SOURCES OF METHYL MERCURY TO FRESHWATER ECOSYSTEMS: A REVIEW[2,3]

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[2] Plenary address to the International Conference on Mercury as a Global Pollutant
[3] Publication #10 of the Experimental Lakes Area Reservoir Project (ELARP).

Abstract. The recent development of sensitive analytical techniques for the determination of MeHg concentrations in water has resulted in a rapid advancement in our understanding of MeHg production and transport in lake and reservoir systems. Results from three recent whole-ecosystem studies have shown that there are three important sources of MeHg to aquatic systems - precipitation, runoff from wetlands, and in-lake methylation. Data from these three studies are used to construct a simple model that illustrates how the relative importance of these sources can vary with rates of atmospheric deposition of MeHg, lake type, percentage of wetlands in the terrestrial catchment and the percentage of water surface area that covers flooded terrain.

1. Introduction

Until quite recently, it was generally believed that the only source of MeHg to freshwater ecosystems was internal (in-lake) production of methyl Hg (MeHg). However, we now know that wetlands can be important external sources of MeHg to lakes (Rudd et al. 1992; St. Louis et al., 1994). This likely explains why fish in brown-water lakes, which receive significant inflow from wetlands, often have high concentrations of MeHg (e.g. Driscoll et al., 1994). The atmosphere may be another important external source of MeHg to some lakes. For example, Hultberg et al., (1994) concluded that atmospheric deposition is an important source of MeHg for drainage lakes located in heavily polluted regions of southern Sweden. The recent recognition of the importance of external sources of MeHg to freshwater ecosystems followed the development of a highly sensitive technique for the determination of MeHg in water (Bloom, 1989; Horvat et al., 1993).

In this paper, I attempt to summarize and synthesize the present understanding of the relative importance of sources of MeHg to lakes and reservoirs (atmospheric, terrestrial and internal). This will be largely done by drawing information from three recent whole-ecosystem studies: Little Rock Lake, WI. (Watras et al., 1994); Lake Gardsjon, southern Sweden (Hultberg et al., 1994); and from studies of MeHg in flooded and unflooded boreal catchments that are being carried out as part of the Experimental Lakes Area Reservoir Project (ELARP), northwestern Ontario. A primary goal of the ELARP is to improve the understanding of the causes of elevated Hg concentrations in fish taken from hydroelectric reservoirs (e.g. Hecky et al. 1991)

Water, Air, and Soil Pollution **80**: 697–713, 1995.

2. Materials and Methods

2.1. SAMPLE COLLECTION

For the three studies discussed in this paper, rainwater and surface-water samples were collected using the stringent clean-hands-dirty-hands protocol described in St. Louis et al., (1994a), Hultberg et al., (1994) and Watras et al., (1994). It is assumed that estimates MeHg in deposition obtained by event rainfall collectors and bulk (IVL) collectors are equivalent. This assumption is based on year-to-year similarity of MeHg deposition rates measured at the same location using rain collectors and bulk collectors (H. Hultberg pers. comm., Hultberg et al., 1994).

2.2. ANALYTICAL

The MeHg data discussed in this paper are comparable. For all three studies, MeHg concentrations were analyzed by GC-CVAFS following aqueous phase ethylation of MeHg (Bloom, 1989, Horvat et al., 1993). The labs analyzing all of these samples (IVL, Brooks-Rand Ltd., Frontier Geosciences and Flett Research Ltd.) have recently successfully participated in an international inter-comparison exercise (Bloom and Horvat, 1995).

3. Results and Discussion

3.1. SOURCES OF MeHg TO FRESHWATER ECOSYSTEMS

Three sources of MeHg to freshwater ecosystems will be considered. Two of the three sources (terrestrial runoff and direct atmospheric deposition onto the lake surface) are external to freshwater systems. The third source is internal and is comprised of MeHg produced in the sediments, the water column and in the intestinal contents of fish.

Atmospheric Deposition:

To evaluate the relative importance of external vs. internal sources of MeHg, atmospheric inputs of MeHg must be accurately quantified. Deposition of MeHg has been measured at several sites in the northern hemisphere and has been found to vary considerably from one region to another. In Table I, the data are arranged in order from lowest to highest deposition rate. There is a ten fold range between the lowest (0.39 mg ha^{-1} yr^{-1}, ELA, northwestern Ontario) and highest deposition rates (1.9-4.0 mg ha^{-1} yr^{-1}, southern Sweden).

TABLE I.

MeHg in wet/bulk deposition collected in several regions of the northern hemisphere[1].

Region	Wet/Bulk Deposition mg ha^{-1} yr^{-1}	Reference
ELA NW Ontario	0.39	St. Louis et al., (this issue)
N. Sweden	0.70	Munthe and Iverfeldt, (1994)
Wisconsin	0.88	Fitzgerald et al., (1991)
S. Finland	1.1	M. Verta pers. comm.
E. Sweden	2.0	Munthe and Iverfeldt, (1994)
W. Sweden	2.9	Munthe and Iverfeldt, (1994)
S. Sweden	1.9-4.0	Munthe and Iverfeldt, (1994) Hultberg et al., (1994)

[1] Adapted from St. Louis et al. (this issue).

MeHg deposition in the equatorial Pacific is likely even lower than at ELA. Although an annual deposition rate was not reported, concentrations of MeHg at three sampling locations in the equatorial Pacific average <0.01 ng/L (below the analytical detection limit, Mason et al., 1992). For comparison, average MeHg concentrations at ELA are 0.04 ng/L (St. Louis et al., 1995).

At the present time, the origin of MeHg in deposition is not known but may be directly or indirectly related to industrial activity. For example, the two most remote sites listed in Table I (ELA and northern Sweden) have the lowest deposition rates, while the highest rates are in southern, western and eastern Sweden which are relatively close to industrialized areas of Europe. The intermediate sites (northern Wisconsin, southern Finland), while not remote, are somewhat removed from heavily industrialized areas. The undetectable concentrations of MeHg in equatorial Pacific rain suggest that the source of MeHg in rainfall is terrestrial.

In addition to the amount of MeHg measured in rainfall and bulk collectors (Table I), MeHg inputs via litterfall (i.e MeHg attached to fallen needles, leaves and twigs) may also be important. Hultberg et al., 1994 reported that MeHg deposition via litterfall is equal to wet/bulk deposition in the Lake Gardsjon area of southern Sweden. However, the source of MeHg in litterfall is not known. It could be atmospheric in origin or it could be produced on the surface of leaves and needles. It is also possible that the MeHg in litterfall is not all newly produced or deposited but is instead recycled from soil emissions or by root translocation. If the latter are true, it would not be correct to include litterfall in estimates of deposition. On the other hand, if MeHg in litterfall is of atmospheric origin, then present wet/bulk loading estimates (Table I) are underestimates of total MeHg deposition and this could lead to over estimates of rates of MeHg production in lakes and wetlands by mass-balance calculations.

Terrestrial catchments as sources/sinks for MeHg:

Terrestrial catchments that contain wetlands have been identified as important sources of MeHg to downstream aquatic systems (Rudd et al., 1992; St. Louis et al., 1994a). Wetland areas of catchments at the ELA contributed 26 to 79 times more MeHg per unit area to downstream water than did purely upland areas of catchments that contained no wetlands (saturated organic soils, St. Louis et al., 1994a). This finding appears to be of general importance as wetlands have also been identified as important sources of MeHg by recent studies in Wisconsin and northern Sweden (Bishop et al., 1994: Hurley et al., 1994; Krabbenhoft et al., 1995). Also, Driscoll et al., (1994) reported a significant relationship between the percentage of near-shore wetlands in Adirondack lake catchments and the MeHg concentration of lake water.

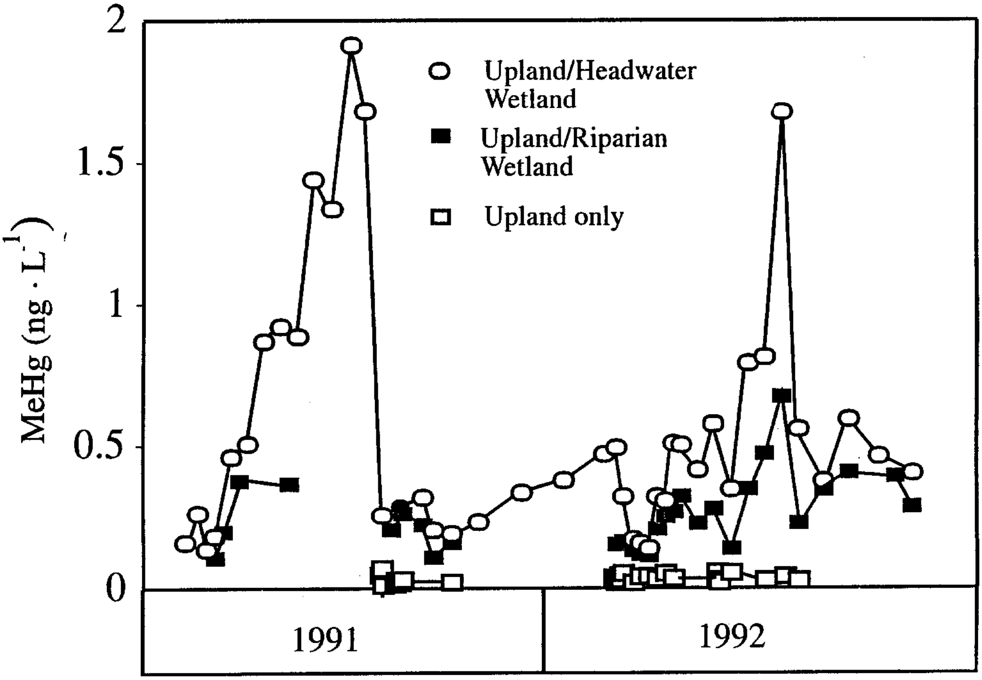

Figure 1. Concentrations of MeHg in stream water exiting three types of terrestrial catchments at the ELA, northwestern Ontario.

The ELARP is intensively studying the production, storage and export of MeHg in wetlands (Fowle et al., 1994; Heyes et al., 1994; Moore et al., 1994). The project is also studying, at the subcatchment level, the transport of MeHg from uplands (Allan et al., 1994, St. Louis et al. 1994a). Figure. 1 shows that the conclusions of St. Louis et al., (1994a), which presents data from the first year of the ELARP study, have been consistent on the longer term. That is, concentrations of MeHg from a purely upland catchment are uniformly low (<0.1 ng L^{-1}). Concentrations of MeHg are intermediate in value (0.1-0.6 ng L^{-1}) in a stream draining a catchment that is composed of upland terrain and stream-side wetland areas (riparian wetlands) that receive water from the uplands. MeHg concentrations are very high in a stream draining a catchment that is composed of uplands and a large (4.3 ha) continuous area of headwater wetland (0.1-1.9 ng L^{-1}, Figure 1).

TABLE II

MeHg export from three types of terrestrial catchments at the ELA, northwestern Ontario.

Catchment	Per Cent Wetland	1991 (mg ha^{-1} yr^{-1})	1992 (mg ha^{-1} yr^{-1})
Upland	0	0.07	0.08
Upland/ Riparian Wetland	14	0.32	0.87
Upland/ Headwater Wetland	16	0.96	1.14

The export of MeHg from these catchments follows a similar pattern to concentration, with the purely upland catchment consistently exporting about ten fold less MeHg per hectare than catchments that contain wetlands (Table II). The export of MeHg also depends on the seasonal distribution of precipitation. MeHg concentrations in runoff from wetland containing catchments are highest during midsummer (Figure 1; St. Louis et al. 1994a). Thus, stream flow during midsummer, which can be quite variable depending on the timing and quantity of precipitation, is very important. For example, in the combination upland/riparian wetland catchment, stream flow was interrupted during midsummer 1991 by a prolonged drought and annual export during 1991 was less than half of the 1992 export when stream flow was continuous (Table II). In contrast, in the catchment containing the large headwater wetland, storage of water sustained stream flow during the dry summer, and export of MeHg was only slightly lower in 1991 than in 1992.

This pattern of MeHg concentrations and export in runoff from three different types of catchments (purely upland, upland/riparian wetland, upland/headwater wetland) is consistent at least within the ELA area. Very similar MeHg concentrations and export have also been found in the outflow from two other purely upland catchments, two other catchments that are combinations of uplands and riparian wetlands and one other catchment with a large area of continuous wetland (St. Louis et al. 1994b). This predictability means that it is possible to begin to model, for other boreal locations with similar atmospheric inputs, MeHg output from terrestrial surfaces using knowledge of the type and percentage of wetlands in upland terrain, the seasonal precipitation and predicted runoff (see later discussion).

Average annual input-output budgets for the three types of catchments for 1991-93 (Table III, St. Louis et al., 1994) show that catchments containing wetlands exported MeHg because they were net MeHg producers. The capacity of wetlands for producing MeHg can be fully appreciated by estimating the rate of MeHg production per hectare of wetland. For example, the combination upland/riparian wetland catchment consists of 86% upland terrain and 14% wetland area adjoining the stream that drains the catchment. If the whole catchment receives MeHg in precipitation at a rate of 0.39 mg ha^{-1} yr^{-1} and the upland area of the catchment exports MeHg at a rate of 0.07mg ha^{-1} yr^{-1} (Table III), then the wetland area must be producing MeHg at a rate of 4.7 mg ha^{-1} yr^{-1} to sustain the annual export from the catchment of 0.78 mg ha^{-1} yr^{-1}. Even if it is assumed that input from wet precipitation should be doubled by including litterfall (Hultberg et al., 1994), the wetland areas would still need to produce MeHg at a rate of 4.4 mg ha^{-1} yr^{-1} to support the measured export. This MeHg production rate is comparable to the estimated rate of MeHg production in ELA lake sediments (5.0 mg ha^{-1} yr^{-1}, see later discussion).

TABLE III

Average annual production of MeHg by terrestrial catchments at the Experimental Lakes Area, northwestern Ontario during 1991-1993 (ranges in parentheses). All values are in (mg ha^{-1} yr^{-1}).

Catchment	Wet Precipitation	Export	Production
Upland	0.39 (0.32 to 0.41)	0.07 (0.06 to 0.08)	-0.32 (-0.26 to -0.35)
Upland/ Riparian Wetland	0.39 (0.32 to 0.41)	0.78 (0.32 to 1.14)	0.39 (-0.09 to 0.82)
Upland/ Wetland Headwater	0.39 (0.32 to 0.41)	1.9 (0.96 to 2.4)	1.48 (0.55 to 2.11)

TABLE IV

Retention or demethylation of MeHg in upland catchments. All values are in (mg ha^{-1} yr^{-1})

Catchment	Wet Precip.	Wet + Dry Precip.	Export	% Retention or Demethylation
Gardsjon Upland	4.0[1]	8.0	2.0	75
ELA Upland	0.4[2]	0.8[3]	0.07[2]	91

[1] Hultberg et al. (1994)

[2] St. Louis et al. (1994)

[3] Assuming wet equals dry deposition as in Hultberg et al. (1994)

In contrast to wetlands, the ELARP study (St. Louis et al., 1994a; Allan et al., 1994) and other research (Hultberg et al., 1994; Lee et al., 1994) have demonstrated that uplands are sinks for MeHg in precipitation (Table III, IV). The fate of MeHg retained in uplands is unknown. Some is stored in soils (Lee et al., 1994). Feather mosses, which contain very high concentrations of MeHg (Moore et al., 1994), may also be important upland storage sites (although production of MeHg in these mosses may also explain these high concentrations). It is also possible that some of the MeHg "retained" by uplands is demethylated rather than stored in the soils or mosses but demethylation in upland soils has not been studied.

Even though a large percentage of MeHg is retained and/or demethylated in upland terrain (75% at Lake Gardsjon, southern Sweden, and about 91% at ELA, Table IV), runoff of the residual MeHg from uplands may be an important source to lakes in regions where atmospheric inputs are very high. For example, at Lake Gardsjon, MeHg runoff from an upland catchment is about 30 fold greater per unit area than at ELA (because of higher precipitation inputs and lower percentage retentions, Table IV). Also in contrast to ELA, runoff of MeHg from purely upland areas appears to be an important source of MeHg to lakes in southern Sweden. Hultberg et al. (1994) found that the amounts of MeHg entering Lake Gardsjon from upland runoff and direct precipitation were of equal importance (Figure 2). It was estimated that together these two inputs are sufficient to account for all MeHg accumulated by fish on an annual basis (Figure 2).

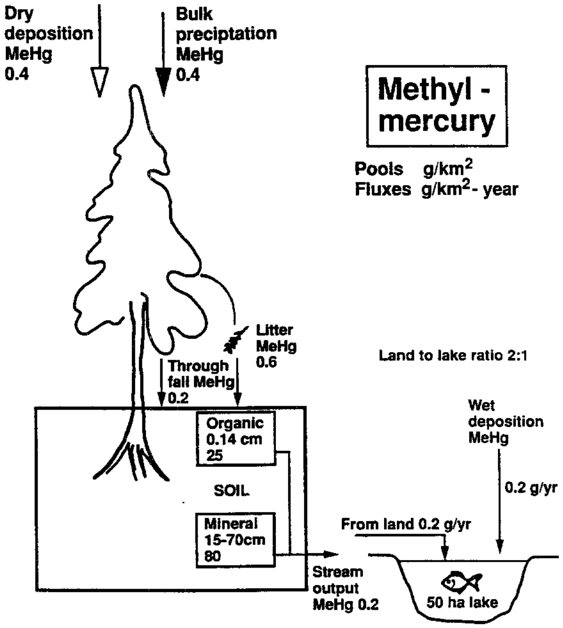

Figure 2. Pools of MeHg and inputs of MeHg to a 50 ha lake in southern Sweden with a 100 ha watershed. Inputs from direct wet deposition (0.2g/yr) and runoff were 0.2g/yr were sufficient to account for annual MeHg bioaccumulation by fish. From Hultberg et al. (1994).

In-Lake Production of MeHg:

Originally it was thought that all MeHg in freshwater ecosystems was produced internally and that methylating bacteria active in the sediments were the only source of internal MeHg production (e.g. Jensen and Jernelov, 1967). Later it was found that internal production also occurs in the water column (Furutani and Rudd, 1980; Parks et al., 1989), in the external slime layer of fish (Jernelov, 1972) and the intestinal contents of fish (Rudd et al., 1980). More recently, flooded terrestrial surfaces have been shown to be important internal source of MeHg to reservoirs (Hecky et al., 1991). While there is no doubt that methylation occurs in these sites, quantitative determinations of the rates of methylation and of the relative importance of these internal sources has eluded researchers for decades (Winfrey and Rudd, 1990).

The reason that our understanding of internal MeHg production is so vague is that there no methods for the measurement of natural rates of Hg methylation or demethylation. Isotopic methods that have been used for many years, only determine relative rates of methylation and demethylation and the ratios of methylation to demethylation (M/D, Furutani and Rudd 1980; Ramlal et al., 1986). While these methods are useful in determining sites of methylation and factors influencing rates of methylation and demethylation (e.g. Bodaly et al. 1993), for two reasons they do not give quantitative rate information (Winfrey and Rudd, 1990). First, high specific activity isotopes ($^{203}Hg^{2+}$ and $^{14}CH_3Hg^+$) have not been available, necessitating the addition of high concentrations of cold carrier Hg^{2+} or CH_3Hg^+. Second, methods have not been developed for the determination of the proportion of the isotope that is available to the methylating or demethylating populations. Thus the specific activity of the Hg or MeHg isotopes that the microbes use is unknown. For the measurement of methylation, Stordall and Gill (1994) have recently made progress on the first shortcoming by developing techniques that reduce the amount of Hg^{2+} carrier that is added to a sample. However, completion of a quantitative isotopic assay awaits development of methods for the measurement of the bioavialability of the added Hg^{2+}. To date, there has been no attempt to develop a quantitative isotopic method for the measurement of demethylation rates.

A second approach that is under development is to determine natural rates of net methylation in sediments using wet chemistry. For this approach, the net methylation rate is the sum of two separate measurements: 1) the flux of MeHg across the sediment-water interface and 2) the accumulation of MeHg on solid sediments with time. Methods for the flux measurement have been developed Sellers et al. (1994) but determination of rates of MeHg accumulation on the solid sediments is difficult because of the large background pool of MeHg that is attached to the sediment particles (P. Sellers and C. Gilmour pers. comm.). Probably some combination of the isotopic and wet chemistry approaches will be used in the future to obtain natural rates of methylation and demethylation.

Even though the quantitative methods for sediment methylation are not yet available, it is possible to obtain whole-lake estimates of net methylation rates using a mass-balance approach. For example, in the English/Wabigoon system, where large amounts of Hg were added from a chlor-alkali plant, an annual net methylation rate of 22 mg ha^{-1} yr^{-1} for the entire river-lake system was estimated using input-output budgets (Parks et al., 1989). More contaminated reaches of the system were estimated to have annual rates about 10 fold higher than for the whole-ecosystem. A second whole-ecosystem methylation rate was obtained for a seepage lake (the treatment basin of Little Rock Lake, Wi.; Watras et al., 1994) using measured inputs of MeHg to the lake, as well as sediment trap fluxes and sediment accumulation of MeHg. In this case, the rate of 30 mg ha^{-1} yr^{-1} was considered to be a maximum estimate because it may have included some recycling of MeHg from particulate sedimentation to the water column (Figure 3).

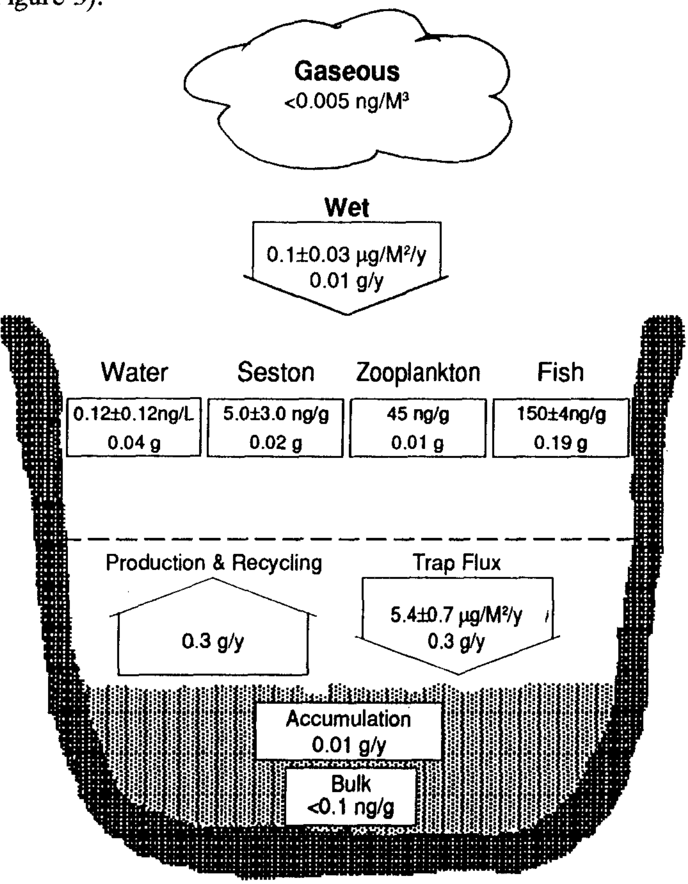

Figure 3. MeHg budget for the treatment basin of Little Rock Lake, WI. From Watras et al. (1994).

The mass-balance approach is also being used by the ELARP study to determine whole-ecosystem rates of Hg methylation before and after flooding of a 14.3 ha wetland. Input-output budgets and production and transport of MeHg within the experimental wetland were studied for two years prior to flooding (1991-92) and will be followed for at least 3 years after flooding in 1993.

Prior to flooding, MeHg concentrations in the outflow of the 2.4 ha central pond in the experimental wetland averaged 0.1 ng/L (0.05 to 0.28 ng/l). After 1 month of flooding, MeHg concentrations increased dramatically and peaked at a concentration of 2.3 ng/L (about 20 fold above preflood values, Rudd et al. in prep.).

TABLEV

Inputs to the model used to estimate the relative importance of direct atmospheric precipitation, terrestrial runoff and in-lake production as sources of MeHg to freshwater systems. Watershed and lake areas are in ha, MeHg inputs from all sources are in mg ha^{-1} yr^{-1}.

Simulation Lake/Reservoir	Lake Area (ha)	Watershed Area (ha)	% Wetland in Watershed	% Flooded	Direct Precip.[1]	Upland Runoff[2]	Wetland Runoff[3]	In-Lake Production[4]	Flooded Production[5]
Lake (Fig. 4a)	50	5, 100 or 500	0-100	0	0.4	0.1	3	5	-
Lake (Fig. 4b)	50	5, 100 or 500	0-100	0	0.4	0.1	3	30	-
Lake (Fig. 5a)	50	5-505	15	0	0.4, 0.9 or 4	0.1, 0.22 or 1.0	3	30	-
Lake (Fig. 5b)	50	5-505	15	0	0.4, 0.9 or 4	0.1, 0.22 or 1.0	3	5	-
Reservoir (Fig. 6a,b)	50	500	15	0-80	0.4, 0.9 or 4	0.1, 0.22 or 1.0	3	5	130

[1] Direct precipitation inputs are taken from measured values obtained at ELA (St.Louis et al., this issue), Wisconsin (Fitzgerald et al., 1991), and in southern Sweden (Hultberg et al., 1994). [2] It is assumed that upland runoff equals 25% of precipitation because uplands at ELA retained or demethylated 75% of MeHg in rain (Table IV).

[3] The mid range of export of MeHg from ELA catchments that contain wetlands (St. Louis et al., 1994).

[4] In-lake production rate of 5 mg ha^{-1} yr^{-1} is the average MeHg flux from undisturbed cores taken from wetland ponds at ELA (ELARP unpub. data). The 30 mg ha^{-1} yr^{-1} value is from Watras et al., 1994.

[5] The rate of MeHg production from flooded terrestrial areas (26 times flux of undisturbed ELA cores) was estimated from the minimum increase in MeHg flux observed after flooding of wetland 979 at ELA.

Annual input-output budgets show that there was a 26 fold increase in outflow of MeHg from the experimental catchment after flooding during the summer of 1993 (Rudd et al. in prep.). Early (first summer) post-flood data suggest that the large increase in loss of MeHg from the experimental catchment was the result of increased methylation and was not due to leaching of MeHg from plants and peat after flooding. This was concluded because the mass of MeHg in flooded plant tissues increased after flooding rather than decreasing, as would have been expected if leaching had been important (Heyes et al., 1994). MeHg also appears to be increasing in peat after flooding (unpub. ELARP data). Hence the estimated 26 fold increase in MeHg outflow is a minimum estimate of the increase in net methylation because a portion of the newly produced MeHg was bound by the plant tissues and peat. A more accurate estimate of the increase in methylation rate following flooding will be determined after further sample analyses. These results substantiate Hecky et al. (1991) who concluded, using indirect data, that there was a large increase in net methylation following flooding by reservoir development in northern Manitoba.

3.2. MODELLING THE RELATIVE IMPORTANCE OF MEHG SOURCES TO AQUATIC ECOSYSTEMS

Using the data from the three whole-ecosystem studies, a simple mathematical model was developed to examine the relative importance of atmospheric, terrestrial and in-lake sources of MeHg to lakes and reservoirs. With the limited amount of data presently available, this modelling exercise is useful primarily for evaluating differences in the relative importance of MeHg sources to lakes, and for establishing directions of future research (i.e. the model is not a predictive tool).

Inputs to the model included lake area, watershed area, and percent wetland in the watershed. Other inputs were fluxes of MeHg from direct precipitation to the lake surface, runoff from uplands, runoff from wetlands, and in-lake production.

Importance of watersheds as sources of MeHg:

Simulations of the relative importance of the watershed as a source of MeHg to lakes were made by manipulating three inputs to the model: 1) percent wetland in the watershed, 2) the ratio of watershed to lake area, 3) in-lake rate of MeHg production. For this exercise, fixed inputs to the model were the rate of direct precipitation onto the lake surface, and the areal rates of MeHg runoff from purely upland catchments and from wetlands. The values for all of these model inputs were measured values. The rationale for their choice are given in Table V.

Figure 4a gives simulations for three lakes that are 50 ha in area, which have in-lake methylation rates of 5 mg ha^{-1} yr^{-1} and are located in a region of low atmospheric precipitation (0.4 mg MeHg ha^{-1} yr^{-1}). One of the lakes is a seepage lake with a 5 ha watershed the other two lakes are drainage lakes with 100 and 500 ha watersheds. For the drainage lake with a 500 ha watershed, when only 15% of the watershed area was wetland, about 50% of the MeHg input to the lake originated from the watershed. This percentage of wetland is common to many catchments in Canadian the boreal forest. In contrast, for a seepage lake (5 ha watershed, 50 ha lake) only 6% of total MeHg input originated from the watershed even if 100% of the watershed was composed of wetland (Figure 4a). This simulation is consistent with Watras et al. (1994) who concluded that in-lake production of MeHg was the major source of MeHg for Wisconsin seepage lakes

In Figure 4b, all factors are the same as in Figure 4a., except that in-lake methylation was set at 30 mg ha^{-1} yr^{-1} (Watras et al., 1994). In this case, the relative importance of the watershed as a source of MeHg to seepage lakes was extremely low even if 100% of the watershed was wetland. For a 500 ha:50 ha drainage lake, if the watershed was 15% wetland, about 18% of total MeHg inputs was from the watershed and if 100% of the watershed was wetland, 55% of total input was from the watershed. For this drainage lake situation, where in-lake methylation rate was high and atmospheric input was low, this simulation suggests that both the watershed and internal production were important sources of MeHg.

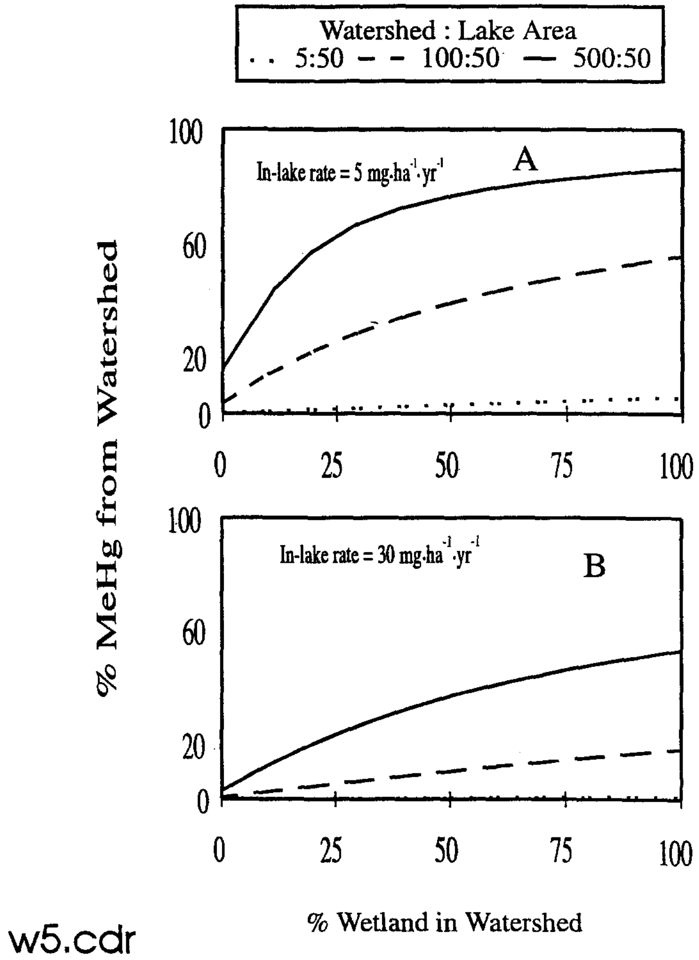

Figure 4. The relative importance of the watershed as a source of MeHg as a function of the watershed:lake area ratio, the % wetland in the watershed, and the in-lake methylation rate.

Importance of atmospheric precipitation as a source of MeHg:

Simulations of the possible importance of precipitation as a source of MeHg to lakes were made by manipulating the following inputs to the model: 1) watershed: lake area ratio, 2) rate of direct precipitation onto the lake, 3) rates of internal methylation. For this exercise, fixed inputs to the model were the percentage wetland in the watershed (15%) and the flux of MeHg from wetland areas 3 mg ha^{-1} yr^{-1}. It was assumed that 75% of the MeHg present in precipitation was retained or demethylated in upland watersheds (Tables IV,V).

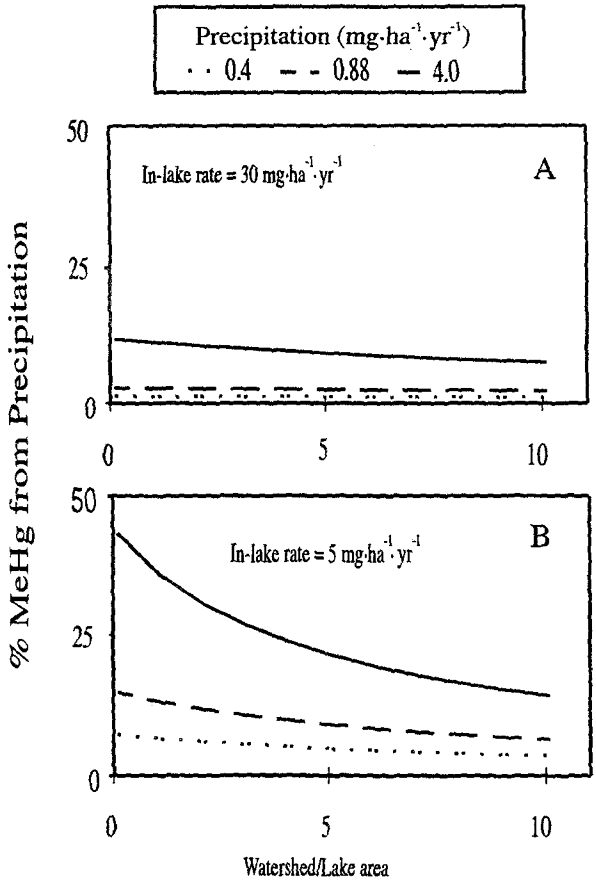

Figure 5. The relative importance of precipitation onto to the lake surface as a source of MeHg as a function of the watershed:lake area ratio, the MeHg precipitation rate, and the in-lake methylation rate.

Figure 5a gives simulations for three 50 ha lakes with internal methylation rates of 30 mg ha^{-1} yr^{-1}. At all three levels of MeHg in precipitation (Table I,V), inputs of MeHg to the lake surface would be of minor importance for both seepage and drainage lakes. This simulation is consistent with Watras et al. (1994) who concluded that input of MeHg from precipitation was of minor importance to a seepage lake (Little Rock Lake, WI). The simulations shown in Figure 5b suggest that if the internal methylation rate is reduced to 5 mg ha^{-1} yr^{-1}, that in regions of high MeHg in precipitation, direct inputs of MeHg to the lake surface could be important for seepage lakes (up to 40% of total input) and significant for drainage lakes (>14%). If the total impact of the high precipitation rate is considered (by summing the direct inputs to the lake surface plus the elevated export from upland watersheds), the importance of precipitation could be >24% of total input for drainage lakes with a watershed: lake area ratios greater than 10:1 (simulation not shown). In general, these simulations support Hultberg et al. (1994) who concluded that precipitation can be an important input of MeHg to drainage lakes as well as seepage lakes in high precipitation areas. However, the simulations also predicted that at least 25% of MeHg was produced internally even in the extreme case of the low level of internal methylation rate (5 mg ha^{-1} yr^{-1}) and high MeHg deposition rate (4 mg ha^{-1} yr^{-1}). This is contrary to Hultberg et al. (1994) who concluded that internal methylation was unimportant in southern Swedish drainage lakes because MeHg inputs from precipitation and runoff equal annual uptake of MeHg by fish (Figure 3). Assuming there is significant internal methylation in southern Swedish lakes, as the model suggests, total MeHg inputs must be higher than annual fish uptake. This suggests that there must be significant internal demethylation in the southern Swedish lakes which would be necessary to balance the MeHg input-output budgets.

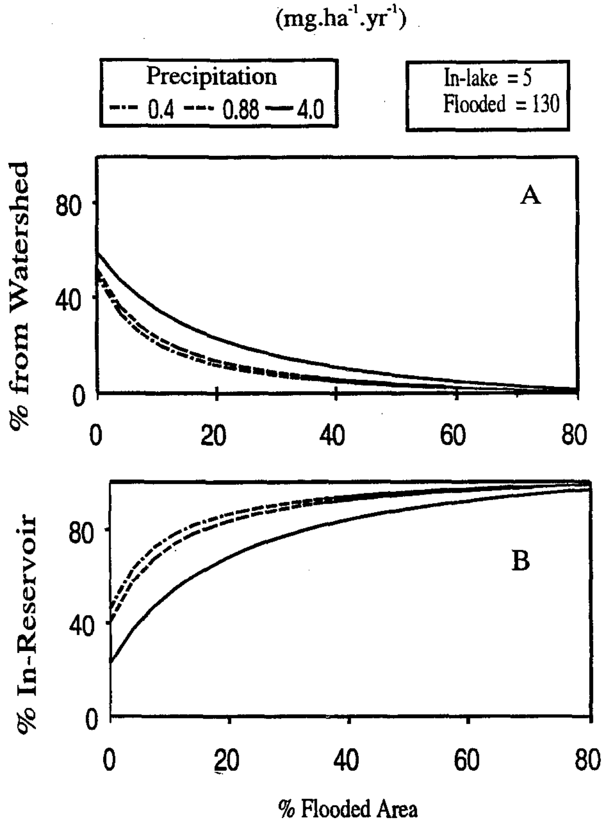

Figure 6. The relative importance of the watershed (a) and the in-reservoir production (b) as sources of MeHg to a reservoir as a function of the percentage of reservoir surface area that is flooded and MeHg input via direct precipitation.

Importance of flooded areas as sources of MeHg:

Simulations of the importance of flooded areas as sources of MeHg were made by manipulating two inputs to the model: 1) the percentage of reservoir surface area that was flooded terrain, and 2) the level of atmospheric deposition of MeHg (Table V, Figure 6). For this exercise, fixed inputs to the model were, the flux of MeHg from the former lake sediments (5 mg ha^{-1} yr^{-1}) and from flooded areas (130 mg ha^{-1} yr^{-1}), the areas of the watershed and former lake surface, the export of MeHg from wetland areas, and the percentage catchment area that is wetland (Table V).

The simulations are plotted as percentage of total MeHg input from the watershed (Figure 6a) and from internal reservoir production (Figure 6b). Both ways of looking at the reservoir situation show that the most important source of MeHg to a reservoir is internal production if the % flooded area of a reservoir surface exceeds about 10% of the reservoir area. The amount of MeHg in precipitation does not change the situation markedly because of the importance of internal production. Even in the extreme situation (simulation not shown), where 100% of the reservoir catchment is wetland and only 10% of the reservoir surface is flooded terrain, internal production is still equal in importance to watershed input.

These modelling exercises, which are based on measured MeHg fluxes in three systems located at three geographic locations, are consistent with data obtained in other independent studies of MeHg. For example, Driscoll et al. (1994) found a significant relationship between concentrations MeHg and DOC in lake water. They concluded that wetlands are important sources of both MeHg and DOC to lakes and this observation is consistent with the modelling results (Figure 4). Model simulations were also consistent with present understanding of MeHg fluxes in reservoirs. For example, Hecky et al. (1991) found large (2-3 fold) increases in the Hg concentrations of pike following flooding of Southern Indian Lake, Manitoba even though the surface area was increased only 20% by flooding (Newbury et al. 1983). They conclude that flooded terrain is the most important source of MeHg, which is also consistent with the model (Figure 6). The success of this model in generally simulating the results of recent studies indicates that the straightforward modelling approach used here is adequate to model sources of MeHg to freshwater systems.

4. Conclusions

Recent research has shown that there are three important sources of MeHg to lakes - internal production, inputs from watersheds that contain wetlands, and atmospheric inputs. Modelling of data from three recent whole-ecosystem studies demonstrates that under different circumstances each of the three sources can be important for lakes. For reservoirs, the model indicates that internal production of MeHg is always very important .

The success of the modelling exercise also demonstrates that with further research it should be possible to predict accurately MeHg inputs using the straightforward approach described here. Most urgently required are field studies that quantify fluxes of MeHg under different environmental circumstances. For example, studies are needed:

1) to improve knowledge of total rates atmospheric deposition of MeHg at different geographic locations (i.e. is MeHg in litterfall important component of atmospheric deposition?)

2) to determine if MeHg export from wetlands is higher in regions of high atmospheric deposition than regions of low atmospheric deposition (i.e. is export from wetlands internally controlled?)

3) to develop methods that accurately determine rates of methylation in lakes and wetlands.

4) to develop methods that accurately determine rates of mercury demethylation in uplands, wetlands and in lakes.

Acknowledgments

C. Kelly provided valuable insights to the modelling exercise. D. Bodaly, R. Hecky, A. Heyes, C.Kelly, D. Knauer, M. Paterson, N. Roulet, and V. St. Louis provided many useful suggestions during ms. preparation. The ELARP research was funded by the Department of Fisheries and Oceans, Manitoba Hydro, Ontario Hydro, Hydro Quebec and NSERC.

References

Allan, C.J., Heyes, A., Roulet, N.T., and Moore, T.R.: 1994, Abstract, Presented at the International Conference on Hg as a Global Pollutant, Whistler, British Columbia.

Bishop, K., Lee, Y.H., Pettersson, C. and Allard, B.: 1994, Abstract, Presented at the International Conference on Hg as a Global Pollutant, Whistler, British Columbia.

Bloom, N.S.: 1989, Can. J. Fish. Aquat. Sci., 46: 1131-1140

Bloom, N.S.: 1992, Can.J. Fish. Aquat. Sci., 49: 1010-1017.

Bloom, N.S. and Horvat, M.: submitted, Water Air Soil Pollut., (This volume).

Driscoll, C.T., Scholfield, C.L. Munson, R. and Holsapple, J.: 1994, Environ. Sci. Technol., 28: 136-143.

Fitzgerald, W.F., Mason, R.P. and Vandal, G.M.: 1991, Water, Air, and Soil Pollut., 56: 745-767.

Fowle, B.A., Heyes, A., Moore, T.R., and Roulet, N.T.: 1994, Abstract, Presented at the International Conference on Hg as a Global Pollutant, Whistler, British Columbia.

Furutani, A. and Rudd, J.W.M.: 1980, Appl. Environ. Microbiol. 40: 770-776.

Hecky, R.E., Ramsay, D.J. Bodaly, R.A. and Strange, N.E.: 1991, In: Advances in Hg Toxicology (T. Suzuki et al., eds.), Plenum Press, New York.

Heyes, A., J.W.M. Rudd, Moore, T.R., and Roulet, N.T.: 1994, Abstract, Presented at the International Conference on Hg as a Global Pollutant, Whistler, British Columbia.

Horvat, M., Bloom, N.S. and Liang, L: 1993, Anal. Chim. Acta, 281: 135-152.

Hultberg, H., Iverfeldt, A. and Lee, L.H.: 1994, In: Hg Pollution: Integration and Synthesis (C.J. Watras and J. Huckabee, eds), Lewis Pub., Boca Raton, FL, 313-322.

Hurley, J.P., Benoit, J.M. , Babiarz, C.L. Andren, A.W. and Webb, D.A.: 1994, Abstract, Presented at the International Conference on Hg as a Global Pollutant, Whistler, British Columbia.

Jensen, S. and Jernelov, A.: 1967, Nature (London), 223: 753-754.

Jernelov, A.: 1972, In: Environmental Hg contamination (R. Hartung and B.D. Dinman, eds.) Ann Arbor Science Publishers Inc.

Krabbenhoft, D.P., Benoit, J.M., Andren, A.W., Babiarz, C.L., Hurley, J.P., and Andren, A.W.: 1995, Water Air Soil Pollut., (This issue).

Lee, Y.H., Bishop, K., Hultberg, H., Pettersson, C., Iverfeldt, A. and Allard, B.: 1994, Abstract, Presented at the International Conference on Hg as a Global Pollutant, Whistler, British Columbia.

Mason, R.P., Fitzgerald, W.F., and Vandal, G.M.: 1992, J. Atmos. Chem. 14: 489-500.

Moore, T.R., Heyes, A. and Bubier, J.: 1994, Abstract, Presented at the International Conference on Hg as a Global Pollutant, Whistler, British Columbia.

Munthe, J. and Iverfeldt, A.: in press, In: Hg Pollution: Integration and Synthesis (C.J. Watras and J. Huckabee, eds.), Lewis Pub.

Newbury, R.W., McCullough, G.K., and Hecky, R.E.: 1984, Can. J. Fish. Aquat. Sci. 41: 548-557.

Parks, J.W., Lutz, A, and Sutton, J.A.: 1989, Can. J. Fish. Aquat. Sci. 46: 2184-2202.

Ramlal, P.S., Rudd, J.W.M. and Hecky, R.E.: 1986, Appl. Environ. Microbiol. 51: 110-114.

Rudd, J.W.M., Furutani, A. and Turner, M.A.: 1980, Appl. Environ. Microbiol., 40:777-782.

Rudd, J.W.M., Kelly, C.A., St. Louis, V., and Bodaly, R.A.: 1992, Abstract presented at the International Conference on Hg as a Global Pollutant, Monterey, California.

Sellers, P., Kelly, C.A., Rudd, J.W.M., and St. Louis, V.: 1994, Abstract presented at the International Conference on Hg as a Global Pollutant, Whistler, British Columbia.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Beaty, K.G., Bloom, N.S. and Flett, R.J.: 1994a, Can. J. Fish. Aquat. Sci. 51: 1065-1076.

St. Louis, V.L., Rudd, J,W,M., Kelly, C.A., Roulet, N.T., Heyes, A., Beaty, K.G., Bloom, N.S., and Flett, R.J.,: 1994b, Abstract, Presented at the International Conference on Hg as a Global Pollutant, Whistler, British Columbia.

St. Louis, V.L., Rudd, J.W.M. and Kelly, C.A.: 1995, Water Air Soil Pollut., (This issue).

Stordall, M.C., and Gill, G.A.: 1994, Abstract, Presented at the International Conference on Hg as a Global Pollutant, Whistler, British Columbia.

Watras, C.J., and 20 others; 1994, In: Hg Pollution: Integration and Synthesis (C.J. Watras and J. Huckabee, eds.), Lewis Pub., Boca Raton FL, 153-180.

Winfrey, M., and Rudd, J.W.M.: 1990, Environ. Toxicol.. Chem. 9: 853-869.