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Sinks and sources of methylmercury in a boreal catchment

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Abstract. A simple, catchment-scale, cascade model was used to assess the importance of sinks and sources of methylmercury (MeHg) in a boreal catchment that contains a forested upland, a lowland peatland and a small lake. The three compartment model was run using realistic flow rates and atmospheric loading of MeHg, and the model was constrained by observed concentrations of MeHg in each compartment. Assuming no internal sinks and sources of MeHg, modelled catchment yields showed reasonable agreement with field observation, but the predicted internal MeHg concentrations in each compartment were implausible. Only when sources and sinks of MeHg are added to the three compartments do MeHg-pool concentrations fall into the range of those measured in the field. To maintain both catchment-scale and compartment-scale continuity, the upland and peatland were net sources of MeHg (0.0007 and 0.1065 mg ha^{-1} d^{-1} respectively), and the lake a net sink (-0.2215 mg ha^{-1} d^{-1}). These source/sink rates are 1.73, 259 and -539 times the input of MeHg via wet precipitation input for the modelled ice-free season. Sensitivity analysis revealed that the volume of runoff delivered to the peatland by the upland area, peatland size and porewater MeHg concentration in the peatland are important controls on catchment MeHg yield, and that contemporary atmospheric deposition of MeHg is insignificant compared to the sources of MeHg within the catchment.

Introduction

There is a debate on the role that catchment physiography plays in methylmercury (MeHg) production. Although it is not contested that demethylation processes (e.g. oxidation, complexation, binding) are at work in the terrestrial portions of catchments, there are differences in opinion regarding the importance of methylation. Some researchers suggest that MeHg in precipitation is sufficient to account for catchment yields of MeHg in runoff in some landscapes; hence by inference Hg methylation in the catchment soils/water is unimportant or insignificant relative to the atmospheric deposition (e.g. Hultberg et al. 1995). St. Louis et al. (1994) observe similar or higher MeHg catchment yields in Northern Ontario to that of southern Sweden but atmospheric inputs of MeHg are much smaller. St. Louis et al. (1994)

and Branfireun et al. (1996) conclude that *in situ* methylation processes contribute significantly to catchment MeHg output and that peatlands appear to be a locus of MeHg production. This conclusion is supported by other recent work (Bishop et al. 1995a, b; Krabbenhoft et al. 1995; Hurley et al. 1995).

"Black box" catchment input-output budgets may indicate that atmospheric MeHg inputs account for a significant proportion of MeHg outputs. However, sources and sinks of MeHg within the catchment may be very large, but go unnoticed if the net within-catchment budget is comparable to other inputs. The results of recent covered-catchment experiments have attempted to dismiss the latter (e.g. Hultberg et al. 1995), but the results have not been definitive.

Our objective in the present study is to develop a simple hydrology model and use it as a heuristic tool to test the relative importance of wet MeHg deposition and internal sinks and sources of MeHg on variations in MeHg yield for a low boreal headwater catchment.

Model description

The model comprises two coupled sub-models, hydrologic volumes and fluxes and net MeHg sinks and sources (Figure 1). The model operates on a daily time step and simulations are one year long. The model simulation starts after the end of snowmelt and assumes saturated conditions at the beginning of the open water season and zero flow during the winter. The catchment simulated was based on a small headwater catchment (632) in the Experimental Lakes Area, northwestern Ontario, Canada which is a site of ongoing research into boreal catchment hydrology and MeHg dynamics (Branfireun et al. 1996; Branfireun & Roulet, in press).

The hydrology sub-model is a simple cascading reservoir system with precipitation, and evapotranspiration and catchment outflow as the major input and outputs, respectively, to three sub-catchment reservoirs (upland, peatland and pond). The sub-model considers each catchment unit as a "bucket" which flows into the next sub-catchment compartment at a rate determined by the drainage coefficient *D*, and the amount of water in the "bucket". The sub-model's data requirements are the volume of each catchment reservior and it's saturated volumetric soil moisture, which are set at the beginning of each run. All other values are generated by the model (e.g. precipitation; net radiation) and are tailored to field data from the reference catchment. This limits the model's application to the reference catchment but this simple structure simulates this catchment's hydrologic response, storage volumes, and fluxes between the catchment units reasonably well, therefore

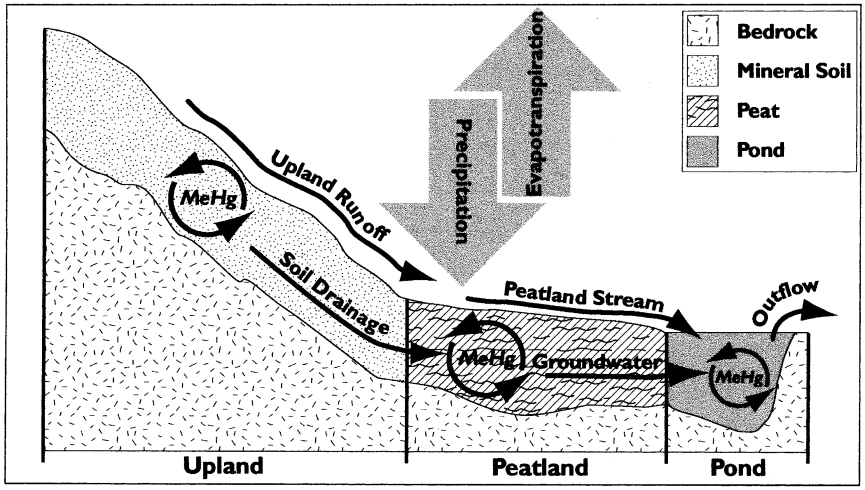

Figure 1. Schematic diagram of the model reservoirs and fluxes.

satisfying our desire to capture the hydrology and to test our hypotheses about the importance of sources and sinks of MeHg.

The MeHg sub-model uses net MeHg production, which encompasses a wide variety of (largely unknown) biotic and abiotic processes, as the input and output of MeHg to each reservoir which are sufficient to maintain equilibrium concentrations. The equilibrium concentrations are based on field data from the reference catchment and are set at the beginning of each model run. This approach was taken because of the absence of information in the literature regarding *in situ* methylation and demethylation processes in terrestrial and wetland environments.

Hydrology sub-model

As discussed above, the hydrology sub-model is a simple cascading reservoir system with all units in m^3 of water. The upland was allocated an area of 20 ha with 75% soil cover at 1 m depth (allowing for exposed bedrock areas). The peatland was assigned an area of 2 ha with 100% organic soil coverage (peat) at a depth of 2 m. The pond was given an area of 0.8 ha with a depth of 1 m. Initial volumes of water in the reservoirs are based on field data and assume saturated conditions. These volumes are 67500 m^3 for the upland (assuming a uniform 45% volumetric soil moisture), 32000 m^3 for the peatland (assuming a uniform 80% volumetric soil moisture), and 8000 m^3 for the pond.

Precipitation is generated using a subroutine based on the probability of rain on a given day (p = 0.22; determined from ELA precipitation records). If rain is selected, then a storm magnitude (based on monthly averages from

the ELA) is determined randomly within a specified range weighted towards smaller, 'normal' magnitude storms. Daily total evapotranspiration over the upland and peatland surfaces, and evaporation over the pond is calculated as:

$$E = \frac{\frac{Q^* + Q_G}{1+\beta}}{L_v} \tag{1}$$

where E is the mass of water evaporated (Kg m^{-2} d^{-1}), Q^* is the net radiation incident at the surface (MJ d^{-1}), Q_G is the ground heat flux (MJ d^{-1}), β is the Bowen Ratio (unitless), and L_v is the latent heat of vaporization. Potential Q^* is generated as a function of latitude (Charles-Edwards 1982). Random variability ("cloud effect") in Q^* is introduced which varies Q^* by 0 to 90% on any given day. On days with rain, Q^* is reduced by 50%. Modelled Q* agrees well with actual Q* data from field studies at the ELA catchment (Roulet, unpublished data, 1993). Q_G is set at 10% of Q^* for the forested upland and peatland, and 0% of Q^* for the pond, except for in the spring when Q_G is set to 30% of Q^* for the pond to account for heating of the water (Roulet et al., in press). β was determined from representative values from the literature (Oke 1987; Roulet et al., in press) and set at 0.2 for the pond, 0.4 for the peatland and 0.6 for the forested upland. It is assumed that evapotranspiration from the upland occurs from the soil covered areas only, and that no evapotranspiration occurs on days when it rains.

Changes in the amount of water in a state variable is determined as:

$$V_{\mathrm{H_2O}}(t) = V_{\mathrm{H_2O}}(t - dt) + (I_1 + I_2 + I_3 \ldots - O_1 - O_2)dt \tag{2}$$

where $V_{\mathrm{H_2O}}$ is the volume of water in the state variable at time t, $V_{\mathrm{H_2O}}(t - dt)$ is the volume of water in the state variable at the previous time interval and I_x and O_x are inputs and outputs to the state variable, respectively.

The source of water to the model catchment is precipitation. This is the same as that in the study catchment at ELA since there is no inter-basin transport of groundwater. Evapotranspiration and catchment outflow are the two outputs. Fluxes from the upland to the peatland are upland surface runoff and soil drainage, and from the peatland to the pond are a peatland stream and groundwater. Fluxes within the catchment may generally be described as:

$$F(t) = (V_{\mathrm{H_2O}}(t) - V_{\mathrm{sat}})D \tag{3}$$

where $F(t)$ is the magnitude of the flux at time t (m^3 d^{-1}), V_{sat} is the volume of the 'full' reservoir and D is the drainage coefficient which ranges between 0.001 and 0.8 for all fluxes (smaller for slow, insensitive fluxes such as peatland groundwater; larger for responsive, episodic fluxes such as overland flow

(see Branfireun & Roulet, in press)) and determines the rate at which excess water in each reservoir may drain via that pathway. *D* was determined by trial and error, manually calibrating the hydrograph responses and magnitudes of the model fluxes to approximate those of the study catchment (632). Fluxes via upland runoff, peatland streamflow and catchment outflow pathways are only permitted to occur when the volume of their corresponding state variables exceeds V_{sat}, and upland soil drainage may only occur uninhibited if volumetric soil moisture in the upland soils is in excess of 20%.

Methylmercury sub-model

The sub-model for MeHg is nearly identical in form to that of the hydrology sub-model, with the exception that the units for this sub-model are mass of MeHg (ng), the fluxes are controlled by MeHg concentration in free porewater (mass of MeHg in the reservoir multiplied by the volume of water in the reservoir; all water in the reservoirs is assumed to be mobile and completely mixed) and the magnitude of the flux of water, with reservoir volumes and water fluxes being determined by the hydrology sub-model. Inputs of MeHg by precipitation are determined using [MeHg] data for the ELA area from St. Louis et al. (1995), with storm concentrations allowed to vary randomly between 0.010 and 0.179 ng L^{-1}. The equilibrium MeHg concentration of each reservoir is variable to allow for the testing of relative importance of each state variable in determining final pond concentrations.

The model is run to resolve the MeHg export from the basin, and the initial model runs are constrained by the known concentrations of MeHg in each reservoir. This allows us to determine the net sinks/sources of MeHg needed to maintain observed MeHg concentrations in the reservoirs when the initial conditions are set to that representative of measured field values and assumed to be in steady-state.

The analysis of the potential role of sources/sinks of MeHg, the impact of MeHg in precipitation, and the effects of upland and peatland size are examined using two different model scenarios and sensitivity analysis.

The role of MeHg sources and sinks

To determine the role of MeHg sources and sinks in the catchment compartments, two different model scenarios are used. In scenario 1, the model is run with wet deposition of MeHg as the sole MeHg input. Initial MeHg concentrations for the three reservoirs are set at 0.2 ng L^{-1} [MeHg], 2.0 ng L^{-1} [MeHg] and 0.2 ng L^{-1} [MeHg] for the upland, peatland and pond respectively, representing concentrations measured in the field (Branfireun et al. 1996; A. Heyes, unpublished data, 1995; B. Branfireun, unpublished

data, 1996). In reality these concentrations would not be distributed evenly throughout the volume of water in each reservoir given the heterogeneity of MeHg in the landscape, but these values represent an estimated average concentration. 2.0 ng/L represents a very conservative estimate for MeHg concentrations in the peat porewater, as concentrations in excess of 7 ng/L have been measured at this site (Branfireun et al. 1996).

In scenario 2, net MeHg sinks/sources are added to scenario 1, in which MeHg will be removed/added based on the assumption that the amount of MeHg in each reservoir will remain relatively stable over the model run (i.e. the concentration of MeHg in each compartment is in 'steady-state'). If the MeHg concentration in the reservoir at time *t* is different from the equilibrium concentration, then:

$$\textit{Net\_Sink/Source}_t = K_{MeHg}(\textit{MeHg}_{eq} - \textit{MeHg}_{t-dt}) \quad (4)$$

where $\textit{Net\_Sink/Source}_t$ is the amount of MeHg (ng) added to, or removed from, the system at time *t*, K_{MeHg} is the rate constant for MeHg production/destruction, $\textit{MeHg}_{eq}$ is the equilibrium mass of MeHg in the reservoir (ng) which is set at the beginning of the model run (the same concentrations as used in scenario 1), and $\textit{MeHg}_{t-dt}$ is the amount of MeHg in the reservoir at the previous time step (ng). K_{MeHg} is set to 0.5 to simulate the relatively rapid equilibration of porewater MeHg concentrations observed in the field (Heyes, unpublished data, 1995).

Results

For all of the model scenarios, the simulated mean contribution of MeHg by wet deposition to the entire catchment was 0.0004 mg ha^{-1} d^{-1} [MeHg], which is comparable to that reported by St. Louis et al. (1994). Modelled and measured MeHg yields for precipitation and catchment yields from the different model scenarios are found in Table 1. Simulation results in Table 1 are mean values derived from a 30 run Monte Carlo simulation in which all randomly generated parameters were independently and randomly varied. These include 4 parameters which control rainfall occurrence and magnitude, 2 parameters which control cloud cover and Q^* and 1 parameter which controls the concentration of MeHg in rainfall.

Scenario 1

With the initial concentrations set at 'realistic' levels, concentrations of MeHg in the upland showed little variation, with a maximum occurring at the height

Table 1. Actual and modelled catchment MeHg depositions and yields. Model results are means and standard errors from a 30 run Monte Carlo simulation in which all randomly generated parameters were varied independently and randomly.

	Mean deposition of yield of MeHg (mg/ha/d)	Standard error	Yields/annual precip. input
Actual precipitation[1]	0.0004	–	–
Modelled precipitation	0.0004	0.00002	–
Actual catchment yield (upland dominated)[2]	0.0009	–	2.25
Actual catchment yield (peatland dominated)[2]	0.0036	–	9.00
Modelled catchment yield (scenario 1)	0.0052	0.00038	12.75
Modelled catchment yield (scenario 2)	0.0026	0.00036	6.51
Modelled upland net MeHg source	0.0007	0.00009	1.73
Modelled peatland net MeHg source	0.1065	0.00879	259
Modelled pond net MeHg sink	−0.2215	0.01466	−539

[1]Data from St. Louis et al., 1995.
[2]Data from St. Louis et al., 1994.

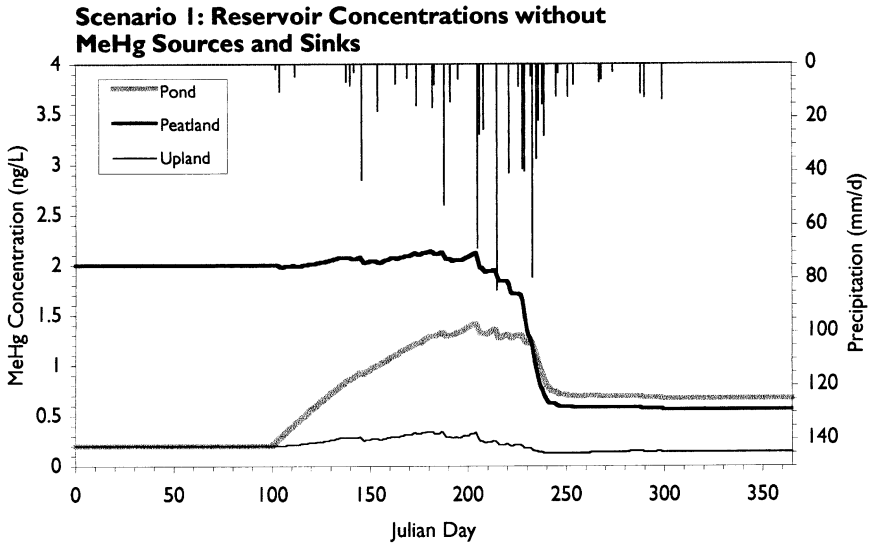

Figure 2. MeHg concentrations in the three reservoirs for a model run *without* net MeHg sinks and sources.

of the summer period when fluxes out of the reservoir were at a minimum (Figure 2). Concentrations dropped to below initial levels by the end of the model year.

Peatland MeHg concentration behaved quite differently. The initial concentration of 2.0 ng L^{-1} was maintained until mid-summer, after which

the concentration rapidly dropped to a minimum of 0.56 ng L^{-1}. Subsequent undocumented model runs revealed that MeHg concentration above approximately 0.75 ng L^{-1} could not be sustained, suggesting that production of MeHg *in situ* may be important. MeHg export appeared to be controlled by high runoff events with substantial decreases in concentration coinciding with large storms during high water table conditions.

Pond MeHg concentration increased rapidly at the beginning of the model run, stabilizing at between 1 and 1.4 ng L^{-1}, nearly an order of magnitude above the initial concentration and measured field values. This suggests that demethylation processes may significantly control pond concentrations. The catchment yield of MeHg calculated from the outflow flux was 0.0062mg ha^{-1} d^{-1} [MeHg].

Scenario 2

Sink and source fluxes were added to the upland, peatland and pond, as defined in equation 4, to maintain concentrations at or about the initial levels. The source and sink fluxes regulated the amounts of MeHg in the upland, peatland and pond quite effectively, allowing for normal fluctuation as a result of dilution and flushing effects, particularly due to large storms (e.g. day 240; Figure 3). Peatland concentration reached a maximum of 2.88 ng/L at mid-summer, whereas upland and pond concentrations were maintained about their initial values. The catchment yield of MeHg calculated from the outflow flux was 0.0031 mg ha^{-1} d^{-1} [MeHg].

The results presented in Table 1 indicate that when sources and sinks of MeHg are included in the model, the upland and upland are mean net sources of MeHg (0.0007 and 0.1065 mg ha^{-1} d^{-1}) which are 1.73 and 259 times larger than the simulated atmospheric input of MeHg to the entire catchment. The pond is a mean net sink for MeHg (-0.2215 mg ha^{-1} d^{-1}) which is 539 times larger than the atmospheric input.

Sensitivity analysis

Sensitivity analyses were performed to determine the effects on catchment yield of upland and peatland size, the magnitude of atmospheric MeHg deposition, and the equilibrium concentrations of MeHg in the peatland reservoir, since the results of scenario 2 indicate that it is the primary source of MeHg in the catchment. All sensitivity analysis were performed using the scenario 2 model structure (i.e. sinks and sources of MeHg were included, and where catchment yield = 0.0031 mg ha^{-1} d^{-1} under initial conditions.

The catchment MeHg yield is sensitive to changes in peatland area relative to the rest of the catchment (Figure 4). In this sensitivity analysis, the upland

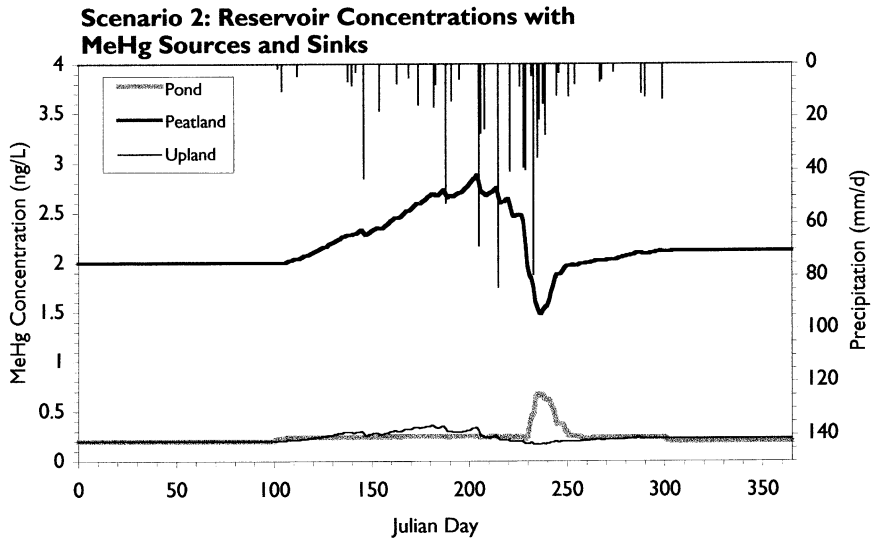

Figure 3. MeHg concentrations in the three reservoirs for model run *with* net MeHg sinks and sources.

and pond areas were unchanged while the peatland area was varied from 0.2 to 4 ha. Catchment yields were largest with relatively large peatland areas, and decreased with increasing upland area-peatland area ratio. Upland yield was constant at 0.0012 mg ha^{-1} d^{-1}, whereas peatland yield increased markedly with increasing upland area-peatland area ratio as a result of the increased flushing rate of the smaller peatland volume relative to the upland. The catchment yield decreases with increasing upland area-peatland area ratio in spite of this since the size of the pond MeHg sink remains constant, offsetting the increased yield from a relatively smaller peatland area.

Similarly, the catchment yield is sensitive to the size of the upland relative to the peatland (Figure 5). Catchment yield increases rapidly with increasing upland area (peatland area held constant at 2 ha) with a maximum yield of approximately 0.0036 mg ha^{-1} d^{-1} occurring with an upland area-peatland area ratio of 20:1, and decreases with increasing ratio. Peatland and upland yields are similar to those observed in the previous sensitivity analysis, and decreasing catchment yield at higher upland area-peatland area ratios suggests that the relatively much larger uplands are capable of delivering large volumes of low MeHg runoff which counteract the influence of the higher MeHg peatland runoff contributions. Both of the above scenarios become somewhat implausible at higher upland area-peatland area ratios, as the overall basin physiography would not be expected to scale proportionally, particularly with regard to pond characteristics. For example, very large catchments would

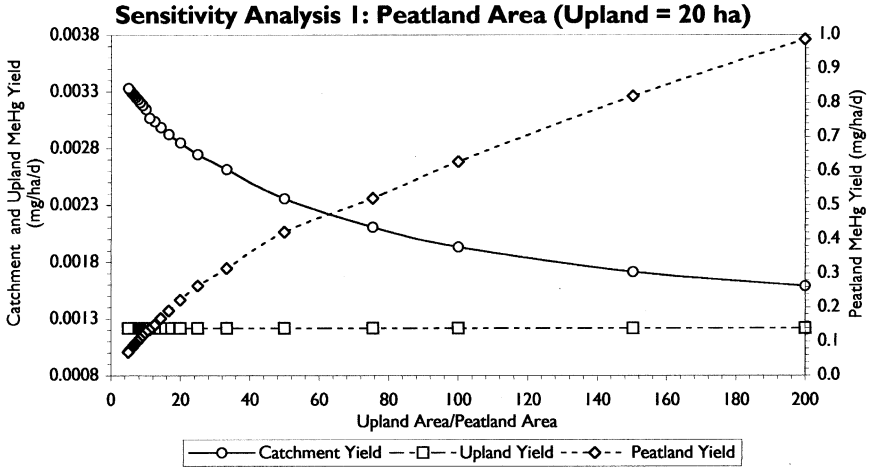

Figure 4. Results of peatland area sensitivity analysis. Peatland area was varied from 0.1 ha to 4 ha and upland and pond areas were constant at 20 ha and 0.8 ha respectively.

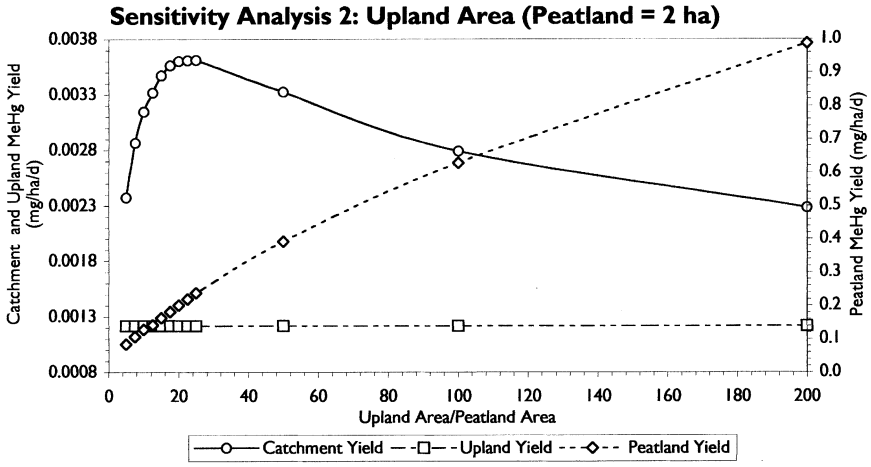

Figure 5. Results of upland area sensitivity analysis. Upland ara was varied from 5 ha to 400 ha and peatland and pond areas were constant at 4 ha and 0.8 ha respectively.

be expected to have larger, deeper lakes associated with them which could represent much larger sinks for MeHg, thus regulating the catchment yields significantly.

Sensitivity analysis in which the amount of MeHg deposited in precipitation over the catchment was varied by factors of 0 to 15 times ELA deposition revealed that catchment yield remained virtually unchanged (0.0031 mg ha^{-1} d^{-1}), even at 15 times deposition (Figure 6). This model suggests that

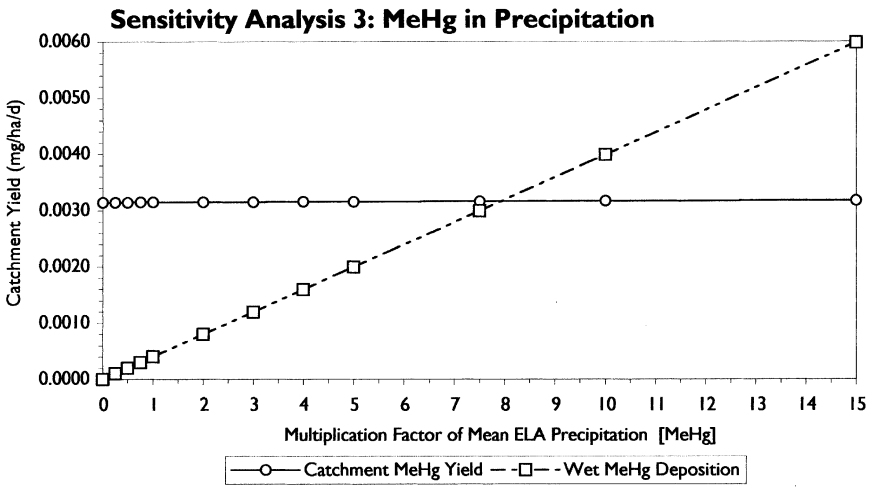

Figure 6. Results of precipitation MeHg sensitivity analysis. The precipitation MeHg used in the model based on ELA records was varied by a factor of 0 to 15 to simulate various degrees of loading.

contemporary deposition of MeHg plays an insignificant role in influencing the magnitude of catchment yield in catchments containing peatlands.

Catchment yield is also extremely sensitive to the concentrations of MeHg found in the peatland reservoir. Realistic yields are only found between 2 and 4 ng L^{-1} for this simulation which agrees with measured field concentrations. This finding suggests that accurate quantification of the 'active' pool of MeHg in peatlands is important if it is to be incorporated into catchment-scale budgets or process-based models.

Discussion

When realistic initial concentrations of MeHg are used and no net MeHg sinks/sources are included (as in scenario 1), concentrations in the upland generally vary between 0.20 and 0.40 ng L^{-1}, which is consistent with measured field concentrations (Branfireun, unpublished data, 1995). This finding suggests that net methylation in this type of environment may be about zero (i.e. methylation and demethylation processes are either negligible or roughly in balance).

A much different situation is found in the peatland and pond. The peatland reservoir is incapable of maintaining the initial concentrations of MeHg likely as a result of flushing with low MeHg upland runoff, particularly during large runoff events. The conclusion of this simulation is that if concentrations are to

be maintained at the observed level in the peatland, there needs to be an additional source of MeHg to the system. Conversely, the relatively high volume, high concentration fluxes entering the pond elevate pond concentrations to nearly seven times the observed concentrations, indicating that MeHg must be being removed from the pond. The mean catchment yield calculated in scenario 1 (0.0052 mg ha^{-1} d^{-1}) is 1.69 times larger than that found by St. Louis et al. (1994) for the catchment on which this model is based (0.0036 mg ha^{-1} d^{-1}), but is not unreasonable. However, the behaviour of reservoir MeHg concentrations render this simulation implausible.

In scenario 2, the model was inverted to ask, "What are the net sources and/or sinks needed in the various compartments of the catchment to maintain the reservoir concentrations and basin yield, given the observed atmospheric loading?". This scenario confirms that a source of MeHg (0.1065 mg ha^{-1} d^{-1}) to the peatland over 250 times the MeHg input by precipitation (Table 1). Even given gross errors in the model parameterization, there is clearly a large source of MeHg to the peatland area. This scenario also indicates that MeHg is being removed from the pond reservoir (0.2215 mg ha^{-1} d^{-1}), at a rate over 500 times that of MeHg input by precipitation. The mean catchment yield of 0.0026 mg ha^{-1} d^{-1} is within 30% of that found by St. Louis et al. (1994), and is subject to variability in precipitation volume and timing, and MeHg concentration. What is important is that the catchment yields are in rough agreement while preserving a realistic concentration regime in the three reservoirs through the addition of methylation and demethylation fluxes.

Sensitivity analyses confirm the importance of the peatland reservoir as a source of MeHg to the system (Figures 4 and 7), and also indicate that important role of the upland portion of the catchment not as a source of MeHg, but as a source of runoff which serves to flush high MeHg water from the peatland to the pond (Figure 5). Most importantly, this simulation clearly indicates that contemporary atmospheric deposition of MeHg has little or no influence on catchment MeHg yield in catchments containing peatlands because of the magnitude of the sources and sinks found within the catchment.

These results are limited by the assumptions made in the formulation of the model. The assumption that MeHg concentrations are in equilibrium in the reservoirs, and that MeHg is transferred conservatively between compartments of the catchment are potentially the greatest sources of error in this study. To relax these assumptions to allow for *in situ* methylation, demethylation and the mobility of MeHg through oxic, anoxic, mineral and organic soils in the model structure requires greater understanding of the factors that control the transport and transformation of (Me)Hg than is currently found in the literature.

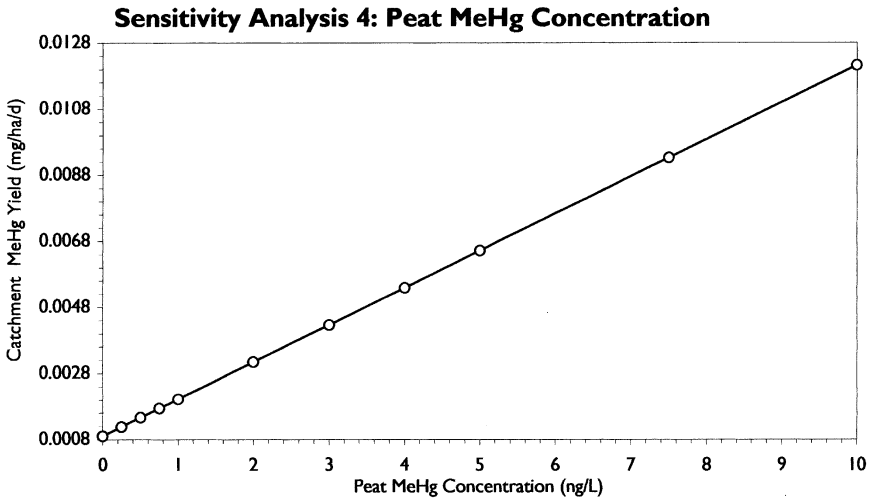

Figure 7. Results of peat porewater MeHg concentration sensitivity analysis.

Possible sources and sinks of methylmercury

MeHg in the porewater of peatlands may be derived from the methylation of *in situ* inorganic Hg in decaying organic matter, and/or the equilibration of porewater MeHg concentrations with MeHg in the plant tissues and organic sediment. The store of inorganic Hg in peatland vegetation and pore water is more than sufficient to provide enough Hg^{2+} for *in situ* methylation (Moore et al. 1995), and porewater MeHg concentrations have been found to rapidly equilibrate with the high concentrations of MeHg in plant tissue and sediments, likely through diffusion (Heyes, unpublished data, 1995). We hypothesize that biotic methylation may be a major source of MeHg in peatlands, as suggested by previous research (e.g. Branfireun et al. 1996).

The large sink of MeHg in the pond may be attributed to a variety of demethylation processes including oxidation, and uptake by sediments and/or plants and biota (biodilution). More importantly, lakes have recently been found to be large sinks of MeHg via an abiotic photodegradive pathway (Sellers et al. 1996). This model simulation independently confirms this finding, and further testing of this model incorporating the empirically derived rates of MeHg photodegradation from Sellers et al. (1996) would be valuable.

Summary

The results of this preliminary model suggest that cycling of Hg species may be going on at a tremendous rate *within the catchment*, and interpretations

regarding the role of the landscape in methylation/demethylation processes must be made with great care.

It is difficult to draw comparisons between the results found here and field data derived elsewhere because of differences in catchment characteristics and our assumptions regarding the behaviour of MeHg in natural systems, but the model results indicate that, although the catchment yield found under a no net methylation scenario may be realistic, the internal concentration regime is inconsistent with that observed in the study catchment in the ELA. The model results indicate that: the peatlands must be a large source of MeHg (consistent with St. Louis et al. 1994; Branfireun et al. 1996); the amount of MeHg which must be destroyed by demethylation in the pond system to maintain measured field concentrations is consistent with the large photodegradive MeHg sink found by Sellers et al. (1996) and; contemporary atmospheric deposition of MeHg is not a significant component of MeHg budgets in catchments containing peatlands. This suggests that post-industrial MeHg contamination of "pristine" lakes may be the result of the enhancement of Hg methylation or inhibition of MeHg demethylation by the deposition of some other atmospherically-derived industrial pollutant (e.g. SO_4^{-2}; see Gilmour & Henry 1991) or through some change in the bioavailability of the large volumes of inorganic mercury which are held in the catchment soils and sediments. Work is ongoing to elucidate these mechanisms. This simulation does not consider the impact of atmospheric deposition of inorganic Hg, which must also contribute to the pool of Hg methylated *in situ*. The importance of this atmospheric Hg in the catchment Hg cycle is unknown.

These large internal sources and sinks indicate a need for improved understanding of the mechanisms of Hg cycling within catchments before conclusions regarding sinks or sources of MeHg may be drawn. This finding also has more wide ranging implications for those modelling any biogeochemical system using a "black box" input-output approach, where the potential for internal transformations larger than the inputs and outputs combined may exist.

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