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An examination of current Hg deposition and export in Fenno-Scandian catchments

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Abstract. The input and output flux data of total Hg (THg) and methylmercury (MeHg) from three catchments located in different geographical regions in Sweden and one catchment in southern Finland were compared to elucidate the role of current atmospheric Hg/MeHg deposition with regard to waterborne Hg/MeHg output.

There was a negative co-variaton between the open field THg inputs and the ratio of THg output to open field input. The highest ratio (and lowest input) occurring in N. Sweden and S. Finland, while the lowest output ratio (and highest inputs) occurred in southwest Sweden. A much larger variation was found in the ratio of output to open field input for MeHg (14 to 160%). Examinations of MeHg input/output data in relation to catchment charateristics suggest that riparian peat, mires and wet organic soil contributed to the large MeHg output from certain catchments, probably due to *in situ* production of MeHg. This finding is consistent with other studies which have found that catchment characteristics such as wetland area, flow pathways, seasonal temperature and water flow are important in controlling the output of MeHg. These catchment characteristics govern the fate of the contemporary input of Hg and MeHg as well as the mobilization of the soil pools.

Introduction

Input of anthropogenic mercury (Hg) and methylmercury (MeHg) to the terrestrial ecosystem has resulted in a large accumulation of Hg/MeHg in soils (Aastrup et al. 1991). Although only a very small fraction (0.01 to 0.04%) of the catchment store of Hg and MeHg is transported annually from the soil to surface water, this is an important source of MeHg accumulated in the fish of Swedish and Finnish drainage lakes (Håkanson et al. 1988; Verta 1990). Recent results from integrated catchment studies on Hg/MeHg cycling in Sweden and Canada have identified factors influencing the load of Hg/MeHg in runoff and the processes controlling the transport of MeHg/Hg from soil to runoff water (St. Louis et al. 1994; Lee et al. 1995; Bishop et al. 1997, 1995a, 1995b; Pettersson et al. 1995; Krabbenhoft et al. 1995; Munthe

et al. 1997; Rudd et al. 1995). Flow paths, climate and catchment character were found to be the most important factors regulating the biogeochemical and hydrological conditions which have an impact on the output of MeHg/Hg in runoff water. St. Louis et al. (1996) concluded that wetlands are important sites of long-term MeHg production in boreal ecosystems.

Input of Hg to forests occurs both by wet and dry processes in the forms of precipitation/open field deposition (OF), throughfall (TF), and litterfall (LF) (Iverfeldt, 1991; Munthe et al. 1995). Dry deposition is an important process in a coniferous forest for THg in both LF and TF. The dry deposition of atmospheric Hg occurs through different mechanisms, such as deposition of particulate Hg, adsorption onto plant surfaces by gaseous divalent forms or in situ oxidation of elemental mercury to forms with lower vapor pressure. Hg^0 uptake through stomata may also be an important pathway at elevated air concentrations (Lindberg et al. 1992; Hanson et al. 1995). Dry deposition of MeHg has also been shown to be significant (Hultberg et al. 1994; Munthe et al. 1995). In Fenno-Scandian catchments, litterfall is a major pathway for Hg/MeHg input to soil. The litterfall contributes about half of the annual input to the forest floor (Hultberg et al. 1994; Munthe et al. 1995).

The importance of atmospheric deposition for litterfall THg/MeHg concentrations relative to mobilization of Hg/MeHg from soil pools up to the crown canopy cannot yet be resolved. Both sources are sufficiently large to sustain the present level of catchment output of Hg/MeHg. This study is focused on determining whether there are any regional trends across Fenno-Scandia in the ratio between catchment output and input fluxes of Hg/MeHg. This study also investigated the relationship between flow paths, climate, catchment character and output of MeHg and THg in Fenno-Scandia.

Study sites

This study includes three catchments in Sweden and one catchment in southern Finland (Figure 1 and Table 1). Gårdsjön is the catchment exposed to the highest levels of atmospheric THg and MeHg deposition. Paroninkorpi, Svartberget and V. Dybäcken are exposed to lower levels of deposition. The bedrock in the study areas consists mostly of acidic, weathering-resistant, granite and gneiss covered by podsolized till soil of different thicknesses. The forest soils are predominantly podzols, characterized by a distinctive humus layer on the top of the mineral soil. The Svartberget catchment is drained by two tributaries. One of the tributaries starts at the outlet of a mire (which comprises 16% of the total catchment area), and there is a band of riparian peats adjacent to the tributaries. The Paroninkorpi catchment has no peatland, but gentle slopes with substantial organic soil deposits. The vege-

Figure 1. Site location of catchments in Sweden and in Finland.

tation in all catchments is dominated by coniferous forests. The understory vegetation is mostly moss (*Sphagnum spp*.) near the streams (Svartberget and Västra Dybäcken) or near the outlet (Gårdsjön). Physiographic characteritics of all sites are given in Table 1.

Table 1. Selected physiographic and hydrologic characteristic of the study catchments.

Region/site	Area (km^2)	Catchment characteristics	Precip. (mm)	Runoff mm/yr	TOC mg C/L
Sweden					
Southwest					
Gårdsjön (58°04′ N, 12°01′ E)	0.037	Upland with thin soil and small area of wetland (ca. 5% of total area)	1112	586	7.8 (avg.)
Central					
V.Dybäcken (60°05′ N, 13°47′ E)	0.3	Svamp forest with peat and abundant swamp mosses along the stream channel (5.6% of total area)	660	369	10–34
North					
Svartberg (64°14′ N, 19°46′ E)	0.5	Upland containing riparian peat and a mire (16% of total area), and with sphagnum near the stream	711	375	15 (avg.)
Finland					
South					
Paroninkorpi (61°00′ N, 24°45′ E)	0.035	No peatland and low catchment slopes with thick organic soil	630	537	19.7 (avg.)

Methods

The details of the sampling equipment and procedures for THg and MeHg analysis have been described elsewhere (Iverfeldt 1991; Lee et al. 1994b).

Inputs of MeHg and THg to the whole catchments are from wet deposition (OF and TF) and litterfall. As TF data were not available for Svartberget and V. Dybäcken, only OF data were used in the input/output mass-balance budgets. Deposition (OF and TF) of THg/MeHg was determined monthly using bulk samplers. The collection bottles were pre-acidified with 2.5 ml of HCL (Merck Suprapur). The litterfall samples were collected using nylon nets mounted on aluminium frames. The deposition of THg and MeHg to the V. Dybäcken catchment was not available. As the V. Dybäcken catchment is situated in area with no obvious local air (Hg) pollution sources, regional OF data collected from Aspvreten (Kindbom et al. 1995) was used in the V. Dybäcken calculations.

Surface water sampling for THg/MeHg chemistry was carried out at the catchment outlet weirs at least once per month, biweekly for Gårdsjön and Paronikorpi, three to four times per month during high flow for Västra Dybäcken, and for Svartberget intensive sampling was conducted during the spring flood as well as during July 1993 and July 1994.

The MeHg measurements were performed using a GC-CVAFS technique with aqueous phase ethylation and distillation/dichloromethane extraction preseparation steps (Horvat et al. 1993). The methods summarized in Lee et al. (1994b) were considered when choosing an appropriate and validated pre-treatment procedure to isolate MeHg from the sample matrix. Total Hg analysis was performed using the gold amalgamation method following BrCl oxidation and $SnCl_2$ reduction and CVAFS detection (Bloom & Crecelius 1983; Iverfeldt 1991). The detection limit for both THg and MeHg is 0.06 ng/L (three standard deviation of blanks). The precision (relative standard deviation) for replicate analyses of the same samples is 5% at concentration of greater than 0.1 ng/L for both THg and MeHg.

The annual output fluxes of THg and MeHg from each catchment were calculated by multiplying the daily flow by an estimate of the daily THg and MeHg concentration in stream water. The daily concentration values were arrived at by linear interpolation of measured concentration between consecutive sampling occasions. The daily flow data are based on continuous flow monitoring except for V. Dybäcken. For V. Dybäcken interpolation was also used to estimate the daily flow between consecutive sampling occasions.

Results

The input and output data from all catchments are presented in Table 2 as well as Figures 2 and 3. The ratio of MeHg fluxes between the output and input from OF had a large variation (14% to 160%) in different catchments while the THg ratio varied from 17% to 63%. The OF data for THg and MeHg indicated that a large gradient existed for both THg and MeHg, with the highest deposition values in southwest Sweden, lower values in central Sweden and S. Finland, and the lowest values in northern Sweden. In contrast to the input fluxes, there were smaller differences in THg output, but MeHg output varied more than THg output. Inputs of THg and MeHg in LF were much greater than those in OF (2 to 12 times). The largest difference between LF and OF deposition of both THg and MeHg was found in Paroninkorpi.

A three-year record of runoff from Svartberget (from 1993 to 1995) (Figure 4 and Figure 5) shows a strong seasonal trend in the monthly output of MeHg (which starts from a low value during the spring flood and increases throughout the summer before declining again. THg output, on the other hand, peaked during spring snowmelt at the same time as MeHg output was low. A strong seasonal trend in the MeHg monthly output was also found at the V. Dybäcken (based on 1.5 years of data) and Paroninkorpi (based on one year of data) catchments. High THg output during the spring flood occurred at Paroninkorpi and Svartberget (Figure 5).

Table 2. Annual input/output fluxes in g km^{-2} yr^{-1} for THg and MeHg in catchments during 1993 to 1995.

	Input fluxes				Output fluxes				Output/OF	
	OF		LF		LF/OF		Runoff		(%)	
	THg	MeHg	THg	MeHg	THg	MeHg	THg	MeHg	THg	MeHg
Gårdsjön	10.4	0.21	23.0	0.55	2.2	2.6	1.8	0.03	17	14
V. Dybäcken	(5)*	(0.1)*					1.4	0.16	28	160
Svartberget	3.1	0.07	21.3	0.39	6.8	5.6	1.3	0.11	42	157
Paroninkorpi	5.1	0.1	59.5	0.64	11.7	6.4	3.2	0.09	63	90

* Regional data (Kindbom et al. 1995).

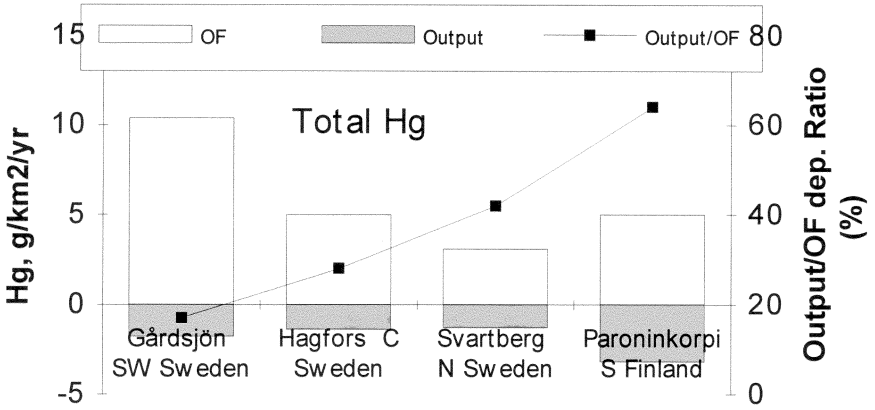

Figure 2. Annual input(OF)/output fluxes for total mercury in catchments.

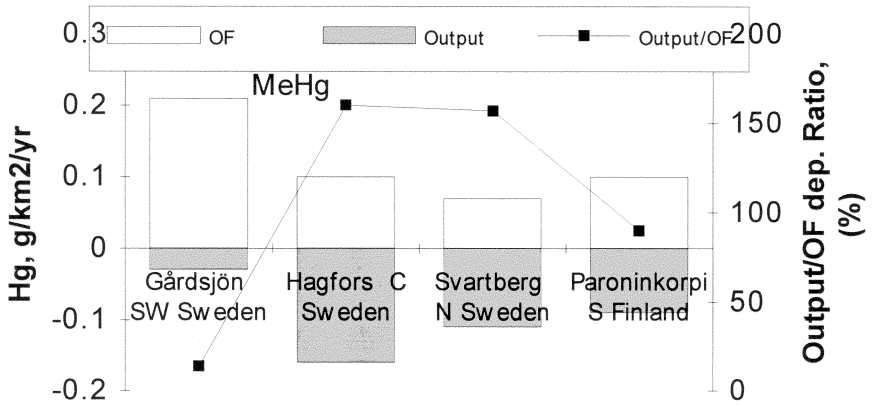

Figure 3. Annual input(OF)/output fluxes for methylmercury in catchments.

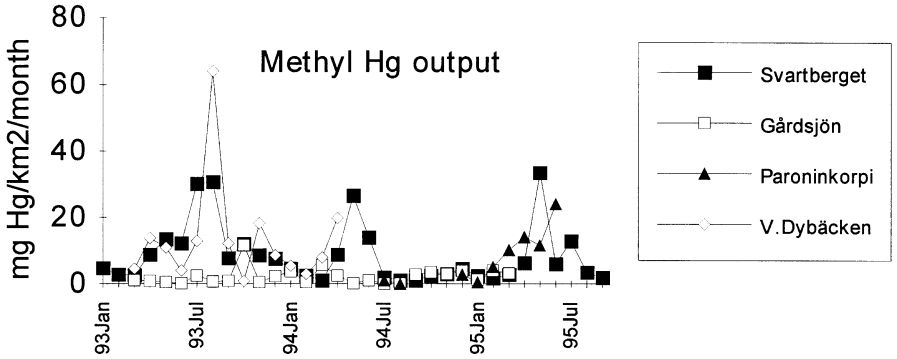

Figure 4. Monthly average output (mg month^{-1} km^{-2}) of methylmercury from catchments.

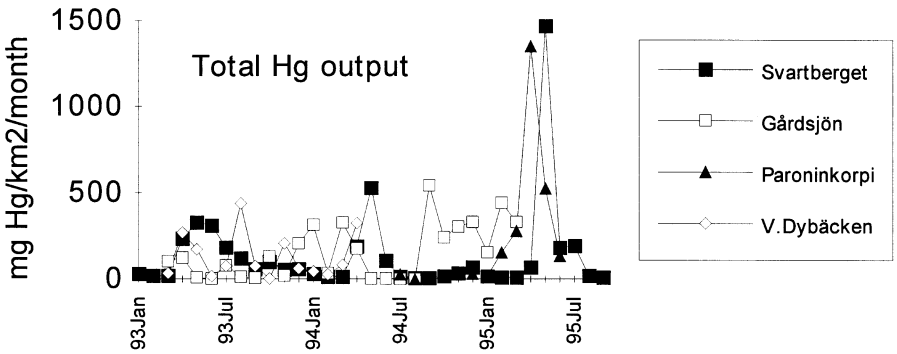

Figure 5. Monthly average output (mg month^{-1} km^{-2}) of total mercury from catchments.

Discussion

In Svartberget, previous studies have reported (Pettersson et al. 1995; Bishop et al. 1995b) that the variation in THg output was largely controlled by the major flow pathways (and DOC level) in runoff. The flow condition was an important factor in influencing output flux. During periods of high discharge, especially during spring floods, the major water flowpathways were superficial and passed through soil layers rich in Hg and total organic carbon (TOC). This may have caused increased THg and TOC levels (Pettersson et al. 1995) in runoff compared to the flow during low discharge periods when the water flows through deeper soil layers with lower Hg content (Lee et al. 1994a; Bishop et al. 1995b). As the spring flood comprises a major portion of the annual catchment runoff for northern Sweden and southern Finland as compared to central and southwest Sweden, a snow-rich winter can double the annual THg output from catchments in northern Sweden (Bishop et al.

1995a). Gårdsjön and V. Dybäcken, where spring flood was not the dominant runoff event, had lower THg output during the spring. In these catchments, the catchment output of THg during periods of high discharge in the autumn and winter can be a more important influence on the yearly output of THg (Figure 5) (Munthe et al. 1997).

The output of THg from Paroninkorpi was much higher than from the other catchments. One possible reason is that the low slope of the catchment (characterised by substantial organic soil deposits) may result in the major flow pathways being frequently routed through superficial soil layers during storm flow, consequently increasing THg and TOC levels (cf. Table 1) in runoff.

The high THg outputs during spring, and the superficial, organic rich flow paths at Paroninkorpi resulted in higher output/input OF flux ratios for THg in southern Finland and northern Sweden compared to that in southwest Sweden. Methylmercury, however, did not exhibit a similar regional trend in the ratio between output and input (OF) fluxes.

Soil temperature and soil moisture are two fundamental parameters controlling the rate of most biogeochemical processes. Indications of their influences on MeHg output from the field study from Svartberget catchment are shown in Figure 4 by an increase in MeHg concentration during the summer, most pronounced during the wet summer of 1993.

The sources of MeHg from the forest areas of catchments may have been controlled by the net methylation rates in wet soil (riparian peat and mire) and in wet stream bed material (sphagnum/moss). The ongoing stable isotope study of MeHg production in forest soil at Gårdsjön has found that the methylation rate of inorganic Hg was much higher in wet sphagnum and wet organic soil than that in dry conditions (Munthe et al., in preparation). Methylmercury and THg contained in organic material (stream sphagnum/moss in Svartberget and V. Dybäcken) are rapidly decomposed due to the high biological activity in riparian environments (Moore et al. 1995), resulting in a potential for methylation as well as for mobilization and transport of Hg to streams.

The sum of the wet deposition and litterfall of MeHg in the catchment at Svartberget (0.46 g km^{-2} yr^{-1}) was less than that at Gårdsjön (0.78 g km^{-2} yr^{-1}) and Paroninkorpi (0.75 g km^{-2} yr^{-1}), while MeHg output from Svartberget (0.11 g km^{-2} yr^{-1}) was higher than that from Paroninkorpi (0.09 g km^{-2} yr^{-1}) and much higher than that from Gårdsjön (0.03 g km^{-2} yr^{-1}). This suggests that the local conditions for net production and runoff mobilization of MeHg in wetland/riparian soil and wetland plants at Svartberget overshadowed the effect of contemporary MeHg inputs. For THg there was a positive co-variation between the output fluxes and the contemporary inputs (LF + OF). Figure 6 shows that the ratio of THg fluxes between the output

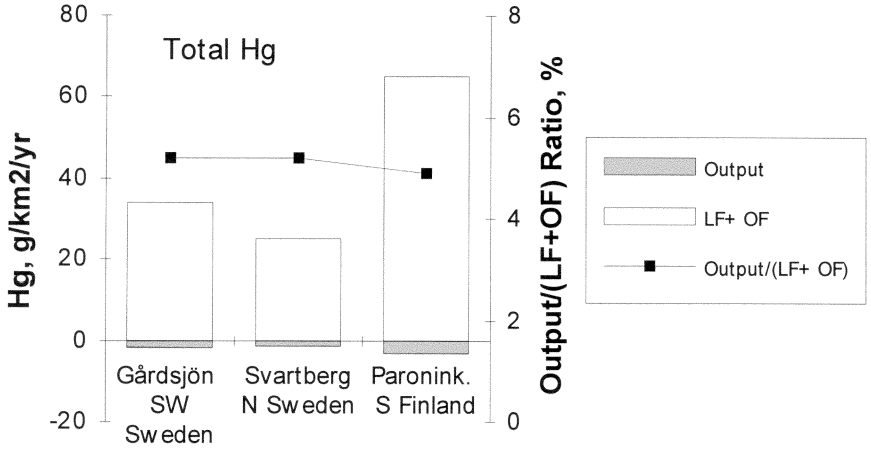

Figure 6. Annual input(LF + OF)/output fluxes for total mercury in catchments.

and input from (LF + OF) in different catchments was very similar. Since we do not know how much of litter input is new input, the influence of litterfall as atmospheric input on the THg output remains unclear.

To satisfactorily distinguish the role of contemporary THg/MeHg deposition, relative to the historical accumulation of Hg in soils with regards to current runoff outputs of THg/MeHg will require advances in the understanding of mercury cycling in the terrestrial ecosystem, especially with regards to the spatial distribution of key processes. Results from the comparison of regional input/output data indicate that contemporary deposition of THg/MeHg does not directly govern the output of MeHg/THg in runoff. Instead it appears to be catchment characteristics, such as organic matter content in the soils and hydrological dynamics, in the presence of a large catchment store of Hg/MeHg, (that is being added to each year by atmospheric deposition), which determines the current THg/MeHg output.

Conclusions

There was a significant difference in the output/input OF flux ratio for THg from southernwest Sweden where it was lowest, to northern Sweden and southern Finland where it was highest. Methylmercury had a a larger variation (14 to 160%) in the flux ratio between output and input (open field deposition) at the different catchments, due mainly to the variations in wetland types (riparian peat, mire and wet organic soil) and wetland areas.

The results from regional comparisons of input/output data suggest that the atmospheric deposition of MeHg/Hg is not directly controlling mobiliza-

tion and output from forested catchments. Catchment characteristics such as wetland area, flow pathways and seasonal variation in temperature and water flow are more important in influencing the fate of the Hg and MeHg deposited on the catchment in any given year, such as controlling the rate of net MeHg production and its accumulation, and in remobilizing the historically accumulated storage of THg and MeHg.

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References

Aastrup M, Johnsson J, Bringmark E, Bringmark I & Iverfeldt Å (1991) Occurrence and transport of mercury within a small catchment area. Water Air Soil Poll. 80: 445–454

Bishop KH & Lee YH (1997) Catchments as a source of mercury/methylmercury in boreal surface waters. In: Sigel A & Sigel H (Eds) Metal Ions in Biology, Vol. 34 (pp 113–130). Marcel Dekker, Inc., New York

Bishop KH, Lee YH, Pettersson C & Allard B (1995a) Methylmercury output from the Svartberget catchment in northern Sweden during spring flood. Water Air Soil Poll. 80: 445–454

Bishop KH, Lee YH, Pettersson C & Allard B (1995b) Terrestrial sources of methylmercury in surface water: The importance of the riparian zone on the Svartberget catchment. Water Air Soil Poll. 80: 435–444

Bloom NS & Crecelius EA (1983) Determination of mercury in seawater at subnanogram per litre levels. Mar. Chem. 14: 49

Hanson PJ, Lindberg SE, Tabberer TA, Owens JG & Kim KH (1995) Foliar exchange of mercury vapour: Evidence for a compensation point. Water Air Soil Poll. 80: 373–382

Horvat M, Liang L & Bloom NS (1993) Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part II Water. Anal. Chim. Acta 281: 153–168

Hultberg H, Iverfeldt Å & Lee YH (1994) Methylmercury input/out and accumulation in forested catchments and critical loads for lakes in southwestern Sweden. In: Watras J & Huckabee JW (Eds) Mercury Pollution: Integration and Synthesis (pp 313–322). Lewis Publishers, Boca Raton, FL

Håkanson L, Nilsson Å & Andersson T (1988) Mercury in fish in Swedish lakes. Environ. Pollut. 49: 145–162

Iverfeldt Å (1991) Occurrence and turnover of atmospheric mercury over the Nordic countries. Water Air Soil Poll. 56: 251–265

Kindbom K, Sjöberg K, Munthe J & Lövblad (1995) Luft- och nederbördskemiska stationsnätet inom PMK. Resultat från 1994. IVL Rapport B1206. Swedish Environmental Research Institute (in Swedish)

Krabbenhoft DP, Benoit JM, Andren AW, Babiarz CL & Hurley JP (1995) Mercury cycling in the Allequash Creek watershed, northern Wisconsin. Water Air Soil Poll. 80: 425–433

Lee YH, Bishop KH, Pettersson C, Iverfeldt Å & Allard B (1995) Subcatchment output of mercury and methylmercury at Svartberget in northern Sweden. Water Air Soil Poll. 80: 455–465

Lee YH, Borg GCH, Iverfeldt Å & Hultberg H (1994a) Fluxes and turnover of methylmercury: Mercury pools in forest soils. In: Watras CJ & Huckabee JW (Eds) Mercury Pollution: Integration and Synthesis (pp 329–341). Lewis Publishers, Boca Raton, FL

Lee YH, Munthe J & Iverfeldt Å (1994b) Experiences with the analytical procedures for the determination of methylmercury in environmental samples. Appl. Organomet. Chem. 8: 659–664

Lindberg SE, Meyers TP, Taylor GE, Turner RR & Schroeder WH (1992) Atmosphere/surface exchange of mercury in a forest: Results of modeling and gradient approaches. J. Geophys. Res. 97: 2519–2528

Moore TR, Bubier JL, Heyes A & Flett RJ (1995) Methyl and total mercury in boreal wetland plants, experimental lake area, northwestern Ontario. J. Environ. Qual. 24: 845–850

Munthe J, Haraldsson C, Parkman H, Lee YH & Iverfeldt Å (Manuscript in prep) A stable isotope study of methylmercury production and turnover in forests soils. Methods development and initial results

Munthe J, Hultberg H & Iverfeldt Å (1995) Mechanisms of deposition of methylmercury and mercury to coniferous forests. Water Air Soil Poll. 80: 363–371

Munthe J, Lee YH, Hultberg H, Iverfeldt Å, Borg GCH & Andersson BI (1997) Cycling of mercury and methylmercury in the Gårdsjön catchments. In: Skeffington R & Hultberg H (Eds) Experimental Reversal of Acid Rain Effact: The Gårdsjön Covered Catchment Experiment. John Wiley & Sons, London. In press

Pettersson C, Bishop KH, Allard B & Lee YH (1995) Relations between organic carbon and methylmercury in humic rich surface waters from Svartberget catchment in northern Sweden. Water Air Soil Poll. 80: 971–979

Rudd JWM (1995) Sources of methyl mercury to freshwater ecosystems: A review. Water Air Soil Poll. 80: 697–713

St. Louis VL, Rudd JWM, Kelly CA, Beaty KG, Bloom NS & Robert JF (1994) Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. Can. J. Fish. Aquat. Sci. 51: 1065–1076

St. Louis VL, Rudd JWM, Kelly CA, Beaty KG, Robert JF & Roulet NT (1996) Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. Environ. Sci. Technol. 30: 2719–2729

Verta M (1990) Mercury in Finnish forest lakes and reservoirs: Anthropogenic contribution to the load and accumulation in fish. In: Publications of the Water and Environment Institute, National Board of Water and the Environment, Finland, 6