Inputs and outputs of mercury from terrestrial watersheds: a review

D.F. Grigal

Abstract: This review focuses on mercury (Hg) inputs and outputs in temperate and boreal terrestrial systems. It covers deposition via throughfall and litterfall, whose sum (ca. 38 μg m^{-2} a^{-1}) is greater than that via precipitation (ca. 10 μg m^{-2} a^{-1}). Outputs considered include volatilization, soil sequestration, and streamflow. The former is highly uncertain, but the mean rate (11 ng m^{-2} h^{-1}) over a growing season is equivalent to about 32 μg m^{-2} a^{-1}. Modern rates of soil sequestration (ca. 5 μg m^{-2} a^{-1}) and streamflow fluxes (ca. 2 μg m^{-2} a^{-1}) balance the annual budget. The majority of the uncertainty in the budget is related to volatilization. Nonetheless, a large fraction of atmospheric Hg is likely a product of continuing deposition and volatilization. Watershed characteristics related to streamflow fluxes of both Hg and methylmercury (MeHg) are discussed. Both runoff concentration and flux of Hg are weakly and inversely related to watershed size. Dissolved organic carbon (DOC) and particulates are important carriers of Hg; watershed activities that affect either affect Hg flux. Runoff flux of MeHg is skewed with about 80% of observations less than 0.15 μg m^{-2} a^{-1}. Although there is no pattern of MeHg flux with watershed size, there is a strong positive relationship between flux and wetland area. Wetlands are a site of MeHg production and their presence increases water residence time; both increase MeHg flux. Concentrations of MeHg in streamflow from watersheds with wetlands are near the current water quality criterion, and effective control measures in those watersheds appear problematic.

Key words: deposition, non-point pollution, methylmercury, wetlands, dissolved organic carbon (DOC).

Résumé : Cette revue porte sur les entrées et sorties de mercure (Hg) dans les systèmes boréaux et tempérés. Elle couvre les dépositions via la canopée et la chute des litières, dont la somme (ca. 38 μg m^{-2} an^{-1}) est plus grande que la précipitation au sol (ca. 10 μg m^{-2} an^{-1}). Les sorties prises en compte incluent la volatilisation, la séquestration au sol et le lessivage. Ce dernier est très peu certain, mais le taux moyen (11 ng m^{-2} h^{-1}) au cours d'une saison de croissance est l'équivalent de 32 μg m^{-2} an^{-1}. Les taux modernes de séquestration au sol (ca. 5 μg m^{-2}an^{-1}) et les flux par lessivage (ca. 2 μg m^{-2} an^{-1}) balancent le budget annuel. La majeure partie de l'incertitude dans le budget implique la volatilisation. Néanmoins, une forte proportion du Hg atmosphérique résulte vraisemblablement de dépositions et de volatilisations continues. On discute les caractéristiques des bassins versants reliées aux flux de lessivage du Hg aussi bien que du mercure méthylé (MeHg). La teneur du ruissellement ainsi que le flux de Hg sont faiblement et inversement reliés à la dimension du bassin versant. Le carbone organique dissout (DOC) et les particules sont d'importants vecteurs du Hg, et les activités des bassins versants qui les affectent, affectent également le flux de Hg. Le flux par ruissellement du MeHg est biaisé, avec environ 80 % des observations inférieures à 0.15 μg m^{-2} an^{-1}. Bien qu'il n'y ait pas de

D.F. Grigal. Department of Soil, Water, and Climate, 439 Borlaug Hall, 1991 Upper Buford Circle, University of Minnesota, St. Paul, MN 55108, U.S.A. (e-mail: dgrigal@soils.umn.edu).

patron de flux du MeHg selon la dimension du bassin de drainage, il y a une forte relation positive entre le flux et la surface de terrain humide. Les terres humides constituent un site de production de MeHg et leur présence augmente le temps de résidence de l'eau; les deux augmentent le flux de MeHg. Les teneurs en MeHg dans les ruisseaux provenant de bassins versants bordés de terres humides rencontrent les critères usuels de qualité de l'eau, et les mesures correctives efficaces dans ces bassins versants apparaissent problématiques.

Mots clés : déposition, pollution non-ponctuelle, mercure méthylé, terres humides, carbone organique dissous (DOC).

Introduction

Mercury (Hg) occurs in two oxidation states in environmental media: Hg^0 (metallic, Hg(0)) and Hg^{2+} (mercuric, Hg(II)). Under ordinary conditions, Hg(0) vaporizes readily and is easily transported in the atmosphere. Natural sources of Hg to the atmosphere include degassing of the earth's crust through volcanos and diffusion from ore bodies (Nriagu 1979). Human activities such as mining and associated smelting, burning of fossil fuels, and industrial uses of Hg in chloralkali plants, paints, batteries, medicine, and dentistry have significantly increased the global reservoir of atmospheric mercury since the beginning of the industrialized period (Fitzgerald et al. 1998). This Hg is widely distributed via atmospheric processes, and deposition from the atmosphere to terrestrial and aquatic systems, even those in remote areas, has led to the recognition of Hg as a toxic global pollutant (Fitzgerald et al. 1998; Jackson 1997).

Aquatic systems are considered most sensitive to Hg toxicity, with nearly all concern directed at methylmercury (MeHg). It can be concentrated more than a million-fold in the aquatic food chain. It can cross the barrier that normally protects the brain from toxins in the blood stream and is a potent neurotoxin, penetrating the placenta and exposing the fetus. Point sources are important in delivering Hg to aquatic systems, but atmospheric Hg deposition, either directly to the aquatic system or indirectly via deposition to terrestrial watersheds and its subsequent transport, is also significant (Fitzgerald et al. 1998; Schroeder and Munthe 1998). Fish far from obvious sources of Hg emissions have been found to have MeHg levels of concern to human health (U.S. EPA 1997), leading to fish consumption guidelines and health advisories in Scandinavia, North America, and elsewhere. For example, 35 states in the U.S.A. have at least one waterbody under an Hg advisory, and six states have statewide advisories (U.S. EPA 1997). Although nearly all Hg in fish is MeHg (U.S. EPA 1997), the cycling of total Hg (HgT) is of concern because an important environmental source of MeHg is biological methylation, first shown by Jernelöv (Schroeder and Munthe 1998).

Regulation of pollutants in aquatic systems has historically emphasized point sources. More recently, non-point or diffuse sources have received increasing attention, as illustrated by the U.S. Environmental Protection Agency's concept of total maximum daily load (TMDL) (U.S. EPA 1999). Atmospheric deposition of Hg is a classic example of a non-point source of a contaminant. Although direct Hg deposition from the atmosphere can be important, terrestrial watersheds are the proximate source for most Hg in aquatic systems. Simply on an areal basis, terrestrial watersheds receive more Hg from the atmosphere than do aquatic systems. Between 5 and 25% of atmospheric Hg deposited on upland terrestrial basins reaches the associated lakes (Krabbenhoft and Babiarz 1992; Krabbenhoft et al. 1995; Lorey and Driscoll 1999; Swain et al. 1992), contributing between 5 and 85% of the total Hg loading depending on the terrestrial-to-lake surface area ratio (Krabbenhoft et al. 1995; Lindqvist et al. 1991; Lorey and Driscoll 1999; Swain et al. 1992). There is some evidence that the proportional contribution of Hg by terrestrial watersheds has increased as Hg loadings to the watersheds have increased with time (Lorey and Driscoll 1999).

The significance of the non-point contribution of Hg from terrestrial watersheds to aquatic systems depends on biogeochemical processes in the watershed, including deposition of atmospheric Hg, its storage in ecosystem components, its transfer among components, and its loss either as a gas or in solution. Although biogeochemical behavior of some non-point pollutants such as nitrogen and phosphorus

is fairly well understood in terrestrial watersheds, understanding of Hg behavior is incomplete. Fluxes of Hg both in and out of terrestrial watersheds can be as solids, liquids, or gases, and their measurement, especially of the gaseous pathways, is challenging. System pools usually are considerably larger than are fluxes so that uncertainties in their measurements leads to an inability to draw any firm conclusions about short-term trends in pool sizes and of fluxes influencing them. Elemental budgets of Hg in terrestrial systems are often "balanced" by an unmeasured residual term.

Although Hg contamination in remote areas is generally considered to be the result of atmospheric deposition (Fitzgerald et al. 1998), there is an opposing view that emphasizes the importance of natural geologic sources (Rasmussen 1994*a*). Part of the disagreement is based on conflicting reports of Hg concentrations and amounts. One of the keys to understanding Hg in the environment is cognizance of the level of technical sophistication required for analysis of the low levels of Hg found in many environmental media. Ultra-clean analytical approaches were rare before the mid-1980s, and hence reports published before that time must be approached cautiously (Fitzgerald et al. 1998). Some early techniques such as neutron activation analysis (Låg and Steinnes 1978) or radiotracers (Landa 1978*a*) have provided valid data.

This review will focus on Hg cycling, especially inputs and outputs, in terrestrial systems in the temperate and boreal zones. It will cover wet deposition and a detailed discussion of various forms of dry deposition that result in Hg in both throughfall and litterfall. Outputs considered include soil sequestration, volatilization, and losses in solution, primarily in streamflow. In the latter case, watershed characteristics that are related to fluxes of both Hg and MeHg will be discussed. The role of disturbance in altering Hg loss will also be evaluated. The data collected in the review will be synthesized to create a nominal input–output budget for Hg in terrestrial systems, and this budget will be related to both current concerns about Hg pollution of aquatic systems and to global Hg cycling.

There will be no attempt to review all papers on the topic; the literature is very large and continues to grow. Instead, the emphasis will be on representative studies and especially those focused on watersheds that are not near point sources of atmospheric Hg. Most research has been carried out on forested watersheds, but available data from other land uses, such as agriculture, will also be included. Information from studies in systems with high concentrations and contents of Hg, usually as a result of industrial activity, will be included only where relevant. Because of the plethora of reports, in many cases data will be aggregated from pertinent reviews rather than from original literature.

Histograms have been used to summarize the literature, providing a succinct description of the data, including its central tendency and variability. Many distributions are skewed and are often lognormal, and the geometric mean is used as a more appropriate measure of central tendency than the arithmetic mean. If distributions are more nearly normal, the geometric and arithmetic means are numerically similar. Some empirical relationships have been developed. These may reflect an underlying mechanism or principle or may simply reflect a coincidence of numbers. The authenticity of general trends that transcend sites and dates, albeit with high uncertainty, gains credibility when the plethora of other factors that influence the individual response of a unique site or date is considered. In all cases, however, such relationships should be considered to be hypotheses and not facts.

Inputs

Atmospheric concentrations

The three major Hg species in the atmosphere are elemental Hg(0) in the vapor phase, gaseous inorganic Hg(II) compounds (also termed reactive gaseous Hg; RGM), and particulate-phase Hg (Hg(p)) (Shroeder and Munthe 1998). Elemental Hg is capable of being aerially transported for tens of thousands of kilometres from its source, Hg(II) for a few tens to hundreds of kilometers, and Hg(p) at intermediate distances depending on particulate size and mass (Schroeder and Munthe 1998). Nearly all the Hg in the atmosphere occurs as Hg(0) (>95%), but the relative amounts of Hg species can be altered by oxidation–reduction reactions (Iverfeldt and Lindqvist 1986; Munthe 1992; Munthe et al. 1991). Total

gaseous Hg (TGM) concentrations over the open ocean show a general linear increase from south to north from about 1 ng m^{-3} at 40°S to about 2.2 ng m^{-3} at 45°N (data from Fitzgerald and Mason (1996)). Concentrations over land are similar although somewhat higher (Gill et al. 1995; Iverfeldt et al. 1995; Kvietkus et al. 1995; Lindberg et al. 1992; Schroeder 1994; Schroeder et al. 1995) and are influenced by both location, such as distance to point sources, and methodological issues, such as season of sampling, the period of time over which a sample was collected, and the number of observations included in a reported value.

There is some evidence for a long-term decrease in TGM and hence related decreases in deposition to terrestrial surfaces. There has been about a 2% decline per year in TGM on the west coast of Sweden over the period 1980 to 1992, and more recent observations are more nearly normally distributed compared to earlier lognormal distributions, implying fewer episodes of high TGM (Iverfeldt et al. 1995). Wet deposition of HgT has declined even more, about 7% per year (Iverfeldt et al. 1995). These declines are consistent with declines in Hg concentrations in ryegrass leaves (*Lolium multiflorum*), used as a biological monitor for Hg deposition in south Sweden, of about 10% per year over the period 1990 to 1994 (Xiao et al. 1998).

Atmospheric concentrations of Hg(p) are about two orders of magnitude lower than those of TGM (Guentzel et al. 1995; Keeler et al. 1994; Keeler et al. 1995; Lamborg et al. 1994; Lamborg et al. 1995). Because Hg(p) is subject to both washout by precipitation and dry deposition, its low atmospheric concentrations are not indicative of the role it can play in creating regional patterns of Hg deposition. Such patterns depend on both the size and mass of the particulates (Schroeder and Munthe 1998), precipitation frequency (for washout), and the nature of the receiving surface (for dry deposition). All these variables make the role of Hg(p) in total Hg deposition very site-specific.

Precipitation

Although atmospheric Hg is dominated by Hg(0), gaseous Hg(II) is much more soluble and is the dominant form in precipitation (Fitzgerald and Mason 1996; Porcella 1994). In a global pattern similar to that of atmospheric TGM concentrations, Hg concentration in precipitation over land generally increases from south to north (Mason et al. 1994). Although Hg deposition in precipitation depends on both volume and Hg concentration, it follows a trend similar to that of concentration (Mason et al. 1994). These generalized trends obscure a great deal of variation. Both gaseous and particulate forms of Hg(II) may contribute to the regional differences in wet deposition in spite of the well-mixed atmospheric load of Hg(0) (Fitzgerald and Mason 1996). Although concentrations of Hg in precipitation vary widely, from less than 1 to more than 1000 ng L^{-1} (Downs et al. 1998), the extremes are likely due to variation associated with sampling over short time periods or with samples collected near point sources of Hg.

A compilation of reports from unpolluted North Temperate areas indicates that most volume-weighted annual average concentrations of HgT in precipitation are in the range of 5 to 20 ng L^{-1}, with a mean of 16 ng L^{-1} (Fig. 1). Annual precipitation does not vary widely over most areas where Hg has been studied in terrestrial watersheds because most are forested and in temperate or boreal zones. The distribution of reports of wet deposition of Hg (Fig. 2), therefore, looks similar to that of precipitation concentration (Fig. 1), with about 60% of observations in the range of 5 to 15 μg m^{-2} a^{-1} and a mean of 10 μg m^{-2} a^{-1}. The average concentration of MeHg in precipitation is about 1% of that of HgT (Downs et al. 1998; Fitzgerald et al. 1994; Hultberg et al. 1994; Iverfeldt et al. 1996; Lamborg et al. 1995; Meuleman et al. 1995; Munthe et al. 1995; Schwesig and Matzner 2000; St. Louis et al. 1995), as is its average reported wet deposition (Driscoll et al. 1998; Fitzgerald et al. 1994; Hultberg et al. 1994; Iverfeldt et al. 1996; Lamborg et al. 1995; Lee et al. 2000; Munthe et al. 1995; Rudd 1995; Schwesig and Matzner 2000; St. Louis et al. 1995; St. Louis et al. 1996). Loadings of MeHg in wet deposition in Scandinavia, especially from the Gårdsjön watershed in southern Sweden, are at the high end of the distribution and are related either directly or indirectly to industrial activity (Rudd 1995). Variations in MeHg to HgT ratios in inputs to watersheds are not related to variations in ratios in streamflow (Lee et

Fig. 1. Volume-weighted mean annual Hg concentration in precipitation reported in studies from Ontario (Mierle 1990; Mierle and Ingram 1991; St. Louis et al. 1996), northern U.S.A. (Burke et al. 1995; Glass and Sorensen 1999; Hoyer et al. 1995; Kolka et al. 1999*a*; Lamborg et al. 1995), Florida (Guentzel et al. 1995), Siberia (Meuleman et al. 1995), central Europe (Schwesig and Matzner 2000), and Scandinavia (Jensen and Iverfeldt 1994; Munthe et al. 1995) (*n* = 54).
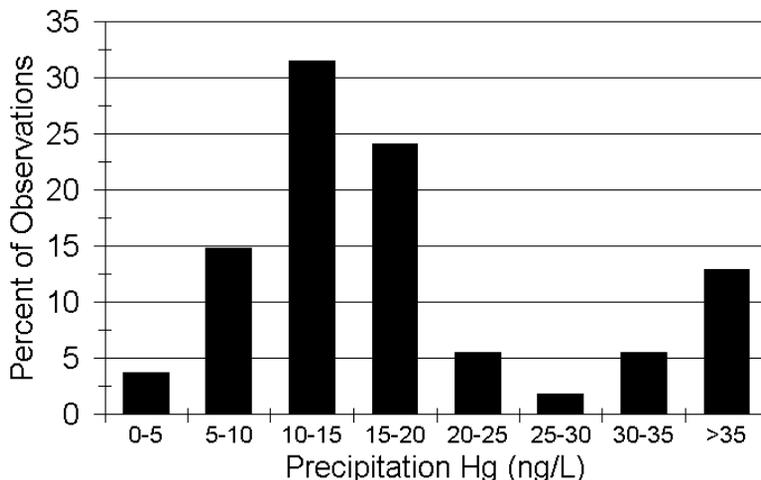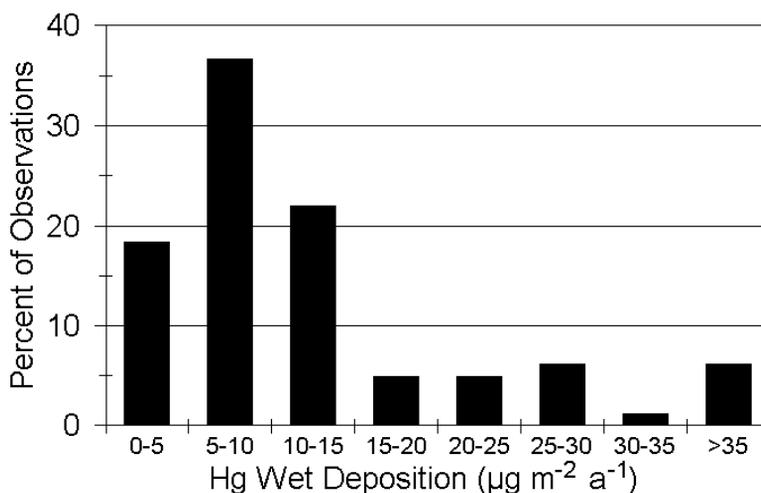

Fig. 2. Annual wet deposition of Hg to terrestrial systems reported in individual studies from Ontario (Mierle 1990; Mierle and Ingram 1991; St. Louis et al. 1996), northern U.S.A. (Burke et al. 1995; Fitzgerald et al. 1994; Glass and Sorensen 1999; Hoyer et al. 1995; Kolka et al. 1999*a*; Lamborg et al. 1995), Florida (Guentzel et al. 1995), central Europe (Schwesig and Matzner 2000), Scandinavia (Iverfeldt 1991*a*; Jensen and Iverfeldt 1994; Lee et al. 2000; Munthe et al. 1995), and as tabulated by Jensen and Iverfeldt (1994) and Kolka (1996) (*n* = 82).

al. 2000; Schwesig and Matzner 2000); differences in MeHg loadings are not as important to terrestrial as to aquatic systems.

Fig. 3. Annual deposition of Hg in open field precipitation, via throughfall, and via litterfall in forests in studies from Scandinavia (Driscoll et al. 1994*a*; Iverfeldt 1991*b*; Lee et al. 1998; Lee et al. 2000; Munthe et al. 1995), central Europe (Schwesig and Matzner 2000), and the U.S.A. (Grigal et al. 2000; Guentzel et al. 1998; Kolka et al. 1999*a*; Lindberg 1996; Rea et al. 1996).
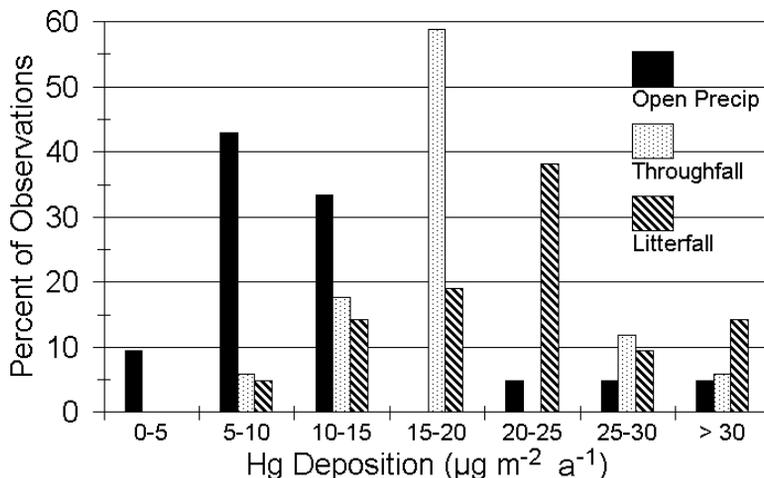
Dry deposition

Dry deposition, deposition to surfaces during precipitation-free periods, also contributes atmospheric Hg to terrestrial systems. About 25% of total Hg deposition directly to lakes in north central Wisconsin, U.S.A., was dry deposition of Hg(p) (Lamborg et al. 1995). Because of the large area of receptor surfaces, dry deposition of Hg is much more important in forests. Fluxes in throughfall, water reaching the ground under forest canopies during precipitation, have been used to directly estimate total wet plus dry deposition for atmospheric constituents such as the Na^+ cation and SO_4^{-2} anion (Johnson and Lindberg 1992). These estimates can be used if precipitation quantitatively removes previously deposited material and if foliar leaching of internal plant sources of the material is negligible (Lindberg et al. 1994). These conditions, but especially the latter, are satisfied in the case of Hg. Substantially more total Hg is deposited as throughfall in forests than is reported in open precipitation (Fig. 3). The ratio of the geometric means of inputs via throughfall ($17 \, \mu g \, m^{-2} \, a^{-1}$) to those from open precipitation ($9.7 \, \mu g \, m^{-2} \, a^{-1}$) (Fig. 3) is 1.8, slightly greater than the 1.5 suggested by Munthe et al. (1995). Simply to use that ratio to estimate Hg deposition to forests, however, obviates some important details about the process.

First, throughfall is not merely wet deposition plus washoff of adsorbed Hg(p). Measurement of atmospheric Hg(p) and assumptions of reasonable velocities for its dry deposition lead to significant underestimates of Hg in throughfall (<10% of measured) (Lindberg et al. 1994; Rea et al. 1996). The most likely sources of Hg in throughfall are considered to be adsorption of gaseous Hg(II) and capture and oxidation of Hg(0) by the canopy (Lindberg et al. 1994). Secondly, the use of a simple ratio erroneously assumes that all forest canopies are identical in their role in Hg deposition via throughfall. The deposition of Hg to a forest via throughfall depends on both the efficiency of the canopy in capturing Hg, whether gaseous or particulate, and the characteristics of the canopy that influence volume of both throughfall and related stemflow (water flowing down the branches and the bole of the tree to reach the ground) (Helvey 1971). The influence of these relationships on Hg can be illustrated by contrasting annual throughfall deposition under a black spruce (*Picea mariana*) canopy ($19.5 \, \mu g \, m^{-2} \, a^{-1}$) compared to under an adjacent deciduous aspen (*Populus tremuloides*) canopy ($9.3 \, \mu g \, m^{-2} \, a^{-1}$) (Kolka et al.

1999*a*). These large differences presumably arose because of the greater efficiency of the more dense spruce canopy in trapping atmospheric Hg. The ratio of Hg deposition in throughfall to that in the open was 1.4 for aspen but 3.0 for spruce, very different from the overall ratio of 1.5 suggested by Munthe et al. (1995).

In the few studies that have reported both MeHg and HgT in open precipitation and throughfall, the average ratio of MeHg to HgT in open precipitation is about 1.5 times higher than that in throughfall (1.5 vs. 0.9 %, respectively). Ratios are highest and differences are greatest in coniferous forests in southern Sweden (3 vs. 1.2 %, Munthe et al. 1995; Munthe et al. 1998), differences are virtually non-existent in coniferous forests in northern Sweden (about 1.7 %, Lee et al. 2000), and ratios are slightly lower in open precipitation in both coniferous and deciduous forests in central Europe (0.4 vs. 0.5 %, Schwesig and Matzner 2000). As stated earlier, variations in MeHg to HgT ratios in inputs to watersheds are not related to variations in ratios in streamflow (Lee et al. 2000; Schwesig and Matzner 2000). Other factors, to be discussed later, much more strongly affect the ratio in streamflow.

Litterfall

If adsorption of gaseous Hg(II) and capture and oxidation of Hg(0) by the canopy are likely sources of Hg in throughfall (Lindberg et al. 1994), and if Hg strongly binds to organic matter (Meili 1991), it is unlikely that all of the adsorbed Hg will be removed from the canopy during precipitation events. It is therefore logical that litterfall, dropping of senescent leaves, is a major pathway of Hg flux from the atmosphere to forested terrestrial watersheds.

Foliar uptake

The source of foliar Hg appears to be almost exclusively the atmosphere. Several greenhouse and laboratory studies have indicated that Hg uptake from soil is limited, with roots acting as a significant adsorption site for Hg and hence a barrier for its further transport to foliage (Beauford et al. 1977; Godbold and Hüttermann 1988; Hogg et al. 1978*a*; Lindberg et al. 1979; Mosbæk et al. 1988; Rao et al. 1966). These studies are consistent with field observations. For example, foliar concentrations of Hg in red pine plantations were inversely related to Hg in soil, but positively related to length of the growing season and hence duration of plant physiological activity (Fleck et al. 1999), implying Hg uptake from the atmosphere rather than from soil. Similarly, although positive relationships were reported between Hg concentrations in the atmosphere and pine needles in an Hg mining area, no relationship existed between Hg concentrations in needles and roots, implying soil was not the source of the Hg (Barghigiani et al. 1991). Calculations based on annual transpiration and soil water Hg concentrations indicate that <10% of annual Hg deposition in litterfall is likely due to root uptake and subsequent sequestration in leaves (Johnson and Lindberg 1995; Lindberg 1996), and measurement of HgT and MeHg concentrations in xylem sap in mature spruce and pine in Sweden indicate that only about 10% of HgT and about 3% of MeHg in litterfall could be accounted for by root uptake and sequestration (Bishop et al. 1998).

Foliar uptake of Hg presumably occurs through open stomata, with subsequent binding and oxidation of the Hg(0) (Du and Fang 1982). Experimental data with graminaceous plants indicated that uptake of Hg(0) was not limited by stomatal resistance, but by the binding and oxidation step described by a residual term, mesophyll resistance (Du and Fang 1982). Modeling of Hg deposition to the surface of a forest canopy confirmed that mesophyll resistance dominated exchange (Lindberg et al. 1992). As a result, simple analogies of Hg(0) uptake with that of other common gases such as O_3, SO_2, and NO_2 are inappropriate (Lindberg et al. 1992). Another potential source of Hg is RGM (Stratton and Lindberg 1995). Because of its high deposition velocity, this Hg species would accumulate in foliage (Barton et al. 1981; Guentzel et al. 1998).

There is also evidence that foliar emission of Hg occurs. Maintaining Hg(0) atmospheric concentrations near ambient levels in gas exchange chambers, Hanson et al. (1995) observed that foliar exchange of Hg(0) was balanced around a critical atmospheric concentration or compensation point, with uptake

occurring at concentrations above that point and emissions below that point. The compensation point was species specific, but it ranged from about 10 to 25 ng m^{-3} for tree seedlings, considerably higher than observed average atmospheric TGM concentrations. Lindberg (1996) has measured substantial emissions of gas-phase Hg(0) from the forest canopy and suggested that the source is transport of the gas from soil to leaves via the transpiration stream. The very low solubility of Hg(0) in lakewaters and sediment porewaters, albeit up to 50 times higher than atmospheric concentrations (Lindqvist et al. 1984; Vandal et al. 1995; Watras et al. 1994; Watras et al. 1995), makes that source unlikely to lead to significant Hg(0) efflux, <0.2 μg m^{-2} a^{-1}. Siegel et al. (1974) also measured volatile Hg loss from vascular plant leaves at room temperature, but this was neither MeHg nor dimethyl Hg, nor was it gas-phase Hg(0). Fluxes from the canopy appear to be under stomatal control.

Although foliar emissions of Hg may occur, evidence is overwhelming that foliage is a net sink for atmospheric Hg. In conifers, Hg concentrations increase with needle age (Barghigiani et al. 1991; Bombosch 1983; Fleck et al. 1999; Rasmussen 1995), and in both coniferous (Rasmussen 1995) and deciduous trees (Lindberg 1996), Hg concentrations also increase over the growing season. As a general rule, conifer needles tend to have higher concentrations than deciduous leaves from trees at same location, perhaps because conifer collections usually include older needles (Rasmussen et al. 1991). There is also the suggestion that plants of lower stature have higher concentrations than trees from the same location (Rasmussen et al. 1991). This would be consistent with foliar uptake from a soil source of gaseous Hg(0) (Lindberg et al. 1992). Concentrations of Hg in non-vascular plants (mosses, fungi, and lichens) are nearly an order of magnitude higher than those in vascular plants (Moore et al. 1995). Whether these higher concentrations are related to increased adsorption of atmospheric Hg(0) or of soil-based gaseous Hg(0) is unclear.

Flux

Both the quantity of litterfall and its Hg concentration are important in affecting inputs to forested watersheds. Firstly, litterfall mass in forests has a strong positive relationship with actual evapotranspiration (AET) (Meentemeyer et al. 1982), an index of growing season length and quality. Forests in areas with longer growing seasons are likely to have both a greater quantity of litterfall and higher Hg litter concentrations as a consequence of a longer period of foliar uptake. Secondly, there are great contrasts in foliar concentrations of Hg, apparently depending upon atmospheric concentrations and differences in uptake efficiency. Although there is a general increase in Hg concentration with needle age, concentrations in needles from central Europe are much higher than those in needles from relatively remote North American sites (Barghigiani et al.1991; Bombosch 1983; Fleck et al. 1999; Rasmussen 1995). For example, in a Hg mining area in Italy, pine needle Hg concentrations were up to 4000 μg kg^{-1}, associated with TGM concentrations of 600 ng m^{-3} (Barghigiani et al. 1991). Most reported tree foliar concentrations are much lower, with the majority in the range 10 to 50 μg kg^{-1} and a mean of those reports near the midpoint of that range (24 μg kg^{-1}) (Barghigiani et al. 1991; Bombosch 1983; Fleck et al. 1999; Grigal et al. 2000; Lindberg 1996; Moore et al. 1995; Rasmussen et al. 1991; Rasmussen 1994*b*; Rasmussen 1995; Zhang et al. 1995). Leaves in litterfall have concentrations 1.5 to 2 times those reported in foliage (Grigal et al. 2000; Lindberg 1996; Rea et al. 1996) because of Hg accumulation over the entire growing season compared to foliage collected near the midpoint of the season. Litterfall includes not only leaves but also bark, twigs, reproductive parts, and other overstory components; an average of about 70% is leaves (Meentemeyer et al. 1982). Concentrations of Hg in the other litterfall components have been rarely reported but can be much higher than in leaf litter (Grigal et al. 2000).

There is a consistent trend of higher inputs of Hg via litterfall than via either open precipitation or throughfall (Fig. 3). In co-located studies, the ratio of the mean annual Hg wet deposition in the open (9.7 μg m^{-2} a^{-1}), that in throughfall (17 μg m^{-2} a^{-1}), and that in litterfall (21 μg m^{-2} a^{-1}) (Fig. 3) is 1:1.8:2.2, not greatly different than the ratio of 1:1.5:3 suggested by Munthe et al. (1995). As explained earlier, however, those overall ratios of means may obscure many important differences

within and among sites. Atmospheric deposition of Hg to lakes is much less than that to forests in the same geographic location because the lakes lack the forest canopy and hence those surfaces for both dry deposition and foliar uptake. Deposition of Hg to lakes ranges from approximately equal to about 25% higher (Lamborg et al. 1995) than wet deposition in the open (Fig. 2), or only about one-fourth that of Hg deposition to forests (sum of throughfall and litterfall). Deposition to vegetation of low stature, such as to grasslands, is likely to be intermediate between that to lakes and to forests because of differences in total surface area for interception, but data are rare. Dry particulate deposition of Hg over an open field in Ontario, Canada, was non-detectable, but based on a limited number of vertical profiles deposition of RGM to vegetation was estimated as 40 to 110 μg m^{-2} a^{-1}, 1.5 to 3.5 times greater than wet deposition (Barton et al. 1981). Similarly, using grass as a bioindicator, annual dry deposition in southern Sweden was estimated to be 42 μg m^{-2} a^{-1} $\pm$ 40% (Xiao et al. 1998), higher than most estimates of Hg deposition via litterfall (Fig. 3). The high uncertainty of both these estimates does little to clarify the question of Hg deposition to low-stature vegetation.

Litterfall may also be a source of MeHg to terrestrial ecosystems, either of atmospheric origin or produced in the plants (Rudd 1995). In northwestern Ontario, Canada, tree and shrub leaves had a low ratio of MeHg to HgT (1.1%, Moore et al. 1995). In the few studies that have reported both HgT and MeHg in litterfall, it appears that the average ratio of MeHg to HgT is nearly identical to that in open precipitation (1.5%) (Lee et al. 2000; Munthe et al. 1995; Munthe et al. 1998; Schwesig and Matzner 2000), but is higher than that in throughfall (0.9%). Because the ratio in precipitation and litterfall is so similar, an atmospheric origin of MeHg is more likely than is production within the plants. Higher ratios in litterfall than in throughfall can also lead to an inference that vegetation may preferentially adsorb MeHg as compared to HgT. As in many cases, the average obscures some important differences among sites. In some locations, the ratio of MeHg to HgT in litterfall was nearly twice that in open precipitation (1.7 vs. 1.1%, Lee et al. 2000; 0.8 vs. 0.4% , Schwesig and Matzner 2000), while in others the ratio was higher in open precipitation than litterfall (3 vs. 2.4%) and both ratios were higher than in throughfall (1.2%) (Hultberg et al. 1995). Litterfall does contribute MeHg to watersheds, but usually as a small proportion of HgT.

Summary

Deposition of Hg by direct precipitation in the open in unpolluted North Temperate areas is the range of 5 to 15 μg m^{-2} a^{-1} (60% of observations) with an overall mean of 10 μg m^{-2} a^{-1}. Atmospheric deposition of Hg to forests is about four times open precipitation (38 μg m^{-2} a^{-1}) because of additions via throughfall, washoff of dry deposition, and litterfall, dropping of senescent leaves that have accumulated atmospheric Hg. Atmospheric deposition of Hg to lakes is only about one-fourth that to forests in the same geographic area because the lakes lack the forest canopy and hence surfaces for both dry deposition and foliar accumulation. Deposition of MeHg is only about 1% of HgT deposition, and variations in ratios of MeHg to HgT in deposition do not appear to be related to variations in ratios in streamflow from watersheds.

Outputs

Loss of Hg from terrestrial ecosystems can be either as a gas or in solution. The first pathway has implications for Hg in the atmosphere, including concentrations and deposition to other systems, while the latter has implications for aquatic systems and human health. The strong binding of Hg to organic matter, including dissolved organic matter (DOM) (or dissolved organic carbon (DOC)) in waters and soil organic matter (SOM), is critically important to its behavior in the environment (Meili 1991). Although ligands such as OH$^-$ and Cl$^-$ have some theoretical importance, in most cases "It is mainly the physical fractioning of soil organic matter (dissolved vs. adsorbed) that determines the behavior and distribution of Hg in soils." (Schuster 1991), and "... chloride complexation is not quantitatively important ... in most soil and fresh water systems ..." (Skyllberg et al. 2000). It is generally acknowledged, then, that

"Studies at the watershed level have shown that Hg^{2+} is the predominant form of Hg in soils and surface waters and that it is associated with organic substances." (Skyllberg et al. 2000). The binding of Hg to organic matter appears to be exclusively associated with reduced S groups whose concentration in natural systems is high enough to bind all Hg(II) (Xia et al. 1999; Skyllberg et al. 2000).

Volatilization

Because of the relatively high vapor pressure of Hg(0) at ambient conditions, Hg can be lost from terrestrial watersheds by volatilization. Most research has emphasized loss from soils, where volatilization is presumed to require three steps, reduction of Hg(II) to Hg(0), diffusion or mass transport of Hg(0) to the soil surface, and diffusion or mass transport of the Hg(0) across the soil–air boundary layer into the atmosphere (Zhang and Lindberg 1999). If Hg(0) is present in soil as a gas, in solution, or adsorbed, the first step is obviated. The reduction of Hg(II) can potentially be accomplished by both biotic and abiotic agents. In an adaptation to Hg toxicity, microbes can enzymatically reduce Hg(II) to Hg(0). This reduction is induced by toxic levels of Hg, and below the minimum Hg threshold concentration there is usually no induction and hence no reduction (Baldi 1997). Levels of Hg(II) found in uncontaminated environments are usually lower than that threshold (about 10 ng L^{-1} in solution, Morel et al. 1998). Microbial Hg reduction is also unlikely in anaerobic environments; presence of organic sulfides in such environments may strongly bind Hg, reducing its toxicity so that the microbial enzyme systems are not induced (Baldi 1997).

Both early and more recent laboratory work have shown that when Hg(II) is applied as salts to soils, a rapid loss of 10 to 30% of the Hg occurs within 10 to 15 days (Hogg et al. 1978*b*; Landa 1978*b*; Schlüter et al. 1995). The pattern of loss is a rapid initial rate followed by a sharp decline to low rates, suggesting an abiotic reduction mechanism because of lack of a lag phase characteristic of enzyme induction. The Hg(II) reduction has been attributed to a reaction with DOM in soil solution, with the rate decline attributed to the decreasing availability of Hg for reduction because of binding with SOM (Schlüter et al. 1995). Because of the much greater concentration of DOM than Hg(II) in soil solution, it can be described as a pseudo-first-order reaction with the rate linearly related to the Hg(II) concentration. Another potential agent of reduction is sunlight, either by direct photolysis of Hg compounds or by photolysis of other reactants that then reduce Hg(II) (Zhang and Lindberg 1999). Such reactions are unlikely in closed-canopy forests, but could be important in open agricultural areas. Because of the plethora of reactants and conditions in terrestrial environments, many other reduction reactions could also occur. In particular, wet areas in the landscape such as near stream channels or microtopographic depressions are usually strongly reducing environments and could provide conditions leading to significant Hg(II) reduction.

Many other factors can influence Hg volatilization. Both the vapor pressure of volatile Hg species and biotic or abiotic reaction rates are temperature dependent, and higher temperatures increase rates of Hg loss in the laboratory (Landa 1978*c*). Temperature dependence of volatilization in the field is more difficult to assess because of the interactions of temperature with other environmental factors. In general, however, highest rates of Hg volatilization have been reported in summer as compared to other seasons and during the day as compared to night (Schlüter 2000). In a boreal forest in Sweden, Hg that was deposited to the soil surface during the winter was apparently emitted or re-emitted during the remainder of the year (Schroeder and Munthe 1998). Similarly, Hg concentrations in the organic-rich aspen forest floor in Alberta, Canada, declined from high levels in spring following snowmelt through the summer to a minimum in August, and then increased in autumn, a time of both leaffall and cooler temperatures (Dudas and Cannon 1983). These observations could be interpreted as volatilization by higher summer temperatures of labile forms of Hg that were deposited during the winter. Finally, in portions of a peat core from an ombrotrophic bog in Spain that were deposited during periods of globally cool climate, up to 50% of the Hg was represented by Hg(0); in other parts of the core nearly all ($>$80%) Hg(II) was bound to organic matter (Martinez-Cortizas et al. 1999). The supposition was that cool temperatures

during peat formation retained the Hg(0), while warm temperatures led to volatilization of that species. All these data imply that a significant portion of Hg that is deposited on terrestrial landscapes may be extremely labile and that simply moderately warm temperatures are sufficient to volatilize that portion without any other mechanism being invoked.

In addition to temperature, other soil properties also affect volatilization rates, including soil water content, pH, and clay and SOM content. In the laboratory, Hg losses from soils were maximized at field capacity compared to either air-dry or nearly saturated soils (Landa 1978*b*). Some field observations indicate increased rates of volatilization with increases in soil water content, such as following a rainfall event (Zhang and Lindberg 1999). This has been provisionally attributed to displacement of adsorbed Hg(0) by water molecules. The diffusion and mass transport of Hg(0) within the soil are affected by soil water. Saturation and filled soil pores would be expected to reduce both processes, whereas dry soils would be associated with higher transport rates. Reduction of Hg(II), however, may be inhibited in dry soils. Finally, as stated earlier, wet areas in the landscape could provide conditions leading to significant Hg(II) reduction. In general, Hg volatilization tends to increase with increase in soil pH (Schlüter 2000). Higher volatilization also seems to be associated with lower clay and SOM contents, associated both with lack of binding and therefore stabilizing sites for Hg(II) and with an increase in pathways for diffusion (Schlüter 2000). The movement of Hg(0) across the soil–air boundary layer into the atmosphere also depends on environmental conditions such as barometric pressure (or its change), wind speed, and turbulence (Kim et al. 1997). Another complicating factor in determining the magnitude of volatilization from soil is the evidence that Hg(0) vapor is also adsorbed by soils. Experimentally, such adsorption was roughly correlated with soil carbon (C) content, and retention was predominantly by organo-complexes. Little adsorbed Hg was subsequently lost under ambient conditions (Landa 1978*a*). Although undocumented, a possibility exists that Hg(0) could also be adsorbed by the abundant charcoal found in some soils, remnants of historical fires. The balance between Hg(0) production and adsorption ultimately determines the net flux of Hg from soil.

As might be expected when so many factors potentially affect Hg volatilization, reports of rates vary widely and have high uncertainty, from <1 ng m^{-2} h^{-1} to about 90 000 ng m^{-2} h^{-1} (Fig. 4). In those reports, the mean for sites enriched in Hg through mining or other contamination is 1300 ng m^{-2} h^{-1}, while that for unenriched background sites is 11 ng m^{-2} h^{-1} (Zhang and Lindberg 1999). Lindberg (1996) reported net emission flux from the soil at Walker Branch Watershed, Tennessee, during spring, summer, and fall to be about 7.5 ± 7.0 ng m^{-2} h^{-1}. This net flux was the summation of periods of fluxes from the atmosphere to the soil and of emissions from the soil.

The potential of foliar exchange of Hg(0) around a compensation point (Hanson et al. 1995) was discussed earlier. Using best-available though uncertain data, and including gas-phase exchange of Hg(0) between the atmosphere and both the forest canopy and the soil, Lindberg (1996) estimated that atmospheric deposition of Hg to Walker Branch Watershed, Tennessee, on a summer day was only about one-third of the losses, the largest of which were canopy emissions of gas-phase Hg(0). The source of the additional Hg was either the soil pool or deposition during the dormant season when canopy emissions would be absent. This conclusion is tentative because of both the history of the site, near industrial sources of Hg, and high uncertainty in the measurements. Although measured throughfall and litterfall were nearly equivalent to estimated atmospheric deposition to the canopy, gasous emissions from the canopy had a coefficient of variation of $\pm 80\%$. As mentioned earlier, the very low solubility of Hg(0) makes transport of the gas from soil to leaves via the transpiration stream puzzling. If, however, these emissions are generalizable to other forests, then they have a significant impact on global Hg budgets (Lindberg 1996). The complexity of gaseous Hg flux to and from both terrestrial and aquatic systems can be summarized, "Because of its persistence in the environment and its proclivity to cycle ... a large portion of the mercury in the atmosphere today may consist of recycled mercury stemming from previous releases from both natural and anthropogenic sources." (Schroeder and Munthe 1998, p. 818).

The dynamics of MeHg volatilization from soils differs from that of Hg(0) because of the greater

Fig. 4. Frequency distribution of reported rates of Hg flux by volatilization measured over terrestrial surfaces. Rates over *Background* and *Enriched* surfaces from Zhang and Lindberg (1999) ($n = 8$ in each case), rates over *All* surfaces from Schlüter (2000) ($n = 37$).
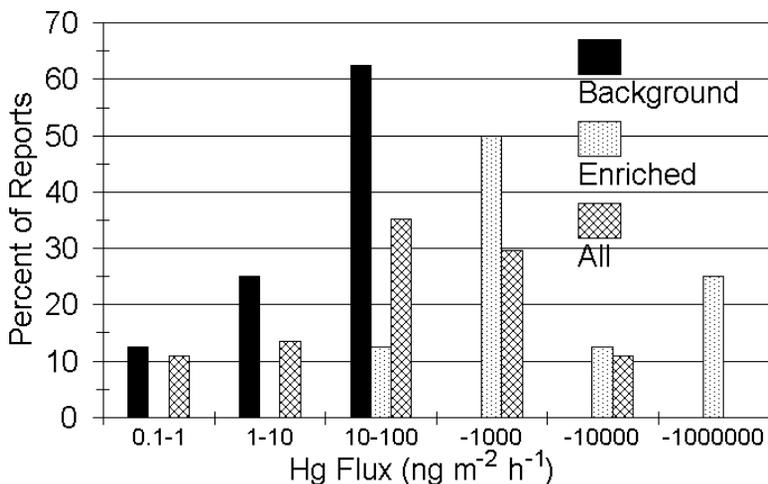
toxicity of the compound, its lower binding to SOM, but also because of its relatively low abundance. Concurrent work with Hg(II) added as $HgCl_2$ and MeHg added to soil as CH_3HgCl showed characteristics of biotically induced reduction in the loss of MeHg, including presence of a lag phase (Schlüter et al. 1995). More Hg was volatilized when applied as MeHg than as $HgCl_2$, but the results must be interpreted cautiously because rates of application exceeded natural levels by five to six orders of magnitude. Both greater rates of biotic detoxification of MeHg and the lower binding of MeHg to SOM were cited as reasons for the difference in volatilization of the two Hg compounds (Schlüter et al. 1995).

Solution losses

Soil solution and groundwater

Presence and transport of Hg in soil solution and groundwater, both in temperate (Aastrup et al. 1991) and tropical soils (Roulet and Lucotte 1995), is closely related to the presence and mobility of DOC or DOM. In general, Hg concentrations are very low in soil solution and groundwater, and Hg transport in lower soil horizons and groundwater is limited. For example, in a boreal landscape in Sweden with glacial till over bedrock, there was a general decrease in Hg concentration in soil solution from the surface (14 ng L^{-1}) to groundwater samples at 100 to 165 cm (7 ng L^{-1}) (Aastrup et al. 1991). Dominant soil solution flux was horizontal, not vertical, in this landscape, and over three-fourths of the downslope transport of Hg occurred in the upper 50 cm. Similarly, soil solution concentrations decreased from near 5.5 to about 3 ng L^{-1} from 20 to 70 cm in depth in the Gårdsjön watershed, Sweden (Lee et al. 1994). In Germany, Hg concentrations in mineral soil solution were below detection limits of 15 ng L^{-1}, but concentrations in groundwater in nearby peatlands were about 20 ng L^{-1} and solutions from the upland forest floor were highly variable but ranged up to 130 ng L^{-1} (Schwesig et al. 1999). Similar high near-surface Hg concentrations in soil water were reported from northern Sweden, where HgT declined with depth from about 150 ng L^{-1} at the surface to about 18 ng L^{-1} at 50 cm (Bishop et al. 1998). The nearly order of magnitude range in concentrations over shallow depths is striking. Low soil water concentrations have also been reported in hardwood stands in Tennessee, U.S.A., 5 ng L^{-1} at 5 cm depth (Lindberg 1996). Concentrations of Hg in deeper groundwater have not been widely

reported, but data from the north-central U.S.A. indicate that they are even lower than those in soil solution (2–4 ng L^{-1}, Krabbenhoft and Babiarz 1992; 1 ng L^{-1}, Grigal et al. 2000).

Even extreme laboratory situations have failed to find significant vertical transport of Hg through soil. For example, following a high rate of Hg application in simulated acid rain (about 50 and 400 years of annual deposition of HgCl$_2$ over about 20 days), the uppermost 1 to 2 cm of soil cores contained 85 to 96% of the applied Hg (Schlüter et al. 1995). Similarly, Hogg et al. (1978b) applied HgCl$_2$ to undisturbed soil cores and leached them with sewage effluent of relatively high pH (8.5) and high concentrations of cations and anions compared to waters in undisturbed systems. They failed to find movement of Hg below 20 cm, but other cations including Ca^{2+}, Mg^{2+}, K$^+$, and Zn^{2+} were progressively leached in a similar experiment. A variety of moderate extractants failed to remove the applied Hg; only 6 N HCl, which progressively dissolves inorganic colloids and hydrolyzes organic matter, was effective (Hogg et al. 1978b). There are reports of vertical Hg movement in the field, but also under extreme conditions. Fifteen years following a single application of sewage sludge containing 3000 to 5000 μg kg^{-1} Hg to an agricultural site in New York, U.S.A., the surface soil layer (upper 20 cm) had an Hg concentration of 640 μg kg^{-1} compared to about 150 μg kg^{-1} in the control (McBride et al. 1999). Total HgT loading to the site had been extremely high, 4.5 kg Hg ha^{-1} (4.5×10^5 μg m^{-2}) (McBride et al. 1997). Concentrations of Hg in soil solution at 60 cm in the control were below detection limits compared to 130 ng L^{-1} at the treated site. The transport of several heavy metals, including Hg, was presumably enhanced by high DOM in the sludge leachate (McBride et al. 1999).

In conclusion, groundwater and soil solution that are low in DOM are also likely to be low in Hg so that vertical transport of Hg is minimal. However, a caveat must be attached to that conclusion. There is the possibility that Hg, with DOM, could be transported quite deeply in highly structured soils through preferential flow paths (Jardine et al. 1989a). This Hg could reach groundwater, at least during storms (Jardine et al. 1990). There is also evidence, however, that in most cases this DOM and presumably associated Hg will be adsorbed by the soil matrix as the solutions move through the soil (Jardine et al. 1989b). Similarly, although vertical Hg flux was minimal in moist peat soils, drying led to shrinkage of the soils, and resulting cracks provided pathways for significant Hg flux (Lodenius et al. 1987).

There are limited data on MeHg concentrations in soil solution, including groundwater. Similar to HgT, MeHg is low in groundwater, ranging from below detection limits of 0.02 ng L^{-1} (Krabbenhoft et al. 1995) to about 0.2 ng L^{-1} (Branfireun et al. 1996). Observations of higher MeHg concentrations in soil solution near the surface (e.g., Branfireun et al. 1996) imply that the major source of MeHg is via surficial or near-surface processes. Relatively high ratios of MeHg to HgT in soil solution have been reported at Gårdsjön, southern Sweden, with an average of about 21% of Hg present as MeHg and nearly identical ratios in both discharge and recharge areas (Lee et al. 1994). These ratios are driven by relatively low HgT concentrations (4 ng L^{-1}) associated with high MeHg concentrations (about 0.9 ng L^{-1}). In northern Sweden, concentration of both HgT and MeHg in soil solution declined with depth, with MeHg about 0.24 ng L^{-1} at the surface to about 0.01 ng L^{-1} at 50 cm (Bishop et al. 1998), and ratios of MeHg to HgT ranging from 0.05 to 0.2%, with a tendency for a decrease with depth (Bishop et al. 1998). In contrast with Gårdsjön, high HgT concentrations (geometric mean about 40 ng L^{-1}) were associated with low MeHg (geometric mean about 0.07 ng L^{-1}). The high ratio of MeHg to HgT at Gårdsjön may be due to high levels of atmospheric deposition of MeHg (Hultberg et al. 1994), but data from either organic surface horizons of mineral soils or organic horizons in a fen and bog in Germany show MeHg concentrations similar to those reported at Gårdsjön (1.2 ng L^{-1}) (Schwesig et al. 1999). Concentrations of HgT in Germany, however, were much higher (25 ng L^{-1}) and therefore ratios of MeHg to HgT were only about 5%. Reports from Ontario, Canada, did not include HgT, but MeHg concentrations were lower in recharge than in discharge areas (0.4 versus 1.8 ng L^{-1}) (Branfireun et al. 1996). In summary, both the HgT and the MeHg concentrations in soil water are highly variable, as is the resulting ratio between them. From the limited available data, the ratio of MeHg to HgT in soil water can be expected to range from about 0.15 to 15%.

Streamflow

Water flux

Loss of Hg by streamflow is controlled by water flux from terrestrial watersheds. Baseflow, streamflow between storm or snowmelt periods, represents outflow from groundwater aquifers that are recharged by percolating soil water. Baseflow would be expected to be low in Hg. Runoff, synonymous with stormflow, is water the origin of which is storms or snowmelt. Runoff is derived from channel precipitation, precipitation falling directly on the flowing stream; overland flow, precipitation that has reached the stream without infiltrating into the soil surface at any point; and interflow, subsurface stormflow that has moved through the soil during at least part of its journey to the stream (Hewlett 1982). Overland flow, produced when rates of precipitation or snowmelt exceed soil infiltration rates, leads to very sharp peaks and recessions of stream hydrographs and is often considered to be the dominant source of runoff (Horton 1933). Although overland flow occurs in agricultural soils, roads, lawns, parking lots, areas subject to livestock trampling, and similar situations (Dunne 1978), it has not been observed or described in undisturbed humid forested areas except under unique conditions (Chorley 1978; Dunne 1978; Hewlett 1982).

Interflow, common in humid forested watersheds, is caused by differential rates of vertical percolation through soil and may occur in more than one soil horizon (Hewlett 1982). The rapid stream response of many forested watersheds to storms is explained by preferential flow through soil macropores, which can occur even in very dry soils (Wilson et al. 1990), and by the development of a variable source area (Hewlett 1974). The variable source area is the part of the watershed that contributes to stormflow, varying in size with the storm and with antecedent conditions; entire watersheds do not contribute to stormflow. Many hydrologic characteristics of lower slope positions increase the importance of near-stream interflow (Helvey and Hewlett 1962). Interflow discharging directly into the stream bed increases streamflow, expands the stream channel network, and increases the size of the source area, often by overflowing temporarily flooded low areas (Hewlett and Nutter 1970). The concept of the variable source area is well established and has potential ramifications to Hg transport. Near-stream areas of the watershed are generally high in SOM and likely Hg and hence are sites where Hg–organic complexes will be mobilized to enter streams during storms. Because of high soil water content, these areas are also likely to have reducing conditions and be sites of both reduction of Hg(II) to Hg(0) and of methylation.

Dissolved Hg

The close relationship between Hg and DOC in solution is well documented (e.g., see citations in Joslin (1994), and many more recent) (Fig. 5). Relationships from around the Northern Hemisphere have similar slopes, about 0.2 ng Hg per 1 mg DOC, with differences in intercepts probably related to whether or not particulate Hg is included. The relationship between DOC and Hg is considered to have strong explanatory power for the transport of Hg from terrestrial to aquatic systems (Driscoll et al. 1995; Johansson and Iverfeldt 1994; Joslin 1994; Lee et al. 1998; Kolka et al. 1999b; Mierle and Ingram 1991). In spite of similarities (Fig. 5), there are regional (Johansson and Iverfeldt 1991) and local differences in the Hg–DOC relationship.

Data from a single location help demonstrate the variability that can be expected. Data were collected on the Marcell Experimental Forest, Minnesota, U.S.A., and included biweekly streamflow samples from six watersheds and concurrent interflow samples from the organic forest floor and from the top of the B mineral horizon at 40 cm (Fleck 1999). The change in Hg concentration with change in DOC is markedly different between the streamflow and interflow samples (Fig. 6), with streamflow very near that reported for other locations (0.17 ng Hg per 1 mg DOC) but interflow through both organic and mineral soil horizons having both greater change (about 0.40 ng Hg per 1 mg DOC) and greater intercept at 0 DOC (about 13 ng L^{-1} compared to 2.8 ng L^{-1}) (Fig. 6). The greater Hg enrichment of interflow than streamflow DOC may be associated with hydrophobic versus hydrophilic organic matter.

Fig. 5. Reported empirical relationships between total Hg concentration and dissolved or total carbon concentration in solution. NY = lakes in the Adirondack Mountains, New York, U.S.A. (Driscoll et al. 1995); MN-s = first-order streams in northen Minnesota, U.S.A. (data from Fleck 1999); Sc = forest streamflow in Sweden (from Meili 1991); WI-l = lakes in northern Wisconsin, U.S.A. (Watras et al. 1996); WI-*r* = rivers in Wisconsin, U.S.A. (Babiarz et al. 1998); MN-l = lakes in northern Minnesota (Sorensen et al. 1990).
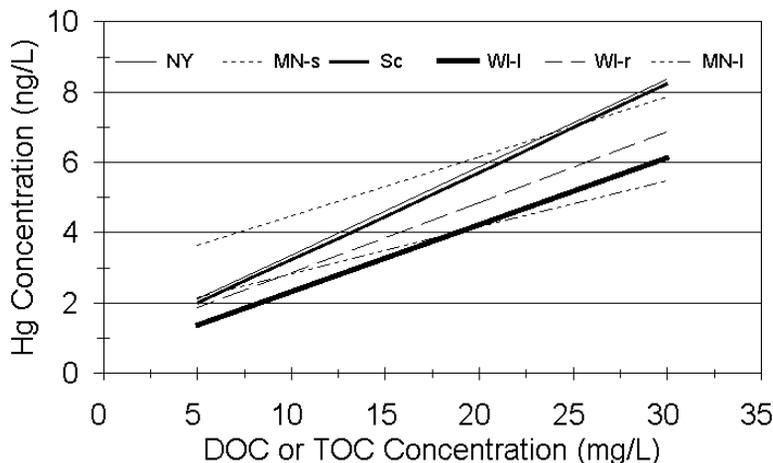

Concentration of hydrophobic organic matter is higher in interflow, with a positive relationship between it and HgT, while no such relationship exists in streamflow (Fleck 1999). Varshal et al. (1996) note that fulvate complexes dominate in the solution phase of river waters, while humic complexes dominate in soils or particulate organic carbon (POC). Export of HgT from watersheds in northern Ontario was very closely related (r^2 = 0.95) to the export of humic material (Mierle and Ingram 1991). The greater intercept of the interflow waters (Fig. 6) suggests the presence of other forms of Hg, either unlikely Cl salts (Skyllberg et al. 2000) or particulates, including POC. Interflow only occurs when soils are saturated, primarily during snowmelt with lesser occurrences during summer storms or autumnal rains, and these conditions are likely to mobilize particulates.

Particulate-bound Hg

In many systems, most of the annual Hg flux is transported during spring floods and high flow periods both because of an increase in Hg concentration and the contribution of these events to the annual water flux (Johansson and Iverfeldt 1994). Short periods during spring flow can carry 50 to 90% annual Hg flux of a watershed (Aastrup et al. 1991; Johansson et al 1991; Mason and Sullivan 1998; Sukhenko et al. 1992). The relationship between Hg and DOC degrades during these high flow events (Bishop et al. 1995*a*; Bishop et al. 1995*b*; Johansson et al. 1991; Mierle 1990; Pettersson et al. 1995; Sukhenko et al. 1992), and a major reason for the increase in Hg concentration is particulate transport. Aastrup et al. (1991) observed large organic particles in soil solution from upper soil horizons, but decreasing amounts downslope and none in deep groundwater, and they suggested that these particles could be the main carriers of Hg in the watershed. A single summer storm event in an agricultural watershed in Wisconsin transported 70 times more particulate matter and 20 times more Hg than normal flow (Babiarz et al. 1998). In a small, relatively steep (average slope 35%) hardwood watershed in New York, U.S.A., 60 to 75% of the annual Hg export from the watershed was by particulates during high-flow events (Scherbatskoy et al. 1998). Particulate Hg (total – dissolved) was highly correlated with the organic fraction of suspended sediment, suggesting that the Hg was associated with POC. In five small watersheds in Minnesota, U.S.A., Kolka et al. (1999*b*) found poor correlations between monthly

Fig. 6. Empirical relationships between total Hg concentration and dissolved organic carbon concentration in interflow through organic surface horizons (O, $n = 220$), mineral subsurface horizons (M, $n = 270$) , and first-order streams (S, $n = 340$) in the Marcell Experimental Forest, Minnesota, U.S.A., from 1993–1998 (data from Fleck 1999).
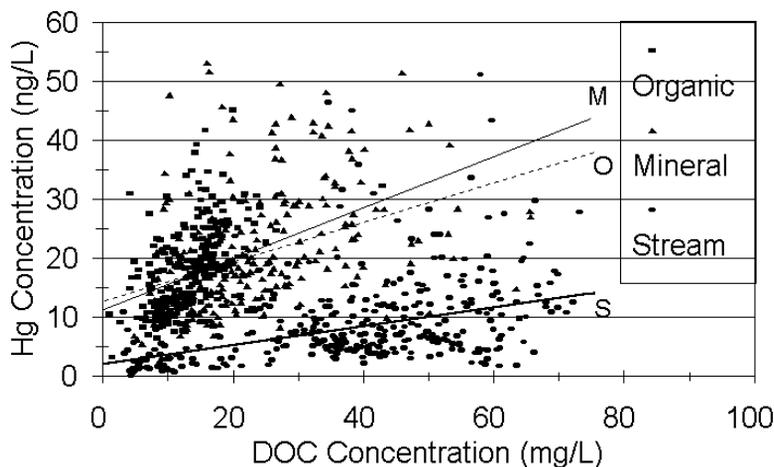
HgT and DOC or total organic carbon (TOC), but significant positive relationships between HgT and POC, operationally defined as the difference between TOC and DOC. Although POC accounted for only 10 to 20% of the carbon transported from the watersheds, it was associated with 52 to 80% of the HgT transported. Others have also considered particulates to be important in Hg transport, with the Hg concentration curve following the hydrograph during frequent episodic events (Allan and Heyes 1998).

Particulates have also been implicated in Hg transport in large watersheds. Nearly three fourths of the Hg load of the St. Lawrence River Basin, Canada, 1.34×10^6 km^2, with a variety of land uses including agriculture, forest, and urban, was particulate (Quémerais et al. 1999). Similarly, virtually all the transport of Hg in the Minnesota River basin, draining about 44 000 km^2 of largely agricultural land, was by particulates assumed to be primarily mineral and derived from surface erosion (Balogh et al. 1997). The origin of this material was demonstrated by monitoring overland flow from a cultivated area in the watershed during snowmelt (Balogh et al. 2000). Due to particulates, concentrations of Hg were much higher in overland flow (about 20 ng L^{-1}) than in snow (1 ng L^{-1}). In this case, true overland flow (Hortonian) occurred and a minimum of 70% of the Hg particulate fraction was derived from soil. The Hg concentration of the particulates, 52 μg kg^{-1}, was very similar to that reported for particulates in the river system (46 μg kg^{-1}) (Balogh et al. 1998a) and for the silt plus clay soil fraction both across the north-central U.S.A. (52 μg kg^{-1}, Nater and Grigal (1992)) and the prairie soils of Alberta, Canada (53 μg kg^{-1}, Dudas and Pawluk (1976)). These data demonstrate that mobilization of soil materials is important to Hg transport in cultivated watersheds.

The ratio of particulate to dissolved Hg is affected by land use. Compared to export from the predominantly agricultural large river system (Balogh et al. 1997), there was about an order of magnitude lower annual-sediment-yield (particulates) per unit watershed area and only about one-third the annual Hg yield per unit watershed area in two adjacent large basins (20 000 and 51 500 km^2) (Balogh et al. 1998a). The smaller watershed, the St. Croix basin, is predominantly forested with wetlands; the larger watershed, the Upper Mississippi basin, has a mix of forest and agriculture. These differences in land use influenced both particulate and dissolved Hg, with both higher Hg concentrations in particulates (191 and 86 μg kg^{-1}, respectively, compared to 46 μg kg^{-1}) (Balogh et al. 1998a) and higher dissolved Hg (1.9 and 0.79 ng L^{-1} compared to 0.41 ng L^{-1}, Balogh et al. 1998b) in the other watersheds than in

Table 1. Distribution coefficients (particulate Hg (ng kg^{-1}) divided by dissolved Hg (ng L^{-1})) reported or calculated from the literature (all means or medians).

Location	log K_d (L kg^{-1})	Reference
Large rivers north-central U.S.A.	4.4	Balogh et al. 1998*a*
Minnesota 1st order streams	4.7	Fleck 1999
Wisconsin rivers (spring)	4.8	Hurley et al. 1995
Wisconsin rivers (fall)	4.9	Hurley et al. 1995
Wisconsin rivers	4.9	Babiarz et al. 1998
Texas estuaries	4.9	Stordal et al. 1996
Wisconsin lakes	5.2	Hurley et al. 1994
Lake Michigan tributaries	5.5	Hurley et al. 1996
St. Lawrence River and tributaries	5.5	Quémerais et al. 1999
Lake Michigan	5.7	Mason and Sullivan 1997

the agricultural watershed. In spite of lower concentrations, higher particulate flux led to higher Hg flux from the agricultural watershed. In a study of 39 river systems in Wisconsin, U.S.A., Hurley et al. (1995) associated elevated HgT flux with land use, with particulate Hg important in agricultural watersheds and dissolved Hg important in forested watersheds with wetlands. In an urban river near Washington, D.C., storm flow associated with particulates was the major vector for Hg transport (Mason and Sullivan 1998).

Although particulates are important in transporting Hg, there are difficulties in ascertaining their absolute importance. First, there are analytical difficulties associated with their determination, especially at low particulate concentrations. Another difficulty is measurement during appropriate times. To understand the actual contribution of particulates to Hg flux and the contributions of single events to the annual Hg load, samples must be collected during episodes of high flow. Simply using weekly or monthly grab samples for Hg and particulate determination will not appropriately weight the data for flux determination.

Despite these difficulties in determining the role of particulates in transport, it is interesting that the log of the distribution coefficient, K_d, is surprisingly uniform among a variety of studies and systems (Table 1). The mean of these studies, 5.1 ± 0.4 L kg^{-1}, indicates that the Hg concentration associated with particulates is generally high. However, in storm events from agricultural areas with significant mineral particulates, the values of log K_d are likely to be lower than this mean (2.8, Babiarz et al. 1998; 3.4, computed from Balogh et al. 2000). The ratio of organic to mineral matter in particulates affects both K_d and particulate Hg concentration, with stronger binding associated with higher organic content (e.g., Mason and Sullivan 1998).

Resulting flux

Overall patterns

Mean annual streamwater Hg concentrations from streams and rivers, collected over multiple years or sites ($n = 79$), ranges over one order of magnitude, from 1.2 to 20 ng L^{-1} (Babiarz et al. 1998; Johansson et al. 1991; Kolka 1996; St. Louis et al. 1996; Westling 1991). Annual fluxes of Hg, from an even wider variety of watersheds ranging from very small first-order watersheds (minimum 0.6 ha, Gårdsjön G1 (Munthe et al. 1998)) to very large river basins (maximum 1.34×10^8 ha, St. Lawrence River, Canada (Quémerais et al. 1999)), have a near-normal frequency distribution with about 75% of observations in the range of 1 to 3 μg m^{-2} a^{-1} and a mean of 1.7 μg m^{-2} a^{-1} (Fig. 7). This relatively small range of flux is surprising. Many scientists stress the importance of DOC, particulates, area of

Fig. 7. Frequency distributions of annual Hg flux from very large watersheds (Minnesota River, St. Croix River, Upper Mississippi River, U.S.A., (Balogh et al. 1998*b*); St. Lawrence River, Canada, (Quémerais et al. 1999)); moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998); first-order streams in northern Minnesota, U.S.A. (Kolka 1996), Vermont, U.S.A. (Scherbatskoy et al. 1998), Ontario, Canada (Mierle 1990; Mierle and Ingram 1991; St. Louis et al. 1996), Scandinavia (Driscoll et al. 1994*a*; Iverfeldt et al. 1996; Lee et al. 1995; Lee et al. 1998; Lee et al. 2000; Munthe et al. 1998), and central Europe (Schwesig and Matzner 2000); and miscellaneous reports tabulated by Bishop and Lee (1997, 6 reports), Driscoll et al. (1998, 6 reports), and Kolka (1996, 9 reports) (*n* = 121).
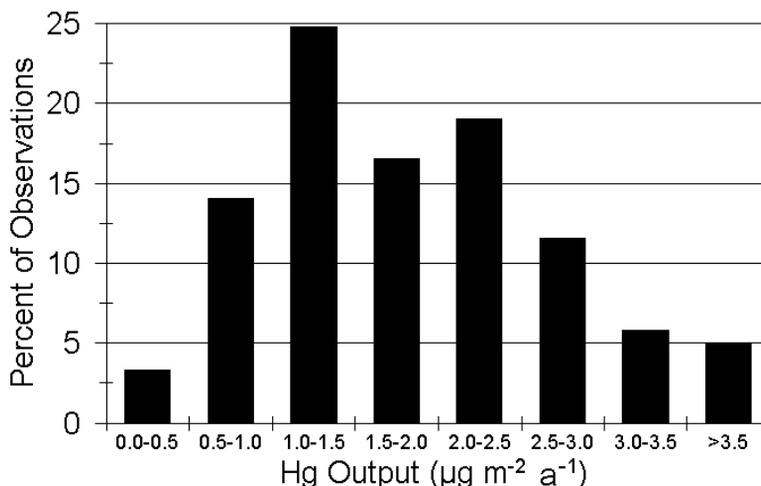

peatlands, frequency of episodic events, and other factors to explain variation among sites or years in their annual flux data. Although all these factors are likely to be important, these nuances are apparently averaged out to create a relatively uniform Hg flux from a variety of systems (Fig. 7).

Although the main concern involving toxicity of Hg is MeHg, as described above, only a small proportion of the Hg in both inputs and pools of the terrestrial Hg cycle is present as MeHg. In the case of MeHg flux from terrestrial to aquatic systems via streamflow, however, the situation becomes more complex. Flux of MeHg from watersheds is very skewed, with about 80% of observations $<0.15\ \mu\mathrm{g\ m^{-2}\ a^{-1}}$ (mean = 0.06 $\mu\mathrm{g\ m^{-2}\ a^{-1}}$) (Fig. 8). On the basis of averages, flux of MeHg is only about 4% of HgT flux. However, some of the measured MeHg fluxes are substantially higher than the mean (Fig. 8), and the explanation for those fluxes lies in watershed characteristics.

Watershed characteristics

Topography — Because of the close relationship between Hg and DOC, watershed factors that increase DOC export are also likely to enhance Hg export. The DOC concentrations of 337 lakes in the northern U.S.A. and in Canada were positively related to the ratio of drainage area to lake area and negatively related to watershed slope and both lake area and depth (Rasmussen et al. 1989). At the extremes, highest DOC was likely in small, shallow headwater lakes with relatively large, low-sloped watersheds and rapid water turnover, while the lowest DOC was associated with large, deep, higher-order lakes with small, steep, direct drainage areas and slow water turnover. Both thin, rocky soils and presence of coniferous vegetation led to increased DOC. Wetlands are also a major source of DOC (Eckhardt and Moore 1990). In general, long water residence times in terrestrial systems lead to higher DOC in associated lake waters and should also lead to higher Hg concentrations. Concentration of Hg in water, sediments, and fish from 81 lakes in northern Minnesota, U.S.A., was positively related to total organic

Fig. 8. Frequency distributions of mean annual MeHg flux from moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998); first-order streams in Ontario, Canada (St. Louis et al. 1996), central Europe (Schwesig and Matzner 2000), and Scandinavia (Driscoll et al. 1994*a*; Iverfeldt et al. 1996; Lee et al. 1995; Lee et al. 1998; Lee et al. 2000; Munthe et al. 1998); and miscellaneous reports tabulated by Bishop and Lee (1997, 6 reports) and Driscoll et al. (1998, 6 reports) (*n* = 53).
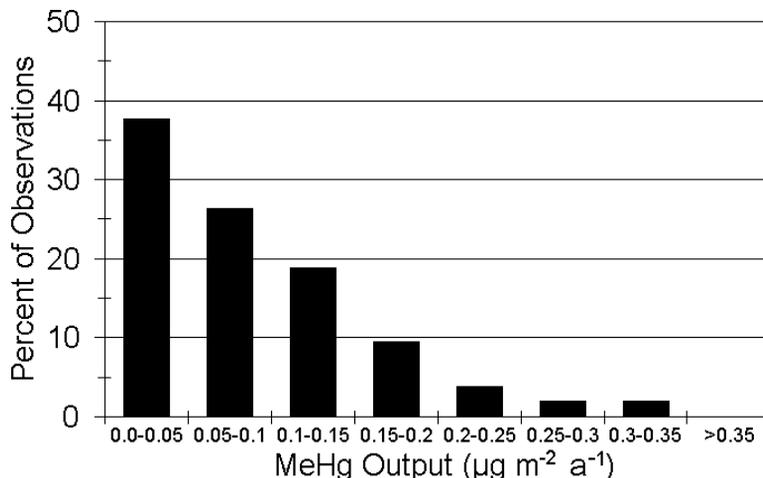

carbon (TOC) in solution (Sorensen et al. 1990) and to those watershed factors that could plausibly affect TOC, including positive relationships with the proportion of the watershed that was forested and lake water turnover time and a negative relationship with lake surface area. Similar positive relationships between lake water DOC and Hg and negative relationships with lake size have been reported from Wisconsin, U.S.A. (Watras et al. 1995). In the Adirondack Mountains, New York, U.S.A., Driscoll et al. (1994*b*) stressed that DOC in lakes and the watershed characteristics that influence it were the most obvious factors regulating the concentration and availability of both Hg and MeHg. Lee et al. (1998) summed up these characteristics with respect to Hg transport from the Svartberget watershed in Sweden, "... variation in the (total Hg) output was largely controlled by the major flow pathways and DOC levels in runoff." During periods of high flow, flow paths were surficial and passed through soils layers rich in Hg and C, leading to higher HgT and DOC than during low discharge periods when water flowed through deeper soil layers with lower Hg and C (Lee and Iverfeldt 1991; Lee et al. 1998).

Size — Flux of Hg via streamflow is weakly related to watershed size, with a clear tendency for lower annual flux with increasing watershed size (Fig. 9, $r^2 = 0.22$). Even though the relationship is weak, its existence over a range of about eight orders of magnitude of watershed size encompassing a broad range of systems lends it some credibility. Flux depends on both Hg concentration and on water yield, and size and water yield could co-vary. Concentration of HgT is also inversely related to watershed size, albeit more weakly, based on data from very large watersheds (Minnesota River, St. Croix River, Upper Mississippi River, U.S.A. (Balogh et al. 1998)); St. Lawrence River, Canada (Quémerais et al. 1999)); moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998); first-order streams in northern U.S.A. (Kolka et al. 1999*b*; Krabbenhoft et al. 1995; Scherbatskoy et al. 1998), Ontario, Canada (Mierle 1990; St. Louis et al. 1996), central Europe (Schwesig and Matzner 2000), and Scandinavia (Iverfeldt et al. 1996; Iverfeldt and Johansson 1988; Lee et al. 1995; Lee et al. 1998). The best-fit line, including the correction term for bias (Beauchamp and Olson 1973), is

[1] $\ln(\text{Hg concentration (ng L}^{-1})) = 2.02 - 0.063 \times \ln(\text{Area (ha)}), r^2 = 0.13, n = 47.$

Fig. 9. Relationship of annual Hg flux and watershed area. Data from very large watersheds (Minnesota River, St. Croix River, Upper Mississippi River, U.S.A. (Balogh et al. 1998*b)*; St. Lawrence River, Canada (Quémerais et al. 1999)); moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998); first-order streams in northern U.S.A. (Kolka et al. 1999*b*; Krabbenhoft et al. 1995; Scherbatskoy et al. 1998), Ontario, Canada (Mierle 1990; St. Louis et al. 1996), central Europe (Schwesig and Matzner 2000), and Scandinavia (Iverfeldt et al. 1996; Iverfeldt and Johansson 1988; Lee et al. 1995; Lee et al. 1998; Lee et al. 2000). Best-fit line, including correction term for bias (Beauchamp and Olson 1973), $\ln(\text{Hg flux } (\mu\text{g m}^{-2}\text{ a}^{-1})) = 0.89 - 0.068 \times \ln(\text{Area (ha)})$, $r^2 = 0.22$, $n = 49$.
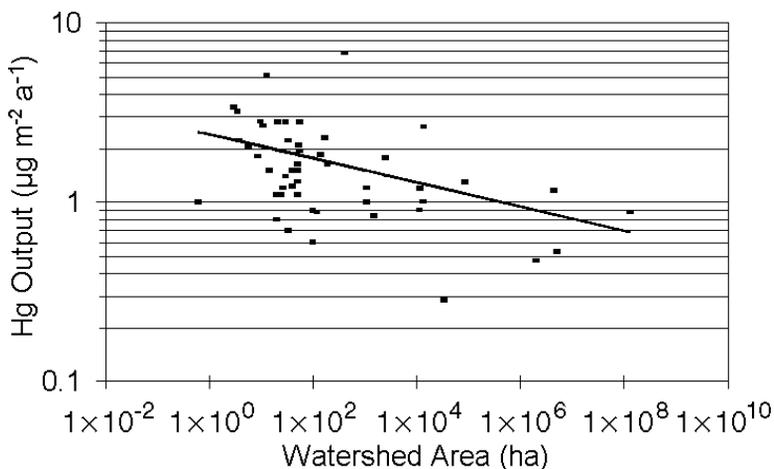
An algebraic solution for water yield, using the best-fit statistics for Hg flux and concentration, indicates less than a 7% change in water yield with increase in watershed size from 1 to 10^6 ha. In these data, size and water yield do not strongly co-vary and the decrease in both Hg concentration and flux with watershed size is therefore not simply due to change in water yield. One possible explanation for the decline in Hg may be less effective transport processes to streams and rivers in larger watersheds. Another possible explanation may be loss of Hg from the stream or river by in-stream processes such as volatilization and sedimentation. The rapid decrease in flux with watershed size, and hence with stream order, indicates more active processing of Hg in small systems, similar to the case of nitrogen export (Peterson et al. 2001). The data upon which this relationship is based were collected from systems that were not near significant sources of Hg contamination. In contrast, urban watersheds in New York, U.S.A. (Bigham and Vandal 1996) have Hg streamflow flux that is four to five times greater than predicted from the relationship with watershed size (Fig. 9). The higher flux in these watersheds is due to local sources of atmospheric Hg, reduced area of permeable soil due to paving, other non-point sources of Hg to the streams, and continual anthropogenic disturbance as compared to non-urban systems (Bigham and Vandal 1996).

There is no pattern of MeHg flux with watershed size ($r^2 = 0.01$, $n = 22$), based on data from moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998) and first-order streams in Ontario, Canada (St. Louis et al. 1996), central Europe (Schwesig and Matzner 2000), and Scandinavia (Iverfeldt et al. 1996; Lee et al. 1995; Lee et al. 1998; Lee et al. 2000).

Studies of HgT and MeHg flux are contradictory. St. Louis et al. (1996), for example, found no relationship between HgT and MeHg in waters from Ontario, while Watras et al. (1995) found such a relationship in Wisconsin. These contradictory results emphasize that export of HgT and MeHg are influenced differently by terrestrial factors such as DOC, particulates, area of peatlands, and frequency of episodic events (Lee et al. 1995). For example, two watersheds in Sweden that differed in wet MeHg inputs by a factor of three, associated with about a two-fold difference in both volume of precipitation and of streamflow, had comparable streamflow MeHg flux ($0.12 \ \mu\text{g m}^{-2}\text{ a}^{-1}$) (Lee et al. 1995). Wet

deposition alone was not a good indicator of either MeHg concentrations or flux in streamflow (Lee et al. 1995).

Wetlands — Transport of Hg to lakes is frequently linked to presence of wetlands in the watershed. Because most studies have been conducted in northern forested watersheds, the term "wetlands" usually refers more specifically to peatlands. The role of peatlands in Hg transport is paradoxical. Budgets indicate significant Hg sequestration in peatlands (Benoit et al. 1994; Grigal et al. 2000). It is therefore logical to hypothesize that Hg flux from watersheds should be reduced when wetlands are present, and this hypothesis has support in the literature (Borg and Johansson 1989; Johansson et al. 1991; Lindqvist et al. 1991; Zillioux et al. 1993). Presence or absence of wetlands in watersheds in northwestern Ontario had no discernable effect on HgT retention, neither reducing nor enhancing it (St. Louis et al. 1996). Because wetlands (peatlands) are a major source of DOC (Eckhardt and Moore 1990), their presence may also be hypothesized to increase Hg streamflow flux. This hypothesis, too, has support in the literature (Babiarz et al. 1998; Driscoll et al. 1994*b*; Kolka et al. 1999*b*; Mierle and Ingram 1991; Watras et al. 1995). With a diverse data set from the literature, ranging from first-order basins (minimum about 3.5 ha, Paroninkorpi, Finland (Lee et al. 1998)) to very large watersheds (maximum 5.15×10^6 ha, Upper Mississippi basin (Balogh et al. 1998*a*)) and excluding watersheds reported as having no wetlands, there is a weak positive relationship between the percent of the watershed in wetlands and the annual HgT flux (Fig. 10, $r^2 = 0.19$, $n = 24$). One of the difficulties of determining such a general trend is assessing what is meant by the term wetlands in the literature. Some watersheds are clearly either wholly upland or wetland, but other descriptions are more problematic. For example, a watershed may be described as having no wetlands but "... low watershed slopes with thick organic soils." (Lee et al. 1998) or containing a "... riparian zone ... of deep peat" (Lee et al. 1995). Such areas may be functionally equivalent to wetlands in acting as a source of Hg and DOC, but no estimates of their area are provided. In addition, in very large watersheds wetlands are usually located nearer the headwaters, and their influence on Hg and DOC may become diluted as the waters reach higher-order rivers. It appears, however, that the role of wetlands as sources of DOC and associated Hg surpass their role as Hg sinks, so that Hg export is increased by wetlands in the watershed (Fig. 10).

The potential of wetlands and especially peatlands to act as sources of MeHg is reported so frequently that it is nearly axiomatic (Driscoll et al. 1994b; Hurley et al. 1995; Lee and Hultberg 1990; St. Louis et al. 1994; Watras et al. 1995). Such a relationship is confirmed over a diverse array of watersheds and indicates about a three-fold increase in MeHg flux with an increase in wetland area from 1 to 10% and a further three-fold increase from 10 to 50% (Fig. 11, $r^2 = 0.38$). This increase in flux is accompanied by a weak positive relationship between percent wetland and MeHg concentration (Fig. 12, $r^2 = 0.14$). In spite of the problem of defining wetlands, the relationship between wetlands and MeHg flux is quite strong. The increase in MeHg concentration with area of wetland in the watershed (about 0.01 ng L^{-1} per % in the range 1 to 10% wetland, Fig. 12) is similar to that reported for lakes in northern Wisconsin, U.S.A. (0.007 ng L^{-1} per %, Watras et al. 1995) but only about one-third that reported with area of near-shore wetlands for lakes in the Adirondack Mountains, U.S.A. (Driscoll et al. 1994*b*, 0.03 ng L^{-1} per % wetland). Wetlands located somewhere in the watershed are less significant sources of MeHg to lakes than are wetlands directly on the lakeshore. These empirical relationships do not directly address the mechanistic origin of the MeHg.

The increase in flux of MeHg with increase in wetland area (Fig. 11) is greater than the increase in flux of HgT (Fig. 10) and an algebraic solution of the two regressions yields the equation,

[2] $\ln(\text{MeHg/HgT}(\%)) = +1.1 + 0.3 \times \ln(\text{Wetland}\%)$.

Equation [2] indicates an increase in the ratio of MeHg to HgT from about 3% at 1% wetland to a maximum of about 12% at 100% wetland. These ratios are comparable to those reported in streamflow

Fig. 10. Relationship between the proportion of wetlands in a watershed and the annual Hg flux in streams and rivers from very large watersheds in the midwestern U.S.A. (Balogh et al. 1998), moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998) and first-order streams in Minnesota, U.S.A. (Kolka et al. 1999*b*), Ontario, Canada (St. Louis et al. 1996), New York, U.S.A. (Driscoll et al. 1998), and Scandinavia (Lee et al. 1995; Lee et al. 1998). Watersheds without wetlands not included. Best-fit line, including correction term for bias (Beauchamp and Olson 1973), ln(Hg flux (μg m^{-2} a^{-1})) = -0.21 + 0.26 × ln(Wetland %), $r^2 = 0.19$, $n = 24$.
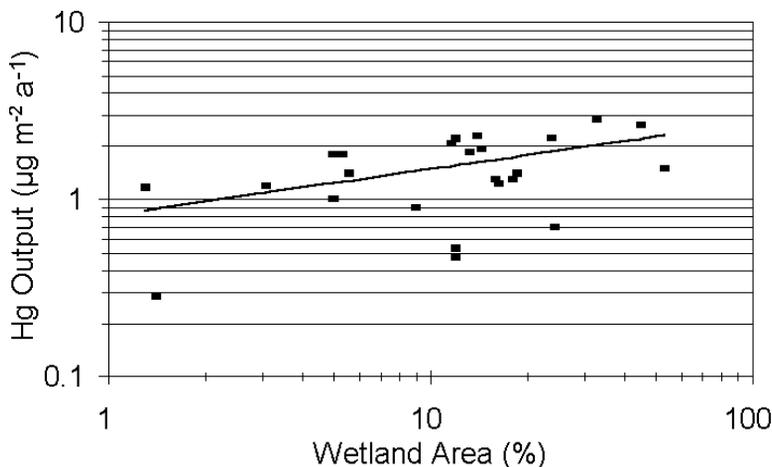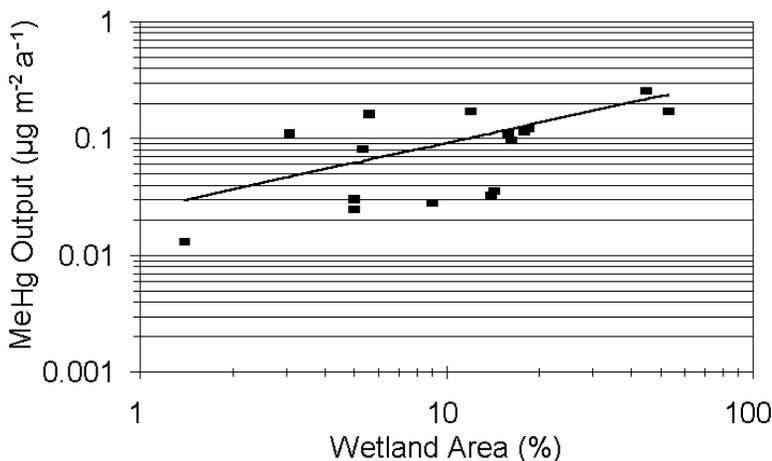

Fig. 11. Relationship between the proportion of wetlands in a watershed and the MeHg flux in rivers and streams from moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998) and first-order streams in Ontario, Canada (St. Louis et al. 1996), New York, U.S.A. (Driscoll et al. 1998), and Scandinavia (Lee et al. 1995; Lee et al. 1998). Watersheds without wetlands not included. Best-fit line, including correction term for bias (Beauchamp and Olson 1973), ln(MeHg flux (μg m^{-2} a^{-1})) = -3.71 + 0.57 × ln(Wetland %), $r^2 = 0.38$, $n = 16$.

(Lee et al. 1995; St. Louis et al. 1996; Westling 1991) and may indicate an upper limit of about 10 to 15% in the ratio of MeHg to HgT, perhaps related to the balance between methylation and demethylation in terrestrial systems.

The flux of MeHg from watersheds has seasonality related to biological activity. Concentrations of MeHg are highest in flow from wetlands during midsummer (Rudd 1995). Although the runoff

Fig. 12. Relationship between the proportion of wetlands in a watershed and the MeHg concentration in rivers and streams from moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998) and first-order streams in Ontario, Canada (St. Louis et al. 1996), New York, U.S.A. (Driscoll et al. 1998), and Scandinavia (Lee et al. 1995; Lee et al. 1998, Westling 1991). Watersheds without wetlands not included. Best-fit line, including correction term for bias (Beauchamp and Olson 1973), ln(MeHg concentration (ng L^{-1})) = -1.95 + 0.25 × ln(Wetland %), r^2 = 0.14, n = 23.
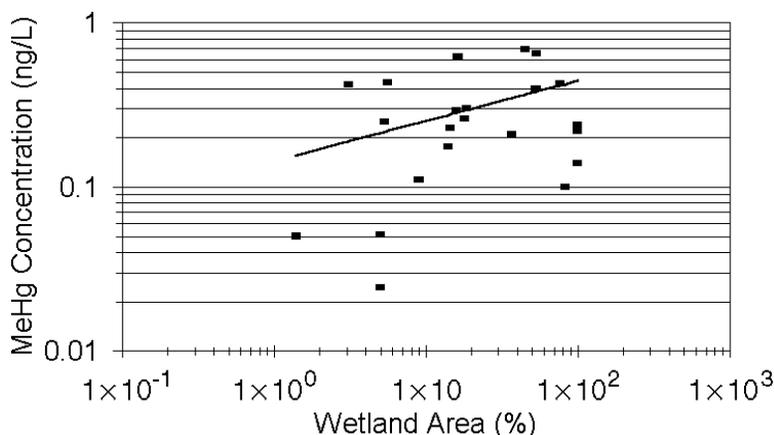
associated with snowmelt in spring accounted for about one fourth of the water flux and about one third of annual output of HgT from a small watershed in northern Sweden, it only accounted for slightly >10% of the MeHg flux which continued to increase to a maximum in August (Bishop et al. 1995*b*). Less than 5% of HgT transported during the spring thaw from watersheds of seven rivers in Wisconsin, U.S.A., was MeHg, but that ratio increased to about 15% in autumn, presumably as a consequence of the flushing of soil pore waters in late summer (Babiarz et al. 1998). Concentration of MeHg in pore-water also increased from spring to summer in a watershed in Ontario, Canada (Branfireun et al. 1996). The highest concentration of MeHg in base flow was during a very warm dry period, and 53% of the annual mass flux of MeHg from the watershed occurred during one summer storm. Surface stream flow across a peatland was the most important flux path for MeHg, while groundwater discharge from the peat was an insignificant contributor because of both low water flux and MeHg concentration (Branfireun et al. 1996). Near-surface pore-water concentrations of MeHg were high in peatland discharge zones and lower in recharge and lateral flow zones. Annual production rates of MeHg in wetlands are about 0.3 μg m^{-2} a^{-1} compared to 0.5 to 3 μg m^{-2} a^{-1} for lakes and 13 μg m^{-2} a^{-1} for recently flooded areas (Rudd 1995). Driscoll et al. (1998) measured rates of MeHg production in a beaver pond of 0.45 μg m^{-2} a^{-1} of pond area, with highest rates during low-flow conditions. They suggest that the recent increased beaver populations in forested areas, rebounding from very low levels near 1900, may have led to increased MeHg production due to inundation of terrestrial landscapes, with a gradual decline to current rates of production as ponds matured.

Although wetlands provide suitable conditions for production of MeHg (Rudd 1995), they also affect the hydrologic response of a watershed. Both flow paths and residence times are extremely important for mobilization of MeHg (Bishop and Lee 1997; Branfireun et al. 1996). As the proportion of wetlands in a watershed increases, stormflow (flood) peaks are attenuated because of temporary water storage in those relatively flat landscape elements. The attenuation is proportional to the logarithm of percent of wetlands, and the shape of the relationship (Fig. 13) is very similar to that describing the increase in MeHg flux from watersheds (Fig. 11). The flood attenuation is equivalent to an increase in water residence time in the watershed, allowing greater interaction with the porewaters in the wetlands.

Fig. 13. Relationship between the proportion of wetlands in a watershed and both the reduction in flood peak flow (stormflow) from watersheds in the midwestern U.S.A. (Verry 1997) and the mean annual MeHg flux (see Fig. 11).
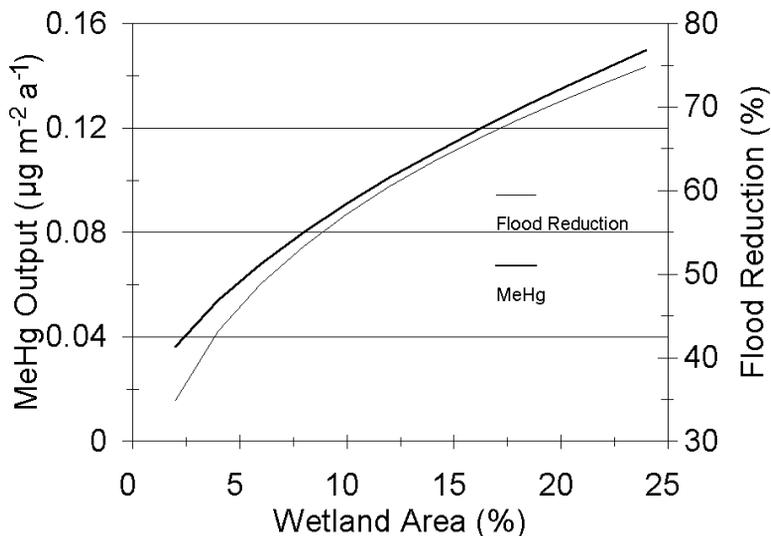
Wetlands therefore increase MeHg flux from terrestrial to aquatic systems both because they act as sites of production and because they increase water residence time. In a few cases, uplands, usually sinks for MeHg, have been reported to be sources (Rudd 1995). Although each watershed is unique in its streamflow regime and mix of land cover, as reflected in the lack of a relationship between MeHg flux and watershed size, wetlands are especially important as sources of MeHg. The flow of waters through them, its residence time, and the season of residence all affect MeHg transport to aquatic systems. It is ironic that wetlands, sacred landscape elements that both regulation and legislation attempt to protect from disturbance, are the single most identifiable source of MeHg from terrestrial to aquatic systems.

Fire or other disturbance

Fires are common in nearly all forests, particularly those in the boreal zone. High temperatures during burning of foliage and small twigs of trees should lead to volatile loss of associated Hg. Similarly, loss of soil C by fire should lead to loss of Hg because of the close association between soil C and Hg. For example, there was about a 50% loss of C from the forest floor following a spring forest fire when the soil was relatively moist from recent snowmelt (Slaughter et al. 1998), and even greater losses could be expected from fires in mid- to late-summer when soils are dryer. Fires are common in peatlands, creating layers of charcoal and reducing peat accumulation (Kuhry 1994) and also likely leading to loss of accumulated Hg. In the Okefenokee Swamp, Georgia, U.S.A., an inverse relationship between percent ash and Hg concentration with depth in peat contrasted with either no relationship or a positive relationship between ash and other metals (Casagrande and Erchull 1976). The increased ash content of the peat is an indicator of oxidizing conditions, either induced by warm dry climatic conditions or by fire, and its inverse relationship with Hg indicates Hg loss under those conditions in contrast with accumulation of other metals.

Fires can also alter the hydrology of the site, with effects varying with environment. A forest fire in semi-arid New Mexico, U.S.A., mobilized both organic matter and Hg and increased their transport to a reservoir (Caldwell et al. 2000). Concentrations of HgT increased six fold and of MeHg by about 30-fold in reservoir sediment compared to that deposited before the fire. In contrast, there was no increase

in MeHg in zooplankton in boreal lakes in Québec, Canada, associated with forest fire (Garcia and Carignan 1999). In this environment, burning did not increase transport of Hg, presumably because it did not increase transport of DOC from terrestrial watersheds to lakes (Garcia and Carignan 1999).

Reduced transport of DOC from a terrestrial watershed, by about 50% over a 20-year period, was attributed to a combination of dry, warm temperatures and associated forest fires in the Experimental Lakes Area, Ontario, Canada (Schindler et al. 1996). This reduction in DOC would be expected to reduce transport of Hg to the lakes and also to affect in-lake Hg reactions (Schindler et al. 1996). The reduction in DOC transport was ascribed almost wholly to reductions in water flux from the terrestrial watershed to the lake, about 11 mm per year over the 20-year period (Schindler et al. 1996).

Forest harvest also affects DOC transport, and should therefore affect Hg. Most studies have measured only DOC and not Hg, and results vary. In some cases, harvesting has had little effect on total DOC (McLaughlin et al. 1996; Meyer and Tate 1983), in others harvest has increased DOC export (Neal et al. 1992; Qualls et al. 2000), and in still others relatively little change has occurred (McDowell and Likens 1988). These differences in response emphasize the importance of hydrologic regime and soil properties in affecting DOC export (Moore 1987). In a study that measured Hg but not DOC, Garcia and Carignan (1999) reported an increase in MeHg in lake zooplankton associated with recent logging in Québec, presumably because of associated increased transport of DOC.

Other disturbances also affect Hg flux. Based on numerous studies, initial cultivation of previously undisturbed soils and attendant increased microbial activity and erosion leads to a loss of 30% or more of the original SOM (Mann 1986). A logical deduction would be that cultivation should similarly reduce Hg by a combination of volatile and particulate losses. Tillage of forest soils significantly increased Hg concentrations in understory plants in Finland compared to either harvested and untilled or unharvested areas (Leinonen 1989), implying increased volatilization of Hg(0) and subsequent foliar uptake following tillage. A logical deduction would be that cultivated soils should have reduced Hg compared to uncultivated soils. Reported differences in Hg between undisturbed and cultivated soils, however, do not appear to be large. For example, in Alberta, Canada, soils that had not been cultivated had Hg concentrations ranging from 20 to 35 μg kg^{-1} (Dudas and Pawluk 1976), while similar cultivated soils ranged from 20 to 40 μg kg^{-1} (Dudas and Pawluk 1977). In southwest Siberia, the range of Hg concentrations among different types of cultivated soils was from 21 to 33 μg kg^{-1} (Anoshin et al. 1996), not appreciably different than that in uncultivated soils. In both cases, however, cultivation significantly affected those horizons very high in SOM, appreciably altering the high-organic LFH horizons in Canada (Dudas and Pawluk 1976) and the A_o and A_s horizons in Siberia (Anoshin et al. 1996). For these horizons, at least, cultivation clearly enhanced the loss of SOM and Hg. Cultivation also is a major cause of erosion (particulate transport) in watersheds (Pimental et al. 1995); particulates are important for Hg flux in many systems.

Because wetlands are a major source of DOC (Eckhardt and Moore 1990), peatland drainage for forest production could lead to increased Hg flux. There was no clear evidence of greater HgT flux from drained as compared to undrained peatlands in central and south Sweden, but MeHg flux increased from drained peatlands with about 70% of the MeHg associated with humic materials (Westling 1991). The highest concentrations of both HgT and MeHg occurred in streamflow following dry periods with low ground water and low water flow, climatically induced water fluctuations. In contrast to that reported lack of difference in HgT flux with drainage, Simola and Lodenius (1982) used Hg accumulation in annual sediments in two comparable lakes to assess peatland drainage. Rates of Hg accumulation in sediments increased in the lake with drained peatlands in the watershed, from 30 μg m^{-2} a^{-1} to over 100 μg m^{-2} a^{-1} temporally associated with the drainage; there was no such increase in the lake whose watershed had no drainage.

Table 2. Literature values for important fluxes of the terrestrial Hg cycle as documented in this review.

Category	Units	Mean	25th Percentile	75th Percentile	N
Inputs					
Open Precipitation	μg m^{-2} a^{-1}	9.6	6	15	82
Throughfall	μg m^{-2} a^{-1}	17	15	19	17
Litterfall	μg m^{-2} a^{-1}	21	17	25	21
Outputs					
Volatilization	ng m^{-2} h^{-1}	11	8	28	8
Streamflow HgT	μg m^{-2} a^{-1}	1.7	1.2	2.4	121
Streamflow MeHg	μg m^{-2} a^{-1}	0.06	0.03	0.12	53

Summary

Volatilization is an important Hg flux from terrestrial systems. Its measurement is highly uncertain with measured rates from soils having a central tendency near 10 ng m^{-2} h^{-1}. Gas-phase exchange of Hg(0) between the atmosphere and the forest canopy may be the largest mechanism of loss of Hg from terrestrial systems, but data are limited and uncertain. Watershed factors that increase hydrologic export of DOC are likely to increase Hg export. Particulates are also important in Hg transport, especially in steep or erosive systems such as cultivated land, but their absolute significance is difficult to determine because their episodic nature makes measurement difficult. Transport of Hg in lower soil horizons and groundwater is minimal. Fluxes of Hg from a wide variety and size of watersheds do not range widely, with about 75% of observations in the range of 1 to 3 μg m^{-2} a^{-1} and a mean of 1.7 μg m^{-2} a^{-1}. Concentration and flux of HgT from watersheds are weakly and inversely related to watershed size. Flux of MeHg from watersheds is very skewed with about 80% of observations less than 0.15 μg m^{-2} a^{-1}, but some fluxes are substantially higher. Although there is no pattern of MeHg flux with watershed size, there is a strong relationship between MeHg flux and wetland area. Finally, the degree and kind of disturbance in terrestrial watersheds can influence Hg flux. In most cases, it appears that disturbance increases Hg efflux via either volatilization or in runoff.

Synthesis and integration

A central question is what happens to the Hg that is deposited in terrestrial systems? Is it sequestered or is it quickly lost? What are the pathways of loss? The answer to this question has strong implications for the efficacy of measures to minimize both point and non-point sources of Hg to the atmosphere and to aquatic systems.

### Budget balancing/volatilization

There are three possible fates for Hg inputs into terrestrial systems; they may be sequestered within the system, lost via hydrologic flux, or lost via volatilization. Before each of these fates is discussed in more detail, a simple exercise leads to an interesting conclusion. Using the means of the fluxes of Hg documented in this review (Table 2), annual input to forests, the sum of throughfall and litterfall, is about 38 μg m^{-2} a^{-1}. This input can be partially accounted for by streamflow output, about 2 μg m^{-2} a^{-1}, leaving a difference of 36 μg m^{-2} a^{-1}. Volatilization for a period of about 4.5 months at the mean rate, 11 ng m^{-2} h^{-1} (Table 2), would balance the budget. If this computation is valid, then most of the Hg annually deposited on terrestrial ecosystems is simply returned to the atmosphere. Is this simple exercise valid?

Sequestration of Hg in terrestrial systems surely occurs, especially in peatlands, and some scientists believe that the forest floor layer in upland soils has sequestered nearly all the anthropogenically derived Hg (Aastrup et al. 1991; Borg and Johansson 1989; Johansson et al. 1991; Lee and Iverfeldt 1991). There are sufficient reduced S sites in SOM to bind all available Hg(II) (Skyllberg et al. 2000). Historical (pre-industrial) rates of Hg deposition can be estimated from the relative increase in Hg accumulation from the pre-industrial to the modern period in sediments in lakes and peatlands. A necessary assumption is that only the rate of deposition and not other factors influencing accumulation, such as the character of the basin, have changed over that time. Studies of sediment accumulation that have been carried out in north-temperate systems report an average ratio of modern to pre-industrial HgT accumulation of about 3.0 to 3.5 (Benoit et al. 1994; Engstrom and Swain 1997; Lorey and Driscoll 1999). Pre-industrial deposition to forests, including both throughfall and litterfall, would therefore be about 11 μg m^{-2} a^{-1} (38 μg m^{-2} a^{-1} ÷ 3.5). If the modern period extends from 1850 to 2000, and the pre-industrial period is conservatively assumed to extend for 5000 years prior to that (well after deglaciation, which in most of the Northern Hemisphere was about 10 000 BP), then total deposition will have been about 61 mg m^{-2} (55 mg m^{-2} pre-industrial + 5.7 mg m^{-2} modern). Although this deposition compares fairly well with measured Hg accumulation in lakes and peatlands where multiple cores have been measured (lakes, 36 mg m^{-2} (Engstrom et al. 1994); 50 mg m^{-2} (Lorey and Driscoll 1999); peatlands, 40 mg m^{-2} (Benoit et al. 1994)), accumulation in upland soils in north-temperate areas is considerably less, about 8 mg m^{-2} (Lindqvist et al. 1991; Nater and Grigal 1992), although central European sites report accumulations over an order of magnitude higher (Schwesig et al. 1999). If sequestration is linearly related to deposition, then to achieve a current accumulation of 8 mg m^{-2} in upland soils, sequestration rates of 1.4 μg m^{-2} a^{-1} (pre-industrial) and 5.0 μg m^{-2} a^{-1} (modern) are necessary. Short-term studies, less than several decades, cannot detect these changes because pool sizes are too large.

Hydrologic flux is another possible fate for Hg inputs. Deep leaching to groundwater is an unlikely pathway of Hg loss, mainly because of its low Hg concentrations (Johnson and Lindberg 1995). Output of Hg in streamflow depends on both water flux and concentration. Water flux is unlikely to change appreciably because it is driven by the difference between precipitation and evapotranspiration, both of which can be assumed to be historically constant. At current rates of deposition, Hg flux is relatively uniform (Table 2). Assuming minimal groundwater loss, current hydrologic flux is at the mean of observations (Table 2, 2 μg m^{-2} a^{-1}). Because of the small variation in hydrologic flux (Fig. 7), pre-industrial flux could also be conservatively assumed to be about 2 μg m^{-2} a^{-1}.

Sequestration (5.0 μg m^{-2} a^{-1}) and hydrologic outputs (2 μg m^{-2} a^{-1}) therefore currently account for about 20% of annual Hg inputs (38 μg m^{-2} a^{-1}). Volatilization is the remaining possible fate for Hg inputs. In most studies of Hg budgets, Hg volatilization is estimated as a residual, assessed "indirectly" (Watras et al. 1996). In an overall Hg budget for a lake in southern Sweden, estimated volatilization losses from the terrestrial watershed (<1 μg m^{-2} a^{-1}) were <5% of the inputs of 20 μg m^{-2} a^{-1} (Lindqvist et al. 1991). If current net volatilization rates are at the mean of observations (11 ng m^{-2} h^{-1}, Table 2) and occur over a 4-month period, they would account for the remaining 80% of inputs (32 μg m^{-2} a^{-1}). As noted earlier, Lindberg (1996) reported net emission flux from the soil at Walker Branch Watershed, Tennessee, during spring, summer, and fall (6 to 9 months) to be about 7.5 ng m^{-2} h^{-1}. Such volatilization could range from rapid evaporation of deposited Hg(0) (Martinez-Cortez 1999) to reduction of Hg(II) by SOM (Schlüter et al. 1995) or microbes (Baldi 1997) and its subsequent loss. This estimated volatile loss does not include emissions of Hg(0) directly from the canopy to the atmosphere, which Lindberg (1996) considered an important flux in his conceptualization of the Hg cycle during a summer day in Walker Branch Watershed, Tennessee, U.S.A. Because of difficulties in measurement, reported volatilization rates are limited in number and range widely (Fig. 4, Table 2). If volatilization of 80% of the Hg that is deposited to terrestrial surfaces is incorporated into estimates of the global Hg cycle (Mason et al. 1994), then these fluxes to the atmosphere are

Fig. 14. Input–output budget of Hg in terrestrial watersheds. Mean rate refers to the geometric means as summarized in this review. Output by volatilization (gas) based on mean hourly rate extrapolated over 4 months per annum. Output via soil sequestration (soil) based on total soil accumulation of 8 mg m^{-2}. Uncertainty approximated by use of 75th percentile of values, with uncertainty in soil sequestration based on doubling of total accumulation. TF = throughfall; LF = litterfall; Stream = flux in streamflow.
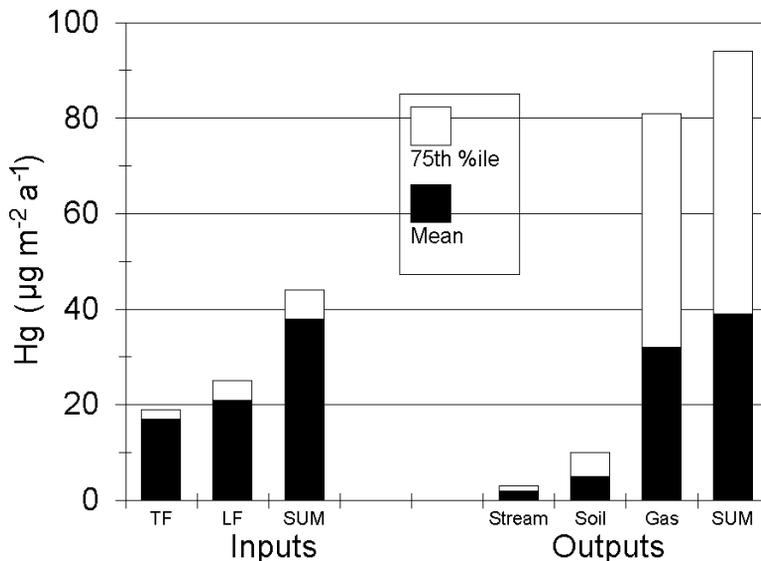
comparable to anthropogenic fluxes. The magnitude of such re-emission has serious implications for control strategies (Jackson 1997).

This input–output budget of Hg in terrestrial watersheds and its associated uncertainties can be succinctly summarized (Fig. 14). At mean rates summarized in this review, the sum of inputs (38 μg m^{-2} a^{-1}) is nearly equal to the sum of outputs (39 μg m^{-2} a^{-1}) (Fig. 14). Uncertainty in these data is not easily defined, but a rough approximation for each of the inputs and outputs is the difference between the mean and the 75th percentile of values. In the case of soil sequestration, with few reports of total Hg accumulation, doubling of total accumulation yields a conservative 100% uncertainty. Using this metric, the uncertainty in volatilization rates is clearly much higher than that of any of the other fluxes (Fig. 14) and in fact is about an order of magnitude greater than that of any other flux. It is clear that terrestrial budgets will not be closed until volatilization is better understood.

Flux to lakes

Although a relatively small proportion of the Hg deposited on terrestrial watersheds reaches aquatic systems, that small fraction is of critical importance to health of those systems. Data from north-central (Swain et al. 1992) and northeastern U.S.A. (Lorey and Driscoll 1999) are consistent in showing that Hg accumulation in sediments increases 25% for each unit area increase in terrestrial watershed area per unit lake surface area. The accumulation rate extrapolated to a lake with no terrestrial watershed has been considered to be equivalent to Hg deposition to the lake surface (Swain et al. 1992; Lorey and Driscoll 1999). As discussed earlier, Hg deposition to lakes is approximately equivalent to open-field deposition; about one-fourth of total Hg deposition to forests. Forested watersheds therefore contribute about 6% of the annual Hg deposition they receive to lakes (25% of 1/4). This value serves as a check of the budget presented above, where hydrologic flux from forests was about 5% (2 ÷ 38) of annual deposition. The difference is trivial considering the uncertainty in all these empirical relationships. This

proportion is consistent with the 5 to 85% of total Hg loading to lakes from terrestrial watersheds, equivalent to lakes with virtually no terrestrial watershed to lakes with terrestrial watersheds nearly four times the lake size. Proportions are likely to level off in larger systems, consistent with the decline in Hg flux in streamflow with watershed size (Fig. 9).

Although 5 to 10% of terrestrial Hg loading reaches lakes, two watershed-specific factors appear to be most important in altering this overall proportion, DOC and particulates. Probably the best evidence for the role of differences in DOC influencing flux is the increase in annual HgT flux with the percent of the watershed in wetlands (Fig. 10), nearly a doubling of flux with an increase in wetland area from 1 to 10%. The probable cause of the increase is the DOC generated in the wetlands. Watersheds with wetlands, especially those wetlands that act as variable source areas, are likely to be disproportionately important sources of Hg to lakes. The importance of particulates in Hg flux is indicated by the degradation of the relationship between Hg and DOC during spring floods and high flow events. In watersheds without significant DOC, particulates can be especially important in transporting Hg to lakes. Watershed disturbances that mobilize particulates, including road-building, cultivation, and some logging practices will increase the flux of Hg to lakes.

In aquatic systems, attention is usually centered on MeHg. Sources of MeHg to lakes include direct precipitation, streamflow from terrestrial watersheds, and in-lake production (Rudd 1995). Simple models demonstrate that under different scenarios any of these sources can be important (Rudd 1995). With that caveat in mind, focus here will be on terrestrial streamflow. Even in that case, variations in MeHg to HgT ratios in atmospheric inputs to watersheds are not related to variations in ratios in streamflow. Internal watershed processes both produce and destroy MeHg, and it is the summation of those processes that ultimately reach lakes. As described earlier, the most important terrestrial watershed property affecting MeHg flux is the proportion of wetland in the watershed, affecting both production of MeHg and water residence time (Fig. 13). The U.S. Environmental Protection Agency has recently issued a water quality criterion for MeHg of 0.3 mg kg^{-1} of fish (wet weight) (U.S. EPA 2001). The criterion was based on a property of fish rather than of water because of the uncertainties associated with both Hg flux from terrestrial to aquatic systems and the bioaccumulation of mercury in aquatic biota. Translation of this criterion to concentration of MeHg in water is therefore tenuous, but it would correspond to an approximate concentration of 0.25 ng L^{-1} MeHg in streamwater using the default fish diet for the general population and about 0.11 ng L^{-1} if the diet is based only on predator fish such as northern pike (*Esox lucius*) and walleye (*Stizostedion vitreum*). In any specific application, actual concentrations would be influenced by site-specific properties such as water pH, temperature, and DOC, and by fish species, age, and trophic level.

Based on the empirical relationship of MeHg concentration with area of wetland in the watershed ($r^2 = 0.14$) (Fig. 12), the criterion based on consumption of all fish would be exceeded at 10% wetland and that based on consumption of predator fish would be exceeded for watersheds with only 1% wetland. Using the stronger relationship between MeHg flux and wetland area ($r^2 = 0.38$) (Fig. 11), and assuming annual streamflow of 50 cm per year, the all-fish criterion would be exceeded in watersheds with about 20% wetland and the predator fish criterion in watersheds with about 4% wetland. It is therefore likely that in many real-world situations, the new criterion is currently exceeded. An obvious method to reduce MeHg flux from terrestrial to aquatic systems would be to reduce the area of wetlands in watersheds. As stated earlier, it is ironic that wetlands, landscape elements that both regulation and legislation have attempted to protect from disturbance, are the single most identifiable source of MeHg in terrestrial systems.

Complexities influencing conclusions

Two factors further affect our ability to draw firm conclusions about Hg cycling. Because of scientific or political interest, and because Hg research requires well-equipped field sites and laboratories, much of the work dealing with Hg cycling has been carried out at relatively few locations. These locations,

such as the watershed of Lake Gårdsjön, southern Sweden; the Svartberget Watershed, northern Sweden; the Experimental Lakes Area in northwest Ontario; and Walker Branch Watershed, Tennessee; provide an important but narrow base upon which to generalize. Unique properties of each site, such as the presence of plumes with high concentrations of industrially generated Hg(0) (Kim et al. 1995), high concentrations of Hg in vegetation (Munthe et al. 1998), or very thin mineral soils associated with windstorms and forest fires (Schindler et al. 1996), illustrate the difficulty of generalizing from a few locations. Data are now being collected and published from many more sites, and those data are sorely needed in order to better allow us to generalize regarding Hg behavior in the terrestrial environment. The METAALICUS Study and other recent research initiatives (Sbick 2000) will help address many questions dealing with Hg and the environment, including some raised in this review.

Secondly, climatic fluctuations are very important to Hg cycling and affect interpretation of the data. For example, long-term studies of HgT and MeHg fluxes (Lee et al. 2000; Munthe et al. 1998) report significant inter-annual variations in fluxes, apparently related to climate. Where atmospheric deposition of Hg was experimentally curtailed, climatically driven variation in flux between the control and treated watersheds were too large to allow discernment of any effect of changes in deposition (Munthe et al. 1998). In an unmanipulated site, variations in output of Hg and MeHg from a watershed were much greater and did not follow the same trends as did variation in atmospheric deposition. Changes in climate had a stronger effect on flux of Hg from terrestrial to aquatic systems than did atmospheric deposition (Lee et al. 2000). Prediction of hydrologic flux of HgT and MeHg is difficult because of between-year variations related to climate and because of the large pool of Hg in soils. Global climate change, whether anthropogenically induced or not, could influence both rates of volatilization and hydrologic fluxes of Hg. Empirical relationships, in particular, can be undermined by change in conditions.

Major implications and limitations

Three major issues arise in this synthesis. First, the potential importance of volatilization, including fire, on Hg budgets of both terrestrial watersheds and of the globe must be better understood. The magnitude of this volatilization has serious implications for industrial control strategies. Secondly, although hydrologic flux of Hg from terrestrial watersheds is less than 10% of inputs, it is an important source of Hg to aquatic systems. Although reduction of Hg flux associated with particulates may be achievable in a few cases, most significant Hg flux is associated with naturally generated DOC. In systems with wetlands and associated DOC, concentrations of MeHg, in particular, already appear to be at or near the current water quality criterion. Finally, because all study sites are unique, and because climate strongly affects Hg cycling, only the most general conclusions about Hg cycling can be made and they must be critically evaluated. The overriding importance of climatic variation and the lack of representativeness of any short series of observations of ecosystems dynamics, including biogeochemical cycling, is cogently emphasized by 31 years of observations at Hubbard Brook, U.S.A. (Likens and Bormann 1995). Credibility is strengthened by relationships that encompass a broad range of systems and climatic variation.

Acknowledgments

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