1992) and its subsequent evasion at the water-air interface are major features of the global Hg cycle (Fitzgerald *et al.* 1984, Iverfeldt 1988). Most recently, fresh water investigations by Vandal *et al.*, (1991) in Wisconsin and Xiao *et al.* (1991) in Sweden have shown a similar and important in-lake Hg° cycle which yields significant Hg° fluxes to the atmosphere. Other natural volatile sources of Hg such as volcanic emanations, biological mobilization, and forest fires can contribute about 30 to 60% to the yearly emissions. The comparatively small estimate for the fluvial flux of Hg illustrates the preeminence of the atmosphere in the transfer of mercury to the world's oceans (Table 11).

Anthropogenic interferences within the biogeochemical cycle of Hg present perplexing and challenging problems. We must be concerned not only with sources, chemical composition, physical state, and direct impact of Hg compounds to natural waters, but with the post-depositional *in situ* bacterial conversion of Hg species to more toxic forms, especially monomethyl mercury. Monomethyl mercury is the principal form of mercury in fish (Westöö 1966, NAS 1978), and it is considerably more toxic than either Hg° or other mercury species. Human exposure to methyl mercury compounds comes almost exclusively from the consumption of fish and fish products.(WHO 1976), although, in certain populations, consumption of marine

TABLE 11

GLOBAL ATMOSPHERIC MERCURY BUDGET

Source	Mercury Flux $(10^9$ g/year)	Reference
Deposition	5-6	Fitzgerald, 1986
	6	Slemr et al., 1981
	7.5	Lindqvist et al., 1991
Emissions		
Anthropogenic	2	Watson, 1979
	3.6	Nriagu and Pacyna, 1988
	4.5	Lindqvist et al., 1991
Natural	2.5	Nriagu, 1989
	3	Lindqvist et al., 1991
Oceanic Sources	2	Kim and Fitzgerald, 1986
Equatorial Pacific	0.2	
Volcanic	0.06	Fitzgerald, 1986
	0.6	Varekamp and Buseck, 1986
Other Continental Sources	1-2	Fitzgerald and Clarkson, 1991
- Crustal Degassing		
- Forest Fires		
- Biological Mobilization		
Fluvial Hg Input	0.2	Gill and Fitzgerald, 1987
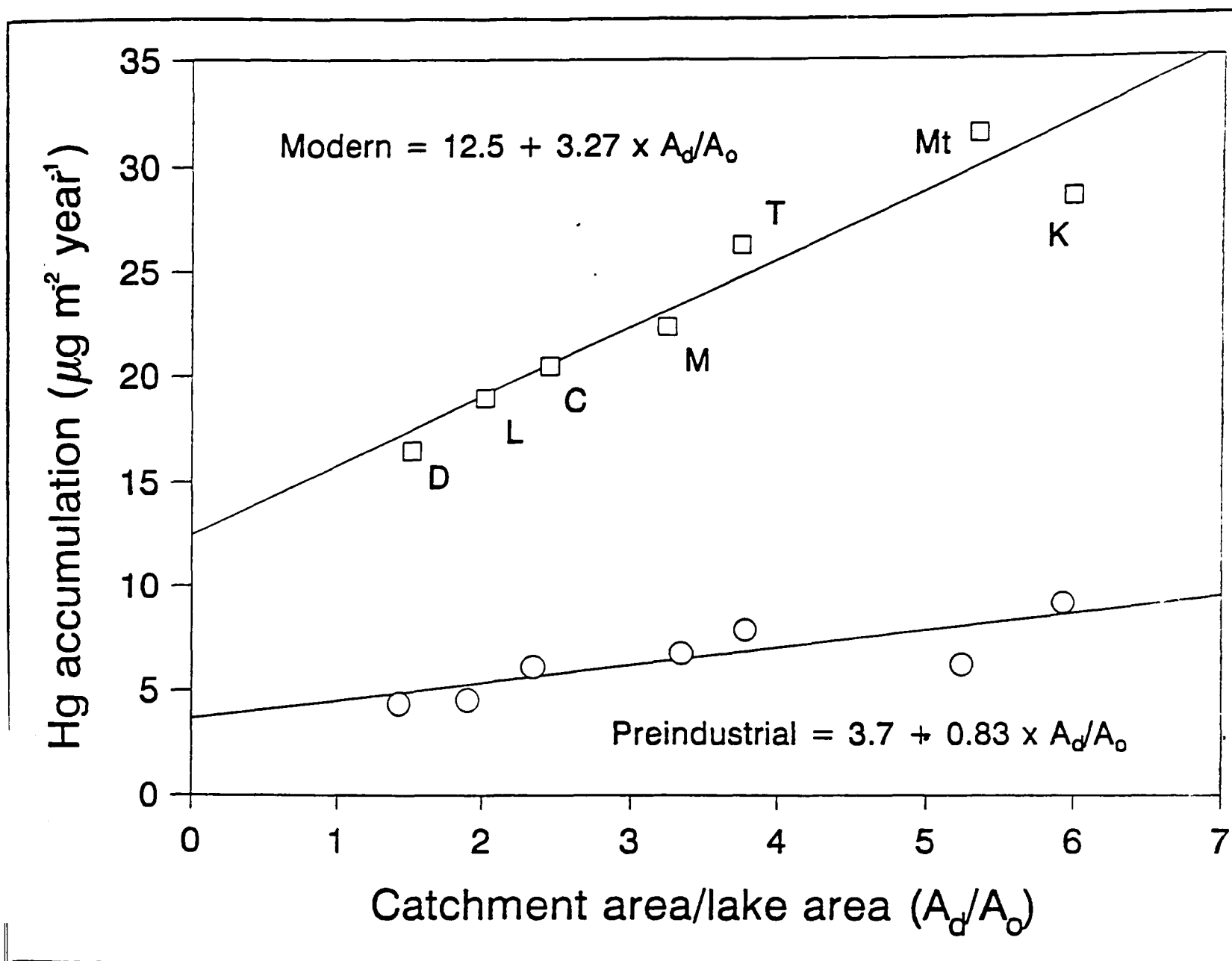
Figure 15. Whole basin accumulation rates for Hg (ug m^{-2} yr^{-1}) are plotted against the terrestrial catchment area to lake area ratio. Modern rates based on the past 10 years are indicated by the filled squares, while the preindustrial estimates (before ca. 1850) are indicated by the filled circles (adapted from Swain et al., 1992).

mammals is a significant source (Fitzgerald and Clarkson 1991). The importance of atmospheric mercury deposition in the aquatic biogeochemistry of Hg has been demonstrated for seepage lakes as part of The Mercury in Temperate Lakes (MTL) Program in Wisconsin (Fitzgerald et al. 1991), and for drainage lakes in Sweden (Lindqvist et al. 1991). Both studies indicate that small increases in atmospheric depositional fluxes of mercury could result in enhanced mercury concentrations in fish, as suggested by Fitzgerald and Watras (1989). These two investigations will serve as a benchmark for assessing the quality of the available information about the atmospheric cycling of mercury and for identifying parts of the cycle where information is needed, especially as it relates to the impact of atmospheric Hg deposition to the Great Waters.

3.3.2   Regional Mercury Cycling and Localized Deposition in North America

A recent and very convincing report documenting increasing rates of atmospheric Hg deposition to lakes in Minnesota and Wisconsin was recently published (Swain et al. 1992). They employed an innovatively simple but effective mass-balance approach to Hg flux information obtained from the sediment record of seven "relatively undisturbed" lakes in Minnesota and Wisconsin. For each lake, multiple cores (7 to 15) were taken, the strata were dated and sedimentation rates established from the ^{210}Pb chronology. Mercury was measured, whole lake Hg fluxes were determined, and the preindustrial and modern atmospheric Hg inputs were inferred.

The results are presented in Figure 15 which has been adapted from Swain et al. (1992). Whole basin accumulation rates for Hg ($\mu g\ m^{-2}\ yr^{-1}$) are plotted against the terrestrial catchment area to lake area ratio. Modern mercury accumulation rates based on the past 10 years are indicated by the filled squares, while the preindustrial estimates (before ca. 1850) are indicated by the filled circles. The intercept of the regression line (catchment area = zero) yields a value that represents the rate of regional atmospheric deposition to the surface of the lake. In addition, the ratio of the intercept to the slope provides the portion of the atmospheric Hg depositional flux to the catchment that is transported to the lake. As indicated in the regression equations (Figure 15), the estimate for present atmospheric deposition of mercury to Minnesota and Wisconsin is 12.5 $\mu g\ m^{-2}\ yr^{-1}$, and preindustrial value is 3.7 $\mu g\ m^{-2}\ yr-1$. This represents an 3.4 fold increase in deposition in recent times. These estimates of substantial anthropogenic enhancement to the mid-continental Hg cycle at approximately 2% yr^{-1} for the past 140 years are consistent with predictions on a global scale (Fitzgerald and Clarkson 1991). For example, approximately two-thirds of the total world's production of Hg has taken place during this century, and anthropogenic releases of Hg to the environment have increased about 3-fold since 1900 (Andren and Nraigu 1979).

The depositional results for Hg as established by the Little Rock Lake budget (Section 8.3), and the whole lake experiments by Swain et al. (1992) yield a consistent estimate of

TABLE 12

TIME INTEGRATED ESTIMATES OF MERCURY DEPOSITION, AS DETERMINED IN PEAT FROM AN OMBROTROPHIC PORTION OF ARLBERG BOG, MINNESOTA
(BENOIT *et al.*, 1992a; 1992b)

Time Period	Mercury Deposition ($\mu g/m^2$-year)
1980 - 1991	24.5 $\pm$ 7.9
1950 - 1980	37.8 $\pm$ 12.3
1935 - 1950	38.2 $\pm$ 12.5
1750 - 1935	10.3 $\pm$ 3.4
Pre-1900	4 $\pm$ 1

present day mercury deposition rates to the mid-continental U.S. Further support is provided by Mierle (1990), who reported a mean wet depositional flux of 10.2 μg m^{-2} yr^{-1} at Dorset, Ontario, which is about 1000 km east of the Minnesota and Wisconsin lakes. This agreement may be misleading and bears careful scrutiny because it suggests that the atmospheric contributions to the mid-continental North America are almost exclusively associated with the global Hg cycle. As noted, Hg°, the principal form of Hg in the atmosphere, has a tropospheric residence time of the order of a year, allowing it to be widely dispersed before oxidization and removal by precipitation or dry deposition. Primary particulate Hg emissions will contribute principally to local and regional deposition. Therefore, one should expect to find the influence of continental sources of particulate Hg in mid-continental Hg deposition. This local-regional particulate Hg would be superimposed on an increasing background of Hg deposition associated with the global cycling of Hg°. Nater and Grigal (1992) have found such a pattern of regional Hg deposition in organic litter and surface mineral soil at forested sites along a 1000 km track from northwestern Minnesota to eastern Michigan. A summary of their results is presented in Figure 16, while the sample locations are indicated in Figure 17. According to these authors, "the observed gradient parallels changes in wet sulphate deposition and human activity along the transect, suggesting that the regional variation in mercury content is due to deposition of anthropogenic mercury, mostly in the particulate form."

An examination of the Hg accumulation profiles versus age of the sediments from representative cores presented in Figure 1 of the Swain *et al.* (1992) work suggests that the whole lake regression analysis will not yield consistent results for other time periods (*e.g.*, 1950 to 1960). Moreover, the number of pre-1980 peaks in the sedimentary record indicates that Hg deposition was variable and possibly larger in the 1950s compared to estimates for the last decade. Temporal variations and localized contributions to atmospheric Hg inputs during the past century are quite evident in the Hg accumulation record for an ombrotrophic portion of Arlberg Bog in northeastern Minnesota (Benoit *et al.* 1992a, 1992b). Arlberg bog is located in St Louis County, Minnesota near the town of Cloquet, about 50 km west of Duluth. The average Hg accumulation (μg m^{-2} yr^{-1}) rates versus time are summarized in Table 12. Average recent Hg deposition is 24.5 $\pm$ 7.9 μg m^{-2} yr^{-1}, which is about twice the estimate from the Little Rock Lake Study (Section 8.3) and the Swain *et al.* (1992) results (Figure 15). Also, and in contrast to the Nater and Grigal (1992) investigation (Figures 16 and 17), atmospheric Hg deposition is greater at this northeastern Minnesota location than in Wisconsin. Local/regional scale gradients in the Hg deposition are evident in temporal deposition where the mean Hg accumulation was approximately 38 $\pm$ 12 μg m^{-2} yr^{-1} between 1935 and 1980, and 10 $\pm$ 3 μg m^{-2} yr^{-1} during 1750 to 1935. Finer resolution from two peat cores indicates that the pre-1900 atmospheric deposition was ca. 4 $\pm$ 1 μg m^{-2} yr^{-1}. Thus, the estimates for preindustrial Hg fluxes from the atmosphere as determined from the Hg distributions preserved in lake sediments and an ombrotrophic peat bog are identical. However, the estimates for recent Hg accumulation differ, and point towards atmospheric scavenging and deposition of Hg in particles near their emission sources.
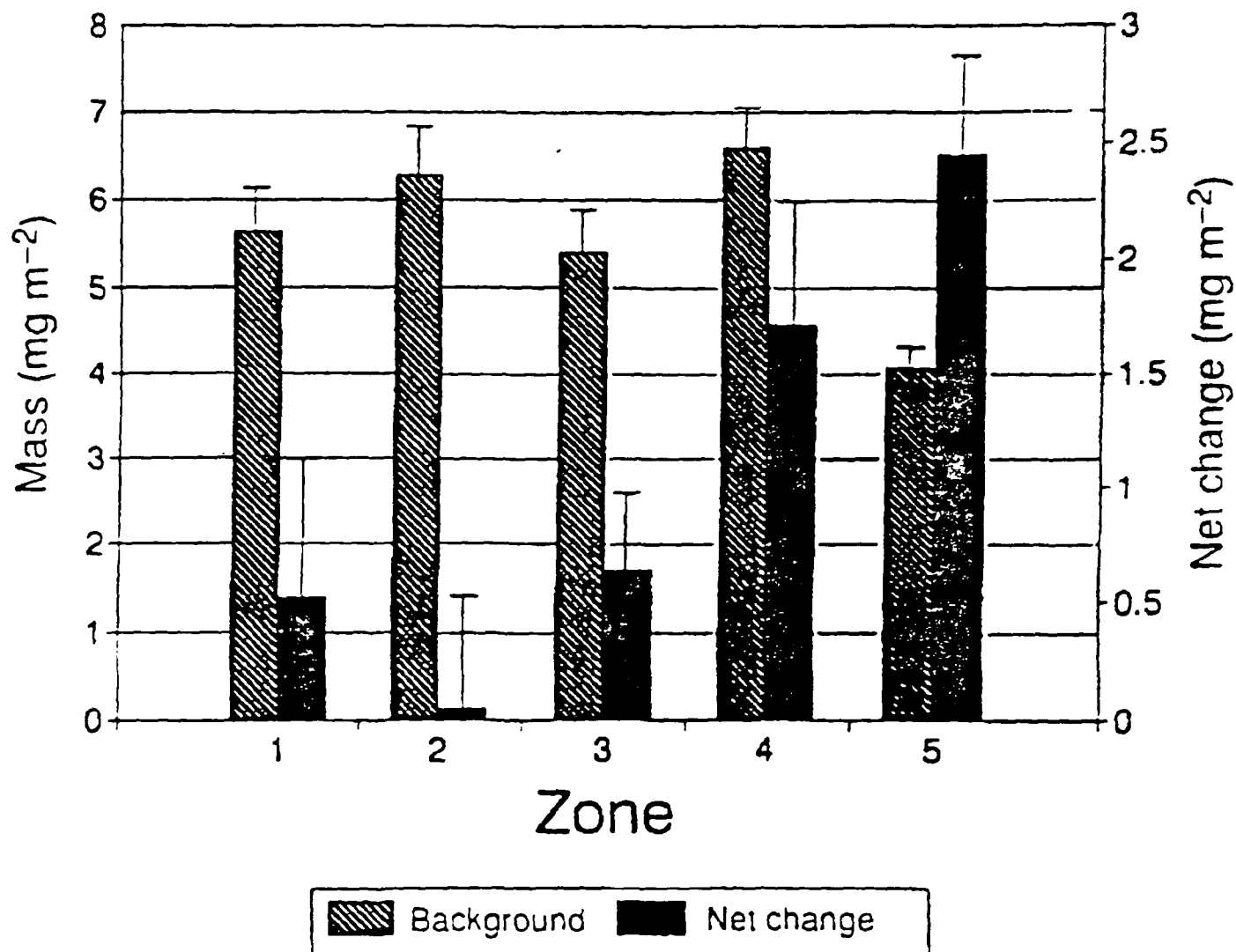
Figure 16. Estimates of the net increase in Hg due to atmospheric deposition compared to predicted geological contributions ("background") along a track between northwestern Minnesota and eastern Michigan (adapted from Nater and Grigal, 1992). The stations appear in Figure 17.
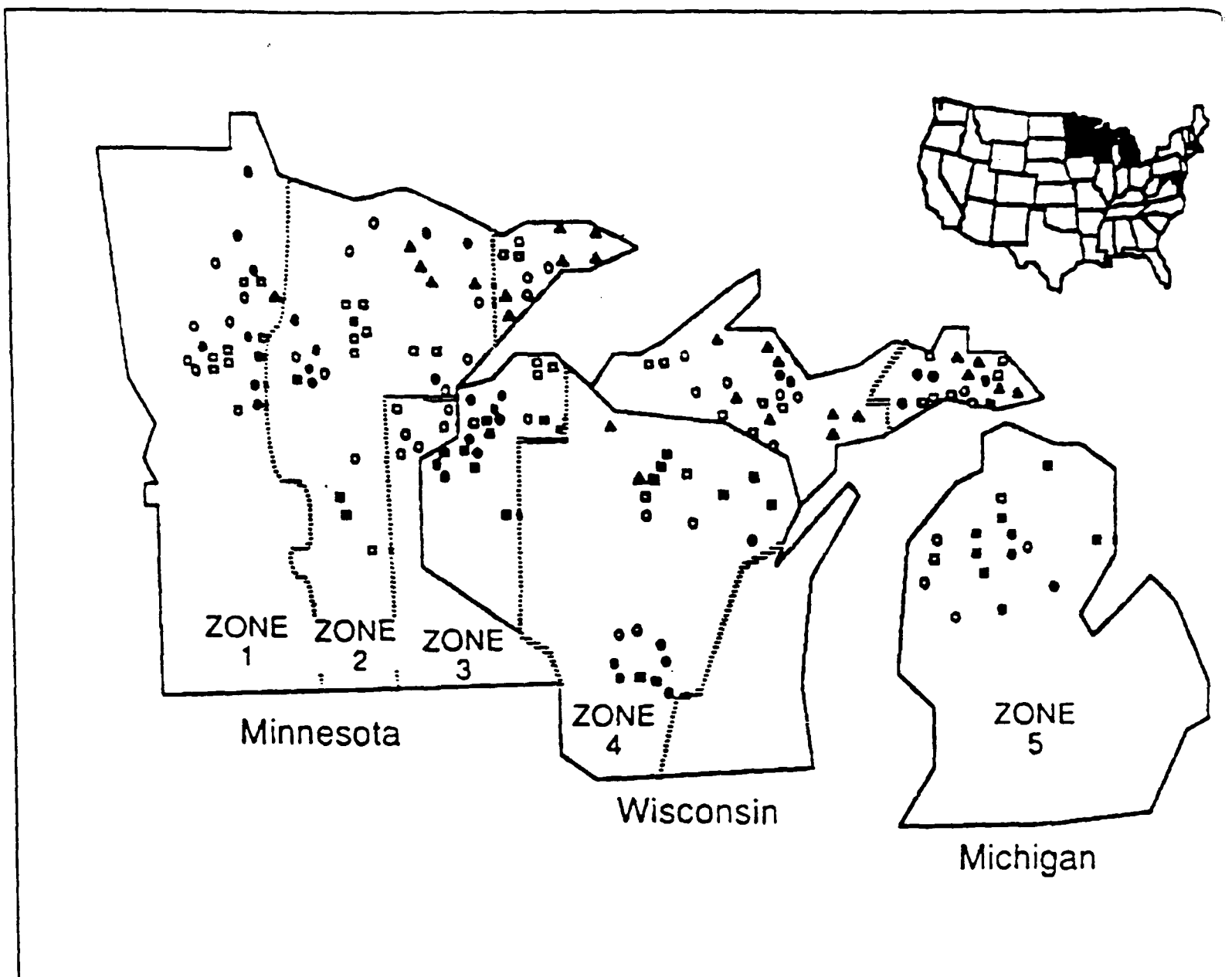
Figure 17. Sampling sites in the five zones established across the Great Lake State (adapted from Nater and Grigal, 1992).

TABLE 13

ANNUAL DEPOSITION AND VOLUME-WEIGHTED CONCENTRATION AVERAGES FOR MERCURY IN PRECIPITATION AT THREE LOCATIONS IN MINNESOTA DURING 1988 AND 1989

(Adapted from Glass *et al.*, 1991)

Site	Year	Deposition (μg/m^2)	Concn (ng/L)	Precipitation Depth (cm)	Sampling Period (Weeks)
Duluth	1988	19.9	22.6	88.5	52
Marcell	1988	15.7	17.7	88.8	48
Ely	1988	16.7	19.7	84.9	47
Duluth	1989	6.5	10.5	62.1	52
Marcell	1989	13.0	18.0	72.2	41
Ely	1989	41.9	81.4	51.4	52

The importance of local Hg emissions and deposition are indicated in another Minnesota study. Glass *et al.* (1991) found a two year average flux of 19 ± 12 μg m^{-2} yr-1 for rain and snow at three sites (Duluth, Marcell, and Ely) in Northern Minnesota. If we assume that an additional 5 μg m^{-2} yr-1 would be contributed by dry deposition, the results are comparable to the Benoit *et al.* (1992a,b) estimates for recent total Hg deposition. This is a further indication of the importance of local sources and site variability in the geographic pattern of atmospheric Hg deposition. As summarized in Table 13, the interannual variations are substantial for the Duluth and Ely sites. The results for Ely, a relatively remote location bordering the Boundary Waters Canoe Area in the Superior National Forest, are particularly puzzling because of the anomalously high concentrations > 100 ng Hg/L of precipitation and the corresponding elevated depositional fluxes reported for the spring of 1989. These unusually high levels are most probably artifacts reflecting contamination incurred during the sample collection and processing procedures. This is a problem common to the study of Hg and other trace metals in the environment (see for example, Patterson and Settle 1976, Fitzgerald and Watras 1989, Fitzgerald *et al.* 1991). We do note that "events" of this magnitude have been observed in the Swedish mercury depositional studies described below.

3.3.3 Localized Atmospheric Hg Deposition: Sweden

The importance of local and regional atmospheric deposition is demonstrated by the extensive study of the tropospheric cycling of Hg over the Nordic countries (Iverfeldt 1991a,b). The results are presented in Table 14, for locations shown in Figure 18 that were chosen to examine south - north gradients of Hg in air and precipitation over a distance of approximately 1500 km, which is comparable to the range covered between northwestern Minnesota and eastern Michigan in the Nater and Grigal (1992) work. In general, average total Hg in precipitation increases from ca. 8 ng/L at the most northerly stations to ca. 40 ng/L at the most southerly site (Figure 19). The latitudinal depositional pattern is particularly pronounced in Norway where with the smallest Hg fluxes observed at the northernmost stations of Överbygd and Jergul (5 and 3 μg m^{-2} yr^{-1} respectively) and the largest at Birkenes (35 μg m^{-2} yr^{-1}), a port on the southern tip of Norway. The variations in annual deposition of Hg are related to the locality and annual wet deposition. For example, Kårvatn, in southeast Norway, with a large annual precipitation of 1430 mm, has a flux of 13 μg m^{-2}/yr, while the southern-most site in the network (Keldsnor, Denmark), with a comparable yearly flux of 17 μg m^{-2} yr^{-1}, has a annual rainfall that is a factor of 3 lower (430 mm). The depositional pattern for the Nordic study closely resembles the average range for the global depositional pattern of Hg as estimated from a limited data base by Fitzgerald (1986).

The importance of regional European sources to Hg deposition in the Nordic countries is evident. The highest levels of Hg in precipitation are associated with air mass trajectories from the south/southeast, mostly from eastern part of Europe. Moreover, episodic effects were evident where concentrations of total Hg in precipitation were > 100 ng/L for southerly air trajectories and these high levels correlated with "exceptionally high concentrations" of soot and

TABLE 14

ATMOSPHERIC WET DEPOSITIONAL FLUXES OF TOTAL MERCURY TO VARIOUS STATIONS IN THE NORDIC COUNTRIES

After Iverfeldt, *et al.* (1991)

Station	No.	Precipitation (mm)	Deposition Rate (μg/m^2-yr)
Keldsnor, DK	1	430	17
Aspvreten, S	2	520	10
Rorvik, S	3	770	27
Birkenes, N	4	1730	35
Tikkakoski, SB	5	720	11
Vindeln, S	6	650	7
Karvatn, N	7	1430	13
Overbygd, N	8	540	5
Jergul, N	9	340	3
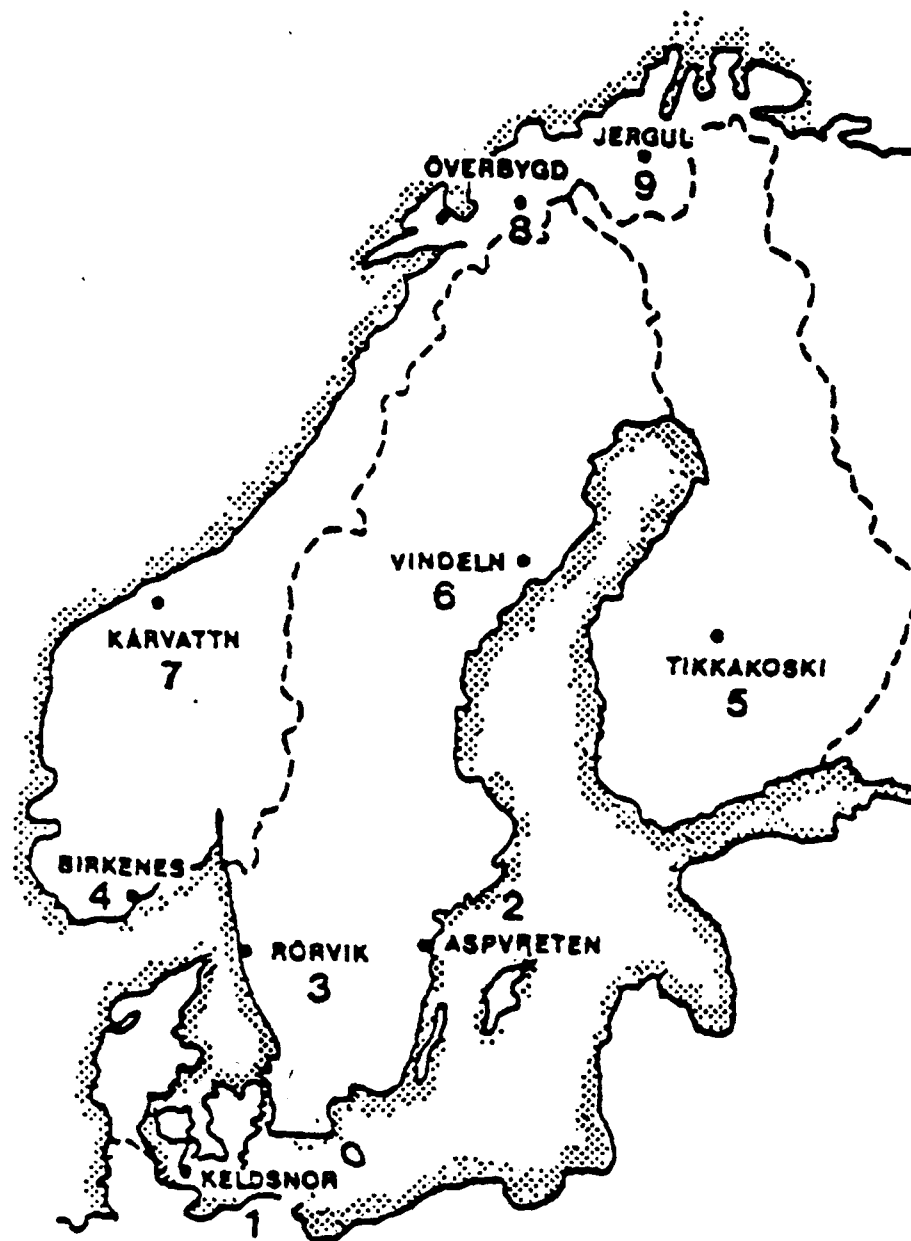
Figure 18.   Stations in the Nordic network study of atmospheric Hg during 1985
to 1989 (from Iverfeidt et al., 1991).
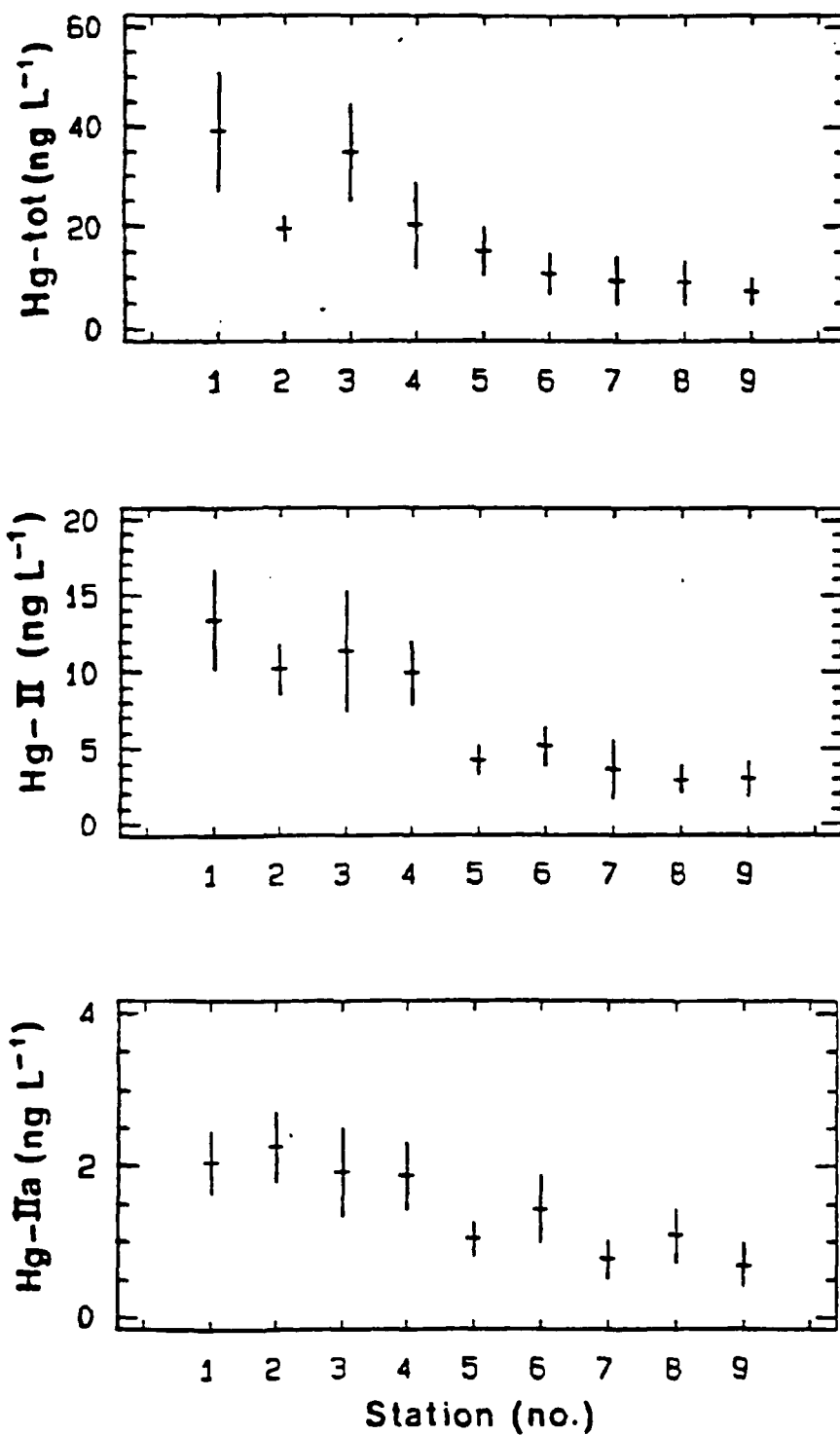
Figure 19.   Mercury in precipitation along the Nordic Sampling Network (Sites
             in Figure 18).

sulfate, as well as low pH. The lead and cadmium concentrations were also about a order of magnitude greater (Iverfeldt, 1991b). In earlier studies in Sweden, Brosset (1987) and Brosset and Iverfeldt (1989) reported a strong correlation between Hg, soot and air trajectories from the eastern part of Europe. Recently, Xaio *et al.*, 1991 reported a good correlation (r= 0.74) between the particulate Hg fraction and soot for air samples collected in Göteborg, Sweden.

3.4   NITROGEN - Evidence of Deposition

Nitrogen and phosphorus are the two primary nutrients required to sustain aquatic biological production. A general ecological axiom is that primary production in freshwater systems is phosphorus limited, while marine systems are nitrogen limited (Hecky and Kilham, 1988). In remote regions, aquatic productivity is often limited by the availability of one or both of these nutrients. However, as the result of anthropogenic inputs, these nutrients are often present at concentrations in gross excess of basic requirements, resulting in a deleterious condition known as eutrophication.

Although a number of earlier works (*e.g.* Correll and Ford 1982, Smullen *et al.* 1982) recognized the ecological significance of the atmospheric deposition of nitrogen in a chemical mass balance for aquatic systems, until recently its import was largely overlooked or underestimated. Much of the current interest has resulted from the recent studies of Fisher *et al.* (1988), Fisher and Oppenheimer (1991), and others (Tyler 1988, Hinga *et al.* 1991) which focus on Chesapeake Bay. These reports concur that 25-40% of the nitrogen loading to Chesapeake Bay is derived from atmospheric deposition (Table 15). Although these studies bring to light the inherent uncertainties in such estimates (particularly with respect to dry deposition and watershed loading estimates), they have underscored the importance of atmospheric deposition and have forced a serious re-examination of eutrophication mitigation strategies in water quality management decisions.

A summary of studies which document the atmospheric input of nitrogen to coastal waters is provided in Table 16. The initial results of Fisher and Oppenheimer (1991) for the Chesapeake Bay have been corroborated by several researchers using somewhat differing approaches. For the other major east coast estuaries, the lower *relative* atmospheric loading of nitrogen primarily reflects the greater degree of anthropogenic influence. For the subestuaries listed, the atmospheric contribution ranges from 7% for Laholm Bay (impacted by heavy agricultural nitrogen inputs) to 100% for Ochlockonee Bay (in an isolated forested watershed which receive minimal anthropogenic inputs). For the coastal seas, the atmospheric input includes direct deposition to the water surface, as little is quantitatively known about the fluvial transport of nitrogen from estuaries to the shelf.

TABLE 15

CALCULATED NITROGEN LOADINGS TO CHESAPEAKE BAY WATERSHED, 1984*

Source	10^6 kg N.yr^1	kg N.ha^{-1}.yr^1	% of Total	% of NPS
Precipitation: Nitrate Ammonium	151 54	9.2 5.1	24 13	26 14
Animal Waste	195	11.9	31	33
Fertilizer	158	9.6	25	27
NPS Subtotal	588	35.9	-	100
Point Sources	41	2.5	7	-
Total	628	38.3	100	-
*Includes the bay.				

From: Fisher and Oppenheimer, 1991.

TABLE 16
ATMOSPHERIC INPUT OF NITROGEN TO COASTAL WATERS

Major Estuaries	Percent Input
Chesapeake Bay	
(1)	39
(2)	35
(3)	25*
Delaware Bay (4)	14
Narragansett Bay (2)	12
New York Bay (2)	10
Long Island Sound (11)	7*
Sub-Estuaries	
Potomac River (5)	28
Rhode River, MD (6)	40
Neuse River, NC (7)	23
Rehoboth/Indian River Inland Bays, DE (8)	8
Laholm Bay, Sweden (2)	7
Ochlockonee Bay, FL (2)	100
Coastal Seas	
North Sea (9)	27**
New York Bight (10)	13**
Baltic Sea (12)	25

*nitrate only
**deposition to water surface only

(1)	Fisher and Oppenheimer 1991	(7)	Fisher et. al., 1988
(2)	Hinga et. al., 1991	(8)	Ritter 1986
(3)	Tyler 1988	(9)	Lancelot et. al., 1987
(4)	Scudlark and Church 1993	(10)	Sinderman and Swanson, 1979
(5)	Jaworski et. al., 1992	(11)	NOAA 1986
(?	Correll and Ford 1982	(12)	Larsson et. al., 1985

The largest uncertainties associated with estimating the relative role of atmospheric deposition of nitrogen to inland and estuarine waters are associated with (1) accurately quantifying dry depositional flux, and (2) determining the indirect atmospheric loading via watershed runoff. The inherent uncertainties in dry flux measurements are subsequently discussed in section 6.0. In terms of wet/dry apportionment of atmospheric deposition, a commonly-employed approximation is that dry and wet deposition provide equal contributions to atmospheric flux. The regional deposition models of Levy and Moxim (1987), Logan (1983), and Sirois and Barrie (1988) indicate that dry deposition accounts for 46-63% of the total atmospheric deposition of $[NO+NO_2+HNO_3+particulate\ NO_3]$. Employing the vegetative throughfall approach, Lovett and Lindberg (1986) gauge the dry deposition of NO_3 to be 60% of the total. For NH_3 and NH_4^+, dry deposition has been reported to comprise 30-63% of the total deposition (Walcek and Chang 1987, Lindberg *et al.* 1986).

Based on the watershed mass balance approach, Fisher and Oppenheimer (1991) estimate that dry deposition accounts for 40-62% of the total atmospheric nitrogen deposition to Chesapeake Bay. Using the same approach, Hinga *et al.* (1991) estimate that dry deposition comprises 42-61% of the total atmospheric nitrogen flux. Recently, the National Dry Deposition Network, a component of the National Acid Precipitation Assessment Program, have initiated inferential dry deposition measurements of gas-phase HNO_3 plus particulate NO_3^- at eight sites in the eastern U.S. Although the relative contribution of dry deposition reported for 1984-87 (30-45%) are somewhat less than the other cited studies, these measurements exclude other potentially significant nitrogen species (such as gas-phase NO_2).

Consistent with our understanding of atmospheric nitrogen emissions and reactivity, for more remote marine areas, far removed in space and time from continental sources, the relative contribution of nitrogen dry deposition is believed to comprise no more than 25% of the total deposition (Duce *et al.* 1991). There is relatively little known about the direct transfer of gas-phase nitrogen to water surfaces. For HNO_3, Lewis (1983) reports that surface waters are a more efficient collector than a dry surrogate surface, but that the opposite is true for NH_4. The air-water gas flux of NO and NO_2 is assumed to be minor since these gases are relatively insoluble and unreactive in water. In coastal marine areas, the deposition of vapor-phase HNO_3 will also be enhanced via the selective scavenging by alkaline marine aerosols (according to the previously elucidated reaction).

In instances where the drainage basin is large relative to the open water (for Chesapeake Bay this ratio is approximately 15:1), the indirect loading can actually exceed the direct deposition to surface waters. The degree of watershed retention, transformation and export of atmospherically-deposited nitrogen depends ultimately on the land usage and geomorphology (Walcek and Chang 1987). Processes which would dictate the degree of watershed retention include the amount, rate and physical nature (rain vs. snow) of precipitation, plant uptake, adsorption and accumulation in soils, removal via crop harvesting, volatilization and denitrification in soils. Furthermore, due to in-stream utilization, only 50-80% of the nitrogen

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entering a feeder tributary from the watershed actually enters the bay proper (Tyler 1988, Hinga *et al.* 1990 and references therein).

4.0   CURRENT UNDERSTANDING OF THE SPECIATION OF CHEMICALS IN THE ATMOSPHERE AND IN PRECIPITATION

4.1   TRACE ELEMENTS - Speciation

Recent investigations in marine and freshwater systems have documented the importance of chemical speciation in the understanding and description of trace element/biosphere interactions. Chemical speciation in aquatic systems reflects a dynamic interaction of biological, chemical, physical, and geological processes. This paradigm has long been applied from a biological perspective in examining the biotransformation of nutrients (*i.e.*, the nitrogen cycle). As analytical methodology has advanced, analogous cycles have become evident for a variety of trace elements as well. Evidence indicates that the chemical form or "speciation" of a trace element is perhaps more important than the total metal concentration in dictating its biological availability, reactivity, and ultimate toxicity. For example, considerable work has been performed by Morel and co-workers (*e.g.*, Morel and Hudson, 1985) which examines the complexation and bioavailability of copper in aquatic systems. Similarly, the Cr(VI) and the As(III) chemical oxidation states exhibit the greatest toxicity in surface waters and sediments.

Trace elements are present in the atmosphere in a variety of aerosol sizes resulting from a variety of natural and anthropogenic sources. The most visible form of aerosols in the stratosphere is from condensation processes during atmospheric redox reactions involving primarily sulfuric acid or neutral sulfate (Junge 1977). The most visible form in the troposphere is that of water vapor condensation (clouds and fog) and dust or haze. Aerosol trace elements exist in super-micron sizes in dust and submicron sizes in haze. The log normal size distribution results from both settling and surface dependent scavenging processes. Both the concentration and enrichment factors (defined later) for trace metals increase with decreasing size in a log normal fashion (Duce *et al.* 1976). The form of trace metal in aerosols depends critically on their origin. In the case of stratospheric or tropospheric haze, they are often the condensation products of volatile emissions. Clouds contain the scavenged and redox solubilized trace elements that result from cloud scavenging and formation. In the case of dust, trace elements are a component of the inherent or adsorbed products of resuspension processes at the earth's surface. Thus rainfall chemistry is the super-condensed product of a primary aerosol and its scavenging chemistry. Most non-crustal atmospheric trace elements are vaporized during high temperature combustion, which preferentially condense on (Linton *et al.* 1976) or form (Smith *et al.* 1979, Natusch *et al.* 1974, Ondov *et al.* 1979, Shendrikar *et al.* 1983, and others) submicron aerosols. However, the low boiling points of some elements (specifically mercury, arsenic, and selenium) allows for a significant vapor phase at standard atmospheric temperatures

and pressures.

Both arsenic (As) and selenium (Se) are greatly enriched in coal. As a result, their global emission inventories are dominated by coal combustion from electric power generation, non-ferrous metal smelting and manufacturing (Mosher and Duce 1987, Walsh *et al.* 1979b). The work of Andren *et al.* (1975), Ondov *et al.* (1979), Shendrikar *et al.* (1983) and others revealed the presence of vapor-phase elemental selenium in coal-fired power plant emissions, presumably as Se(IV) oxide or elemental Se(0). Mosher and Duce (1983, 1987) also present indirect evidence for the existence of vapor-phase selenium in the atmosphere, which may represent natural dimethyl selenide emissions (Jaing *et al.* 1983). Similarly, Walsh *et al.* (1979a) report the existence of vapor-phase As in a variety of marine and continental regimes. However, similar measurements at Lewes, DE did not reveal any vapor-phase As (M. Kitto, Univ. of Maryland, personal comm.). Alkylated arsenic compounds (dimethyl arsine and trimethylarsine) have also been detected at extremely low concentrations (0.1-0.9 ng/m^3) over soil (Johnson and Braman 1975). Such forms are thought to rapidly oxidize to stable oxoacids such as dimethlyarsenic (cacodylic) acid. However, limited measurements of methylated forms of Se and As in precipitation have failed to detect measurable quantities (Andreae, 1980; Cutter and Church, 1986; Scudlark and Church, 1988).

Methylated forms of As (*e.g.*, dimethylarsenic acid) have also been detected in aquatic environments (Andreae 1979, and others), which has been shown to be the result of biologically-mediated reactions. However, due to their high solubilities and low vapor pressures, it is unlikely that such forms tend to appreciably partition into the atmosphere (Andreae 1980). Thus, based on the evidence currently available, while the presence of vapor phases of As and Se may influence their atmospheric reactivity, transport and scavenging, they do not appear to contribute significantly to the net depositional fluxes of these elements.

There exists a paucity of trace element speciation measurements in precipitation. Speciation data are limited to measurements of relative particle loadings and metalloid oxidation states. Most trace elements are dissolved in precipitation, except crustal elements under more dusty conditions (Lim *et al.*, 1991). It has been suggested that the As^{+3}/As^{+5} and the Se(IV)/Se(VI) ratios reflect the redox poise of the attendant air mass, as dictated by the variable concentrations of chemical oxidants (*e.g.*, O$_3$, H$_2$O$_2$) and reductants (*e.g.*, SO$_2$; Scudlark and Church, 1988; Cutter and Church, 1986). Preliminary results of zinc speciation indicates that zinc is almost exclusively in the uncomplexed state, as might be anticipated for an acidic rainwater matrix (Lewis and Church, unpublished data).

4.2   SEMIVOLATILE ORGANIC CONTAMINANTS - Speciation

The transport, fate, atmospheric residence time, and removal processes for organic compounds are largely due to the distribution of the semi-volatile organic chemical (SOC) between the gas and particle phases (Bidleman 1988, Junge 1977, Ligocki *et al.* 1985a,b,

Eisenreich *et al.* 1981, Pankow 1987, Duinker and Bouchertall 1989, Ligocki and Pankow 1989, Foreman and Bidleman 1990). In general, gas-particle distributions are a function of the vapor pressure of the organic compound, the ambient temperature, and the concentration, size, and composition of atmospheric particulate matter. Junge (1977) described gas-particle distributions in the atmosphere using a Langmuir isotherm as:

$$\phi = [c_p/(c_p + c_g)] = c\theta/(p° + c\theta) \qquad [2]$$

where ϕ is the fraction of the compound in the particle phase, c_p and c_g are particle and gas phase concentrations of the SOC in the atmosphere (ng/m^3), respectively, $p°$ is the vapor pressure of the SOC (torr), c is a constant (equal to 0.13 in Junge 1977), and θ is the concentration of total suspended matter in the atmosphere expressed as surface area (cm^2/cm^3). Junge (1977) and others have used this equation to describe the general distribution of SOCs between the gas and particle phase in the atmosphere as a function of increasing $p°$ by plotting (c_p/c_g) (= log $(1-\phi/\phi)$) vs log $cp°$ where the intercept is log $(1/cT)$. It may be expected that c is a function of compound class and therefore constant within that class, and representative of the difference of the enthalpy of desorption of the compound from particulate matter and vaporization of the pure compound (Pankow 1987). Foreman and Bidleman (1990) found that the distribution of n-alkanes, PCBs, PAHs, and other organochlorine pesticides followed the relationship below for Denver aerosol:

$$\log [A(TSP)/F] = 0.830 \log p° = 7.109 \qquad [3]$$

whereas in previous studies, PAHs and organochlorines partitioned to particulate matter differently (Foreman and Bidleman, 1987, Bidleman *et al.* 1986).

Yamasaki *et al.* (1982) collected PAHs in the urban atmosphere of Tokyo using a glass fibre filter followed by a polyurethane foam (PUF) adsorbent. They examined the gas-particle distributions as a function of total suspended particulate concentrations (TSP):

$$\text{Log } K = \log (A(TSP)/F) = m/T + b \qquad [4]$$

where A and F are the concentrations of SOC in the operationally-defined adsorbent and filter, respectively, m and b are constant dependent on compound, and T is ambient temperature in K. Pankow (1987) has shown that, if sampling artifacts are absent or do not affect the gas-particle distribution, then

$$\log c_g/c_p = \log C/TSP + \log p° \qquad [5]$$

where C is a temperature-dependent constant, and $C/TSP = 1/c\theta$. Thus, G/P distributions in the atmosphere are clearly a function of TSP, a surrogate of surface area concentration, a constant related to the difference between the enthalpy of desorption of the SOC from particulate

matter and the enthalpy of vaporization of the pure compound, and T. Pankow (1987) further developed the above relationship using Langmuir sorption theory given

$$K = A(TSP)/F = (990*2\pi MRT)^{1/2}/(N_g A_{TSP} N_o S_o t_o RTe^{QIRT}) \quad [6]$$

where A_{TSP} = specific surface area of aerosol (cm^2/ug), N_g = moles of sorption sites per cm^2 of aerosol, M = molecular weight of compound, N_o = Avagadro's number, s_o = surface area per sorption site (cm^2), t_o = characteristic vibration time (10^{-13} to 10^{-12} sec), Q1 = enthalpy for surface desorption, R = universal gas constant, and T = absolute temperature (K). For a series of similar compounds,

$$K = 1.6 \times 10^4 p^o/N_s A_{TSP} exp([\{Q1-Qv\}/RT] \quad [7]$$

where *Ns is the number of moles of sorption sites per c^2 of particulate matter surface area.* When sorption to the surface is liquid-like, then {Q1-Qv} is 0, and the equation simplifies to

$$K = 1.6 \times 10^4 p^o/N_s A_{TSP} T \quad [8]$$

Thus K is determined by the vapor pressure of the compound, the characteristic surface area of the TSP, and ambient temperature. *Numerous examples of the application of the relationship of log A(TSP)/F or ϕ vs p^{o}L or 1/T for PAHs and organochlorines are in the literature (Junge 1977, Yamaskai et al. 1982, Bidleman et al. 1986, Foreman and Bidleman 1990, Hermanson and Hites 1989, Baker and Eisenreich 1990, Bidleman 1988, Duinker and Bouchertall 1989, Ligocki and Pankow 1989, Manchester-Neesvig and Andren 1988, Eitzer and Hites 1989).*

Pankow (1987, 1988) and co-workers (*e.g.*, McDow 1986, Hart 1990, Hart *et al.* 1992, Ligocki and Pankow 1989) and Bidleman (1988) and co-workers (Cotham 1990, Foreman and Bidleman 1990, Bidleman *et al.* 1986) remind us that the above equations refer to the equilibrium non-specific physical binding of the SOC to atmospheric particles. Possible explanations for the G/P distribution not reflecting equilibrium partitioning include slow kinetics of partitioning (Rounds and Pankow 1990), presence of a non-exchangeable fraction of the particulate-bound compound (Pankow 1988), variability in the sorption characteristics of the atmospheric aerosol (Ligocki and Pankow 1989), and the presence of sampling artifacts (McDow 1986, Hart 1990, Ligocki and Pankow 1989, Bidleman *et al.* 1986, Cotham 1990).

Non-exchangeable material in the particulate phase would result in a plot of log A(TSP)/F vs v^o that is non-linear. Log A(TSP)/F would be lower than expected, and ϕ would be higher than expected. Compounds that may exhibit non-exchangeable behavior include PAHs. A portion of the total aerosol PAH may be occluded within a soot or flyash particles and may not be available to partition to the gas phase. Organochlorines such as PCBs and HCHs are not expected to reflect this behavior. Foreman and Bidleman (1987) and Ligocki and Pankow (1989) have witnessed negative deviations for some PAHs. Pankow (1988) has developed the

expression $\phi = [(100-x)/1+C_p°/TSP) + x]/100$ where x is the fraction of non-exchangeable material. When x = 0, the equation reverts to the Junge-Pankow relationship (equation [2]). The direction of the deviation from the equilibrium condition will always be negative. The magnitude of the deviation increases with increasing p° and x. Pankow (1988) has shown that the "magnitude of the effect can be significant even when the bound fraction is as low as a few percent; the more volatile the compound, the larger the effect." It is difficult to quantify the effect of a non-exchangeable fraction in field data since other factors such as variable sorptive characteristics of atmospheric particulate matter also play a role, although Bidleman *et al.* (1986), Ligocki and Pankow (1989), and Foreman and Bidleman (1990) observed that the magnitude of log K varies little with the source of the atmospheric aerosol.

The times to sorptive equilibrium of SOC gases on atmospheric particles are largely unknown. Rounds and Pankow (1990) adapted a radial diffusion model to the time scales for sorptive equilibrium to both atmospheric aerosols and filter-laden particles. In general, they concluded that SOCs having K < 0.1 m³/ug, the time to sorptive equilibrium is on the order of hours or less, and probably not a problem. For particles collected on filters, the potential for deviations from SOC equilibrium is significant, and depends on the kinetics of the sorption process. In general, the magnitude of the artifacts depend on the duration of sample collection, TSP, the gas phase concentration and temperature. The effect is projected to be most significant for compounds of higher p° that achieve rapid sorptive equilibrium. In this case, the particles on the filter will be at equilibrium with the last parcel of air, which is likely not to reflect the average over the sampling interval. This model is not yet calibrated or verified for atmospheric particles.

Sampling artifacts include adsorption of SOC gases onto the filter, overestimating the particulate fraction, and "blow-off" of SOC gases sorbed to particles collected on the filter, underestimating the particle fraction. Several researchers demonstrate that blow-off during a collection period is significant (Cautreels and Van Cauwenberghe, 1978, Van Vaeck *et al.* 1984) although more recent studies suggest sorption is a bigger problem. Although there is strong evidence to suggest that SOCs may sorb to filters in laboratory and field studies (Bidleman 1988, Bidleman *et al.* 1986, Coutant *et al.* 1988, Ligocki and Pankow 1989, Cotham 1990, McDow and Hutzicker 1990, Hart 1989), the filter-adsorbent combination may not exhibit the problems actively discussed in the literature (Lane *et al.* 1988, Leister and Baker 1993, Kaupp and Umlauf 1992). Zhang and McMurry (1991) calculated that evaporative losses (blow-off) of adsorbed species during atmospheric aerosol sampling is not significant for most SOCs at the pressure drops experienced in typical organic samplers. Hart (1989) has shown that sorption of PAHs and some organochlorines to the quartz front filter does not appreciably alter determination of real G/P distributions. Hart (1989) and McDow and Huntzicker (1990) suggest that volatilization losses and adsorptive gains can be minimized by reducing sampling times as much as possible to minimize fluctuations in temperature and atmospheric concentrations. In addition, a quartz front filter and a backup Teflon filter can be used to estimate the contribution of gas adsorption. These recommendations have been incorporated into a new SOC hi-volume sampler

by Hart *et al.* (1992). Also, many researchers now incorporate two quartz filters in series on a routine basis to estimate field sorption of SOC gases to the filter matrix (Leister and Baker, 1993). The first filter collects the particles and sorbed gases while the second collects only sorbed gases. It is now suspected that this approach overestimates the magnitude of the needed correction (Hart 1989, Hart *et. al.*, 1992). Kaupp and Umlauf (1992) used a conventional glass fibre filter, a low pressure cascade impactor, and a electrostatic precipitator each combined with gas adsorbents to evaluate the importance of the sampling artifacts in the field. They concluded that the G/P distributions were better predicted by the normal filter-adsorbent combination then from the cascade impactor because of particle aggregation in the impactor reducing the exchangeable gas phase concentrations. In any event, they conclude that sampling artifacts for organochlorines such as PCBs, DDT, HCHs, etc. and some PAHs are minimal when proper protocols and media are followed. N-alkanes and other waxy natural materials may still exhibit deviations from equilibrium behavior because they may be transported as waxy aggregates for which the correlative physical parameter is p°_s, the solid vapor pressure.

Seasonal variations in atmospheric SOC concentrations and G/P distributions have been actively investigated (Manchester-Neesvig and Andren 1989, Hermansen and Hites 1989, Hoff *et al.* 1992a) and must inevitably reflect source emissions and the effect of temperature on vapor pressure. Hoff *et al.* (1992a) determined atmospheric concentrations of PCB congeners and many organochlorine pesticides in 143 samples collected in 1988-89 in Egbert, Ontario. This high resolution data set provides the definitive evidence of the seasonal (*i.e.*, temperature) control on atmospheric SOC concentrations. Hoff *et al.* (1992b) developed atmospheric source functions to describe the seasonal behavior of SOCs. Not surprisingly, SOC concentrations were correlated nicely to temperature and to p°_L. The seasonal source functions have been combined with temperature-dependent gas/particle distributions calculated using the Junge-Pankow model to estimate annual wet and dry loadings of numerous chemicals in the Great Lakes region (Eisenreich and Strachan, 1992). The importance of atmospheric speciation of SOCs and the potential applications are clearly described in this report.

Although particle size plays a critical role in atmospheric removal processes, little is known about particle size distributions of atmospheric SOCs. Previous studies of size distributions of trace organic compounds are summarized in Table 17. While several studies of PAH size distributions have been reported, there is only one for PCBs (Holsen *et al.* 1991) and this is only for super coarse particles. Furthermore, the time (minimum sampling time is 1 day) and size resolution of the available data is relatively coarse. Most data have been measured with Sierra (minimum size cut of 0.5 μm) or Anderson (minimum size 1.1 μm) high volume impactors. Mass median diameters of the various SOCs reported with these samplers typically range from 0.5 to 2 μm. Kertesz-Saringer *et al.* (1971) used a Casella impactor with a minimum size cut of 0.28 μm and found that 30 to 50% of the benzo[*a*]pyrene was collected on the glass fibre after filter (<0.28 μm). Miquel and Friedlander (1978) used a Hering low pressure impactor (minimum size cut of 0.06 μm) and found that 75 to 85% of the benzo[*a*]pyrene and coronene in Los Angeles aerosols is associated with particles smaller than

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TABLE 17

SIZE DISTRIBUTION OF MEASUREMENTS OF ORGANIC COMPOUNDS

Chemical	Air Volume (m³)	Sampling Time (Days)	Sampler	Substrates	Reference
PAHs	28000	15	Horizontal Elutriator	GFF	Demaio and Cornz (1966)
Benzo[a]pyrene	200	3 to 30	Casella Impactor	Stages: Glass AF:GFF	Kertesz-Saringer et al. (1971)
Benzo[a]pyrene Benzo[k]fluoranthene	1631	2	Anderson Hivol Impactor	Stages: GFF AF: GFF	Albagli et al. (1974)
PAHs	800-1600	1 to 2	Anderson Hivol Impactor	Stages: GFF AF: GFF	Pierce and Katz (1975)
Benzo[a]pyrene Coronene	4.3	3	Hering Low Pressure Impactor	Stages: Quartz	Miquel and Friedlander (1978)
Ether Extractable Organics	2000	1 to 2	Sub 2-μm; Hivol	GFF	Ketserides and Eichmann (1978)
PAHs Aliphatic and Carboxylic Acids	2500-40000	7 to 35	Anderson and Sierra Hivol Impactors	Stages: GFF AF: GFF	Van Vaek et al. (1979) Van Vaeck and Van Cauwenbergle (1980) Van Vaeck et al. (1979) Van Vaeck and Van Cauwenbergle (1985)
PAHs	800-2000	1	Anderson Hivol Impactor	Stages: GFF AF: GFF	Katz and Cohen (1980)
PCBs	12000-18000	5.5 to 8.3	Noll Rotary Impactor	Mylar Strips; Apiezon L	Holsen et al. (1991)

0.26 μm. However, this impactor operates at pressures significantly below atmospheric, raising the possibility that volatilization of sorbed PAHs may occur during sampling. Thus for SOC data reported to date, mean particle sizes tend to decrease with decreasing impactor cut point. Measurements of SOC size distributions should be made with impactors having size cuts as small as possible. The state-of-the-art for lower size cuts is about 0.05 μm (*e.g.*, MOUDI, Marple *et al.* 1991).

The data of Holsen *et al.* (1991) are interesting in that high PCB concentrations were measured in particles of diameter 2 to 20 μm having estimated deposition velocities of about 4 to 6 cm/sec. If this phenomenon is a general one, then dry deposition of large particles emitted in urban/industrial centers and containing high concentrations of SOCs could dominate atmospheric fluxes to nearby coastal areas (*e.g.*, Lake Michigan near Chicago, IL; Chesapeake Bay near Baltimore, MD; Lake Ontario near Toronto-Hamilton; Long Island Sound near the New York City and New Jersey metropolitan areas.

Most of the measurements in Table 17 were made with Sierra and Anderson high volume impactors. Both of these instruments use glass fibre filters as sample collection substrates on the impactor stages. This leads to two concerns. First, because the impactor jets can penetrate into the GFF, particles that are too small to be collected inertially may be collected by filtration on the filters (Willeke, 1975). Thus a portion of the SOCs that are reportedly associated with coarse particles may, in fact, be from small particles. Secondly, sampling artifacts with glass fibre or quartz filters have been raised. Grosjean (1983) reported that when PAHs were collected on both glass and Teflon filters, the glass/Teflon ratio ranged from 0.25 to 0.8. Furthermore, some organic gases may adsorb on to glass fibre filters (McDow 1986; Hart 1989). Substrates such as Teflon foil are less likely to lead to such artifacts. More recent examinations suggest that the gas adsorption artifact using glass fibre filters may not be as large as first hypothesized for PAHs and organochlorines, somewhat greater for N-alkanes (McDow 1986; Hart 1989; Ligocki and Pankow 1989; Foreman and Bidleman 1991).

4.3   MERCURY SPECIATION IN THE ATMOSPHERE

Most of the Hg species in the troposphere are in the vapor phase (Braman and Johnson 1974, Fitzgerald and Gill 1979, Fitzgerald *et al.* 1981, Slemr *et al.* 1981), and consist almost entirely of elemental mercury (Hg°), as demonstrated by Kim and Fitzgerald (1986). Improved trapping, separation, and detection procedures developed by Bloom and Fitzgerald (1988) have refined our understanding of the partitioning of the vapor phase. These authors showed that Hg° accounts for 95 to 100% of the total vapor phase concentration in a coastal/urban location on Long Island Sound. The remainder species of the vapor phase concentration was monomethyl mercury (MMHg). Greater than 99% of the total mercury present in the near surface marine atmosphere is Hg° (Mason *et al.* 1992). Moreover, recent studies in mid-continental northcentral Wisconsin are showing a similar partitioning with the Hg° fraction generally > 99%.

Monomethyl mercury is much more soluble in water than $Hg°$, and small quantities are present in precipitation. The source of MMHg in the atmosphere is not known.

4.3.1 Mercury Speciation in Precipitation.

An average scavenging ratio (i.e. concentration in rain/concentration in air) observed for mercury in rain collected in Wisconsin was 437 (Fitzgerald *et al.* 1991), and this value is comparable to scavenging ratios found for metals such as lead (Maring *et al.* 1989, Church *et al.* 1991). Although there are limitations to the scavenging ratio approach, it appears that atmospheric Hg wet deposition is analogous to other trace metals (*i.e.*, Pb, Cu, Zn) which exist as particles in the atmosphere (Maring *et al.* 1989, Buat-Menard 1985). Similar conclusions regarding the prominence of the atmospheric particulate Hg cycle in conveying Hg to natural waters were reached in Swedish work (Brosset 1987, Lindqvist *et al.* 1991, Iverfeldt·1991a). The influence of particulate Hg on the composition of Hg in precipitation is shown in Table 18 from Iverfeldt (1991a). He found an on average, > 67% and > 79% of the total mercury in precipitation was filterable at the 0.4 μm size range for two sites, Överbygd, Norway and Keldsnor, Denmark, respectively, in the Nordic Countries Network. The results also show that Hg is associated with large particles (> 10μm) as well as particles between 0.4 μm and 10 μm size classes.

Mercury speciation in precipitation from the MTL Wisconsin studies (Fitzgerald *et al.* 1991, 1993) is shown in Table 19, where measurements of total mercury (Hg_T), reactive mercury (Hg_R) and monomethyl mercury in wet deposition (snow and rain) from these mid-continental rural temperate lacustrine environs are summarized for a two year period (1989 and 1990). Details of the Hg speciation for rain are presented in Figure 20. Several general features are evident in the broad geochemical view provided by the average speciation results in Table 19. Firstly, the average Hg_T was similar for both years (52.5 ± 24.0 and 49.3 ± 20.8 pM) while the average Hg_R was higher during 1990 (41.0 ± 20.6 pM) than during 1989 (13.7 ± 10.6 pM). As noted by Fitzgerald, *et al.*, (1991), the difference between Hg_T and Hg_R is not due to MMHg, which is present in very small quantities (≤ ca. 1 pM; see Figure 20). Rather, the difference is due principally to strong Hg associations with organic substances that are destroyed by the powerful oxidant (BrCl) used in the determination of Hg_T (see Analytical section for details). The authors also suggest that this strongly bound Hg fraction is associated with atmospheric particulates containing organics which may have a significant sulfur content. This interpretation is part of a more general atmospheric particulate Hg scavenging hypothesis emphasizing the influence of atmospheric particulate Hg on the composition in rain. Support for this postulate comes from the scavenging ratio estimates, and the Iverfeldt (1991a) work (Table 18) showing that the filterable or colloidal species dominate the Hg_T in rain.

Predicted Hg_T concentrations in rain based solely on the scavenging of atmospheric particulate Hg are summarized in Table 20. Recent data from the equatorial Pacific are also

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TABLE 18

INFLUENCE OF PARTICULATE MERCURY ON THE COMPOSITION
OF H_g IN PRECIPITATION (AFTER IVERFELDT, 1991)

Station	Avg	> 10 μm Range	SD	n	Avg	>0.4 μm Range	SD	n
Keldsnor, Denmark	64	8-93	22	12	79	49-92	12	10
Overbygd, Norway	42	8-64	20	6	67	24-92	27	5

TABLE 19

SUMMARY OF THE AVERAGE CONCENTRATION OF Hg SPECIES OBSERVED IN WET DEPOSITION FROM NORTHCENTRAL WISCONSIN

Sampling Period	N*	Hg_R (pM)	Total (pM)	MMHg (pM)
Rain 1989	12	13.7 ± 10.6	52.5 ± 24.0	0.78 ± 0.34
Rain 1990	9	41.0 ± 20.6	49.3 ± 20.8	0.37 ± 0.16
Snow 89/89	6	17.5 ± 12	30.0 ± 4.5	0.24 ± 0.11
Snow 89/90	3	8.0 ± 0.75	14.9 ± 3.9	0.52 ± 0.20

*N = number of deposition events sampled

TABLE 20

CALCULATED CONCENTRATION OF Hg IN RAIN BASED ON A SCAVENGING RATIO, $W = 600$ (RANGE 200-1200) AND USING THE FORMULA $W = C_{rain}$ (pg/kg) X 1.2 kg/m^3 ÷ C_{air} (pg/m^3). THE AVERAGE VALUES WERE CALCULATED USING AN AVERAGE SCAVENGING RATIO (W) OF 600 WHILE THE VARIABILITY WAS ESTIMATED USING A RANGE FOR W OF 200 OR 1200 AND THE ACTUAL PARTICULATE CONCENTRATION EXTREMES FOUND AT THESE SITES. THE VALUES FOR W WERE TAKEN FROM THE DATA FOR LEAD REPORTED BY MARING et al. (1989). TABLE ADAPTED FROM MASON et al. 1992

Region	Particle Concentration pg/m^3		Rain Concentration Calculated Measured		
	Range	Ave.	Range	Avg.	Avg.
Pacific	0.2-6	2.6	0.2-30	6	14
Wisconsin 89*	5-62	22	4-310	55	51
Wisconsin 90*	7-77	37	6-385	93	49

*The average particulate concentration and range (all months) found in Wisconsin during 1989 and 1990.
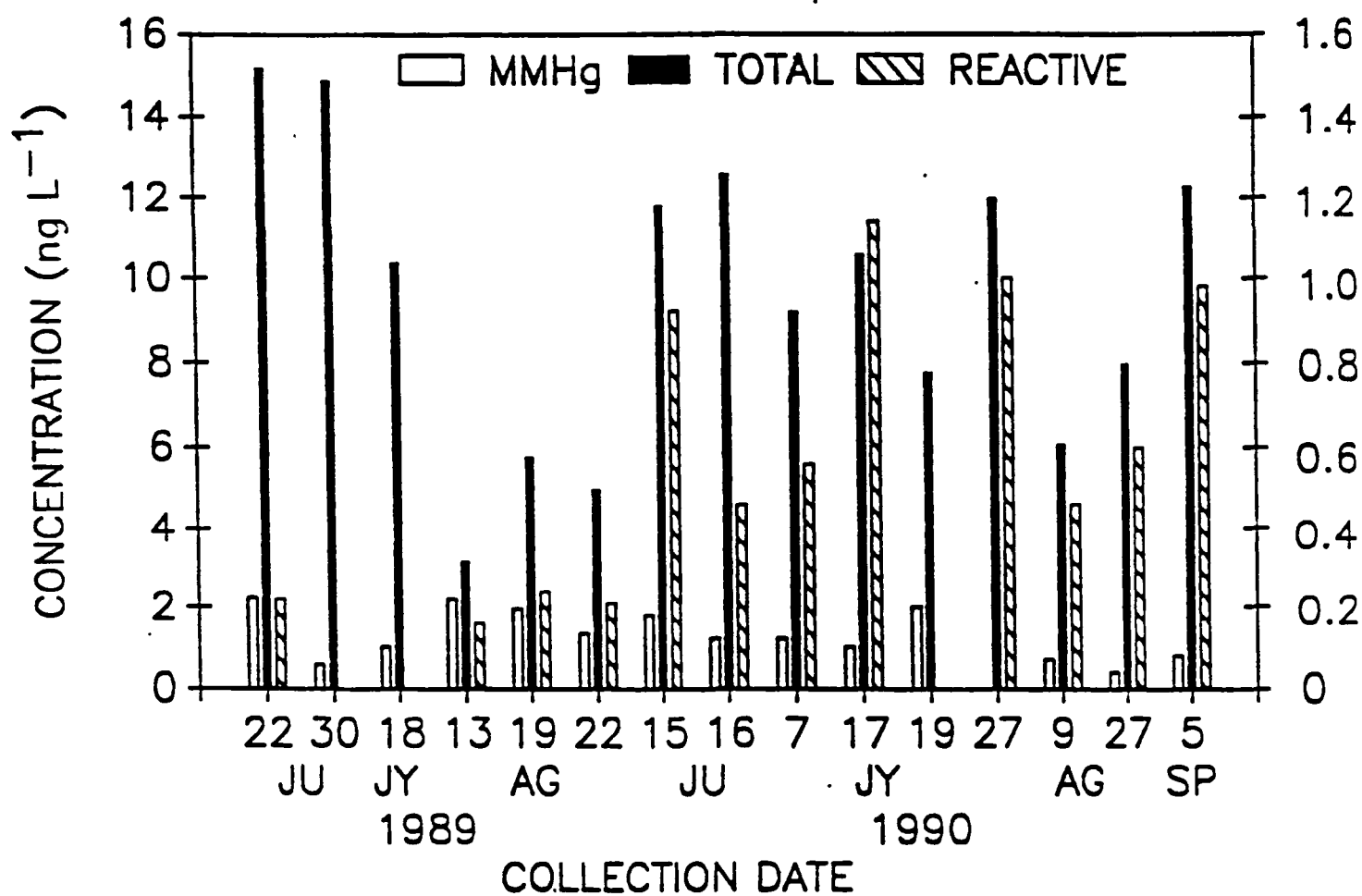
Figure 20. Total, reactive and methylmercury in rain collected in Wisconsin at Little Rock Lake Reference Basin, in 1989 and Max Lake in 1990, adapted from Fitzgerald et al., 1992 and Mason et al., 1991.

included to illustrate and emphasize the integral role particulate Hg plays in determining the composition of Hg in rain. As discussed in Mason *et al.*, (1992) the differences in the Hg content between the equatorial Pacific and mid-continental rains correspond to the atmospheric particulate Hg distribution between these regions. For example, during the studies, the average particulate Hg concentration was 2.6 pg/m^3 in the equatorial Pacific and 22 pg/m^3 and 37 pg/m^3 in Wisconsin in 1989 and 1990, respectively. As illustrated in Table 20, estimates of expected rain concentrations due solely to particulate Hg scavenging are comparable to the observations at both locations. These predictions suggest that the variation in Hg$_R$ and Hg$_T$ between regions and the temporal differences at Wisconsin are a function of the differences in particulate Hg composition and burden. Also, as suggested earlier (Fogg and Fitzgerald 1979; Fitzgerald *et al.* 1983), this depositional behavior indicates that while most of the Hg in the atmosphere is Hg° (> 95%), it is not oxidized and solubilized in processes leading directly to the formation of precipitation. A more general gas-to-particle atmospheric oxidation processes is inferred. Further, Fitzgerald *et al.* (1991, 1993) suggest that Hg$_R$ found in precipitation and atmospheric particulate matter is derived from the atmospheric oxidation products of Hg° in the atmosphe ... This form of Hg is labile and highly reactive in aqueous systems and readily available, for example, to participate in competitive reactions associated with methylation, reduction to Hg°, uptake by biota, and sequestering with humics. The other fraction of the Hg$_T$ in deposition is the operationally defined strongly bound Hg portion ("unreactive" Hg), which raises complex biogeochemical questions as well. For example, are these particles environmentally active? This fraction is likely to be associated with soot and may be strongly bound or sequestered in some type of sulfur-carbon association (Brosset 1987). Perhaps, this unreactive Hg can be solubilized under anoxic and/or sulfitic conditions to yield a species such as Hg(HS)$_2$° which can be bacterially methylated. In lakes, coastal waters, rivers and estuaries, this process could take place at the sediment-water interface as well as in the low oxygen waters of the water column. This would be an insidious process where an apparently unreactive component under oxic conditions would yield MMHg in low oxygen zones of natural waters.

There is a consensus that the principal source of Hg$_R$ in precipitation is the oxidation and dissolution of atmospheric Hg°, and two atmospheric reaction pathways have been postulated. The first argues that Hg$_R$ is derived from a generalized atmospheric oxidation of Hg°, using oxidants such as O$_3$ or OH radicals. This reaction may occur heterogeneously and involve Hg° adsorbed to particles (Fitzgerald *et al.* 1991, 1992). Such a particle conversion hypothesis is supported by Hg(II) washout calculations, and from the direct physical and chemical analysis of rain showing most of the Hg is associated with particles (Iverfeldt *et al.* 1991a,b, Fitzgerald *et al.* 1992, Mason *et al.* 1992). Alternatively, the work of Iverfeldt and Lindqvist (1986) suggests that O$_3$ oxidation of Hg° in clouds could be an important mechanism contributing to Hg$_R$ in rain. The authors predicted an oxidation rate of 0.01 hr^{-1} (88 yr^{-1}) for conversion of Hg° to Hg(II) in clouds, assuming 1 g m^{-3} of liquid water and 23 ppb O$_3$ (a value similar to observed background concentrations). In the absence of O$_3$, the reaction rate is three orders of magnitude slower. However, a residence time of Hg in the atmosphere of approximately 1 yr (Fitzgerald, 1989) based on the global cycle yields an overall conversion rate of approximately 1 yr^{-1}, assuming all

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the Hg in rain is derived from oxidation of Hg°. This calculation represents a maximum conversion rate. Therefore, the reaction investigated by Iverfeldt and Lindqvist (1986), which has a substantially larger rate constant, should not be a predominant mechanism for the oxidation of Hg° in the atmosphere if the reaction occurs at rates comparable to those found in the laboratory. Munthe and Lindqvist (1989) and Munthe (1991) modified this model by suggesting that rapid sulfite ($SO_3^=$) complexation of Hg^{2+} in cloud water would yield $[Hg(SO_3)_2^=]$ with subsequent reduction of Hg^{2+} to Hg°, thereby serving as a potential reverse reaction which limits the net amount of Hg° solubilized. However, insufficient amounts of atmospheric sulfur species are available in the atmosphere over most of the earth's surface (i.e., oceans). Thus, alternative gas to particle conversion processes such as suggested in the other hypothesis must be providing pathways for formation of the Hg_R compounds found in rain.

4.4 NITROGEN - Speciation

The primary component of the earth's atmosphere is unreactive N_2 gas. During high temperature combustion processes, such as the combustion of fossil fuels in transportation and utility sources, atmospheric nitrogen reacts to form oxides of nitrogen ($NO_x = NO + NO_2$). Under varying conditions, the nitrogen oxides can further react via a complex series of photochemical pathways to form a suite of reactive nitrogen species. Although it has been demonstrated that these compounds can be produced from natural sources as well (*e.g.*, NO production by lightning and down mixing of stratospheric NO), anthropogenic emissions are now known to dominate the tropospheric nitrogen budget for eastern North America (Singh 1987, Logan 1983, Galloway and Whelpdale 1980). In fact, the U.S. EPA (1982) estimates that more than 80% of the North American NO_x emissions are from industrial sources.

In contrast with nitrogen oxides, the dominant source of ammonia (NH_3) emissions appears to be biogenic, in particular those associated agricultural practices (*e.g.*, the decomposition of animal excrement and fertilizer production/application, NRC 1979, Apsimon *et al.* 1987). However, there is still some uncertainty about the specific sources of NH_3 emissions. Not only is NH_3 important as a major source of atmospherically deposited nitrogen, but also its atmospheric reactivity greatly influences the formation and deposition of other nitrogen species (for example, the formation of particulate NH_4NO_3 aerosol).

Anthropogenic NO is rapidly oxidized to NO_2, and ultimately to gaseous HNO_3 by photochemically-catalyzed gas-phase reactions. Thus, NO, and NO_2 tend to be deposited (primarily by dry removal processes) fairly close to their source, while vapor-phase HNO_3 is more inclined to be removed (via wet and dry processes) at a greater distance from its source. Both NH_3 and HNO_3 are readily adsorbed onto surfaces, particularly water. For example. Lovett and Lindberg (1986) estimate that as much as 75% of the total nitrogen deposition to a forested watershed was in the form of HNO_3 vapor.

Vapor-phase HNO_3 can also react with NH_3 to form particulate NH_4NO_3. In the marine environment, vapor-phase HNO_3 is also selectively scavenged by alkaline sea-salt aerosols *via* the generalized reaction (Junge 1956, Brimblecombe and Clegg 1988, Savioe and Prospero 1982, Memane and Mehler 1987, and many others):

$$HNO_{3(g)} + NaCl_{(s)} \text{---}> NaNO_{3(s)} + HCl_{(g)} \qquad [9]$$
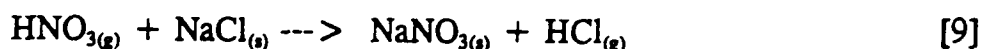
It has also been shown that gaseous NO_2 is similarly scavenged by sea-salt aerosols, particularly in urban environments, according to the generalized reaction (Finlayson-Pitts 1983):

$$2NO_{2(g)} + NaCl_{(s)} \text{---}> ClNO_{(g)} + NaNO_{3(s)} \qquad [10]$$
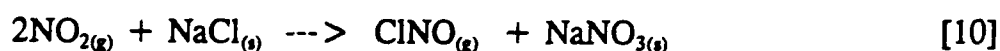
From an ecological perspective, the primary species of atmospherically-derived nitrogen are nitric acid vapor (HNO_3), particulate nitrate (NO_3^-), ammonia (NH_3), particulate ammonium (NH_4^+), nitric oxide (NO), and nitrogen dioxide (NO_2) (Hanson and Lindberg 1991). Less information exists on the deposition of other potentially-important reactive nitrogen species, such as nitrous acid (HNO_2), dinitrogen pentoxide (N_2O_5), or peroxyacetyl nitrate (PAN). Recent data for the wet deposition of dissolved organic nitrogen (DON) suggest this class of compounds may also contribute significantly to nitrogen loading in aquatic ecosystems.

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5.0 CURRENT UNDERSTANDING OF WET DEPOSITIONAL PROCESSES

5.1 GAS SCAVENGING BY PRECIPITATION

Semivolatile organic contaminants (SOCs) are incorporated into water droplets in the atmosphere by a variety of processes. Gas phase SOCs partition across the droplet surface and become dissolved in the bulk liquid. At equilibrium, the magnitude of this partitioning is described by the SOC's Henry's Law constant, which may be approximated as the ratio of its subcooled liquid vapor pressure to it aqueous solubility at the ambient temperature:

$$C_{i,ppt,gas} = [C_{i,g} / H_{i(T)}] \times MW_i \times 10^6 \qquad [11]$$

where $C_{i,ppt,gas}$ is the concentration of nonreactive species i in precipitation resulting from gas dissolution (ng/L), $C_{i,g}$ is the concentration of i in the gas phase (Pa), $H_{i(T)}$ is the Henry's Law constant of i at the appropriate temperature (Pa-m³/mole), and MW_i is the molecular weight of i (g/mole). Raindrops are well-mixed due to the turbulence induced by falling through the air column, minimizing local within-drop concentration gradients. Because mass transfer coefficients of nonreactive organic chemicals across the air-water interface are reasonably large

(*e.g.*, 10^{-11} mol/[cm^2·s·Pa] for PCB congeners), it is generally believed that dissolved concentrations of nonreactive volatile chemicals in falling raindrops are in equilibrium with the corresponding gaseous concentrations in surrounding atmosphere (Scott 1981).

Gaseous species which react in the aqueous phase are much more efficiently scavenged by precipitation, as the aqueous reactions deplete the dissolved species concentration and maintain the diffusive gradients. For example, ammonia is efficiently scavenged by acidic precipitation due to the rapid protonated of ammonia to ammonium. There is some evidence in the literature (*e.g.*, Schomburg *et al.*, 1991) that surface-active organic matter may sequester hydrophobic organic contaminants within rain droplets, effectively maintaining the gas-aqueous concentration gradients across the droplet surface. The scavenging of reactive species is more appropriately modeled as partitioning into an infinite sink.

5.2   AEROSOL SCAVENGING BY PRECIPITATION

Particulate metals and aerosol-bound SOCs can be entrained in precipitation by both below- and in-cloud scavenging mechanisms. Depending on the species, the ambient precipitation pH, and the chemical properties of the scavenged parent aerosol, particulate phases are subsequently solubilized to varying degrees before, during, or after deposition. From the perspective of evaluating atmospheric deposition, the wet flux of trace elements and SOCs includes both dissolved and particulate forms. However, from an ecological perspective, the dissolved component is probably of greatest interest as it is the most readily available. Based on a review of recent data reported at various world-wide locations (Nguyen *et al.* 1990, Nurnberg *et al.* 1984, Gatz and Chu 1986, Lim and Jickells 1990, Scudlark and Church 1993), the phase distribution of trace metals in precipitation appears to be highly variable. Generally, mineral aerosols such as Al are less soluble at ambient pH levels than high temperature combustion condensates such as lead. Often, the speciation of trace elements are altered during sample collection and subsequent acidification.

There is supporting evidence in the literature that the removal of contaminants from the atmosphere by precipitation is dependent on the size distribution of atmospheric aerosols. Slinn *et al.* (1978) derived a semi-empirical relationship between the "collision efficiency" of raindrops and aerosol size. The efficiency of rain to remove particles is predicted to be lowest between 0.1 and 1 μm and increases with decreasing raindrop size. Doskey and Andren (1981) calculated aerosol washout ratios for PCBs for a range of aerosol diameters using the relationship described by Slinn *et al.* (1978) and indicate that PCBs are most likely enhanced in submicron aerosol size fractions. Scavenging ratios for several trace elements have also been shown to depend upon aerosol size (Tschiersch *et al.* 1989).

5.3   FIELD VERIFICATION OF SCAVENGING MECHANISMS

The above description of scavenging by precipitation has been evaluated by coincident collection of air and precipitation samples by several investigators at several locations. Ligocki *et al.* (1985a) reported gas phase scavenging coefficients for a variety of SOCs measured in Portland, OR. Values of the gas phase scavenging coefficients measured at 8°C were three to six times higher than those predicted using Henry's Law constants at 25°C. By correcting these constants to the ambient temperature, they demonstrated that gas and dissolved phases was near equilibrium for several PAHs and other low molecular weight SOCs. Field determined overall (gas + aerosol) scavenging coefficients for many SOCs with vapor pressures less than 10^{-5} torr are often substantially larger than those attributable to gas scavenging along, suggesting that aerosol scavenging is an important process. Scott (1981) suggests that in-cloud scavenging my result in aerosol scavenging coefficients on the order of 10^6. Comparable values for below-cloud scavenging of trace elements range from 10^3 to 10^5 (Slinn *et al.* 1978, Slinn 1983, Talbot and Andren 1983).

More recently, Leister and Baker (1993) have investigated SOC scavenging in the Chesapeake Bay region. Integrated wet-only precipitation samples and air samples were collected at a station adjacent to the bay since July 1990, using a large volume precipitation collector which isolates 'particulate' and 'dissolved' SOCs (as operationally defined by filtration; Baker *et al.*, 1986). In that study, SOC scavenging by precipitation was highly variable, with both the concentration and physicochemical speciation of the SOCs varying substantially between sampling periods (Figure 21). For example, polycyclic aromatic hydrocarbons concentrations in precipitation collected between 26 June and 10 July 1990 are more than ten times greater than those in samples collected in August. Interestingly, PAHs in precipitation collected between 9 and 15 August 1990 existed primarily in the dissolved phase (as determined by *in situ* filtration) while those collected between 15 and 28 August 1990 were more evenly distributed between dissolved and particulate phases. We interpret this as direct evidence that both the magnitudes and the relative importance of various scavenging mechanisms are highly variable. Clearly, the use of a single set of scavenging coefficients to describe the transport for each organic chemical is in error.

5.4   EVIDENCE FROM FOG WATER STUDIES OF ALTERNATE WET SCAVENGING MECHANISMS

Recent studies of fog water have provided intriguing evidence that SOC scavenging by water droplets in the atmosphere is controlled by processes other than gas dissolution and aerosol scavenging. Glotfelty and co-workers (Glotfelty *et al.* 1987, Glotfelty *et al.* 1990, Schomburg *et al.* 1991) measured concentrations of several agrichemicals in fog water and in the interstitial air. The observed gas/dissolved concentration ratios were often much greater than their

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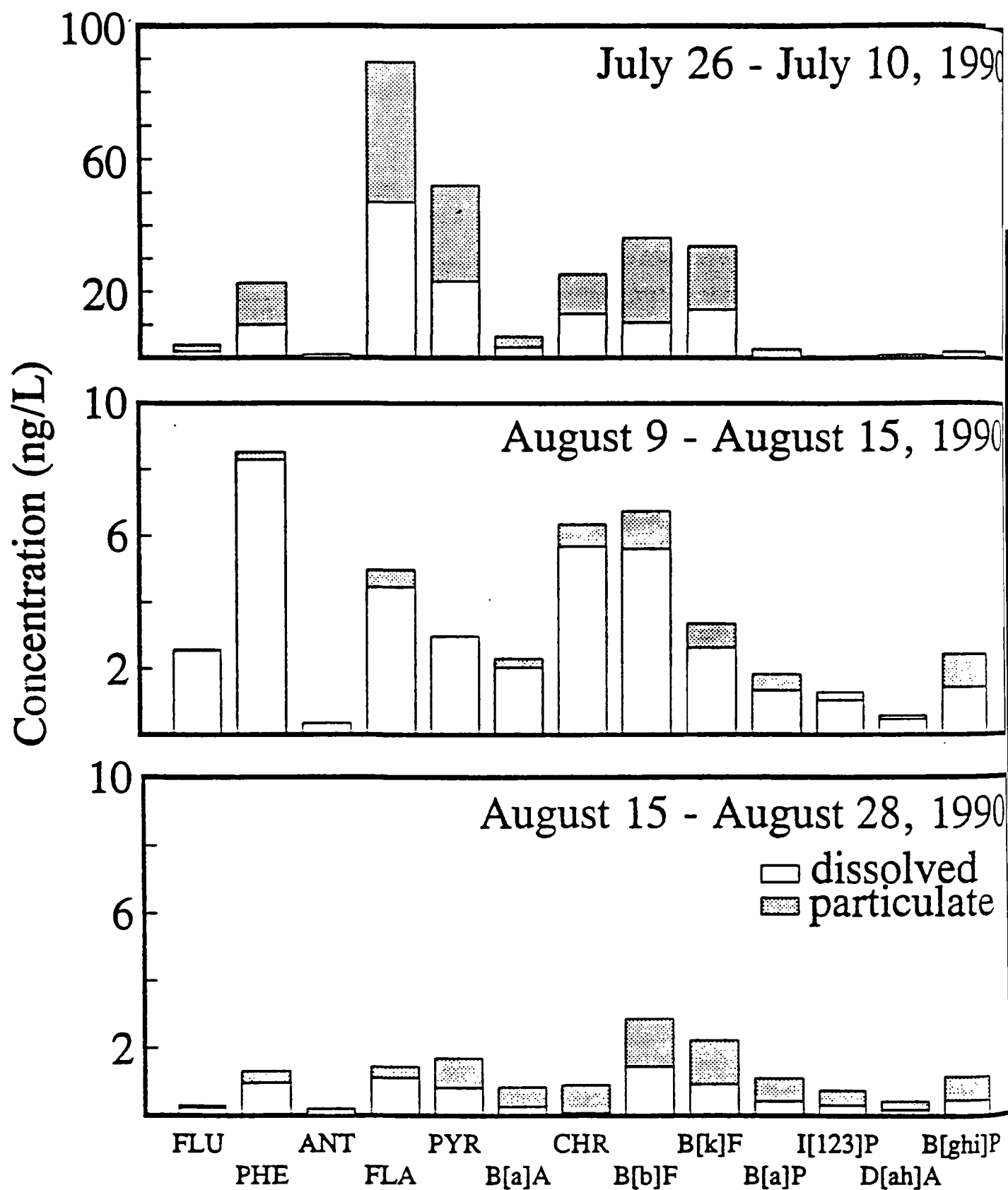
Figure 21. PAH speciation in Chesapeake Bay rainfall
(Leister and Baker, 1992)

corresponding Henry's Law constants, suggesting that the fog water was significantly supersaturated with these chemicals with respect to the gas phase concentrations. The extent of apparent supersaturation was greater for those compounds with larger Henry's Law constants. Glotfelty *et al.* (1987) and, later, Schomberg *et al.* (1991) hypothesized that this enrichment of SOCs in fog water resulted from its complexation by surface-active natural organic matter which was either adsorbed onto the droplet surfaces or was present as colloids within the droplets. Further evidence of the role of natural and anthropogenic organic matter in the enrichment of SOCs is presented in the collaborative studies of fog events in Dubendorf, Switzerland (Czuczwa *et al.* 1988, Leuenberger *et al.* 1988, Capel *et al.* 1990, Capel *et al.* 1991). As with the earlier studies by Glotfelty and coworkers, these investigators measured elevated levels of SOCs in Dubendorf fogwater in far excess of calculated equilibrium values with the interstitial air. Capel *et al.* (1990) reported elevated concentrations of dissolved organic carbon (DOC) ranging from 31 to 260 mg C/L, resulting in significantly lower surface tensions in these urban fog waters. High levels of DOC in surface waters are thought to complex hydrophobic SOCs, lowering their aqueous phase fugacities. Assuming that these fogs scavenge SOCs by the same mechanisms as those operating in clouds, these data suggest that natural organic matter in precipitation may play a substantial, if not controlling, role in scavenging SOCs from the atmosphere.

The field measurements presented above strongly indicate that SOC scavenging by precipitation involves more than the simple Henry's Law-type dissolution of SOC gases and aerosol scavenging. Clearly, both precipitation and fogwater appear to be supersaturated with SOCs relative to the surrounding air, suggesting either that mass transfer out of the droplets is hindered or that alternate mechanisms result in complexed SOCS within the droplets.

6.0 CURRENT UNDERSTANDING OF DRY DEPOSITIONAL PROCESSES

6.1. DRY AEROSOL DEPOSITION

6.1.1. Concepts and Models

Dry aerosol deposition results from the transport and accumulation of aerosol-associated contaminants during periods without precipitation. The theoretical basis of dry aerosol deposition has been discussed extensively in the literature, and the reader should consult the reviews by Davidson and Wu (1988; 1989), Hicks *et al.* (1980; 1986), McMahon and Denison (1979), Sehmel (1980), and Hosker and Lindberg (1982). In general, the magnitude of the dry aerosol contaminant flux is related to the concentration of aerosol-associated contaminant in the air mass. This relationship between concentration and flux is quite complex and non-linear, however, and depends upon characteristics of the atmosphere (*e.g.*, physical stability), upon the nature of the receptor surface (*e.g.*, tree canopy *versus* water), and upon the properties of the

depositing contaminant (*e.g.*, reactivity, aerosol size).

The stability of the atmosphere determines the amount of turbulence and, therefore, the magnitude of aerosol transport in the vertical direction. Near the Earth's surface, a momentum boundary layer exist where the air velocity increases from zero within millimeters of the surface to some constant value with height. A quasi-laminar sublayer of air comprises this millimeter thick layer adjacent to receptor surfaces, where turbulent transport is greatly reduced. A surface layer extends from several meters to tens of meters above the receptor surface. Within the surface layer, vertical turbulent fluxes of momentum and heat are constant with height. Above the surface layer, the planetary boundary layer include the entire region of the atmosphere in which transport is influenced by interactions with the Earth's surface.

Dry aerosol deposition is modeled as a three step transport processes, in which aerosol are carried from the planetary boundary and surface layers through the quasi-laminar layer and are allowed to interact with the receptor surface. Aerosol transport from the planetary boundary and surface layers results from eddy diffusion and sedimentation. The magnitude of eddy diffusion depends upon the amount of turbulence which depends, in turn, on the atmospheric stability. Heat exchange vertically in the atmosphere either contributes to or suppresses turbulent energy. In the case where the air at ground level is colder that than aloft, the air column is stable, turbulence is low, and aerosol deposition by eddy diffusion is limited. Conversely, when the air at ground level is heated, the air column becomes unstable and the increase in turbulence enhances aerosol transport rates. Heating of air at the Earth's surface may result either from solar heating or from the seasonal cooling of large bodies of water.

Aerosol particles larger than one micron may be transported from the planetary boundary and surface layers by sedimentation. Gravitational attraction accelerates aerosol particles towards the Earth's surface and particles increase in velocity until drag forces offset the gravitational forces, as described by Stoke's Law. The magnitude of this terminal settling velocity (*i.e.*, the steady-state velocity when drag and gravitational forces are equal) depends upon the size, shape, and density of the aerosols. Because the terminal settling velocity increases with the square of the aerosol diameter, gravitational settling is an important component of dry aerosol depositional fluxes for those contaminants which are associated with large aerosols.

Once transported to the quasi-laminar sublayer, aerosols move through this sublayer to the receptor surface by a variety of processes, including eddy diffusion, interception, inertial motion, and sedimentation (Davidson and Wu, 1988). Electrostatic forces, thermophoresis, and diffusiophoresis may also assist transport in the sublayer. Aerosols reaching the receptor surface may adhere to or bounce off the surface, depending on the characteristics of both the surface and the aerosol. In addition, specific aerosols or their associated contaminants may react chemically with the receptor surface, maintaining a large concentration gradient within the quasi-laminar sublayer.

Dry aerosol depositional fluxes have been modeled using a temporally- and spatially-variable dry deposition velocity ($v_{d,z,t}$, length/time):

$$F = C_{z,t} \times v_{d,z,t} \qquad [12]$$

where F is the dry aerosol depositional flux (mass/area-time) and $C_{z,t}$ is the concentration of aerosol (or aerosol-associated contaminant) at height z and time t (mass/volume). The overall resistance to transport of aerosols is equal to the reciprocal of the dry deposition velocity. This resistance may be conceptually divided into component resistances resulting from transport in the planetary boundary, surface, and quasi-laminar sublayer, and from interactions at the receptor surface. For most contaminants, the resistance to transport in the planetary boundary and surface layers is quite small relative to those in the sub-layer and at the surface, resulting in large concentration gradients near the Earth's surface. Equations for aerosol deposition velocities derived from the flux of air momentum, boundary layer transport, and interactions with the surface are reviewed by Davidson and Wu (1988).

Aerosol deposition to water surfaces are influenced by the specific properties of the air-water interface. Of particular importance is the exchange of momentum, heat, and water vapor, the potential increase in aerosol size as particles incorporate water, and the role of aerosols produced *via* sea salt ejection and bubble breaking. Slinn and Slinn (1980, 1981) presented a two layer model of particle deposition to water which included transport through a constant flux layer above the surface as well as transport through the surficial boundary layer. Their model included the effect of slip at the water surface and of the growth of hygroscopic aerosols in the high humidity environment at the air-water interface. The Slinn and Slinn model assumes that the surface is a perfect sink (*i.e.*, that there is no surface resistance). Fairall and Larsen (1984) expanded their earlier model to include the influence of sea spray production and atmosphere surface interactions. Williams (1982) accounted for the breaking of waves and the resulting increase in sea surface roughness.

6.1.2. Field Measurements

Methodologies to estimate dry aerosol depositional fluxes have been reviewed previously, including at the National Acid Precipitation Assessment Program (NAPAP) Dry Deposition Workshop in March, 1986, as summarized by Hicks *et al.* (1986). Dry aerosol depositional fluxes are measured directly using a variety of surface analysis methods, in which rates of contaminant accumulation on particular surfaces are measured and depositional fluxes inferred. Alternatively, atmospheric flux methods measure contaminant inventories and speciation in the atmosphere and the corresponding micrometeorology necessary to model aerosol transport. Although progress has been made, there are no methods to *directly* measure dry deposition. Furthermore, there are no unambiguous, widely-accepted methods recognized for the *indirect* estimation of dry deposition. The differing approaches, as summarized and evaluated by Hicks

et al. (1986), Nicholson (1988), Davidson and Wu (1989) and Lindberg (1989) are:

(a)   Inferential micrometeorological techniques based on vertical airborne concentration measurements at one or more levels (*e.g.*, tower-based eddy correlation). Transfer rates from the atmosphere to the surface are obtained via modelling, or where possible, direct measurement of surrogate species (*e.g.* ozone and NO_3^-) and inferring a deposition rate. Due to the complexity and variability in the various processes which control dry deposition, methods which assume a constant deposition velocity from literature values have an inherent large degree of uncertainty. Inferential dry deposition measurements are generally limited to fine particles, under limited terrain conditions (*e.g.* uniform vegetation and adequate fetch) and over relatively short (hrs) time scales.

(b)   Surface analysis techniques, such as the use of surrogate surfaces(*e.g.* Teflon plates, glass microslides), vegetative throughfall/stemflow, and foliar extraction, (Hanson and Lindberg 1991). Surrogate surface techniques are generally applicable only to fine particles over a small spatial scale (cm_2 to m_2), but integrate deposition over relatively long time scales (10s to 100s of hours). A major advantage of surface techniques is that vegetative surfaces more accurately represent deposition to natural surfaces that other approaches cannot physically or mathematically duplicate.

(c)   Watershed mass balance approaches, which have the advantage of integrating measurements over relatively large spatial (ca. 5-10 hectares) and temporal (months-years) scales. The major disadvantage of this technique is that the watershed studied must be well-characterized hydrologically and in terms of internal sources and sinks.

(d)   Regional-scale langrangian and eulerian models (*e.g.*, Levy and Moxim 1989, Eliassen *et al.* 1988), which are typically based on emission inventories rather than concentration measurements. As such, the transfer rates are at the mercy of the input data to the model.

(e)   Isotopic tracers, which can be utilized to infer the total (wet + dry) deposition as well as to apportion the wet and dry fractions (the $^{137}Cs/^{210}Pb$ ratio in precipitation is more than 2X the corresponding ratio in submicron aerosol). Isotopic tracer techniques have the advantage of yielding absolute identification of atmospherically-derived material, and the ability to infer deposition over relatively large spatial scales. Depending on the isotopes utilized, deposition can be estimated on temporal scales ranging from individual events ($^{87}Sr/^{86}Sr$) to decades ($^{137}Cs/^{210}Pb$). Other tracers (*e.g.* ^{35}S, ^{214}Pb, and ^7Be) have been used to specifically measure dry deposition.

6.2   GAS ABSORPTION AND VOLATILIZATION

6.2.1   Importance in the cycling of organic compounds

Little attention has been paid to the role of air-water exchange of semi-volatile organic chemicals (SOCs) in lakes, estuaries, and oceans. Whereas the transfer of low molecular weight, volatile and biologically-mediated gases such as O_2, CO_2, CH_4, H_2S, and 1 and 2 carbon halocarbons have received considerable attention for water quality, carbon cycling, global warming, and other reasons (*e.g.* Thompson and Zafiriou, 1983), SOCs such as PCBs, DDT, HCHs, PAHs, and toxaphene have been largely ignored (see Eisenreich *et al.* 1981, Doskey and Andren 1981, Atlas and Giam 1986, GESAMP 1989). These compounds are derived from major anthropogenic emissions in urban/industrial centers and world-wide agriculture, are transported globally, and are often concentrated in the northern hemisphere atmosphere from 20°N to 45°N (Stanley and Hites, 1991; Ballschmiter *et al.* 1981, Tanabe and Tatsukawa, 1986 and references therein). Recent studies suggest that the air-water exchange of SOCs plays an important role in the mass balancing of inputs to large aquatic systems such as the Great Lakes, the Mediterranean Sea, and the world's oceans (Strachan and Eisenreich 1988, Burns and Villenuve 1988, GESAMP 1989, Atlas *et al.* 1986). For example, the calculated volatilization flux of PCBs out of the North American Great Lakes (Mackay 1989, Swackhamer and Armstrong 1986, Strachan and Eisenreich 1988, Eisenreich 1987) is estimated to be comparable to sedimentation losses. Since planet Earth is approximately 70% water by area, it is not surprising that the problem is one of interfaces. Large aquatic systems such as the Great Lakes, Chesapeake Bay, and the coastal ocean have large surface areas for transfer of chemicals that are unfortunately often close to regions of contaminant input. Air-water transfer of SOCs occurs in both directions; whether absorption or volatilization dominates is discussed below. This section discusses the concepts and models applicable to air-water exchange of SOCs and how these models have been applied in the field.

6.2.2   Concepts and Models

The theory and concepts of air-water exchange and mass transfer of chemicals across water surfaces have been presented (*e.g.*, Liss and Slinn 1983, Brutsaert and Jirkha 1984, Buat-Menard 1986, Wilhelms and Gulliver 1991, Schwarzenbach *et al.* 1992). Air-water exchange refers to the transfer of chemicals across an air-water interface, or air-side and water-side boundary layers (Figure 22). The gas concentration in the atmosphere ($C_{a,g}$) attempts to reach equilibrium with the concentration of gas dissolved in water ($C_{w,diss}$). When equilibrium is achieved, the ratio of the gas activities
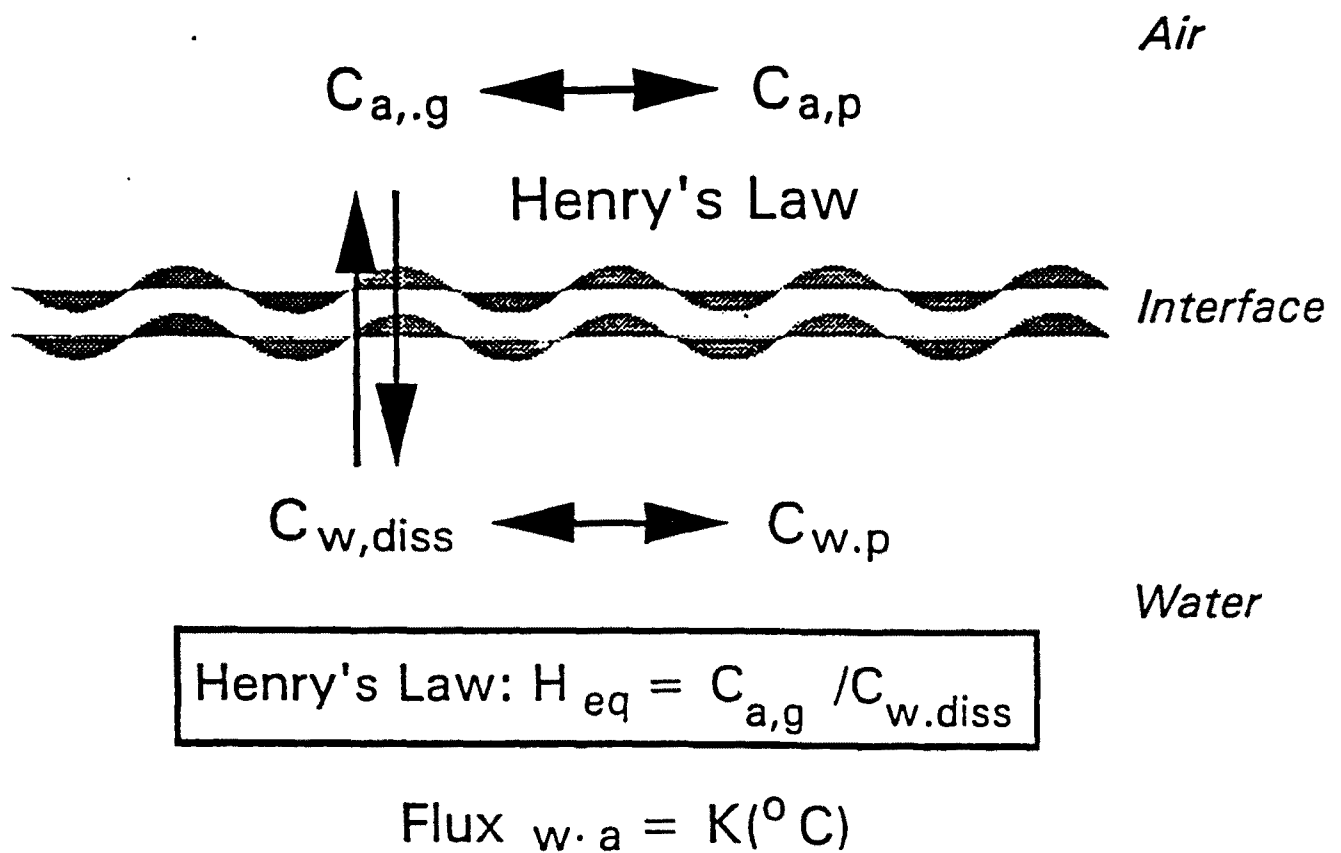
Figure 22. Air-water exchange

in air and water at constant temperature are represented by Henry's Law constant (H = $C_{a,g}/C_{w,diss}$). The direction of chemical transfer is from the water to the air (*e.g.* volatilization) when the activity in the water exceeds the activity (gas phase concentration) in air. Chemical transfer from the air to the water (*e.g.*, absorption) occurs when the activity in the air exceeds the chemical activity in water. The processes of gas absorption and volatilization occur simultaneously, and together contribute to the net flux. The magnitude of mass transfer is controlled by a mass transfer coefficient or piston velocity and the concentration or activity gradient across the interface (Liss and Slater, 1974). Thus, the direction and magnitude of gas transfer is a function of the free concentrations in air and water (activity gradient), wind speed (water side turbulence), temperature, characteristics of the water (water chemistry; surface films), and the physicochemical properties of the chemical compound (Henry's Law constant; octanol-water partition coefficient, vapor pressure, and Schmidt number, Sc).

Air-water exchange may be visualized as diffusive transfer of a chemical across a stagnant film of 0.1 to 1.0 mm thickness. At low wind speeds, insufficient energy exists to stir the air and water films or boundary layers, and a completely stagnant boundary layer is established (Stagnant Two-Film Model). Higher wind speeds generate more turbulence in the boundary layers, and parcels of air and water are forced rapidly to the surface. Exchange is dependent on the renewal rate of air and water parcels (Surface Renewal Model). In highly turbulent seas, gas exchange is enhanced by continual breakup of the surface and generation of a large number of bubbles of great surface area (Bubble Ejection Model). Under turbulence and wind conditions occurring in the Great Lakes and coastal seas, the first two models are most applicable.

The Stagnant Film Model (Whitman 1923, Liss and Slater 1974) describes the transfer of a chemical by diffusion across stagnant air and water films on either side of the air-water interface (Figure 23). The bulk air and water compartments are assumed to be well mixed and offer no resistance to gas transfer. The transfer of chemical at the interface is assumed to be instantaneous, offering no resistance to transfer. The rate of gas exchange or mass flux is equal to $F_{gas} = K_{OL} (C_{w,diss}-C^*)$, where K_{OL} is the overall mass transfer coefficient (m/d), and $C_{w,diss}$ and C^* (mol/m^3) are the free water concentration and the water concentration in equilibrium with the partial pressure of the gas in the atmosphere (P,atm; $C^* = P/H$), respectively. If the concentrations in air and water are expressed as mol/m^3, K_{OL} as m/d, and H as atm m^3/mol, then the chemical flux has units of mol/m^2 day and a positive flux reflects volatilization. The overall resistance to mass transfer is the sum of the resistance across the air and water films: $1/K_{OL} = 1/k_w + RT/Hk_g$ where k_w and k_g are the water film and gas film transfer coefficients (m/day), respectively, R is the universal gas constant (8.2 x 10^{-5} atm/m^3/mol-K), and T is absolute temperature (K). The Henry's Law constant influences both the magnitude of K_{OL} and the concentration gradient. Since H is a function of temperature ($\sim$2.5 fold increase with a 10°C increase), the direction and
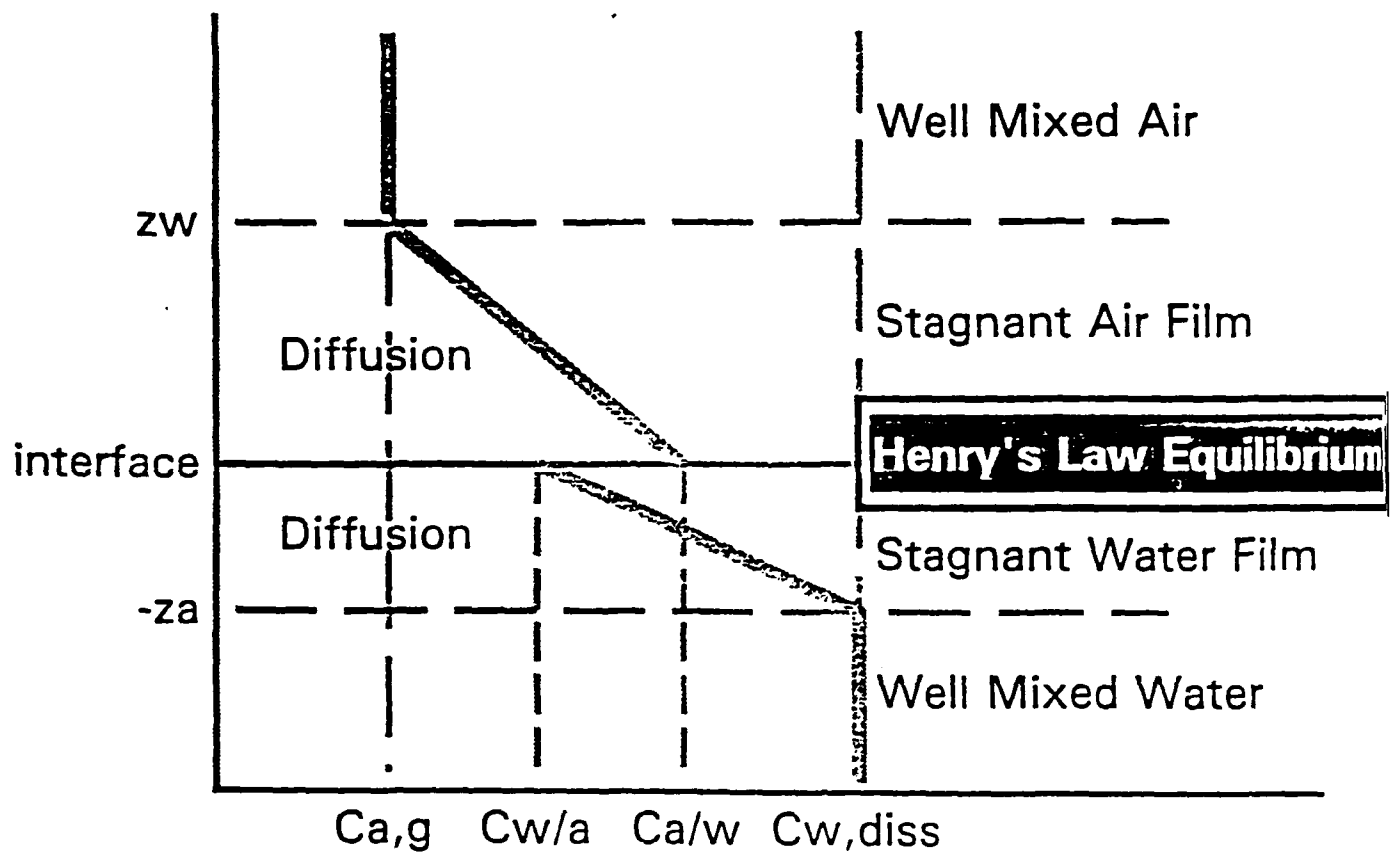
Figure 23. Stagnant Two Film Model

magnitude of gas flux is influenced by the water temperature. The resistance to transfer may arise either in the water or gas film, or a linear combination of the two. Assuming average values for k_w (20 cm/hr) and k_g (2000 cm/hr) resistance to transfer at 25°C is dominated by the water film when $H > \sim 10^{-3}$ atm m^3/mol, and by the gas film when $H < \sim 10^5$ atm m^3/mol. Resistance in both phases occurs when H is between these extremes. Compounds such as PCBs, PAHs, and DDT isomers generally incur resistances in both phases. SOCs with $H < 10^5$ atm m^3/mol volatilize slowly at a rate dependent on H; k_w dominates and the rate is controlled by diffusion through the air. Intermediate and high molecular weight PAHs have H's in this range (Lyman *et al.*, 1990). Examples of Henry Law constants at 25°C are shown in Table 21.

The Surface Renewal Model (Higbie 1935, Danckwerts 1951) involves the periodic renewal of parcels of air and water on either side of the interface with new parcels turbulently mixed to the surface. In mathematical terms, $F_{gas} = (H\sqrt{(r_a D_a)} + \sqrt{(r_w D_w)}](C_{w,diss} - P/H)$ where air parcel renewal rates r_a and r_w are the air and water parcel renewal rates and D_a and D_w the chemical diffusivities in air and water (cm^2/sec), respectively (Schwarzenbach *et al.* 1992). This equation has the same form as that describing gas flux by the stagnant film model with the exception of how the mass transfer coefficients depend on diffusivities. K_{oL} depends on D^1 in the stagnant two film model while k depends on $D^{1/2}$ in the surface renewal model. Enhancements in the surface renewal model have been reviewed by Bennett and Rathun (1972) and Theofannous (1984). New developments in the surface renewal model yield a Boundary Layer Model as described in Deacon (1977) and Hanratty (1991).

The stagnant film and surface renewal models incorporate unmeasurable parameters that must be estimated in the field (*e.g.* the depth of the interfacial zone in the stagnant film model and the renewal rates in the surface renewal model). The stagnant two film model is used oftentimes for its simplicity even though it lacks mechanistic accuracy. Either treatment yields comparable gas fluxes. For convenience, the two film model may be expressed in terms of fugacity (*e.g.*, see Mackay *et al.* 1986). The presence of a surface film may add resistance to air-water transfer (Mackay 1982, Liss 1983, Asher and Pankow 1991) by adding a third resistance film. However, surface films in lakes and seas are sufficiently broken up by turbulence, except under the most calm conditions, that they represent little or no resistance to SOC transfer, at least on longer time scales. However, Mackay *et al.* (1991) argue that SOCs accumulate at the air-water interface by thermodynamic association with structured water at the interface. The net effect is to reduce transfer rates (as observed by experiments conducted by Asher and Pankow (1989) by adding a layer of higher capacity which hinders the diffusion process.

TABLE 21

HENRY'S LAW CONSTANTS OF SEMIVOLATILE ORGANIC CONTAMINANTS

Compound	Log Henry's Law Constant (atm-m^3/mol)
PCBs (1 to 10 Cl)	-3.6 to -4.0
PAHs (1 to 6 rings)	-7.4 to -4.0
Chlorobenzene	-4.6
Tetrachlorobenzene	-2.4
Hexachlorobenzene	-2.9
Lindane (γ-HCH)	-5.6
α-HCH	-5.3
2,3,7,8-TCDD	-4.5

6.2.3 Air and water concentrations

Chemical activities in the gas and water phases are required to assess the direction of gas transfer and activity gradient. On the air side, this requires explicit knowledge of the gas phase concentration. Compounds with vapor pressures $> 10^{-5}$ atm exist predominantly in the gas phase (Junge 1977, Bidleman 1988) and their atmospheric concentration is easily determined. Compounds with vapor pressures between 10^{-5} and 10^{-8} atm are distributed to varying extents between the gas and aerosol phases (Bidleman, 1988). Only the gas phase participates in air-water exchange. Sampling procedures and/or modeling of gas-particle distributions are required to properly assess the gas phase species of interest (see 4.2).

On the water side, the chemical activity is equivalent to the concentration of freely dissolved, unassociated species. As portrayed in Figure 22, SOCs in marine and fresh waters are distributed between the dissolved and particulate phases according to the hydrophobicity of the chemical, and the composition, concentration, and size of the particle population (Karickhoff, 1984, Elzerman and Coates 1987, Schwarzenbach et al. 1992, Chiou 1990). SOCs partition into organic carbon-rich particles, the magnitude of which may be correlated with the fractional organic carbon content of the particles (foc) and K_{ow}. Correlations take the form of $K_p = aK_{ow}^b$ where K_p is the equilibrium partition coefficient (ml/g) and a, b are constants (b ~ 0.7 to 1.0; a depends on compound). For example, Schwarzenbach and Westall (1981) suggest log Kp = 0.72 log K_{ow} + log foc + 0.49. Using this and similar correlations (Karickhof 1984, Lyman et al. 1990), the fraction of chemical (f_d) in the dissolved phase may be calculated as $f_d = 1/[(TSM)k_p + 1]$ where TSM is the total suspended matter concentration (g/L). At typical Great Lakes TSM values of 0.5 to 2 mg/L, PCBs with log Kow values ~ 4.5 to 7.5 are mostly in the dissolved phase (Eadie and Robbins, 1987).

Methodologies to separate dissolved from particulate phases includes the use of high volume filtration through glass fiber quartz filters (nominal pore size of 0.5 to 1 um) and continuous flow centrifugation. This protocol yields "operational" separation of dissolved and particulate species because colloidal size particles pass into the "dissolved phase". Field comparisons suggest that filtration provides a better estimate of the aqueous activity of PCB congeners than does centrifugation (Swackhamer et al. 1993). Gschwend and Wu (1985) and Baker et al. (1986) modeled the distribution of SOCs between the dissolved, suspended, and colloidal phases. Dissolved and colloidal natural organic matter also bind SOCs in dilute solution (e.g., McCarthy and Jimenez 1985, Landrum et al. 1987). Improved methods for measuring dissolved SOC concentrations in natural waters and further characterization of the rates of chemical uptake by aquatic particles are necessary to accurately predict chemical distributions (Baker et al. 1991). Sproule et al. (1991) describe such an in situ sensing device. A further complication is that SOCs may be taken up by aquatic phytoplankton at

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sufficiently slow rates compared to growth kinetics that equilibrium calculations are accurate only in oligotrophic ecosystem (low TSM) and/or at cold temperatures (Swackhamer and Skogland 1991).

6.2.4 Mass Transfer Coefficients

Mass transfer of gases across the air-water interface is a function of wind speed, waves (height, frequency), bubbles (breaking waves), and heat transfer. Laboratory wind tunnel experiments over the last 20 years have elucidated the controls of transfer, especially for gases experiencing liquid (water) control (H > 10-3 atm m3/mol) such as O_2 and CO_2 (for reviews, see Liss 1983, Liss and Merlivat 1986, Brutsaert and Jirka 1984; Wilhelms and Gulliver 1991). Figure 24 (modified from Liss and Merlivat, 1986) shows that liquid phase controlled gases exhibit low transfer rates at low wind speeds measured at 10 to 60 cm above the water surface, corresponding to a smooth surface regime. Transfer rates increase at a transition at 5 ± 3 m/s corresponding to a rough surface regime and the presence of capillary waves. The next transition to higher k_w values occurs in the wave breaking regime at about 10 to 13 m/sec wind speed. K_w is generally found to be proportional to $Sc^{-2/3}$ at low wind speeds (i.e., $k_w \propto D^{2/3}$) under calm conditions, and $k_w \propto Sc^{-1/2}$ (i.e., $k_w \propto D^{1/2}$) in the rough surface regime. Laboratory experiments provide reasonable agreement for k_w with measures of turbulence but may not accurately mimic the complexity of the real environment with respect to bubble formation, spray, boundary effects, etc.

Experimental approaches to determine gas transfer rates in the field include the direct flux method (box), oxygen balance method, profile and eddy correlation techniques, use of natural and bomb-produced ^{14}C, the radon deficiency method, and the use of tracer gases indigenous (e.g., methane) or added (SF_6) to the water. Most of these techniques are most applicable to determining gas transfer coefficients for compounds for which the resistance to transfer is dominated by the water phase (O_2, CO_2, O_3, most PCB congeners, most PAHs, low MW chlorinated solvents). However, the eddy correlation technique may be appropriate for determining gas transfer coefficients controlled by air film resistance (e.g., water vapor). In such studies, k_g has been found to vary linearly with wind speed and therefore expressed as kg $= C_D \times U_{10}$ where C_D is the drag coefficient and U_{10} is the wind speed at 10 m height.

The tracer gas SF_6 has now been used successfully in long term field experiments of gas transfer and mixing in lakes, rivers, and oceans since the first report by Wanninkhof and co-workers (Wanninkhof et al. 1985; 1987; 1991; Wanninkhof, 1986; Ledwell et al. 1986; Watson et al. 1991; Watson and Ledwell 1988; Watson and Liddicoat 1985; and Upstill-Goddard et al. 1990). SF_6 is an excellent tracer of water controlled gases because is has steady, low, and well-defined concentrations in the
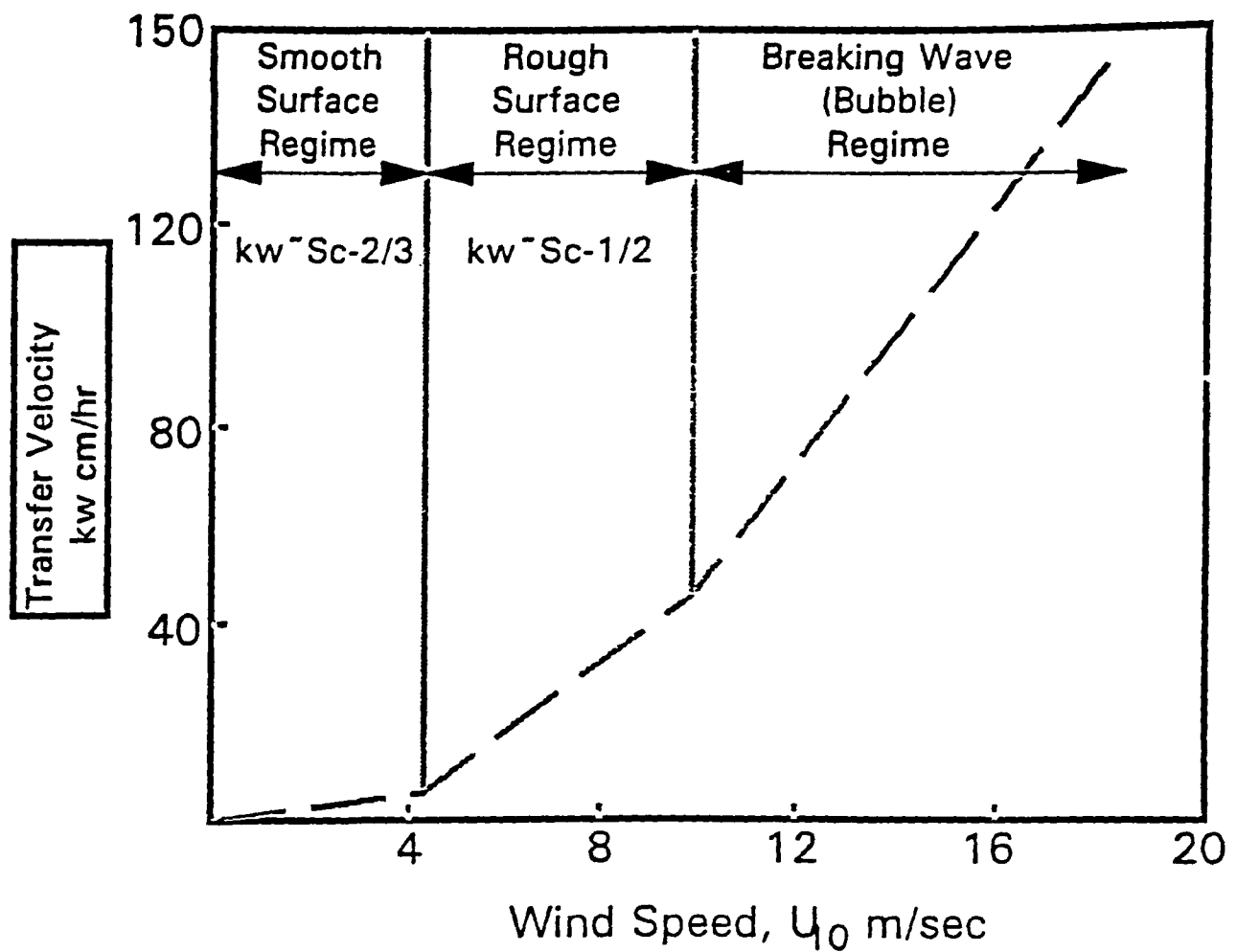
Figure 24. Water phase transfer velocity versus wind speed (modified from Liss and Merlivat, 1986)

ambient atmosphere, is chemically and biologically inert, does not sorb to aquatic particles, is analyzed precisely and accurately at trace concentrations, and its loss rate to the atmosphere is sufficiently rapid to perform experiments to yield k_w values on a daily basis. Liss and Merlivat (1986) took the data of Wanninkhof *et al.* (1985) for gas transfer on a small lake, successfully compared them to previous k_w estimations, and proposed that the following three relationships might be used to determine k_w in various wind regimes up to wind speeds of at least 13 m/sec (u is wind speed at 10m; k_w is normalized to CO_2 having a Sc number of 600; SF_6 has a Sc number of ~1300):

$$k_w = 0.17 \, u \qquad\qquad \text{for } u < 3.6 \text{ m/sec}$$
$$k_w = 2.85 \, u - 9.65 \qquad \text{for } 3.6 < u < 13 \text{ m/sec}$$
$$k_w = 5.9 \, u - 49.3 \qquad\; \text{for } u > 13 \text{ m/sec}$$

These relationships have been applied by GESAMP (1989) to estimate gas transfer in the world's oceans, and others have applied them to PCB exchange in the Great Lakes (Achman *et al.* 1993). Wanninkhof and others have now conducted several SF_6 tracer studies in lakes of different surface areas and in the ocean and have observed a dependence of k_w on the size (fetch and turbulence) of the lake. Wanninkhof *et al.* (1991) have proposed a power law relationship between k_w and wind speed. based upon all data on SF_6 transfer in lake experiments: $k_w = 0.45 \, u^{1.64} \, (Sc_{chem}/600)^{1/2}$. The correlation coefficient was 0.66 indicating there is still considerable scatter and uncertainty in the dependence of kw on wind speed. Livingstone and Imboden (1992) support their approach since k_w is probably a function of both the mean wind speed and the probability distribution of the wind speed. They suggest applying a Weibull wind speed distribution with power law expressions to obtain the effect of wind on k_w. Table 22 is a compilation of literature correlations relating k_w and k_g to wind speed from both laboratory and field experiments.

6.2.5 Field Measurements

Air-water exchange of SOCs in large ecosystems has been difficult to quantify but there is a growing appreciation that it is an important component in whole lake or ecosystem mass balances, and plays a large role in the chemical entry into the food chain. Atlas and Giam (1986), Atlas *et al.* (1986), and GESAMP (1989) have reported that the major mode of PCBs and other organochlorine input to the world's oceans is water absorption of atmospheric gases. Atlas *et al.* (1986) have calculated that of 16.9 x 10^8 g/yr PCBs entering the world's oceans, 70% resulted from air-water exchange. GESAMP (1989) reported similar loadings. In the Great Lakes region, Strachan and Eisenreich (1988) used mass balance calculations for the mid-1980's to suggest that the SOC volatilization dominated all inputs and outputs (Table 10).

Approaches to estimating the direction and magnitude of gas exchange in large

TABLE 22

SOME EMPIRICAL RELATIONSHIPS BETWEEN k_w AND k_g AND WINDSPEED

k_g (cm/hr)	
Mackay and Yuen (1983)	$k_g = 0.0065(6.1 + 0.63U_{10})^{0.5}U_{10}$
Schwarzenback et al. (1992)	$k_{g(water)} = 0.2U_{10} + 0.3$
k_w (cm/hr)	
Mackay and Yuen (1983)	$k_{w(water)} = 1.75 \times 10^4(6.1 + 0.63U_{10})^{0.5}$
Wanninkofh et al. (1985)	$k_{w(SF6)} = 10^4(-8.9 + U_{10})$
Liss and Merlivat (1986)	$k_w = 0.17U_{10}$ for $U_{10} < 3.6$ m/sec
(Sc = 600)	$k_w = 2.85U_{10} - 9.65$ for $3.6 < U_{10} < 13$ m/sec
	$k_w = 5.9U_{10} - 49.3$ for $U_{10} > 13$ m/sec
Wanninkhof et al. (1991)	$K_w = 0.45U_{10}^{1.64}(Sc_{chem}/600)^{0.5}$

aquatic systems include mass balance calculations (based on literature data and measurements in the field), and measurement of activity gradients in the field with calculation of mass transfer coefficients. Atlas and Giam (1986), GESAMP (1989), and Atlas *et al.* (1986) have estimated the atmospheric deposition of organochlorine compounds including PCBs and DDT to the world's oceans including gas exchange based on published data in the literature. In general, the two film stagnant transfer model was applied to the calculation of the global mean gradient across the air-water interface, and mean global wind speeds to estimate mass transfer coefficients. GESAMP (1989) report on the total deposition of organochlorines to the oceans. For example, the mean atmospheric flux (μg/m^2-yr) for some compounds was estimated as: ΣHCH, 14: HCB, 77: Σ-DDT, 165; ΣPCBs, 239. With all the caveats presented, they emphasize that the direction and magnitude of transfer are both uncertain but from 25 to 85% of the total compound deposition is due to gas exchange. Atlas and Giam (1986) provide similar estimates for the ocean. Atlas *et al.* (1986) suggest that PCB transfer to the ocean surface is ~4.5 μg/m^2-yr, significantly lower than the above estimates, and is dominated by air-to-water transfer of gas phase PCBs. Using similar approaches, Doskey and Andren (1981), Murphy *et al.* (1983), Eisenreich *et al.* (1981), Strachan and Eisenreich (1988), and Mackay *et al.* (1986) estimate that the direction of gas transfer for PCBs is from the water to the air (*i.e.*, volatilization) for the Great Lakes, and volatilization represented a dominant component in both the atmospheric deposition and whole lake cycling. The difference in PCB behavior between oceans and the Great Lakes (PCB gas absorption versus volatilization) is likely due to the close proximity of atmospheric sources and the presence of significant inputs to surface waters in the Great Lakes. Strachan and Eisenreich (1988) estimated that volatilization represents about 45% to 87% of total PCB outputs from the Great Lakes. Swackhamer and Armstrong (1986) estimated that PCB volatilization from Lake Michigan was about 5.6 μg/m^2-yr based on a comparison of Lake Michigan and remote lake sediment cores. Swackhamer *et al.* (1988) reported on the gas transfer of PCBs from a remote lake located on an island in Lake Superior. They measured inputs and outputs from all sources except air-water exchange and determined by mass balance that the volatilization flux was ~8.5 μg/m^2-yr (Table 23). Larsson and co-workers (Larsson, 1983, 1985; Larsson *et al.*, 1990) using mass balance techniques in mesocosms and in the field, have shown that PCB contaminated sediments are a source of PCBs available for volatilization to the atmosphere.

Much less information is available on PAHs. McVeety and Hites (1988), using the same approach on Siskiwit Lake, determined that low and medium molecular weight PAHs were lost by volatilization in general proportion to their vapor pressure, and ranged from 0 to 80% of total outputs (Table 23). Strachan and Eisenreich (1988) estimated that benzo[a]pyrene volatilization represented approximately 2 to 19% of total outputs from the Great Lakes in comparison to ~50% from Siskiwit Lake (McVeety and Hites, 1988).

TABLE 23

MASS BALANCE OF PAHs and PCBs IN SISKIWIT LAKE, ISLE ROYALE, LAKE SUPERIOR

(McVeety and Hites 1988, Swackhamer *et al.*, 1988)

Inputs (μg/m^2-yr)			
	Phenanthrene	BaP	PCBs
Atmosphere			
Rain	0.35	0.15	7.3
Snow	0.2	0.05	3.2
Dry Particle	2.85	0.5	3.6
Total	3.4	0.7	14.1
Outputs (μg/m^2-yr)			
Sedimentation	0.7	0.4	5.6
Volatilization	2.7	0.3	8.5
Total	3.4	1.4	14.1

Achman *et al.* (1993a, b) have investigated the air-water transfer of PCBs and PAHs across the air-water interface of Green Bay, Lake Michigan. The strategy was to simultaneously collect air and water samples seasonally from aboard ship at several locations in Green Bay, Lake Michigan in 1989. The fugacity gradients were calculated, and wind speeds measured over the water were used to calculate daily mass transfer coefficients. This is the same strategy that Baker and Eisenreich (1990) applied to determining the flux of PCBs from Lake Superior. Table 24 reports the resulting PCB data and compares them to air-water fluxes reported elsewhere. These data suggest that volatilization fluxes of PCBs of about +50 to +200 ng/m²-day may be a common phenomenon in large, uncontaminated freshwater systems such as the Great Lakes. However, the direction and magnitude of gas transfer depends on season and location, the relative concentrations of compound in the atmosphere and water, and the properties of the chemical (especially H). Achman *et al.* (1993a,b) have compared the air-water exchange of PCBs and PAHs in Green Bay, Lake Michigan in 1989. Figure 25 shows the daily flux of individual PCBs and PAHs at the same location and time in Green Bay. Remembering that H influences both the fugacity gradient and the magnitude of the mass transfer coefficient, PCB behavior is dominated by volatilization while PAH behavior is dominated by absorption. That is, PCBs are being lost from the bay and dramatically influence the over-lake concentrations (Hornbuckle *et al.* 1993) while atmospheric PAHs are a major source to the water. PAHs have lower H values and are dominated by gas phase resistance to transfer. Baker and Eisenreich (1990) drew the same conclusion for Lake Superior.

McConnell *et al.* (1993) have estimated hexachlorocyclohexane fluxes to the Great Lakes based on air and water concentrations determined in 1989 and 1990. They concluded that both a-HCH and g-HCH have net inputs from water to air by gas exchange as follows (ng/m²/yr): a-HCH - Michigan, -2006: huron, -4559; Erie, -121; Ontario, 1196; g-HCH-1691, Michigan; -1748, Huron; -1246, Erie; -1424, Ontario. Although net flux was estimated to be from air to water, calculations showed that volatilization dominated only under warm water conditions in August. The direction, and certainly the magnitude, is a function of season as driven by water temperature and changing air and water concentrations.

To demonstrate the importance of air-water exchange on ecosystem mass balances, Figure 5 depicts the situation for PCBs in Lake Superior today (Jeremiason *et al.* 1993). Important points are: 1) Reservoir of PCBs is ~9000 kg, most in water and sediments; 2) Inputs are ~220 kg/yr while outputs are ~925 kg/yr, ~85% of which is allocated to volatilization; 3)~700 kg/yr PCBs have been lost from Lake Superior on average from 1980 to 1992 very closely matching the volatilization flux; 4) The change in water column concentrations of ΣPCBs of 1.3 ng/L in 1980 and 0.3 ng/L in 1992 results from volatilization; and 5) The residence time of PCBs in Lake Superior is ~4 to 5 years. The magnitude of volatilization of PCBs suggests that PCBs are a major source to the

TABLE 24

ESTIMATED AIR-WATER FLUXES OF PCBS
(+ FLUX = VOLATILIZATION)

LOCATION	PCB FLUX (ng/m^2-day)	REFERENCE
Green Bay	+15 to + 1300 (1-3 m/sec)	Achman *et al.* (1993)
Green Bay	+50 to + 1300 (4-6 m/sec)	Achman *et al.* (1993)
Lake Superior	+19 (still air)	Baker and Eisenreich (1990)
Lake Superior	+141 (5 m/sec)	Baker and Eisenreich (1990)
Lake Superior	+63	Strachan and Eisenreich (1988)
Siskiwit Lake	+23	Swackhamer *et al.* (1986)
Lake Michigan	0 to +13,000	Doskey and Andren (1981)
Lake Michigan	+240	Strachan and Eisenreich (1988)
Lake Michigan	+15	Swackhamer and Armstrong (1986)
Lake Ontario	+81	Mackay (1989)
River Elm, Sweden	+50	Larsson *et al.* (1990)
Oceans	-160 to -450	GESAMP (1989)
Oceans	-4.5	Atlas and Giam (1986)
Oceans	-0.6 to -10	Atlas *et al.* (1986)
Oceans	+12 to - 35	Iwata *et al.* (1993)

GREEN BAY, LAKE MICHIGAN

Site 10, July 31, 1989

Wind Speed = 1 m/s   Water Temp. = 15.6 °C

PCBs   PAHs

−Log HLC (atm m³/mol)   −Log HLC (atm m³/mol)
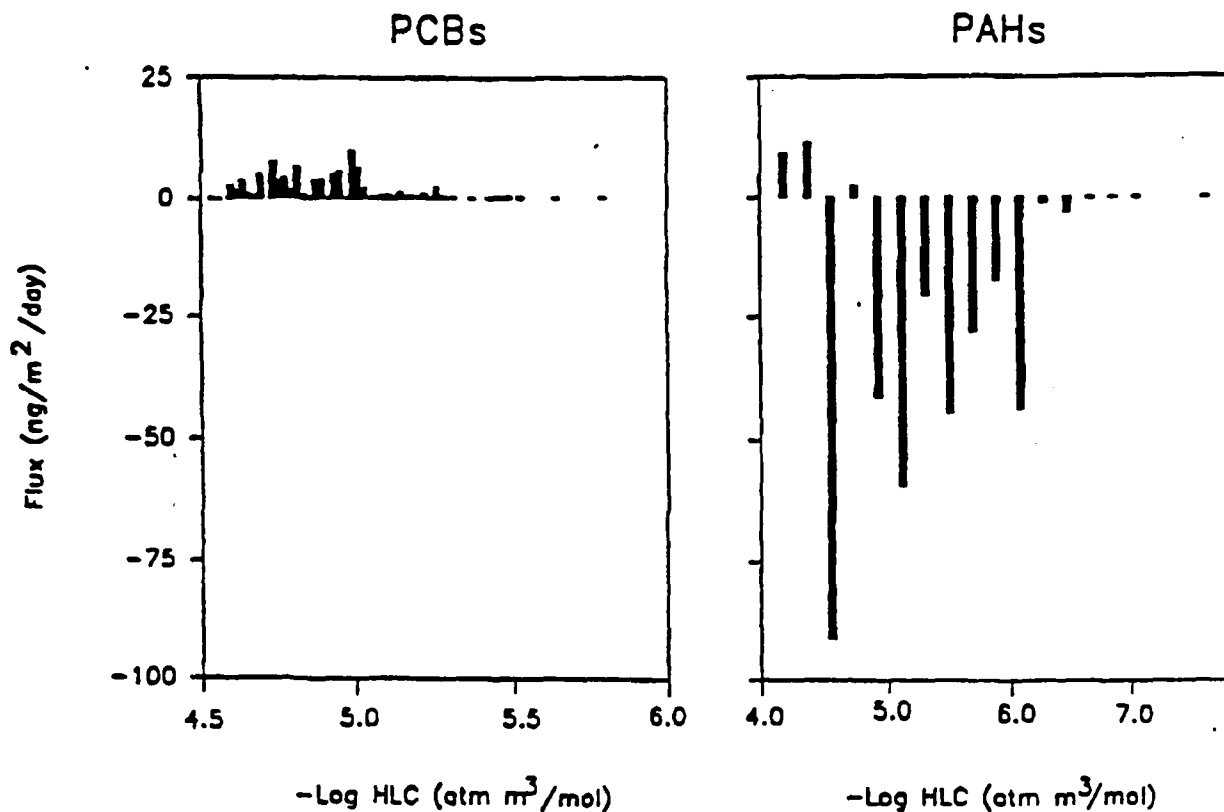
Site 10, October 22, 1989

Wind Speed = 6.5 m/s Water Temp. = 7.6 °C

PCBs   PAHs

−Log HLC (atm m³/mol)   −Log HLC (atm m³/mol)
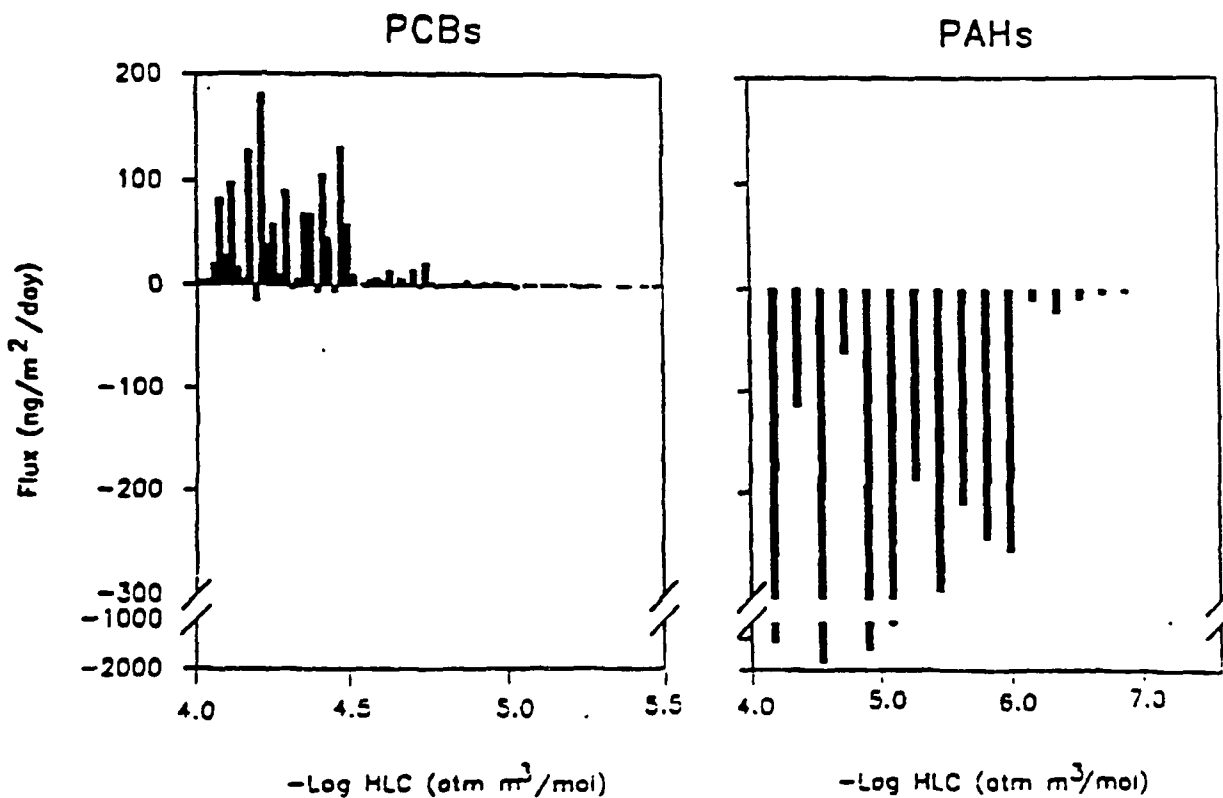
Figure 25. Air-water exchange fluxes of PCBs and PAHs, Green Bay

atmosphere and contribute to global distributions.

7.0 EVALUATION OF CURRENT SAMPLING AND ANALYTICAL PROCEDURES

7.1 TRACE ELEMENTS - Evaluation of current methodologies

7.1.1 Atmospheric Sampling - trace elements

The major techniques used to measure aerosol trace element concentrations include filtration collection on polycarbonate/Teflon filters. Often this is proceeded by differential size separation using dynamic or kinematic techniques such as successive nests of cascade or orifice impactors. The limitation of such filtration techniques is that they either exclude the finest fraction below the filter cut off where higher concentrations of trace elements exist, or they fail to collect the largest fraction where most of the depositional mass exists. Analysis of the filters include direct neutron activation, x-ray fluorescence, or digestion followed by graphite furnace atomic absorption spectroscopy. inductively coupled plasma emission spectroscopy, etc. Dry deposition of aerosols can be measured by exposure of surrogate surfaces of various types, analyzed similar to filters, as mentioned in the previous section of dry deposition of nitrogen.

7.1.2 Precipitation Sampling - trace elements

Due to their typically low concentrations and high potential for contamination, the accurate determination of trace elements in the atmospheric environment requires special equipment, rigorous procedures, and sensitive analytical equipment. Reviews of the historical data on the concentration of trace elements in precipitation (Galloway *et al.* 1982; Barrie *et al.* 1987) cast considerable doubt on the accuracy of reported values and efficacy the techniques utilized. In many of these studies, it is readily apparent that the authors failed to observe the requisite ultra-clean sampling and handling precautions (*e.g.*, Bately and Gardner 1977; Ross 1986), resulting in either gross contamination, or conversely, irreversible losses of certain metals (*e.g.*, lead) to container walls (Chan *et al.* 1983). Furthermore, many laboratories simply do not possess the capabilities to conduct routine analyses in the ng/L range. The reliability of most available databases on the trace metal concentration in precipitation are thus compromised, as are the resultant estimates of wet depositional fluxes.

Most of the first successful attempts to sample atmospheric trace metals were in

remote, open-ocean locations, and involved manual collections and meticulous handling precautions (*e.g.*, Duce *et al.* 1991). More recent studies over continental regions have been conducted using a wide variety of collection devices, handling procedures and analytical techniques. Several recent studies have attempted to specifically address the complexities involved in accurate determination of the trace metal concentrations in precipitation to derive standardized procedures (Ross 1986, Tramontano *et al.* 1987, Keller *et al.* 1988, Vermette *et al.* 1992, Scudlark *et al.* 1992). From these studies, several common considerations emerge:

1. Sampling must be conducted on a wet-only basis. Passive capture of dry fallout is a serious source of contamination. Likewise, bulk (wet + dry) sampling techniques are too easily corrupted to be considered reliable.

2. Polyethylene (LDPE or HDPE) and Teflon^R are the only materials that are compatible with sample contact.

3. To remove metal impurities present from manufacture or prior use, all plasticware must be scrupulously cleaned, which usually involves successive leaching in a series of acid solutions (HNO_3 and HCl).

4. To prevent (or reverse) the adsorption of certain metals on the plastic container walls, the sample must be acidified to below pH 2 with ultra-high purity acid.

5. Depending on the element and its concentration, analysis can be accomplished by a variety of techniques, including graphite furnace atomic absorption spectrophotometry, inductively-coupled plasma atomic emission spectrophotometry, mass spectrometry, and polarography.

Due to the typically low concentrations in precipitation and high potential for contamination, the accurate assessment of trace metals in atmospheric samples requires the strict adherence to a rigorous quality assurance program. Components of such a program should include the routine evaluation of procedural blanks, the use of externally-certified analytical reference samples (*e.g.*, EPA or NIST), and conducting inter-laboratory analytical comparisons, including the use of redundant techniques where possible. Operational blanks provide a comprehensive assessment of the background contamination during sampling and handling. A "field blank", which mimics actual sampling procedures as closely as possible, should be evaluated on a regular (*e.g.*, monthly) basis, or if there is a significant change in the personnel, methods, materials, site activities, or reagents associated with sampling. Such blanks can be utilized to identify and remedy any source of contamination, and to correct apparent precipitation concentrations for background trace metal levels. As a general rule, this correction is required only when the blank contribution exceeds 10% of the average metal concentration (an approximate limit of analytical confidence).

7.2 SEMIVOLATILE ORGANIC CONTAMINANTS - Evaluation of current methodologies

7.2.1 Atmospheric Sampling - SOCs

The separation of gases and particles in field studies is normally accomplished by passing air through a glass fibre, quartz, or membrane filter followed by a solid adsorbent such as polyurethane foam (PUF), XAD-2 resin, and Tenax GC. The filters are extracted and analyzed separately by gas chromatography with electron capture or mass spectrometric detection. The total concentration is the sum of the operationally-defined gas and particle SOC fractions. Yamasaki *et al.* (1982), Bidleman *et al.* (1986), Pankow (1987), and Bidleman (1988) suggest that the G/P distribution may be determined by C_p/C_g or A(TSP)/F which is a function of $p°$ and T. Sampling artifacts which alter the equilibrium G/P distribution such as "blow-off" from collected particles, sorption of gases onto the filter, and degradation and/or transformation of SOCs on the filter may be serious practical problems. The diffusion denuder (Lane *et al.* 1988, Coutant *et al.* 1989) is an alternative to the collection and speciation of SOCs. In a denuder, the gases and particles pass through a denuder section consisting of parallel tubes or concentric cylinders coated with an adsorbent efficient in trapping the SOC gas. The particles pass through the denuder and are collected on a filter. A diffusion separator is similar in theory but minimizes collection and analysis difficulties presented by the denuder and is under active research (Turpin *et al.*, 1992). In the diffusion separator, gases and particles are separated in a short tube based on diffusion differences, and the G/P distribution is determined from the fraction of SOC collected in the annular and core flow in comparison to theory. The denuders should offer definitive data on the G/P distributions in the atmosphere.

7.2.2 Precipitation Sampling - SOCs

Previous studies have used bulk (Glotfelty *et al.* 1991, Webber 1983, EPA 1991) and wet-only (McVeety and Hites 1988, Ligocki and Pankow 1985a, 1985b, Franz *et al.* 1991, Duinker and Bouchertall 1989, Chan and Perkins 1989, Brun *et al.* 1991, Murray and Andren 1992) deposition samplers to collect SOCs in precipitation. Total depositional fluxes estimated from bulk deposition samples are generally quite high, strongly influenced by local contamination, and thought to be unrepresentative of actual depositional rates.

Franz *et al.* (1991) systematically evaluated the performance of several SOC precipitation samplers. Samplers with Teflon-coated and stainless steel collection surfaces, adsorbent and solvent-based isolation systems, and with or without filters were codeployed in central Minnesota for one year. Aside from operational problems (*e.g.*, blown fuses, faulty motors), all samplers efficiently collected SOCs in precipitation. Precipitation frequently backed-up in the sampler

which relied upon gravity to pull the water through an in-line filter, resulting in possible revolatilization of the SOCs. While the solvent-based isolation system (Chan and Perkins 19xx) was efficient at collecting SOCs from precipitation, higher blank levels and problems with transporting solvents may limit the use of this system. The study of Franz *et al.* (1991) and others (Murray and Andren 1992) suggest that rough and hydrophobic Teflon-coated collection surfaces retain particles from precipitation and may adsorb gaseous phase HOCs from the atmosphere. A major problem identified by Franz *et al.* was the relatively small sample sizes collected by their samplers which had collection surfaces ranging from 0.081 to 0.2 m², complicating measurement in the sub-ng/L range.

A wet-only precipitation sampler which automatically collects rainfall and isolates and preserves target HOCs, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and current use agrichemicals is currently in use in the Chesapeake Bay Atmospheric Deposition Study (Leister and Baker, 1993) is designed to operate automatically without intervention for two weeks and meets the following criteria:

1. Wet-only collection. The sampling train is opened to collect precipitation during events, but remains sealed during dry periods to prevent inadvertent contamination.

2. Large sample size. Anticipated HOC concentrations in precipitation range from pg/L to ng/L. To insure that the samples which are collected contain HOCs in excess of the analytical detection limits, this sampler generally collects more than 10 L of precipitation during each deployment period.

3. Inert sampling train. Due to the low analyte levels in the samples, the sampling train is constructed of inert materials (stainless steel and Teflon) to avoid contamination of the samples during the deployment. The sampling train must be cleaned with solvents in the field between samples.

4. Immediate, *in situ* isolation of HOCs from the precipitation. Once collected, HOCs in precipitation may revolatilize, especially if the sample warms during storage. In addition, redistribution of HOCs between dissolved and particulate phases may occur. To limit these artifacts, the particulate and dissolved HOCs are isolated and preserved during each precipitation event.

5. Automated operation. This sampler is to be deployed unattended in the field for at least two weeks.

The sampling train of the CBADS sampler consists of a 1 m² funnel constructed from polished 316 grade stainless steel. The neck of the funnel is attached to a stainless steel vertical tube containing two liquid level sensors followed by a filter holder assembly, which in turn is connected to a resin column. Water is pulled through the sampling train by a peristaltic pump

downstream from the resin column, and stored in a reservoir. The sampling train is covered by a aluminum lid during dry periods which is swung away from the funnel at the beginning of each precipitation event. This sampler has been in continual operation for 2-1/2 years on the shoreline of the Chesapeake Bay, allowing wet depositional fluxes and SOC speciation to be measured.

7.3   MERCURY

The wide spread human-health and environmental worries with mercury as a global and local pollutant has led to growing improvements in the quality of mercury determinations in the environment. It was painful to recognize the extent of inaccurate environmental mercury measurements, particularly in atmospheric and aquatic investigations. Such flaws have been an impediment to understanding the biogeochemical cycling of mercury and assessing the influence from anthropogenic inputs of mercury. The need for accuracy, and high quality, critical experimental designs which incorporate ultra trace-metal clean sampling and analytical protocols must be recognized by scientists involved in mercury research. Here we will present a summary of the state-of-the art with respect to the determination of mercury in the atmosphere and natural waters.

7.3.1   Atmospheric Hg

In general, sampling techniques, apparatus, and protocols for the measurement of Hg in the gaseous and particulate phases follow the well-tested two-stage gold amalgamation methodology developed by Fitzgerald and Gill (1979) for oceanic studies. Briefly, air collections of particulate Hg are made using air filters having a nominal pore sizes approaching ca. 0.3 to 0.45 μm, which is in accord with traditional atmospheric analytical chemical practices. A variety of filter materials are used, including quartz wool plugs (e.g., Fitzgerald et al. 1992, Iverfeldt 1991a,b), quartz and glass fiber filters (e.g., Fitzgerald et al. 1983, Mason et al., 1992, Dumarey et al., 1979), polycarbonate, and teflon substrates. The airborne total gaseous Hg phase (TGM) is operationally defined as the quantity of Hg which passes through the filter and is collected on gold or gold-coated substrates, such as quartz sand or wool (Fitzgerald and Gill 1979; Slemr et al., 1979). The TGM phase has been successfully partitioned into its components using in-line arrangements of stacked columns containing selective adsorbents (e.g., gold; Carbosieve[R]: activated carbon, Carbotrap[R]). Initial partitioning studies indicated that TGM was composed principally of Hg° (Fitzgerald et al. 1981, 1983; Slemr et al. 1981). Most recently, chromatographic separation procedures have been applied to identify specific organo-mercury species, such as dimethyl mercury in addition to Hg° (e.g., Bloom and Fitzgerald 1988, Ballantine and Zoller 1984, Schroeder and Jackson 1984). Applications using the analytical technique developed by Bloom and Fitzgerald (1988) have provided most of the information on the chemical. speciation of the gas phase. The apparatus consists of three atmospheric Hg sampling trains stacks containing the following trapping materials, arranged in sequence to form

a sampling stack.

1. Particulate filter (*e.g.*, quartz wool) / Au (coated quartz sand): yields a total gaseous Hg determination (TGM).

2. Particulate filter (*e.g.*, quartz wool) / Carbotrap^R (graphitized carbon) / Au (coated quartz sand): provides a collection that can be used for direct Hg speciation determinations of alkylated Hg (i.e., MMHg; DMHg) by GC separation and atomic fluorescence detection (CTS).

3. Particulate filter (quartz wool plug): for particulate Hg determinations (PM).

The quartz wool/Au system provides a measure of the TGM concentration (Hg° + alkylated species), while the quartz wool/Carbotrap^R/Au yields a specific determination of the concentrations of DMHg and MMHg. Since Hg° is not trapped very efficiently on Carbotrap^R, most of the Hg° is found on the gold trap, and the total Hg° is obtained from the sum of both traps (Au + Carbotrap^R). Moreover, the sum of the organo mercury species and Hg° found in the Carbotrap^R / Au sampling train should equal the TGM from the separate gold collection. This provides a convenient mass balance constraint. Additional details associated with these various trapping materials can be found in Fitzgerald and Gill (1979), Kim and Fitzgerald (1986), and Bloom and Fitzgerald (1988).

The total gaseous mercury (TGM) analyses are generally conducted by the two-stage gold amalgamation technique (Fitzgerald and Gill, 1979) with detection by atomic fluorescence spectroscopy [(AFS); Bloom and Fitzgerald, 1988]. Currently, the overall atmospheric TGM methodology yields a detection limit of ca. 0.15 ng m^{-3} and a precision of between 10 and 15% at 1.5 ng m^{-3}, based on sample volumes ranging from 0.5 to 2 m^3. Particulate Hg is determined following pyrolysis of the quartz wool plug or filters and trapping on gold. Chemical speciation of the gaseous phase is achieved through analysis of the graphitized substrate (Carbotrap^R) collections using gas chromatographic separation and AFS detection (Bloom and Fitzgerald 1988). The detection limit for the determination of monomethyl mercury and dimethyl Hg is ca. 5 pg m^{-3} The particulate mercury can be analyzed using wet digestion procedures and derivatization with tetraethylborate to determine Hg$_T$, Hg$_R$, and MMHg following procedures to determine Hg species in precipitation (see below).

The precision of measurement can be readily improved by increasing the volumes of air sampled. A precision of < 5% can be achieved, and would be required, for example, to study a current question as to whether Hg° is presently increasing in the global atmosphere as a result of anthropogenic emissions. Indeed, in a recent controversial paper based on non-synoptic data from 7 oceanographic cruises of short duration, Slemr and Langer (1992) concluded that annual atmospheric Hg increases of ca. 1.5% for the Northern Hemisphere and ca. 1.2% for the Southern Hemisphere had occurred for the period between 1977 and 1990. While the inferred

increases do agree with expectations, the precision of measurement appears inadequate, and the experimental design does not account for short time scale variations of both a natural and anthropogenic origin. For example, in a two-month study, Fitzgerald and co-workers (1989) found variations in atmospheric Hg concentration over the northeast Pacific ocean that were comparable to the changes reported for the 13 year period in the Slemr and Langer work. Thus, the very important question of whether Hg is increasing in the atmosphere has not been properly addressed. The desirable approach would use a sampling and analytical strategy similar to the successful Atmospheric Lifetime Experiment Program (ALE). The ALE studies of contemporary temporal changes in the atmospheric concentrations of the freons, methyl chloroform and carbon tetrachloride (Golambek and Prinn 1986) show that two to three years of on-site continuous measurements are necessary to deal satisfactorily with questions of natural variability and to resolve the influence of pollution on constituents such as Hg^o in the atmosphere. In addition, measurements must be carried out in a network context. Stations should selected in both the northern and southern hemispheres. These locations must be remote from significant local and regional sources of Hg^o. For example, the ALE network used sites on the west coast of Ireland, Barbados, Hawaii (Mauna Loa), American Samoa (Cape Matatula), and Tasmania (Cape Grim).

7.3.2   Mercury: Precipitation Sampling and Analysis

At present, the preferred method for collecting rain for mercury studies is on an event basis by trained personnel employing ultra-clean techniques (Fitzgerald *et al.* 1991, 1992, Iverfeldt 1991a,b). Mercury has been examined in rainfall obtained on a autosampling basis (Glass *et al.* 1991) and in a total deposition mode (Lindqvist *et al.* 1991). The unattended collection approach is risky, requires preservatives, and often produces artifacts. Pyrex glass and Teflon collectors have been used quite successfully (*e.g.*, Fitzgerald *et al.* 1991, Iverfeldt 1991a,b, Mason *et al.* 1992). A light funnel constructed from a molded Teflon^R sheet, and contained in an acrylic housing, with a removable acrylic lid is described in Fitzgerald *et al.* (1992), and in Mason *et al.* (1992). It is designed so that rain entering the funnel contacts only Teflon^R parts which were rigorously acid-cleaned prior to use. The sampling protocol should include a continuous program of funnel washings and blanks to insure the integrity of each collection.

The following protocols are used by Fitzgerald and co-workers for rain and snow in the Mercury in Temperate Lakes (MTL) study. The ultra-clean and laboratory prepared rain apparatus (acrylic housing containing the Teflon^R funnel) is placed in an appropriately selected field site. The sampler had been sealed by large clean poly-bags as part of the laboratory preparation. Before sampling, and from a downwind position, the rain collector, wearing clean rainsuits and long poly gloves, removes and carefully stores the bags and acrylic lid. The funnel is rinsed with about 1 L Q water (subboiled distilled low Hg water), from a 2 L Teflon^R bottle that will be used as the collection bottle. The second 1-L aliquot of water is used to take a funnel

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blank. Half of the aliquot is rinsed through the funnel and collected and the other half is retained for analysis without passing through the funnel. As noted, these samples are used to test and monitor the funnels for artifacts and potential contamination. In general, there is no discernable difference between the concentration of Hg in the rinse water and the funnel blank. The funnel is exposed to the atmosphere for the duration of the event. Following the sampling, the rain collectors are carefully covered. An aliquot of rain for ethylation/speciation determinations is decanted into a 100 mL bottle prior to sample acidification. The 100 mL aliquot is frozen and stored for analysis.

Snow samples are taken by scooping snow directly into 1 L Teflon^R jars as soon as possible after a significant snowfall (at least three inches of fresh snow). Great care is taken to maintain sample integrity during collection and shipment. During snow collection operations, the sampling personnel wear particle-free nylon suits (reserved for snow collection) and use arm-length plastic gloves. Snow is collected moving into the wind and away from possible contamination. The jars are wrenched tight, stored, and transported frozen to await analysis. The snow samples for Hg_R and Hg_T determinations are acidified with analyzed reagent grade HCl in a Class 100 clean laboratory, resealed and allowed to thaw at room temperature. The sample for chemical speciation is allowed to thaw without acidification. The samples are analyzed immediately after thawing.

Three different procedures are used in the analysis of rain and snow samples and these measurements provide information on the forms of mercury in precipitation. All procedures rely on the production of volatile Hg species in solution, which are then purged from solution with inert, Hg-free gas and trapped on adsorbing substrate. The determination of "reactive" or "acid-labile" mercury (= Hg_R) involves sample acidification to pH = 1, reduction of ionic Hg and labile Hg to Hg° with $SnCl_2$, aeration of the solution and collection on Au (Gill and Fitzgerald 1987b). The determination of "total" Hg (Hg_T) is similar to the reactive Hg procedure after sample pretreatment with a strong oxidant, BrCl, followed by reduction of the BrCl with $NH_2OH-HCL$, before $SnCl_2$ reduction, sparging and collection on Au (Bloom and Crecelius 1983). Oxidation of the solution with BrCl destroys many strong organo-metal associations and decomposes monomethyl mercury, rendering bound Hg available for $SnCl_2$ reduction. The procedural blank for the reactive Hg determination is 0.025 ± 0.010 ng and the sample size is generally 250 mL, resulting in a detection limit (defined as 3 x the standard deviation of the blank) of 0.5 pM. The blank associated with the oxidation technique is 0.1 ng ± 0.03 ng for a 250 mL sample with a corresponding detection limit of 2 pM. The operationally defined species of Hg based on the wet digestion and reduction/sparging procedures are summarized in Figure 26 (adapted from Lindqvist *et al.* 1991). The operational definitions are given in the figure; we note that Hg-IIa is identical to Hg^R as defined in the MTL studies.

Quantification and identification of mercury species in precipitation involves the ethylation of dissolved Hg in solution using sodium tetraethylborate. The volatile ethyl-Hg derivatives, as well as other volatile Hg species in solution (i.e. Hg° and dimethylmercury) are purged from
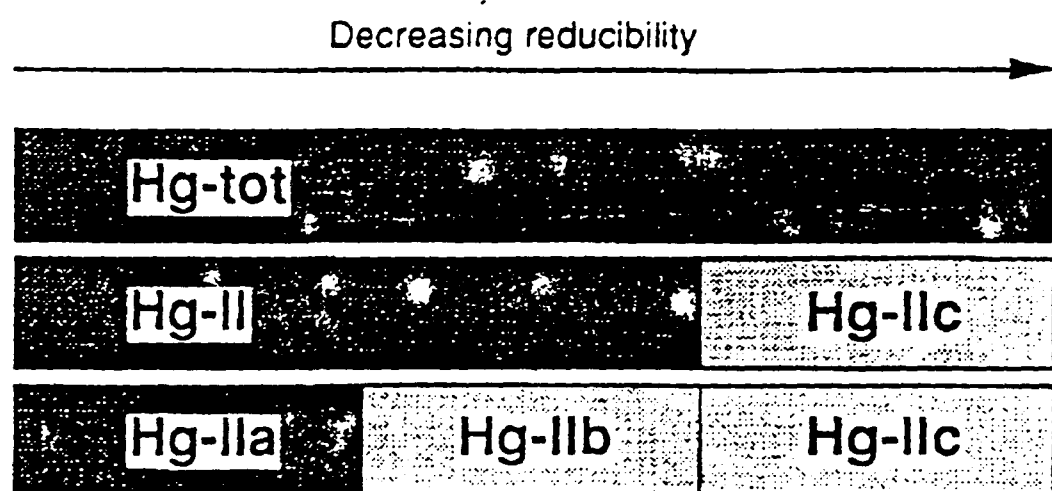
Figure 26. Operationally defined species of Hg based on the wet
digestion and reduction/sparging procedures (adapted
from Lindqvist et al., 1991).

solution, concentrated on Carbotrap[R], separated by cryogenic GC, and detected by atomic fluorescence. The details of the procedure are outlined in Bloom (1989). This method allows for the identification and measurement of methylmercury, as methylethylmercury, labile Hg(II), as diethylmercury, and dimethylmercury and elemental mercury without ethylation. The detection limits are 0.05 pM for methylmercury, and 0.1 pM for Hg(II).

7.3.3 Dissolved Gaseous Mercury in Natural Waters

Geochemical and analytical details associated with investigations the cycling of volatile Hg can be found in Vandal et al. (1991), Fitzgerald et al. (1992), Mason et al. (1992), Xaio et al. 1991). Briefly, lake water and seawater are collected with Teflon[R] coated Go-Flo[R] sampling bottles suspended from Kevlar[R] hydrographic line, using plastic or Teflon[R] weights and messengers. The bottle integrates ca. 1 m depth range. The water is analyzed immediately (ca. 1 to 3 hr) in the clean laboratory, and the samples are maintained near their in-situ temperature until analysis. Dissolved gaseous mercury (DGM) measurements are made by sparging the volatile species from solution using Hg-free argon and trapping on either Au or Carbotrap[R] without pretreatment of the sample. The collection of Hg on Au allows for the measurement of total DGM, and CTS collection allows for separation and identification of the volatile dissolved species by cryogenic GC with AFS detection. The samples are purged in a 2-L pyrex bubbler, and a total sample volume of 4-L is used for each determination. The detection limit for total DGM is 5fM (femtomolar) and 3fM for dimethylmercury.

7.4   NITROGEN

7.4.1   Atmospheric Sampling

Measurement of ambient concentrations of nitrogen species can be divided into two groups based on the reactivity of the nitrogen species. Highly reactive species, such as NO, NO_2, and PAN, which have lifetimes on the order of minutes to hours, must be measured *in situ*. The more stable constituents, such as HNO_3 and particulate NO_3 are typically collected on filters and subsequently analyzed.

A recent review of five major techniques for measuring gas-phase atmospheric NH_3 (Williams et al. 1992) suggests that such measurements can be reliably and accurately performed. However, a similar review of 18 techniques for determining atmospheric HNO_3 concentrations (Hering et al. 1988) indicated a general lack of agreement between the methods (by as much as a factor of four). Very little is known about the deposition of other potentially important airborne nitrogen species, especially NO_2 and PAN (peroxyacetyl nitrate). Thus, for the major nitrogen dry deposition, there would appear to be considerable uncertainty in fundamental measurement.

7.4.2   Precipitation Sampling

The procedures for determining wet deposition are more established, technically less difficult and inherently less uncertain than those for dry deposition. Consequently, in constructing mass balances, estimates of wet loading are fairly well constrained. Largely the result of intense investigations of acid rain, reliable, automated wet-only samplers have been developed for the collection of precipitation for chemical analysis (Galloway and Likens 1978). Similarly, techniques for quantifying the major inorganic nitrogen components in precipitation are common (Technicon 1973, DIONEX 1981).

One uncertainty in estimating nitrogen wet deposition is in integrating the spatial and temporal variability. For example, data compiled by Jaworski *et al.* (1992) for atmospheric nitrogen deposition at ten sites in the Chesapeake Bay watershed varied from 5.8 to 18.1 kg/ha/yr. The data of Fisher *et al.* (1988) varies from 5.68 to 8.49 kg/ha/yr. A similar assessment for six sites in the Delaware Estuary watershed (Scudlark and Church 1993) revealed a 50% variability in the NH_4^+ wet flux and 30% variability in the NO_3^- wet flux.

8.0   CASE STUDIES

8.1   MASS BALANCE OF TRACE ELEMENTS IN ESTUARIES

Estimating the relative atmospheric input and throughput of toxics in an estuary requires some assumptions which has severely limited the accuracy of such estimates in the past. For trace elements, wet and dry deposition to entering the watershed can be largely assimilated by vegetation and soils. Dry fall out accumulating in forest canopies must await washout. The canopy itself can be a source or sink of trace elements, and vegetative ligands may complex and solubilize trace elements (Lindberg and Turner 1988). Likewise, watershed deposition either runs off with secondary weathering components or largely enters the local aquifer to become a ground water component of base flow in streams. Thus, the proportion of atmospherically-derived trace elements which actually cross the fall line into estuarine waters cannot be easily deconvoluted without special studies and the use of tracers. In any case, accurate long term fluvial trace element data are essential. This appears to be beyond the current capability of large-scale monitoring programs (Windom *et al.* 1991).

Much of the flux of trace elements into estuaries occurs during episodic or seasonally short periods of time that correspond to large storm events or spring freshets. Conditions of measurement during these periods of time are often difficult, if not impossible. As such, estuarine mass balances assume steady state between input and output fluxes which are not valid during transient periods of episodic input or seasonal variations. Under such conditions, non-steady state models based on continuity are required.   •

A mass balance of trace elements in the Delaware estuary has been performed using a number of estimates and assumptions (Church 1988). The trace element sources were taken from the following data sets. The primary fluvial flux was calculated as the seasonally averaged concentration at the zero salinity end member times the riverine discharge. In this sense, any ground water fluxes downstream of this point were ignored. Some unknown quantity of the fluvial flux actually includes atmospheric fallout into the watershed. The secondary source from surrounding salt marshes was based on the non-conservative maximum concentration in a representative tidal creek times the net exchange volume of the tidal wedge integrated over the tidal cycle. The primary components of this flux come from both atmospheric fallout into the marsh watershed and from the diagenetic release of sedimentary components. Such components can enter the salt marsh with both upstream terrestrial and downstream marine particulate matter. The oceanic tidal inputs to the bay are hard to quantify but have been attempted using a two layer model and salt balance (Church et al. 1986). Using such an approach, one can close the balance between the trace element sources (rivers and salt marshes) and the sinks (sediment burial and oceanic export) from the Delaware estuary within a factor two. It is thought that the major unknown source in this balance may be that which enters from ungauged ground water whose concentration and flux may be as great as that in the gauged fluvial sources.

The calculations of the percentage atmospheric sources for the Delaware estuary (Table 9) show that there is an net excess (atmospheric versus fluvial sources) of trace elements falling into the watershed versus that which crosses the fall-line. The exception is manganese which shows "negative excess" indicating other sources, which may include weathering, vegetative sources, and benthic flux from the sediments. The amount of trace elements falling directly onto the surface water of the Delaware Bay is small relative to the amount entering by fluvial means. However, as stated above, the fluvial and salt marsh component may include both atmospheric and groundwater components. Again, estimating tidal oceanic inputs, which requires accurate estimates of residual circulation are the largest source of uncertainty in estuarine trace element budgets.

8.2   MASS BALANCE OF SOCS: A PCB BUDGET FOR LAKE SUPERIOR, 1986

The components of a mass balance in aquatic systems such as the Great Lakes are shown in the Figure 1. A mass balance constructed about the water column provides an understanding of the transport and distribution of the chemicals in the lake, an estimate of the residence time that a contaminant is in the ecosystem or any of its parts, and the essential framework for determining the *relative* importance of various input or output sources. Of the potential hydrophobic organic chemicals for which the mass balance can be demonstrated, PCBs have been studied the most because of their bioaccumulation, persistence, ubiquitous distribution in the environment, and alleged toxicity. Eisenreich and co-workers (*e.g.*, Eisenreich, 1987; Baker and Eisenreich, 1990; Baker *et al.*, 1991; Jeremiason *et al.* 1993) have accumulated sufficient

information on Lake Superior that a PCB budget may be constructed and is, therefore, a good example of the paradigm. Lake Superior is the second largest lake on earth after Lake Baikal, is the largest of the Great Lakes possessing >50% of its water volume and approximately 20% of the surface freshwater on earth, has a large lake area to watershed ratio, has a long water residence time of ~ 170 years, is oligotrophic, and is driven primarily by atmospheric interactions (for PCBs). Inputs to the lake include riverine flows (includes municipal/industrial discharges) and atmospheric deposition. PCBs may be lost from the lake by riverine flow (St. Mary's River), sedimentation, degradation, and volatilization.

The inventories of PCBs in the Lake Superior ecosystem are estimated to be:

atmosphere:	~200 kg (~1.2 ng/m^3)
water column:	~7200 kg (~0.6 ng/L)
sediment:	~5000 kg (~6 ng/cm^2)

Riverine inflow and outflow are estimated to contribute 20 to 50 kg/yr and 40 kg/yr, respectively, to the mass balance. Eisenreich and Strachan (1992) estimate that atmospheric deposition of PCBs in the late 1980's was ~167 kg/yr, 125 kg/yr in wet deposition, and 32 kg/yr in dry particle deposition. The burial of PCBs in bottom sediments is ~10 to 50 kg/yr based on detailed analysis of Pb-210 dated sediment cores over the whole lake (Eisenreich, 1987; Baker et al., 1991; Jeremiason et al., 1993). The assumption is made that chemical and biological degradation reactions are negligible in the mass balance. PCBs are lost from the lake by volatilization at a rate of about 600 to 4200 kg/yr (Baker et al. 1990) based on air-water gradients and estimated mass transfer coefficients. Swackhamer et al. (1988) estimated PCB volatilization from Siskiwit Lake on Isle Royale in Lake Superior to be about 720 kg/yr. Measurements of water column PCBs since 1978 suggest a linear loss rate of ~800 kg/yr (1.3 ng/L in 1978 to 0.18 ng/L in 1992). Using the decrease of PCB concentrations in the water column in the mass balance (below) suggests volatilization is about 670 to 750 kg/yr. Assuming the mass budget is balanced by volatilization, then:

INPUTS-OUTPUTS-WATER COLUMN LOSS = VOLATILIZATION = 670 - 750 kg/yr.

According to this mass balance calculation, atmospheric deposition contributes 77% to 89% of 1986 inputs, similar to the earlier calculations of Strachan and Eisenreich (1988). PCB Losses from the lake occur primarily by volatilization which represents nearly 90% of total losses; sedimentation represents only about 5%. This funding is consistent with the earlier calculations of Strachan and Eisenreich (1988), is near the lower end of that estimated by Baker and Eisenreich (1988), and about equal to the estimate of Swackhamer et al. (1988) based on their Siskiwit Lake studies. Given the magnitude and uncertainty of the field measured volatilization rates, this process represents a critical need in the relative loading paradigm.

The estimated residence time (1st order) of PCBs in the water column of Lake Superior

based on the decrease in concentrations over the last 10 to 15 years is 5 to 6 years (Jeremiason *et al.*, 1993). The majority of the decrease in water column concentrations is attributed to volatilization, the rate of which will decrease with decreasing water concentrations. Based on an ecosystem loss rate of 850 kg/yr and an ecosystem inventory of 12,400 kg, a steady state residence time is about 15 years. The system is, of course, not at steady state and the overall system response can only be correctly calculated using dynamic models showing changes in inputs, outputs, and inventories with time.

The mass balance paradigm is a necessary framework to estimate relative loadings of chemical constituents to lakes and estuaries. To correctly do so requires the measurement of concentrations, inventories, and fluxes over time in a precise and accurate manner to statistically demonstrate differences in absolute and relative loadings.

8.3   MERCURY MASS BALANCES

8.3.1   Wisconsin Seepage Lakes

The tropospheric cycling, deposition and air-water exchange of mercury are being investigated in the mid-continental lake region of Vilas County, northcentral Wisconsin (Fitzgerald *et al.* 1991, 1992, Vandal *et al.* 1991). The work is part of a multidisciplinary study of processes regulating the aquatic biogeochemistry of Hg in temperate lakes. The atmospheric Hg flux data were evaluated in a well constrained mass balance Hg budget that was developed for a representative seepage lake, Little Rock Lake (LRL). Little Rock Lake is an extensively studied clear water system that has been divided with a sea curtain into two basins, one of which was untreated (reference pH: 6.1) while the other (treatment) was experimentally acidified. The first year's results for the treatment basin are summarized in Figure 7, from Fitzgerald *et al.* (1991), and as adapted from MTL work to appear in Watras *et al.* (1993), and from preliminary budgets by Fitzgerald and Watras (1989), and Weiner *et al.* (1990).

The estimates of annual depositional fluxes noted for rain (4.5 ± 2.0 μg m^{-2} yr^{-1}), snow (2.3 ± 0.3 μg m^{-2} y^{-1}) and dry deposition (3.5 ± 3.0 μg m^{-2} yr^{-1}) yield a total Hg deposition of 10.3 ± 3.6 μg m^{-2} yr^{-1} for the temperate lake environs. This budget shows that the measured total atmospheric Hg deposition accounts readily for the total mass of Hg in fish, water and accumulating in the sediments of Little Rock Lake. In this mass balance, the data for the fish and sediment were taken from Weiner *et al.* (1990) and the data for the water and seston were obtained from Watras *et al.* (1993). The budget is balanced and the atmospheric Hg exchange well constrained because the net deposition is balanced by the estimated accumulation of Hg in the sediments. In addition, the approximate net accumulation of Hg in the biota of LRL (ca. 0.06 g, assuming a 40% turnover) can be supplied by < 10% of the annual Hg deposition. Fitzgerald *et al.*, (1991) note that "the ecosystem appears delicately poised with respect to atmospheric inputs, since a relatively small fraction of the input readily accounts for the

estimated accumulation of Hg in fish." It is noteworthy that atmospheric deposition of total Hg to the LRL environs is comparable to the estimated depositional flux of Hg at 10 μg m^{-2} yr^{-1} for the northeast Pacific Ocean (Fitzgerald, 1989).

Gaseous Hg the atmosphere and water at LRL was found to be principally Hg° (Vandal et al., 1991). As shown in Figure 7, the evasional losses of Hg° are geochemically significant accounting for about 7% of the input to the treatment basin of LRL. Vandal et al. (1991) demonstrated the biogeochemical importance of Hg° evasion on a broader basis using experimental results from six temperate lakes including the reference and treatment basins of LRL. Seasonal variations were observed with the highest levels of supersaturation for Hg° occurring during the peak stratification period in August. A direct relationship between pH and the degree of saturation for Hg° was also indicated. For example, the evasion:1 flux of Hg° from the reference basin of LRL (1.5±0.9 μg m^{-2} yr-1) is about twice the value estimated for the treatment basin. Further, Fitzgerald, et al. (1991) proposed a reactive Hg(II) substrate hypothesis, in which they hypothesized that in-lake biological and chemical production processes for Hg° and monomethyl mercury were in competition for the reactive Hg substrate, which was suggested to be labile Hg (II) species (Hg$_R$). They postulated that once Hg° is produced in the aqueous phase, it is unreactive and eventually lost from the system. Thus, lakes with limnological conditions favoring Hg° production would be less likely to have elevated levels of Hg in the fish stock. In-lake production and water-air losses of Hg° might function as a potential amelioration mechanism that reduces the Hg$_R$ available for methylation. Conversely, higher biological levels of Hg may occur in lakes where Hg° production processes are inhibited by increased acidity.

Atmospheric depositional fluxes of monomethyl mercury (MMHg) were assessed in a less refined budget for the treatment basin of LRL (Fitzgerald et al. 1991). The atmospheric inputs were estimated using mean concentrations of MMHg observed in snow and rain, yielding 66±28 and 22±8 ng m^{-2} yr^{-1}, respectively, for an annual flux of 88±29 ng/m^2 -yr. While no dry deposition information for MMHg was available, the preliminary data for wet deposition suggested that atmospheric depositional fluxes were insufficient to account for the amounts of MMHg observed in biota. For example, assuming that the MMHg inputs from the atmospheric show a wet/dry partitioning similar to total Hg (i.e., 66% wet and 34% dry), then approximately 0.013 g of MMHg would be delivered to the treatment basin annually. This flux is about 22% of the estimated yearly MMHg accumulation in the fish stock. An in-lake synthesis of MMHg is implicated. This mass balance budget is illustrated in Figure 8, which has been developed using information from Fitzgerald et al. (1991), Weiner et al. (1990), Hurley et al. (1991a,b), Bloom et al. (1991), and Watras et al. (1993).

Additional data for atmospheric deposition of Hg in the Wisconsin MTL study have been reported by Fitzgerald and his co-workers (Fitzgerald et al., 1992). These data are summarized in Tables 25 and 26. The two year average broadens the basis for estimating Hg deposition in these environs. The inputs of Hg$_T$ and MMHg determined for the second year of the study are

TABLE 25

ANNUAL H_g DEPOSITIONAL FLUXES IN NORTHCENTRAL WISCONSIN BETWEEN OCTOBER 1988 AND OCTOBER 1990 (FROM FITZGERALD et al. 1992)

Hg Species	Wet Deposition μg m^{-2} y^{-1}		Dry Deposition μg m^{-2} y^{-1}	
	1988/89	1989/90	1988/89	1989/90
Total	6.8 ± 2.0	8.7 ± 3.7	3.5 ± 3.0	3.9 ± 3.8*
Reactive	2.5 ± 1.3	7.1 ± 3.5	No data	No data
Methyl	0.09 ± 0.03	0.07 ± 0.03	No data	No data

*Estimated from a yearly average of 25 ± 23 pg m^{-3} obtained from the measurements made in the winter and spring of 1989 and the summer data for 1990. A depositional velocity of 0.5 cm sec^{-1} is used (Fitzgerald et al. 1991).

TABLE 26

AVERAGE ANNUAL H₂ DEPOSITION TO LITTLE ROCK LAKE, WISCONSIN DURING OCTOBER 1988 TO 1990 (*DRY DEPOSITION NOT INCLUDED)

Hg Species	Annual Deposition $\cdot \mu g \ m^{-2} \ y^{-1}$
	Oct 1988 to Oct 1990
Total	11.5 ± 3.2
Reactive	$4.8 \pm 1.6^*$
Methyl	$0.08 \pm 0.02^*$

virtually the same as observed during the initial work. There is a significant difference in the deposition of Hg_R to the lake region between years and the authors demonstrate that differences in Hg_R inputs can have profound effects on the Hg° cycle. The role of atmospheric speciation and its relationship to the aquatic biogeochemical cycling of Hg° and MMHg is considered in Section 8.3.3 below.

8.3.2   Drainage Lakes in Sweden

Mercury fluxes to and from a model lake in southern half of Sweden are illustrated in Figure 9, which has been adapted from Johansson et al. (1991). The lake area is 1 km^2 and the drainage area is 10 km^2, and this proportion is representative of the average ratio for Swedish lakes. Wet deposition of Hg is estimated at 20 μg m^{-2} yr^{-1}, about 2.5 times the LRL value of 8 μg m^{-2} yr^{-1} (Table 25). The main source of Hg to the lake is via atmospheric deposition. As summarized in Figure 9, about 5 to 30% of the Hg input from the atmosphere (200 g yr^{-1}) to the catchment will enter the lake through runoff and this waterborne flux (10 - 60 g yr^{-1}) will represent between 50 and 100% of the input from wet deposition. The sediment accumulation of mercury will depend on size of the lake, its biological and chemical character, and on evasional losses (2 to 20 g yr^{-1}) of Hg at the water surface, which are estimated to range from 10 to 100% of the direct wet deposition of Hg (20 g yr^{-1}) to the lake.

There is broad agreement between the Swedish work and the results from the MTL program in Wisconsin. For example, simulation of the Hg flows into and out of a typical Swedish lake clearly demonstrates that atmospheric Hg deposition is the preeminent source of Hg to a drainage lake, and that evasional fluxes of Hg° are significant, although the estimates require refinement. One striking difference between the drainage and seepage lake modelling is the significant portion of the Hg input that is stored in forest soils of the catchment. On average, present atmospheric deposition is greater than the output of Hg in run-off waters by about a factor of 10. Thus, even if anthropogenic Hg inputs were to cease, modern Hg deposition that has accumulated in the soil would continue to be released to the lakes from the forest soils. Indeed, Johansson and co-workers indicate that 70 to 80% of the Hg in the catchment is anthropogenic (Lindqvist et al. 1991), and as a consequence, the watershed transport of Hg to the lakes will remain elevated for long periods of time, perhaps several centuries.

8.3.3 Atmospheric Mercury Speciation: Biogeochemical Implications

A biogeochemical coupling between Hg_R in atmospheric deposition and the Hg° cycle in lakes has been found in the MTL Wisconsin investigation. As discussed (Table 19), there was a substantial difference in the Hg_R composition in wet deposition between 1988-1989 and 1989-1990 and the associated yearly supply of Hg_R to the lakes. A comparison of the estimated inputs

was shown in Table 25. Approximately 3 times more active substrate was introduced in 1989-1990 relative to 1988-1989, yet the Hg_T inputs between years were similar. Indeed, a direct linkage between deposition of Hg_R and in-lake values of $Hg°$ can be demonstrated from the lake-air experiments conducted in the summers of 1989 and 1990. The biogeochemical significance of the in-lake cycling and evasional losses of $Hg°$ was shown by Vandal *et al.*, (1991). In general, the dissolved gaseous Hg (DGM) fraction in the Wisconsin seepage lakes consists principally of $Hg°$ with no significant contribution from volatile organic Hg species, (*i.e.*, dimethylHg [detection limit of 3 femtomolar (fM)]). Experimentally, the air-water partitioning of $Hg°$ is determined from simultaneous measurements of $Hg°$ in the atmosphere and in the lakes. The degree of saturation (%S) for $Hg°$ in lake water relative to the appropriate temperature-corrected equilibrium with the atmosphere (Sanemasa, 1975) is determined using the following relationship:

$$\%S = [(C_{water} \times H)/ C_{air}] \times 100 \qquad [13]$$

$$\%S > 100 = \text{supersaturation in water} \qquad [14]$$

where H = Henry's Law Constant for $Hg°$ and C_{water} and C_{air} = the concentration of $Hg°$ in water and air, respectively. A summary of the 1989 and 1990 $Hg°$ data from August studies in the Wisconsin seepage lakes is given in Table 27 (Fitzgerald *et al.* 1992). Notice that in 1990, the lakes were highly supersaturated with values near the surface ranging from 10.4 (S = 1040%) in Max Lake to 44.6 (S = 4460%) times the equilibrium level in Crystal Lake. In August 1989, supersaturation ranges were from ca. 1.4 to 12 times the saturation concentration. Thus, these large %S values will translate into higher lake to atmosphere fluxes of $Hg°$ than reported previously (Vandal *et al.* 1991). The water-air transfer of $Hg°$ is estimated from the thin film gas - exchange model using the following relationship.

$$F = K (C_{air} H^{-1} - C_{water}) \qquad [14]$$

where, F = gaseous Hg flux into (+) or out of (-) the lake, C_{air} = air concentration of $Hg°$, C_{water} = water concentration of $Hg°$, H = Henry's Law Constant, and K = transfer velocity, 1.5 cm hr^{-1} (0.36 m day^{-1}) for August, 1989 and 1990 (21°C to 24°C). Additional details for lake-air exchange of $Hg°$ calculations are given in Vandal *et al.* (1991).

A demonstration of the biogeochemical importance and dynamic nature of in-lake $Hg°$ production appears in Table 28, where the evasional fluxes from the northcentral Wisconsin study lakes in August 1989 are contrasted with the August 1990 results. In general, with the exception of Max Lake, effluxes of $Hg°$ are ca. 2 to 6 larger in 1990 and interlake differences are significant. Further, the atmospheric deposition of Hg_R was approximately three times

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TABLE 27

DEGREE OF SATURATION FOR ELEMENTAL MERCURY (Hg°) IN NORTHCENTRAL WISCONSIN LAKES

Lake	Date	Hg°(fM) Range	S (%) Range	S (%) Mean and Std. Dev.
Little Rock-Treat.	August, 1989	83 - 107	305 - 345	325 ± 28
Little Rock-Ref.		135 - 200	500 - 740	620 ± 170
Pallette Lake		60 - 355	140 - 1180	605 ± 530
Vandercook Lake		85 - 163	315 - 600	458 ± 202
Max Lake		283 - 297	990 - 1100	1045 ± 78
Little Rock-Treat.	August, 1990	181 - 490	920 - 2790	1703 ± 971
Little Rock-Ref.		214 - 358	1220 - 2040	1536 ± 441
Pallette Lake		92 - 640	340 - 3650	1476 ± 1370
Vandercook Lake		281 - 570	1630 - 3250	2440 ± 810
Max Lake		182 - 546	1040 - 3110	2075 ± 1035
Crystal Lake		90 - 785	350 - 4460	1583 ± 1953
Russett Lake		179 - 1035	660 - 4060	2033 ± 1484

TABLE 28

ESTIMATED AVERAGE EVASIONAL FLUXES FOR AUGUST 1989 AND AUGUST 1990 FOR VARIOUS NORTHCENTRAL WISCONSIN LAKES. FLUXES ARE IN pmol m^{-2} day^{-1}, CALCULATED USING A TRANSFER VELOCITY OF 1.5 cm hr^{-1} (0.36 m day^{-1})

Lake	Evasional Flux in August 1989 (pmol/m^2 day)	Evasional Flux in August 1990 (pmol/m^2 day)
Little Rock-Treat.	25	167
Little Rock-Ref.	50	120
Pallette	85	221
Vandercook	50	92
Max	98	57
Russett	-	143
Crystal	-	274
Average	62 ± 30	153 ± 75
Depositional Flux (Hg_R)	85	260
Depositional Flux (Hg_T)	304	301

greater in August, 1990 relative to August, 1989 (Table 28). The Hg_R input during August 1990 (260 pmol m^{-2}-day^{-1}) was much higher than that of August 1989 (85 pmol m^{-2} day^{-1}). Yet the total Hg (Hg_T) input was similar for both periods: 301 pmol m^{-2} day^{-1} versus 305 pmol m^{-2} day^{-1} (Table 28). A relationship between $Hg°$ evasion and the input of Hg_R is apparent, as the increases in $Hg°$ supersaturation appear to respond to the supply of Hg_R and not to Hg_T.

The principal source(s) of the high levels of supersaturation in the surface waters is not yet known. However, photocatalytic reduction of ionic Hg, bacterial demethylation reactions, organic matter and/or photosynthetic processes may all play a role. Fitzgerald et al. (1992) considered the two most probable sources of $Hg°$ (demethylation and direct reduction) in detail, and the results are illustrated in Figure 27, for (1) the estimated depositional Hg_R input and evasional fluxes of $Hg°$ for Little Rock Lake, (Treatment Basin) and Pallette Lake, respectively, in August 1989 and 1990, and (2) the probable sources of $Hg°$ - demethylation of $Hg°$ and direct reduction of Hg(II). The amounts of MMHg formed in the mixed layer was estimated using the measured epilimnetic Hg_R concentrations in August, 1989 (Bloom, pers. comm.) and measurements in 1990, along with water column methylation rates of 0.01' - 0.3% day^{-1}, determined from laboratory spike experiments (Xun et al., 1987; Korthals and Winfrey, 1987; Gilmour and Henry, 1991). The rate of $Hg°$ formation by demethylation of MMHg must be less than the MMHg formation rate. Thus, the calculations show that demethylation is a minor source of $Hg°$ in the epilimnion of the study lakes. Direct reduction of Hg(II) must be the primary source of $Hg°$ in the epilimnion of these lakes; a similar situation was found for the mixed layer of the equatorial Pacific (Mason and Fitzgerald 1992).

The observed evasion in Little Rock Lake Treatment Basin could be maintained by $Hg°$ formation rates of 8 x 10^{-7} sec^{-1} (7% day^{-1}) in 1989 and 3.3 x 10^{-7} sec^{-1} (2.8% day^{-1}) for 1990. At Pallette Lake, the observed evasion would require $Hg°$ formation rates of 3.3 x 10^{-6} sec^{-1} (28% day^{-1}) in 1989 and 1.4 x 10^{-7} sec^{-1} (1.2% day^{-1}) for 1990. Abiotic production of $Hg°$ (25 x 10^{-7} sec^{-1}; 22% day^{-1}) in the presence of humic acids has been demonstrated in laboratory studies (Alberts et al., 1974). Moreover, the reaction rates indicate that the system response to Hg_R input is rapid with a pulse input of Hg(II) converted to $Hg°$ in the absence of other reactions in about 70 days at a conversion rate of 5% day^{-1} ($t\frac{1}{2}$ = 14 days).

Although the $Hg°$ data is limited to one set of measurements at each lake in each season, these results support the postulate that the production, and subsequent evasion of $Hg°$, are directly linked to the rate of supply of Hg_R. The reactive Hg concentration, therefore, is a measure of the readily available substrate. These rates of conversion are similar to those estimated for the equatorial Pacific (Mason and Fitzgerald 1992), suggesting that analogous processes are involved in these two systems. The similarity between the Hg_T depositional inputs for both seasons suggests further that the unreactive, strongly bound Hg fraction is not directly available for conversion into $Hg°$. It is likely that the strongly bound fraction is transported into the anoxic regions of the lakes (the hypolimnion) or the sediment before any remobilization into a reactive form that can be converted into other Hg species.

AIR   PALLETTE LAKE, 8/89

Hg(II) DEPOSITION Hg^o EVASION
WET: 70   85
DRY: 15

< 1

MMHg ⟵ — Hg(II) ⟶ Hg^o
    < 1   85

PARTICULATE FLUX ↓ ca. 0 (by diff.)

THERMOCLINE   ALL FLUXES IN $pmol/m^2 day$

AIR   PALLETTE LAKE, 8/90

Hg(II) DEPOSITION Hg^o EVASION
WET: 215   221
DRY: 45

◄ 45

MMHg ⟵ — Hg(II) ⟶ Hg^o
    ·45   ►176

PARTICULATE FLUX ↓ 39 (by diff.)

THERMOCLINE   ALL FLUXES IN $pmol/m^2 day$
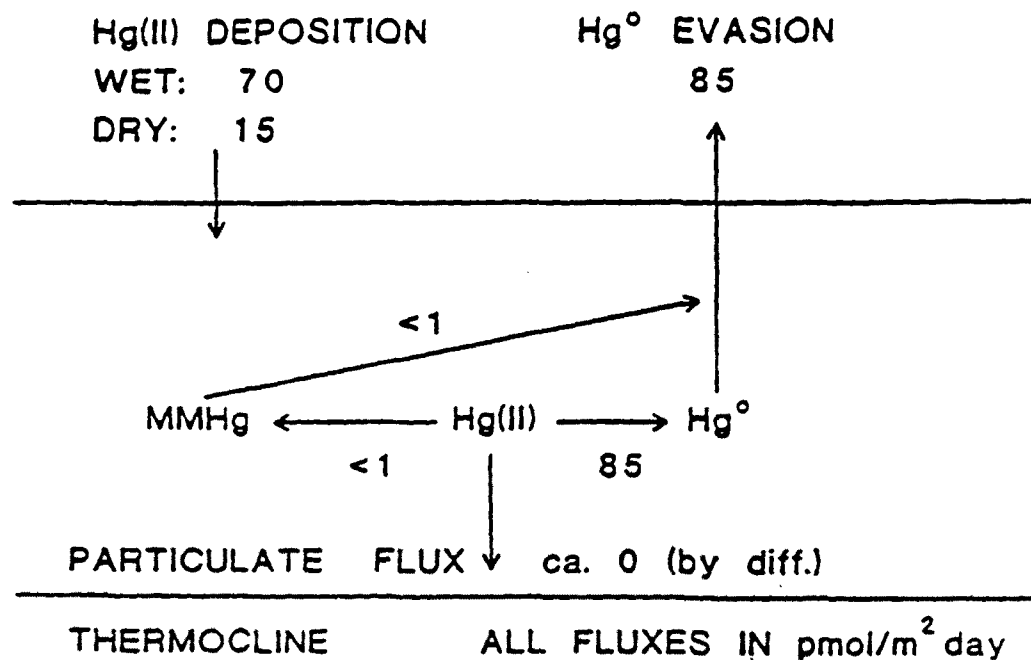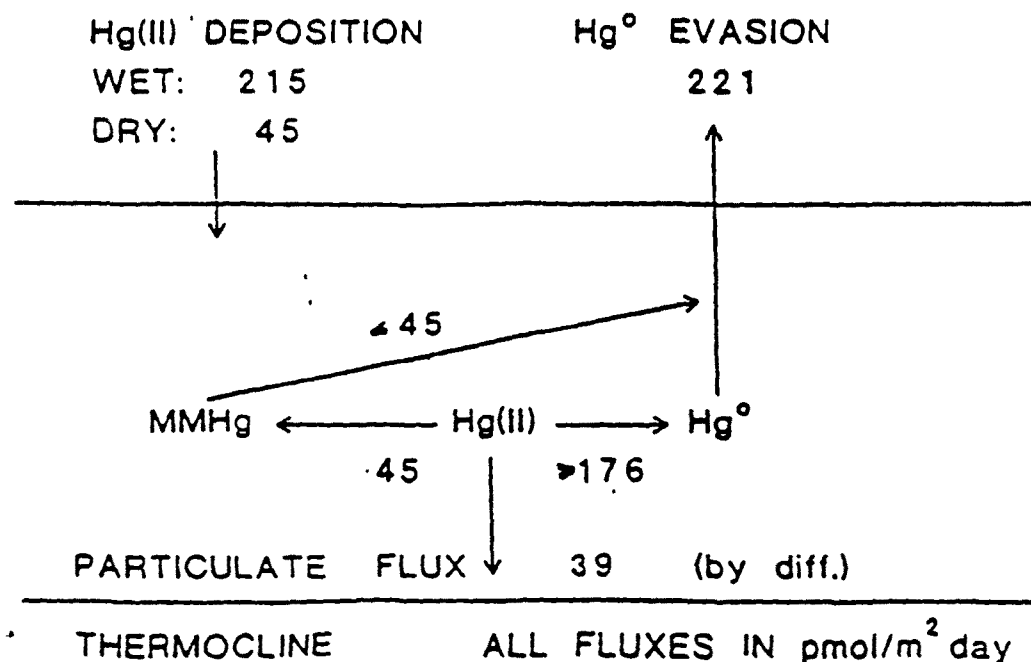
Figure 27b. Modelling the potential pathways for the production and evasion of Hg^o in epilimnion of Pallette Lake, Wisconsin. The amounts of Hg^o produced by demethylation and direct reduction of Hg(II) are estimated and related to the input of Hg_R by atmospheric deposition for the August 1989 and August 1990 experiments.

LITTLE ROCK TREATMENT, 8/89

Hg(II) DEPOSITION
WET: 70
DRY: 15

Hg° EVASION
25

<1

MMHg ← Hg(II) → Hg°
   <1   >24

PARTICULATE FLUX   60   (by diff.)

THERMOCLINE   ALL FLUXES IN pmol/m^2 day

LITTLE ROCK TREATMENT, 8/90

Hg(II) DEPOSITION
WET: 215
DRY: 45

Hg° EVASION
167

<15

MMHg ← Hg(II) → Hg°
   <15   >152

PARTICULATE FLUX   93   (by diff.)

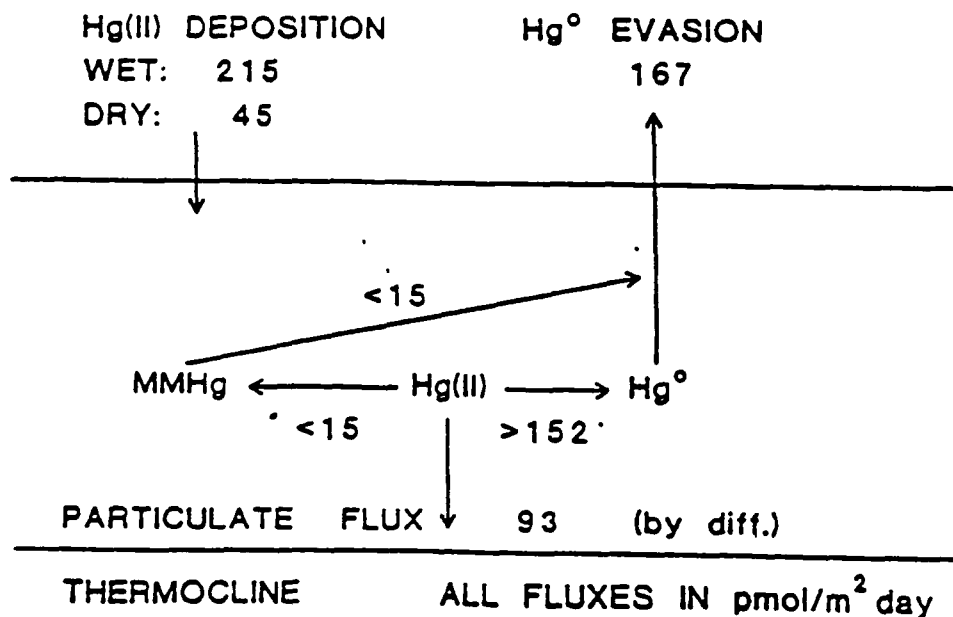THERMOCLINE   ALL FLUXES IN pmol/m^2 day
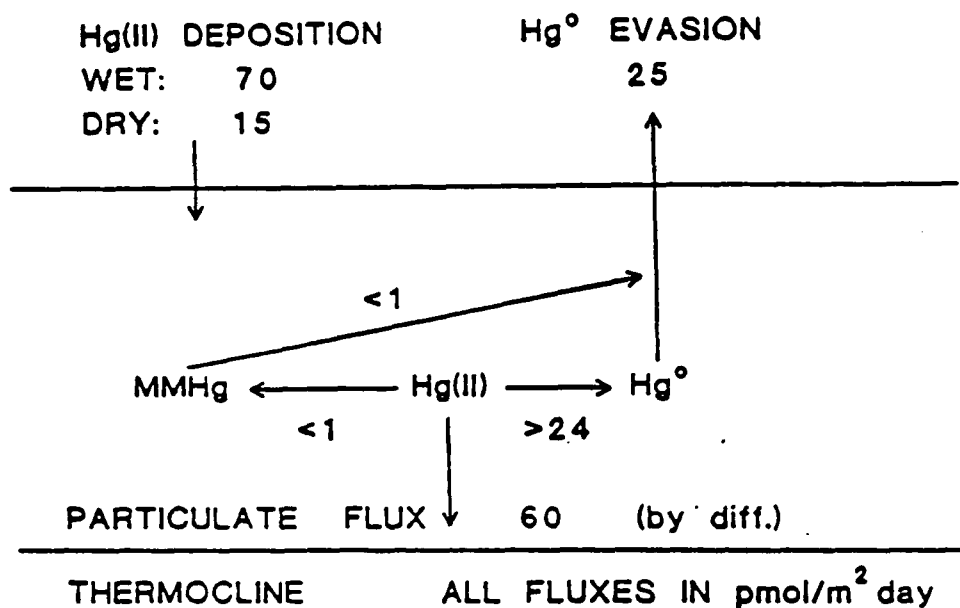
Figure 27a. Modelling the potential pathways for the production and evasion of Hg° in epilimnion of the treatment basin of Little Rock Lake, Wisconsin. The amounts of Hg° produced by demethylation and direct reduction of Hg(II) are estimated and related to the input of Hg_R by atmospheric deposition for the August 1989 and August 1990 experiments.

In the Wisconsin lakes, there was no significant increase in the Hg° concentration during winter ice cover (Vandal, pers. comm.). Iverfeldt (1988) attributed differences in the concentrations of dissolved gaseous Hg, reactive, and total Hg in Framvaren fjord between September 1983 and February 1985 to the lack of atmospheric input during ice cover. While the lack of Hg° formation under the ice could be interpreted as evidence of Hg° production being associated with a process requiring light (*i.e.* primary production or photo-reduction), it is also suggestive of substrate limitation in winter through the lack of atmospheric input. The results from these studies, Iverfeldt's work (1988) and Mason and Fitzgerald (1992) indicate that formation of Hg° in the mixed layer of natural systems is a direct function of the rate of supply of available Hg substrate.

In Table 28, the mass balances for the Wisconsin lakes show that with the exception of Max Lake, atmospheric inputs of Hg_R and Hg_T were larger than the evasional losses of Hg° during the August studies. Other processes removing (or sequestering) Hg_R from the mixed layer limit the available substrate. Particulate uptake and removal from the epilimnion is an important removal mechanism that can deliver substrate for methylation to the hypolimnion or the sediment interface. Net particulate fluxes required to balance the increase in Hg in the hypolimnion of Little Rock Lake Treatment Basin during summer stratification were estimated to be 55 pmol m^{-2} day^{-1} for the summer of 1989 (Hurley *et al.* 1991). This flux most likely accounts for the difference between atmospheric input and Hg° evasion and suggests that this process is a primary competing removal mechanism for epilimnetic Hg(II) substrate.

It is evident that the production and evasion of Hg° in natural waters is a major feature of the aquatic biogeochemical cycling of Hg. Significant effluxes of Hg° have been observed in seepage lakes in Wisconsin as well as in a diverse range of systems such as the open ocean equatorial Pacific (Kim and Fitzgerald 1986), Davis Creek Reservoir, California (Gill and Bruland, 1992), and drainage lakes in Sweden (Xaio *et al.* 1991). We note that Xaio *et al.* made direct flux measurements over soils and lake waters in Sweden, and annual Hg° fluxes from 2 to 20 μg m^{-2} yr^{-1} were estimated for lake regions and ≤ 1 μg m^{-2} yr^{-1} for the coniferous soils investigated. These lake-air fluxes of Hg° are 10 to 100 times the MTL estimates, while Gill and Bruland estimate Hg° emissions at 21 μg m^{-2} yr^{-1}. These higher fluxes coincide with the larger amounts of available Hg in the Swedish lakes and in Davis Creek. Moreover, Mason *et al.*, (1992) have shown that Hg° emissions to the atmosphere are proportional to the availability and supply of Hg_R (the Hg(II) substrate) whether it is atmospherically derived (as in seepage lakes) or supplied principally through upwelling (as in the equatorial Pacific). It is particularly striking that a large fraction of the Hg_R input to the northcentral Wisconsin lakes is returned to the atmosphere. Indeed, and suggested previously (Fitzgerald *et al.*, 1991), lakes with limnological conditions favoring Hg° production would be less likely to have elevated levels of Hg in fish. Moreover, there should be an inverse relationship between Hg° evasion and the accumulation of Hg in sediments for a particular lake (Rada *et al.* 1993).

Interlake variations in Hg° production and evasion are both expected and observed (Table

28). This is consistent with a general physicochemical view of the Hg(II) substrate hypothesis. For example, methylating and reducing processes compete to utilize Hg(II) species, and strong sequestering with organic ligands, or inorganic interactions (*e.g.*, with sulfitic ligands) could reduce the activity of the substrate. Thus, inorganic and organic components, suspended matter, pH, and biological productivity within a lake can alter the availability of the substrate. Vandal *et al.*, (1991) presented evidence suggesting that increasing acidity may reduce the in-lake production of $Hg°$, and that photosynthetic activity may enhance $Hg°$ production. Very few details of the processes affecting production and destruction of $Hg°$ are known. There are many questions concerning short-time scale spatial and temporal variability as well as the importance of photoreduction reactions and redox boundaries (*i.e.*, oxic/anoxic transition zones) in the production of $Hg°$. In addition, the relationships among phytoplankton productivity, microbial populations (*e.g.*, bacterial reduction) and the activity of $Hg°$ should be evaluated. Broadly based $Hg°$ investigations are required, particularly those including atmospheric speciation research, ancillary biological studies and concurrent methylation investigations. Seasonal and spatial data for atmospheric Hg deposition and the evasion of $Hg°$ are limited. This points toward a need to refine input to and efflux estimates from lake waters and to assess, quantitatively, their influences on the overall cycling of mercury in lake systems.

These observations illustrate the value of the chemical speciation approach to our developing understanding of the cycling of Hg in nature. Indeed, they force us to ask and address the following general question: How do such speciation changes in the depositional fluxes of Hg affect the cycling of Hg in aquatic systems, and what causes the variation in the Hg_T and Hg_R composition found in deposition? At present, there are no unequivocal answers to questions concerning the sources and variability of the atmospheric Hg species.

8.3.4 Summary of Mercury Mass Balances

Atmospheric deposition dominates the flux of Hg to lacustrine systems and the open ocean, and it appears that modest increases in atmospheric Hg loading could lead directly to enhanced levels of Hg in biota. The U.S. and Nordic studies of current and historical Hg deposition show broad agreement. Mid-latitudinal preindustrial depositional fluxes of total Hg were ca. 4 μg m^{-2} yr^{-1}, while present day annual fluxes may vary between ca. 10 μg m^{-2} yr^{-1} in rural semi-remote regions to > ca. 25 μg m^{-2} yr^{-1} in places where the presence of local/regional Hg sources is pronounced. The influence of anthropogenic activities on the total Hg cycling is evident, and site specific research must be conducted to assess the impact of human-related interferences in particular localities. However, the more important and subtle concerns are associated with the physical and chemical speciation of Hg deposition. For example, the presence of a significant regional particulate Hg cycle is found in specific chemical analysis of Hg in atmospheric particulate matter and precipitation. Fitzgerald *et al.*, (1991 and 1992) and Iverfeldt (1991a,b) have shown that significant portion of the total Hg in precipitation and in particulate matter is non-reactive to reduction with stannous chloride. Thus, a portion of the Hg_T observed in precipitation at Little Rock Lake and in comparable Swedish regions, is in a particulate form

which is not derived from the oxidation of Hg° in the atmosphere. Moreover, significant differences are evident in the deposition of Hg_R and differences in Hg_R inputs may have profound effects on the Hg° and MMHg cycle in natural waters.

8.4 NITROGEN MASS BALANCES IN COASTAL WATERS

8.4.1 Total Nitrogen

Fisher and Oppenheimer (1991) conducted a comprehensive assessment of the contribution of atmospheric nitrogen deposition to the Chesapeake Bay using two approaches which differed in their assumptions about watershed retention. In their first approach, non-point loadings to the bay (atmospheric, animal waste, sewage and fertilizer) were calculated assuming equal retention in the watershed. Their second approach takes into account the differential retention of nitrogen based on the different land uses and the differing mobility of nitrogen from each source. These authors conclude that 25% of the anthropogenic nitrogen loading to Chesapeake Bay is derived from atmospheric NO_3^-, with another 14% contributed from atmospheric NH_4^+. To address the uncertainties in watershed loading, Tyler (1988) utilized a "transmission factor" to account for two processes. The first, being the most variable, accounted for retention within the watershed, which was land-use specific. The second variable accounted for subsequent in-stream removal due to denitrification. Utilizing this approach, Tyler estimated that atmospheric deposition contributed 19-25% (with about a factor of two uncertainty) of the nitrogen loading to the Chesapeake Bay.

Using an approach similar to Tyler's, but with more refined estimates of watershed retention and in-stream removal, Hinga et al. (1991) contrasted the relative atmospheric loading to four coastal ecosystems, including the Chesapeake Bay. This study also reported high and low estimates based on varying assumptions. This sensitivity analysis revealed widely divergent results (as much as a factor of 50). Overall, their "best estimate" prediction for the Chesapeake Bay supports the earlier results of Fisher et al. (1988), concluding that atmospheric deposition supplies 35% of the nitrogen loading. Estimates for other estuaries range from 12% (Narragansett Bay) to 100% (Ochlockonee Bay), with this difference primarily reflecting differences in the degree of urbanization and land use.

A major shortcoming common to the above studies is that atmospheric deposition was evaluated relative to sources only. However, in terms of ecological impact and overall nutrient dynamics, the throughput of nitrogen, including a consideration of estuarine sinks, is as important as the gross atmospheric loading. For example, while the nitrogen loading to the Delaware Bay is estimated to be 10 times greater than the Chesapeake (Nixon et al., 1986), the assimilatory capacity in the Delaware is considerably greater.

Jaworski *et al.* (1992) have recently attempted a process-oriented mass balance approach by evaluating nitrogen inputs and outputs to the Potomac River Basin, a sub-estuary of the Chesapeake Bay. Of the five major source terms estimated based on direct measurements, they concluded that atmospheric deposition provided 28% of the total nitrogen loading. Scudlark and Church (1993) have examined atmospheric deposition to the Delaware Bay, a more heavily urbanized coastal plain estuary adjacent to the Chesapeake Bay. They conclude that atmospheric deposition provides about 16% of the nitrogen input on an annual basis. However, during late spring and early summer, when the estuary is most nitrogen limited due to maximum rates of primary productivity, atmospheric deposition is estimated to provide 25% of the total nitrogen loading (Figure 28). The greater atmospheric contribution during summer is attributed to increased atmospheric loading (Figure 28) coupled with minimum fluvial inputs because of low river flow.

The ecological consequences of atmospheric nitrogen deposition is not limited to estuarine waters. In fact, it is estimated that as much as 25% of the nitrogen oxide emissions from North America are advected eastward over the western Atlantic Ocean (Galloway and Whelpdale 1987), where they may be efficiently scavenged and deposited (Luke and Dickerson 1987). In coastal (Paerl 1985; Paerl *et al.* 1990) and Gulf Stream (Willey and Cahoon, 1991) waters, atmospherically-derived nitrogen inputs have been shown to enhance primary production. It has also been suggested (Paerl 1988; Fanning 1989) that atmospheric inputs of inorganic nitrogen is inducing in an ecological shift by oceanic phytoplankton from nitrogen to phosphorus limitation (presumably with an accompanying shift in species composition as well). This suggestion is challenged by Jickells *et al.* (1990).

Assessments of atmospheric deposition of nitrogen to oligotrophic waters in the open ocean (Paerl 1985, Knap *et al.* 1986) over an annual time frame suggest that aeolian input provides only a minor influence compared with upwelling (the primary source of available nitrogen far from fluvial influence). However, evaluation of this impact on shorter time scales (Owens *et al.* 1992, Micheals *et al.* 1992) suggest that during episodic events, atmospheric deposition can result in a significant fraction of "new production."

From an oceanographic perspective, nutrient input from shelf exchange processes represents potentially significant source of inorganic nitrogen to estuarine waters which recent published reports (*e.g.*, Tyler 1988, Fisher *et al.* 1991, Hinga *et al.* 1991) have neglected to consider. Hydrologically, classic two-dimensional estuarine exchange involves the net seaward transport of lower salinity water near the surface, with a compensating inflow of higher salinity shelf water along the bottom. For many estuaries, such as the Delaware (Galperin and Mellor 1990) and the Hudson (Oey *et al.* 1985), this two-dimensional exchange results in a net flux (excluding tidal fluxes) of bottom water and associated nutrients into the estuary. Although the bottom water nitrogen concentration is typically small when compared with that in surface water, the large volume flux of water into the bay can result in a large nitrogen input. Consequently, as discussed by Scudlark and Church (1993), such residual circulation may provide a major

Annual

Municipal/Industrial 41.0%

Salt Marsh2.0%

Benthic19.0%

Direct Atmosphere5.0%

Indirect Atmosphere9.0%

Combined LB Rivers 7.0%

Delaware River17.0%

Summer

Municipal/Industrial 49.0%

Combined LB River 4.0%

Benthic14.0%

Direct Atmospheric10.0%

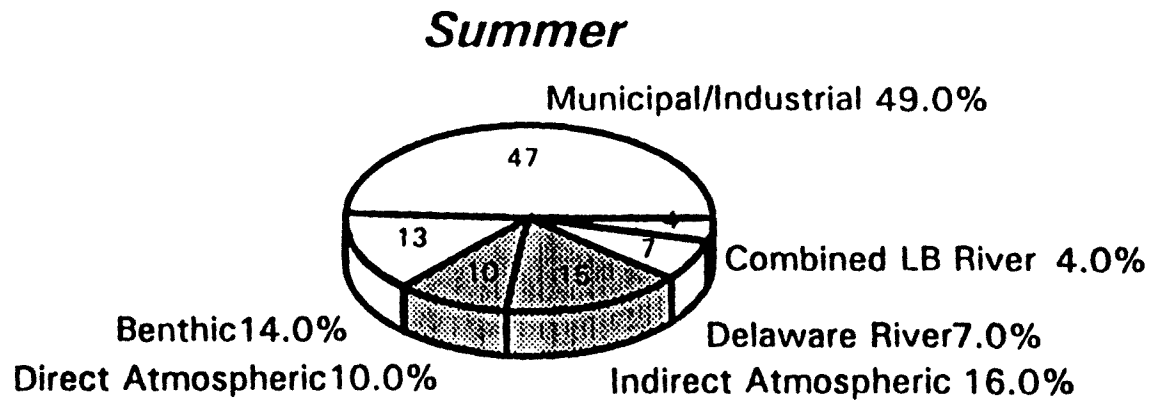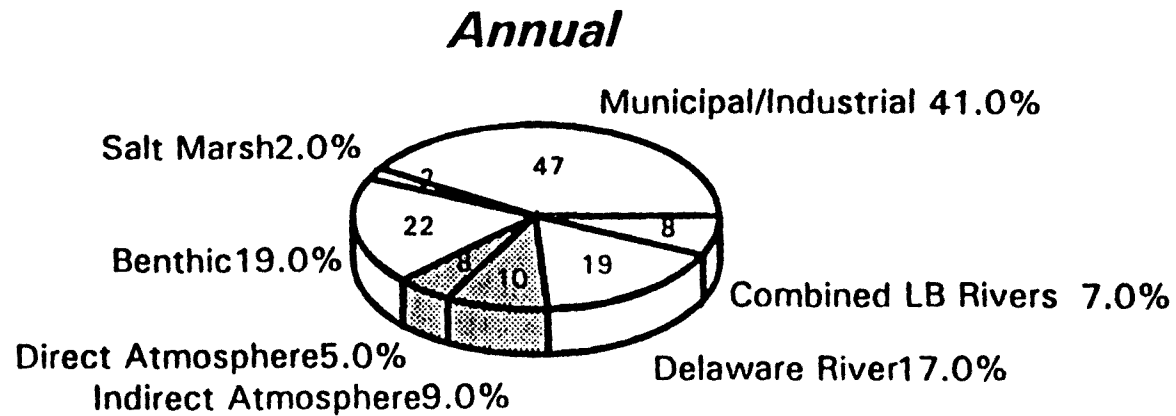Delaware River7.0%

Indirect Atmospheric 16.0%

Figure 28. Seasonal differences in the relative atmospheric loading of inorganic nitrogen to the Delaware Bay

source of inorganic nitrogen to estuarine systems not previously considered. For the previously-cited studies which focus on the role of atmospheric deposition in an estuarine nitrogen budget, inclusion of a significant shelf exchange term would have serious mass-balance implications. Thus, until the role of residual circulation is evaluated, the contribution of atmospheric deposition estimated in these studies should be regarded as relative to landward or continental sources only, and not to total dissolved inorganic nitrogen input.

The temporal variability in atmospheric deposition, fluvial input and primary production are largely overlooked but important characteristics of nitrogen loading to coastal and estuarine waters. For example, the atmospheric input reflected in Figure 28 is based on the long-term (1978-1989) average precipitation composition and rainfall amount. However, the interannual variability in wet deposition of nitrate and ammonium for the same period is as much as 51%. Therefore, assessments based on deposition from a single year may be misleading. On a seasonal basis (Figure 29), maximum rates of nitrogen wet deposition are observed during summer, when primary production in the estuary is most severely nitrogen limited (e.g., D'Elia et al. 1986, Pennock 1987). Based on recent results from the National Dry Deposition Network, the dry deposition of nitrogen appears to exhibit a similar, though less pronounced, seasonal trend (Edgerton et al. 1991).

The episodic nature of wet deposition is revealed by the frequency distribution in Figure 30. While a majority of the events are typically associated with low flux, it is the small number of exceptionally large events which drive the annual flux. For example, the ten largest episodes in Figure 30 (about 10% of the total number) account for 38% of the total annual flux. Furthermore, all of these dominant deposition events occurred during the summer, further supporting the notion of seasonally varying nitrogen deposition. Despite the distinct temporal variability in atmospheric nitrogen fluxes, the ecological response may occur on differing time scales. Fisher et al. (1988) argue that nitrogen inputs during the winter and spring are largely retained and recycled within the estuary. Similarly, atmospheric nitrogen deposited in the watershed will accumulate during the summer and be transported in response to the hydrological cycle (Boring et al. 1988). Thus, residual nitrogen from high input periods may persist in the estuary and watershed sufficiently to influence annual productivity.

While such seasonality in the atmospheric flux of NO_3^- is noted in both the Chesapeake Bay (Lynch et al. 1989, Maxwell and Mahn 1987) and the Delaware Bay watersheds (Figure 29), it is not observed at all sites in the eastern U.S. (Calvert et al. 1985). This can be attributed to either intra-annual variability in regional emissions, or related to the reactivity of NO_x, atmospheric transport and subsequent scavenging of NO_3^- (Wolff 1984, Lindberg 1982). For NH_4^+, summer deposition is generally maximum at all eastern U.S. locations, probably reflecting increased emissions from biogenic sources during warmer weather.

A major limitation in assessing atmospheric nitrogen deposition is that the national wet and dry deposition monitoring networks (e.g., NADP, NDDN) have been designed to
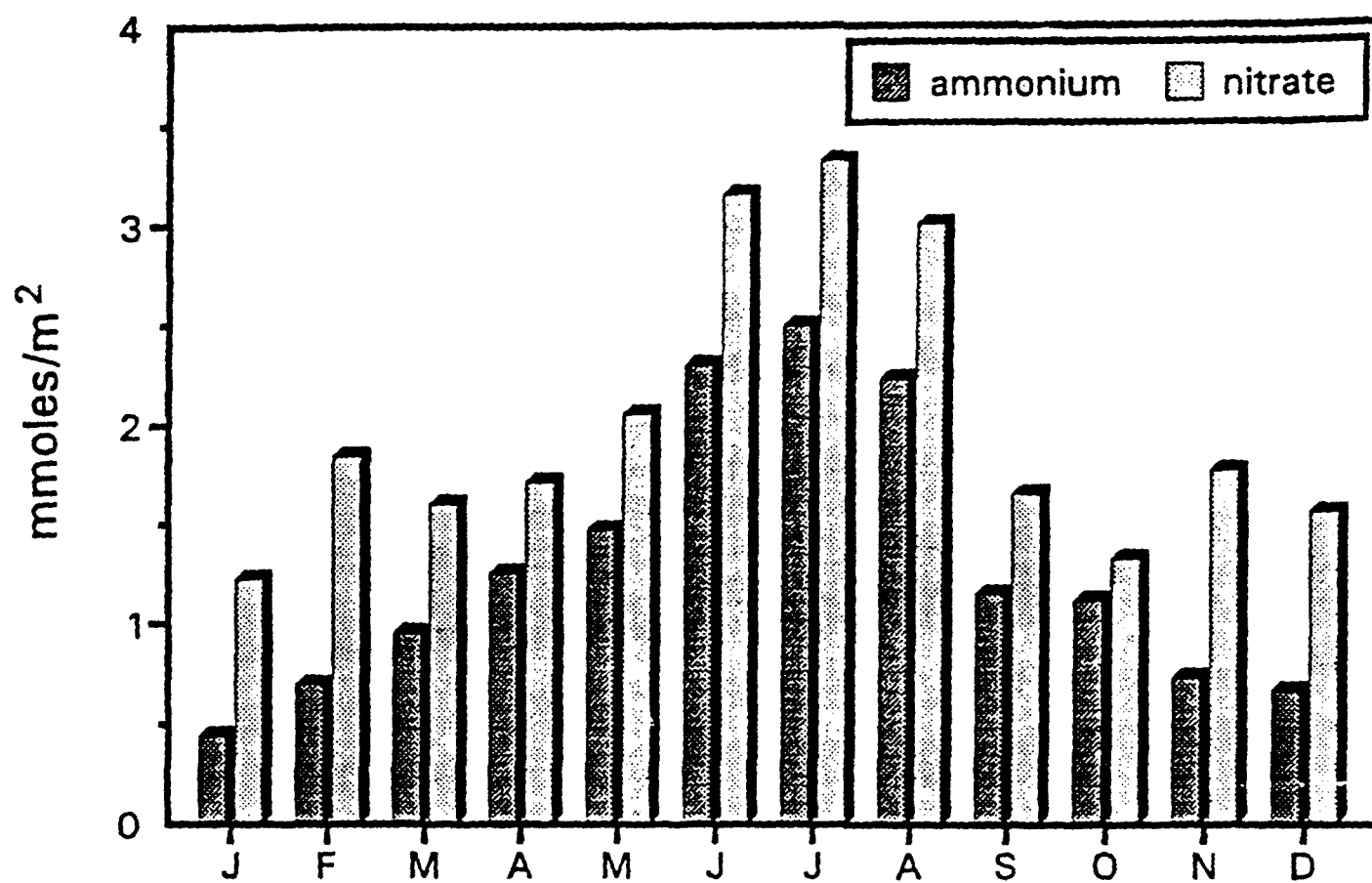
Figure 29. Seasonal variability in nitrogen deposition at Lewes, DE
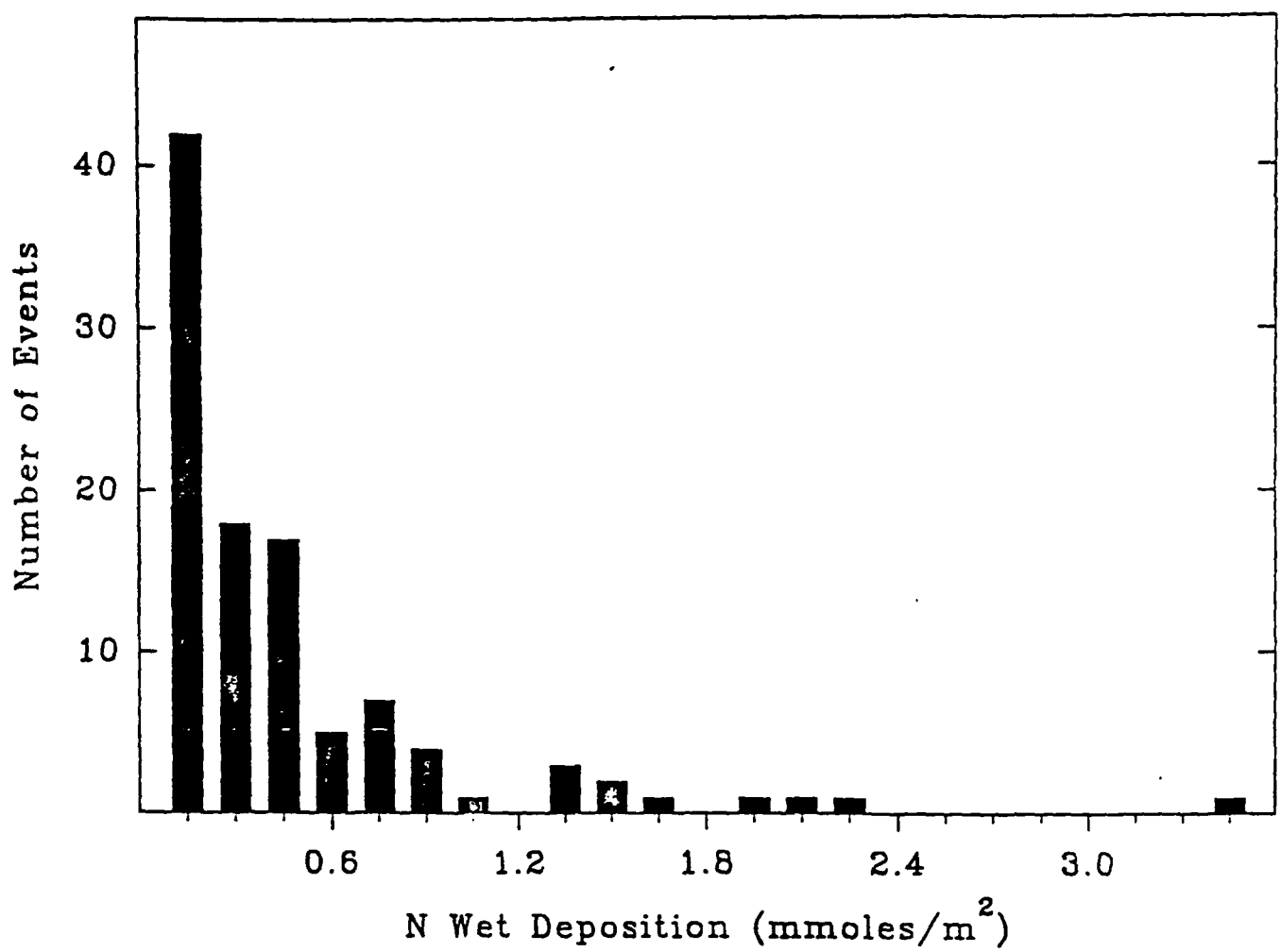
Figure 30. Episodic atmospheric wet deposition of nitrate and ammonium at Lewes, DE, 1990.

intentionally exclude *bona fide* coastal (*i.e.*, shore based) sites in order to exclude complicating influences of sea-salt aerosols on the species of interest (especially SO_4^{-2}). However, deposition of nitrogen to coastal waters can significantly differ from estimated rates extrapolated from inland sites by three mechanisms:

1.   chemical, due to the scavenging of vapor-phase HNO_3 by alkaline marine aerosols;

2.   physical, due to the increased gravitational settling of hygroscopic aerosols under higher relative humidities, and;

3.   meteorological, whereby the atmospheric stability regime over water differs greatly from that over land, due primarily to turbulence resulting from differences in water and air temperatures.

Recently, the NOAA Atmospheric Nitrogen Input to Coastal Areas (ANICA) program has begun to address this shortfall in the Chesapeake Bay, including characterization of the atmospheric stability field over water using buoy-mounted meteorological sensors.

Similarly, atmospheric deposition monitoring networks have been designed so that the sites are regionally representative of their airshed, typically located in rural or semi-remote settings. However, this design inherently excludes the influence of large urban centers, many of which are located along coastal waters. While the magnitude of deposition from the urban emission plume is largely unknown, it would seem that studies to date which rely on national and state monitoring data have underestimated atmospheric deposition.

8.4.2 Dissolved Organic Nitrogen (DON)

Along with NH_3, organic nitrogen forms such as amines and amino acids can be released to the atmosphere from the decomposition and volatilization of organic matter. However, due to the paucity of reliable measurements of organic nitrogen in atmospheric deposition, investigations of the role of atmospheric deposition of nitrogen in mass balances for aquatic systems have focussed completely on inorganic forms of nitrogen. However, the few data available would suggest that atmospherically-derived dissolved organic nitrogen (DON) may provide a small, albeit significant source of external nitrogen to aquatic systems. For example, Mopper and Zika (1987) reported an average concentration of DON (dissolved free amino acids + aliphatic amines) in the western Atlantic Ocean and Gulf of Mexico of approximately $7\mu M$. Likens *et al.* (1983) detected primary amines in precipitation at Hubbard Brook, New Hampshire and Ithaca, New York at concentrations averaging 6 μg C/L. These data agree with observations of Knap *et al.* (1986), Jickells *et al.* (1990) and Jickells *et al.* (unpublished), who measured a total (persulfate oxidation) DON concentration in precipitation from the North Sea, Northeast Atlantic and Bermuda of 6.3-8.7 μM. Similarly, Timperly *et al.* (1985) found that DON (primarily urea) contributed substantially to the overall Nitrogen loading in a New Zealand lake.

Furthermore, and perhaps as importantly, they established that such organic species are readily assimilated by phytoplankton.

These organic nitrogen concentrations can be put in perspective by comparing them with simultaneously-measured concentrations of the major inorganic nitrogen species (NO_3^- + NH_4^+) in precipitation. For the relatively polluted North Sea region, characterized by precipitation concentrations typical of the eastern U.S., DON contributed 16% of the total nitrogen deposition. For Bermuda, more representative of coastal waters of the eastern U.S., DON was found to provide 25% of the total nitrogen wet deposition. Data summarized by Smullen et al. (1982) for Chesapeake Bay indicate that atmospheric deposition of organic nitrogen ($\leq$ 6.8 kg/ha/yr) would increase the total nitrogen deposition by 43%. In contrast, other recent studies of DON in aerosols (Dodd et al. 1984), Rhode Island coastal precipitation (VanNeste et al. 1987), and North Atlantic precipitation (Gorzelska and Galloway 1990), these authors suggest that the atmospheric deposition of organic-N in the eastern U.S. would be less than 10% of the total nitrogen deposition.

Based on these limited measurements, it is difficult to resolve the apparent ambiguity. One simple explanation is that the seemingly divergent results are due to pronounced seasonal and/or spatial variability. If we conditionally accept a value for the average DON concentration in precipitation of $\approx$ 7 μmoles/l (an approximate value on which a number of the cited studies appear to converge), and assume that DON behaves similarly to DIN with respect to wet/dry flux apportionment and watershed retention, the overall atmospheric loading to Delaware Bay is estimated to increase by about 10-15% (Scudlark and Church 1993). However, since we do not have reliable estimates of DON input from other estuarine sources, it is not possible to gauge the impact of atmospheric DON input on an overall nitrogen mass balance. Clearly, a more accurate assessment of the role of atmospherically-derived organic nitrogen in nutrient budgets for the "Great Waters" will require more extensive measurements (both spatially and temporally) of the total concentration and speciation of organic nitrogen compounds in precipitation and surface waters, as well as identification of their sources.

8.4.3 Estimated Response of Nitrogen Loadings to 1990 Clean Air Act Amendments

Provisions of the 1990 Clean Air Act Amendments will "freeze" NO_x emissions at 1990 levels, and presumably not greatly alter the rate of atmospheric nitrogen deposition to coastal waters. However, in order to meet objectives for the reduction in urban ozone levels, further emission reductions may be required. In a preliminary analysis, Buckley and Corio (1992) examined the projected future NO_x emissions and resultant atmospheric nitrogen deposition to the Chesapeake Bay under various emission control scenarios (Figure 31). They predict that only by assertively controlling emissions (44% reduction) over the minimum CAAA requirements would a noticeable reduction (11%) in atmospheric NO_3^- loading to Chesapeake Bay be achieved. It should be noted however that the CAAA do not specifically address sources of atmospheric NH_3, which comprises 30-40% of the total atmospheric nitrogen deposition.
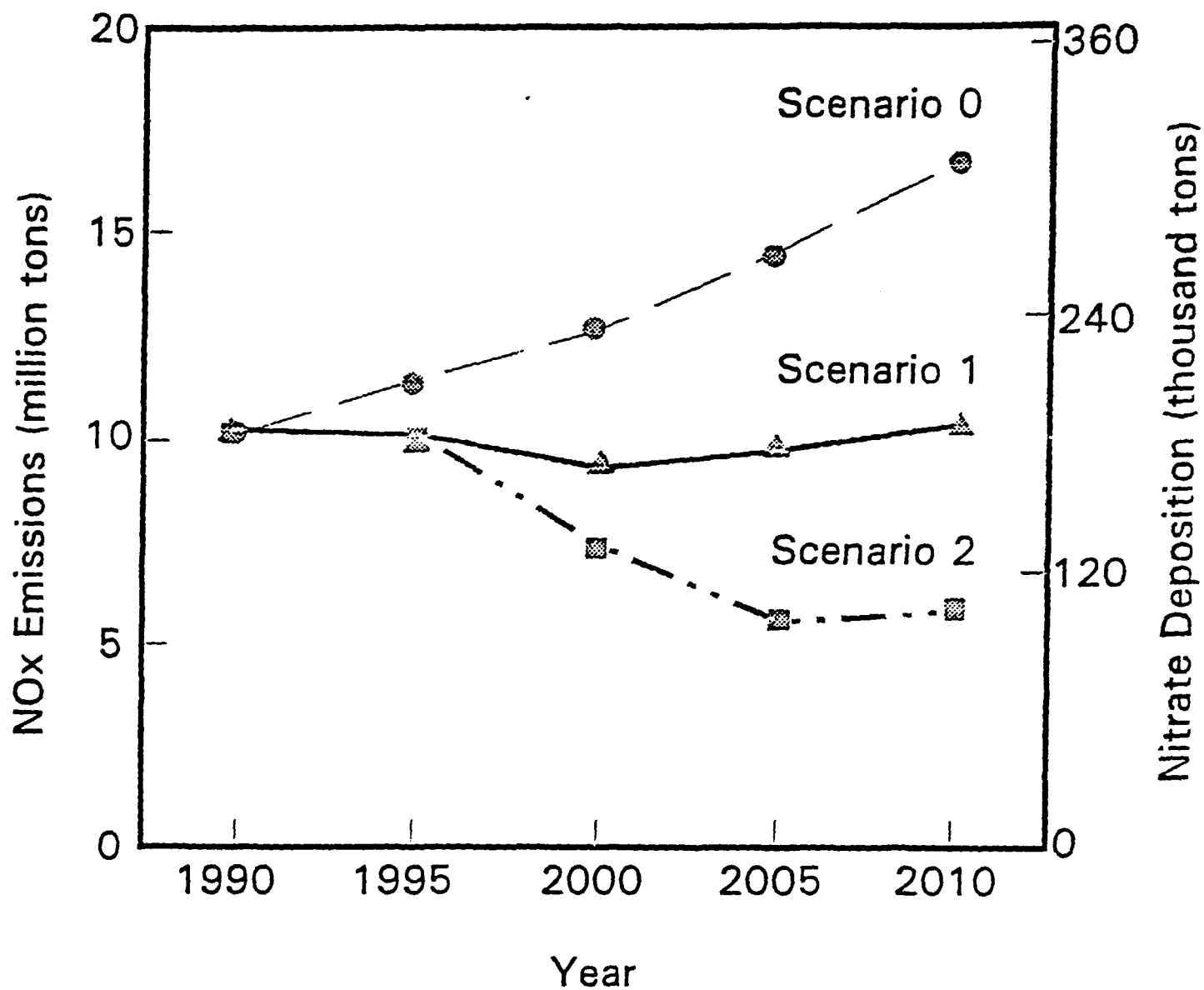
Figure 31. Projected nitrogen emissions and nitrate deposition rates to the Chesapeake Bay under three control scenarios

9.0 CURRENT UNCERTAINTY IN GREAT WATERS MASS BALANCES

There has been tremendous improvements in our understanding to the role of atmospheric deposition in supplying trace elements, mercury, nitrogen, and organic contaminants to surface waters. Many advances have been made in the basic sampling and analytical tools required to make reliable field measurements of atmospheric inventories and wet depositional fluxes. Such measurements require extreme care and are, therefore, not necessarily suitable for large, routine monitoring networks. Nonetheless, during the past ten years it has become possible to accurately measure atmospheric concentrations, speciation, and wet depositional fluxes of many chemicals, and excellent records are evolving at several locations (*e.g.*, Lewes, DE; Chesapeake Bay, Great Lakes region). Due to the inherent variability in atmospheric processes, long-term records, on the scale of decades, will be required to assess changes in atmospheric deposition loadings to the Great Waters. It is left up to the responsible agencies to develop and maintain these long-term programs.

To prioritize future research efforts, the authors of this report have estimated the current uncertainties in the fundamental atmospheric depositional process and assessed their relative importance (Tables 2-5). In general, more reliable measurements of wet deposition are available compared to either dry aerosol deposition or gaseous exchange. While wet deposition can be measured in the field, our ability to predict (*e.g.*, model) contaminant scavenging from the atmosphere by precipitation is highly uncertain, perhaps no better than to within one to two orders of magnitude. Specific studies of wet depositional processes, especially those employing novel geochemical tracers and airborne sampling, are required. While it is important to continue and expand wet deposition measurements and research, much of the research effort must be placed in improving our ability to measure and model dry deposition. In particular, our estimates of dry aerosol deposition are hindered both by a lack of aerosol size distribution information and by our generally poor understanding of the micrometeorological environment above water surfaces. The potentially large contaminant fluxes resulting from the rapid settling of supermicron particles near emission sources (Holsen *et al.*, 1991) as well as the possible elevated fluxes during short-term, intensive meteorological events deserve further study.

Mass balance calculations and measurements of concentration gradients in the field strongly suggest that many organic contaminant are degassing from the Great Lakes, especially during warm summer months. Chemicals such as PCBs, which are no longer produced, may be leaving the Great Lakes back into the atmosphere to be transported and deposited to the world's oceans and to the polar ice pack. The processes by which the Great Waters give these chemicals back to the atmosphere clearly need to be understood, both to predict contaminant levels in these water bodies and to characterize the global redistribution of these persistent chemicals.

In summary, the significant progress made during the past two decades has provided many of the tools required to answered the questions posed by Section 112(m) of the 1991 Amendments to the Clean Air Act. While much remains to be done, the regulatory community will be well served to continue to adopt the geochemical mass balance, emphasizing processes and fluxes of materials, as a rational framework for future endeavors.

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