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# Eight Boreal Wetlands as Sources and Sinks for Methyl Mercury in Relation to Soil Acidity, C/N Ratio, and Small-Scale Flooding

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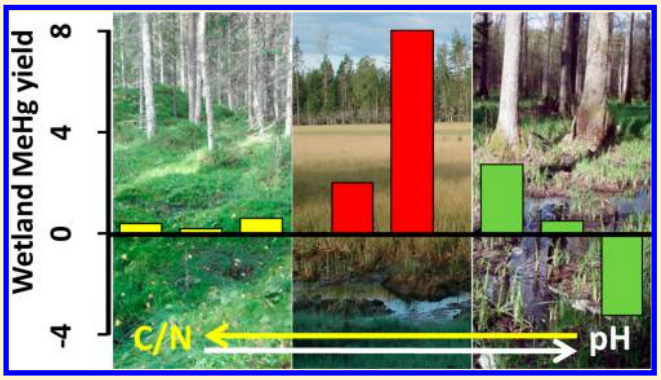
Supporting Information

**ABSTRACT:** Four years of catchment export and wetland input−output mass balances are reported for inorganic Hg ($Hg_{inorg}$), methyl mercury (MeHg), dissolved organic carbon (DOC), and sulfate in eight Swedish boreal wetlands. All wetlands had a history of artificial drainage and seven were subjected to small-scale flooding during the complete study period (two sites) or the two last years (five sites). We used an approach in which specific runoff data determined at hydrological stations situated at a distance from the studied sites were used in the calculation of water and element budgets. All wetlands except one were significant sinks for $Hg_{inorg}$. Seven wetlands were consistent sources of MeHg and one (an *Alnus glutinosa* swamp) was a significant sink. The pattern of MeHg yields was in good agreement with previously determined methylation and demethylation rates in the wetland soils of this study, with a maximum MeHg yield obtained in wetlands with an intermediate soil acidity (pH ∼5.0) and C/N ratio (∼20). We hypothesize that an increased nutrient status from poor to intermediate conditions promotes methylation over demethylation, whereas a further increase in nutrient status and trophy to meso- and eutrophic conditions promotes demethylation over methylation. Small-scale flooding showed no or moderate changes in MeHg yield, maintaining differences among wetlands related to nutrient status.




## INTRODUCTION

Previous reports state that wetlands are environments of net methyl mercury (MeHg) production.[1,2] Large-scale experiments of wetlands[3] and uplands[4] have shown a dramatic increase in net methylation 2−3 years after flooding, followed by a longer period of net demethylation. Thus, there may be a conflict between the current policy of wetland restoration for ecological purposes[5] and an increased production of the neurotoxin MeHg. When hydrologically connected to downstream freshwater ecosystems MeHg produced in wetlands ultimately will end up in fish, which is the main source of MeHg for human intake.[6] Hence, the Swedish national environmental aim of restoring wetlands[7] may further increase today's already critical situation, where approximately half of the Swedish lakes have MeHg levels in fish above the guideline values for consumption.[8]

Freshwater and tidal wetlands have been shown to be sources of MeHg.[9−14] Comparing results from budget studies of MeHg and studies of soil processes in boreal freshwater wetlands may suggest that net MeHg production is linked to acidity and nutrient availability with a maximum net MeHg production observed in wetlands with an intermediate nutrient status, such as "poor fens".[15−17] Because the production of MeHg is primarily linked to the activity of sulfate-reducing bacteria (SRB) in anoxic freshwater environments,[18,19] important controlling factors may include concentrations of total and bioavailable Hg species, as well as the availability of electron acceptors (sulfate), electron donors (low molecular mass organic substances), and pH.[20] Factors in control of demethylation processes in wetlands are less well understood.[21] For inorganic Hg ($Hg_{inorg}$), most studied wetlands have been sinks.[3,9,11,12,22] Dissolved organic carbon (DOC) and reduced sulfur play important roles by affecting the toxicity, speciation, solubility, and mobility of Hg and MeHg.[23,24] Boreal wetlands have generally been reported to be sources of DOC and sinks for sulfate.[3,10]

Here, we report four years of annual $Hg_{inorg}$, MeHg, DOC, and sulfate input−output budgets for eight Swedish, boreal wetlands. In a previous study, potential methylation and demethylation rates determined in the soils of the eight wetland sites were shown to be related to the nutrient status, with maximum net methylation rates and MeHg accumulation observed at an intermediate nutrient status and soil acidity.[15]

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**Table 1. Study Sites Divided into Three Soil Acidity/Nutrient Groups, Their Total Catchment Area, Central Wetland Area (% of Catchment Area), Dominating Vegetation on Wetland, Average Annual Air Temperature Sum (Tsum), pH, and C/N-Ratio in the Central Wetland Soil**

| site | central wetland type | catchment area ($km^2$) | central wetland area ($km^2$) and (%) | dominating vegetation | Tsum[a] (°C) | pH[b] | C/N[b] | group |
|---|---|---|---|---|---|---|---|---|
| SKM | riparian | 0.48 | 0.020 (4.2) | *Carex spp., Sphagnum spp., Polytrichum spp.* | 1950 ± 30 | 4.3 ± 0.1 | 28 ± 1.2 | northern, nutrient poor peatlands |
| SRD | open fen | 1.2 | 0.084 (7.0) | *Carex spp., Sphagnum spp.* | | 4.6 ± 0.1 | 36 ± 4.3 | |
| KSN | dystrophic lake−peatland complex | 1.0 | 0.26 (26) | *Carex spp., Sphagnum spp.* | | 4.8 ± 0.1 | 37 ± 2.4 | |
| LDNA | bog | 0.91 | 0.078 (8.6) | *Calluna vulgaris, Carex spp., Sphagnum spp.* | 2595 ± 70 | 4.6 ± 0.3 | 34 ± 2.4 | peatland nutrient gradient |
| LDNB | fen | 1.1 | 0.028 (2.5) | *Scirpus spp., Carex spp., Sphagnum spp.*, broad-leaved grasses | | 5.1 ± 0.2 | 21 ± 1.8 | |
| GTN | mesotrophic lake−peatland complex | 23 | 0.58 (2.5) | *Phragmites australis, Thypa latifolia, Sphagnum spp.* | 2720 ± 70 | 5.6 ± 0.1 | 19 ± 2.8 | southern, nutrient rich wetlands |
| GDL | artificial wetland | 0.37 | 0.031 (8.4) | *Scirpus spp., Sphagnum spp.* | 2600 ± 30 | 5.8 ± 0.2 | 21 ± 1.5 | |
| EHT | *Alnus* swamp | 0.58 | 0.042 (7.2) | *Scirpus sylvaticus*, N-demanding herbs | 2360 ± 50 | 5.7 ± 0.2 | 14 ± 0.29 | |

[a]Mean annual temperature sum ± SE for 2007−2010, calculated as sum of mean daily air temperature exceeding 5 °C. [b]Soil pore water pH ± SE and soil C/N-ratios ± SE, as reported in Tjerngren et al.[15]

Seven of the wetlands were subjected to small-scale flooding during the study period. We calculated input−output mass balances at the catchment scale by combining chemical data from input and output streams with data on specific runoff obtained either from hydrological stations at nearby catchments or generated from model simulations. The approach was chosen to follow many sites during several years. The main objectives of the study were to determine whether the wetlands were sources or sinks for $Hg_{inorg}$, MeHg, DOC, and sulfate, if the wetland's status as a source/sink changed after small-scale flooding, and if the net MeHg production and export can be linked to soil acidity/nutrient status of the wetland.

## EXPERIMENTAL SECTION

**Site Description.** Seven sites, comprising eight boreal wetlands situated in Sweden, were studied during four complete years: 2007−2010 (Table 1). The wetlands were divided into three groups based on the combination of soil acidity (pH), nutrient status (C/N ratio), climate (air temperature sum), and type of vegetation, as described in more detail elsewhere.[15] In brief, at the three northern sites, Storkälsmyran (SKM), Sjöarödd (SRD), and Kroksjön (KSN), highly acidic (soil pore water pH 4.3−4.8) nutrient poor (soil C/N-ratio 28−37) peat forming wetlands with dystrophic surface waters are developed on gnessic bedrock. The three southern sites, Gästern (GTN), Grundsdal (GDL), and Edshult (EHT), represent relatively nutrient rich (meso-/eutrophic) wetlands, as reflected by pH-values and C/N-ratios in the range 5.6−5.8 and 14−21, respectively. The intermediate group: site Långedalen (LDN) comprises a nutrient gradient, with an upstream, partly drained nutrient-poor ombrotrophic bog (LDNA) having a pH (4.6) and C/N-ratio (34) similar to the northern sites, and a downstream located fen (LDNB) with intermediate acidity and nutrient status (pH 5.1, C/N-ratio 21). All three sites in the southern group had significantly higher pH and lower C/N ratio in the central wetland soil than all sites in the northern group ($p < 0.02$, ANOVA followed by Turkey's multiple comparison test, or their nonparametric analogs). The only exception was SKM, where the C/N ratio of 28 was not significantly different from that of site GDL (C/N = 21). At LDNA, pH was significantly lower and the C/N ratio significantly higher than at all sites in the southern group ($p < 0.005$). At LDNB, pH was significantly higher than that of SKM ($p < 0.01$) and the C/N ratio was significantly lower than those of SRD, KSN, and LDNA ($p < 0.01$). Maps of the central wetlands and their catchments, including data on land use composition, are reported in Figures S1−S13 and Tables S2−S14 (Supporting Information (SI)).

The wetlands all had a history of artificial drainage and were part of restoration projects performed by the land owners. Except at site EHT, the wetland/lake water surface or groundwater level was raised 0.4−1.0 m by artificial damming of the outlet. At site LDN, coniferous trees established after the last drainage was selectively harvested. Although these measures may not restore the wetlands to their former "natural" state, it is a way of using small means to "assist the recovery of an ecosystem that has been degraded, damaged, or destroyed", according to the definition by the Society of Ecological Restoration.[25] Page S3 in the Supporting Information provides a more detailed description of the small-scale flooding at each site.

**Stream Water Sampling and Chemical Analyses.** A detailed description of sampling, sample preparation, and chemical analyses is reported on pages S3−S4 (SI) and elsewhere.[15] Briefly, streamwater from the main in- and outlets of the central wetlands was regularly sampled (in total 29−34 occasions at each site) during 2007−2010, with a focus on the period between spring snowmelt (March−April) and late autumn. Sampling was done at regular intervals but with a bias toward high flow conditions. Subsamples were analyzed for total Hg,[26] MeHg,[27,28] dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC), specific UV-absorbance at 254 nm ($SUVA_{254}$), major anions (Cl, $SO_4^{2-}$), and metal cations (Na, Ca, Mg, Al, Fe). The concentration of inorganic mercury(II), henceforth denoted $Hg_{inorg}$, was calculated as total Hg subtracted by MeHg.

**Atmospheric Deposition and Shallow Groundwater Chemistry.** At each site, data on monthly measurements of Cl and sulfate concentrations in precipitation on open field and in throughfall were taken from the closest situated station of the


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Crown Drip Measurement Network, Swedish Environmental Research Institute (IVL, Göteborg, Sweden). Data for total Hg concentrations on open field was estimated for each site using an average from monthly measurements during 2007−2010 at stations in southern and northern Sweden (IVL, Stockholm, Sweden). Snow samples were collected in acid-washed 1-L FEP-Teflon bottles at the northern sites in February 2010, and at sites LDN and EHT in November 2010. Two sets of shallow groundwater samples ($n$ = 8) were collected in acid-washed Teflon bottles at 40−70 cm depth in four representative soil pits at the northern Swedish sites during low flow conditions in June and high flow conditions in September 2010. All samples were analyzed for pH, total Hg and MeHg, Cl, and sulfate. Groundwater samples were also analyzed for DOC. Data on concentrations of elements/compounds in deposition and groundwater used in the calculations are reported for each site in Tables S2−S14 (SI).

**Water Runoff Data.** For each site, data on daily precipitation and air temperature were taken from the closest situated meteorological station run by the Swedish Meteorological and Hydrological Institute (SMHI, Sweden), and two sets of specific runoff data ($q$ = m$^3$/s/km$^2$) were used in budget calculations: (1) $q$ measured at nearby catchments having hydrological runoff stations included in the SMHI network, and (2) $q$ calculated for nearby catchments using the hydrological catchment model Swedish Hydrological Predictions for the Environment (S-HYPE).[29] The S-HYPE model calculates a mean daily $q$ for a certain type and size of catchment, with main input data including sub-basin areas, land use, soil type, precipitation, air temperature, and elevation. One underlying assumption using this approach is that the studied catchment as a whole has a specific runoff similar to the catchments used to generate the specific runoff. Uncertainties with this approach are discussed on pages S28−S29 (SI). Data on measured or calculated specific runoff from selected hydrological stations and catchments are plotted in Figures S2−S14 (SI). Data on catchment land use, catchment size, and distance to the study site are reported in Tables S2−S14 (SI). At site GTN actual runoff was recorded by a Campbell CR10X data logger at the outlet during 2007−2009, as provided by the Swedish Nuclear Fuel and Waste Management Co (SKB, Stockholm, Sweden).[30] Data were averaged to give a mean daily runoff.

**Water Budgets.** The catchment area delineation at each site was determined using GSD (Geografiska Sverigedata) elevation data from Lantmäteriet (Gävle, Sweden), using the software ESRI ArcGIS (Redlands, CA, USA), having an area resolution of 50 × 50 m (pixel size) and an elevation resolution of 5 m per 100 m, combined with field observations during high flow conditions. Equation 1 was used to calculate inputs of water volume to the central wetland

$$V_{ti}(\mathrm{m}^3) = \sum_{t_i-(t_{i-1})/2}^{(t_{i+1})-t_i/2} q \times A \times 86400 \quad (1)$$

where $V_{ti}$ (m$^3$) is the water volume integrated for the time period (in days) centered at the sampling occasion $i$ ($t_i$), $q$ is the specific runoff (m$^3$/s/km$^2$), $A$ is the area (km$^2$) for which $q$ is assumed rrepresentative, and 86400 the number of seconds in a one day. The integrated time periods (in general 20−40 days) were summarized to give calendar year water inputs to the central wetland of each site ($\Sigma V_{Input}$). Water inputs to the central wetland from inlet streams, direct soil runoff, and at sites SRD, KSN, and GDL contribution from shallow groundwater, are presented in Tables S1−S13 (SI) for each site.

The central wetland objects were considered part of the catchment for which the applied specific runoff was assumed representative and therefore precipitation onto and evaporation from the central wetland sites were not determined. However, for wetlands with open water (sites KSN, GTN, and GDL) precipitation onto and evaporation from the area with open water was determined separately and included in the budget calculations. Evaporation was estimated by a modified Penman equation using monthly average air temperature, latitude, altitude, and wind speed as input parameters.[31] Calculation of the evaporation from open water at site KSN, year 2007, is reported in Table S21 (SI). Snow accumulated during winter (December−March) on the KSN lake was included as a separate water input during the period of snowmelt. The southern sites with open water (GTN and GDL) did not accumulate any snow during winter. The output from the central wetland was calculated as $V_{Output} = \Sigma V_{Input}$ at SKM, SRD, LDN, and EHT, whereas at sites with open water (KSN, GTN, and GDL), the output from the central wetlands was calculated as $V_{Output} = \Sigma V_{Input}$ − evaporation. Artificial flooding had a limited effect on water budgets, both in terms of water volumes and lag time effects. Damming of the outlet of a wetland resulted in a delay in runoff which was calculated as the time required filling the additional volume of water in the reservoir. During this time period no water export was allowed.

**Catchment Exports and Wetland Yields.** Masses of catchment export (output), as well as input to and output from the central wetlands were calculated for $Hg_{inorg}$, MeHg, DOC, sulfate, and Cl using eq 2

$$Mass_{\text{Input or Output}} = C_{ti} \times V_{ti} \quad (2)$$

where $C_{ti}$ is the mass per liter of $Hg_{inorg}$, MeHg, DOC, and sulfate determined in input and output streams at sampling occasion $t_i$, and $V_{ti}$ is the volume of water integrated for the time period centered at the sampling occasion, as determined by eq 1. Stream inlet concentrations were also used to calculate masses of direct soil runoff to the central wetlands, assuming properties for these soils similar to those for the soils drained by the stream. Annual masses of input and output were calculated by a summation of all sampling occasions during a calendar year. Dry and wet atmospheric deposition of $Hg_{inorg}$, sulfate, and Cl onto the central wetlands were included as input, whereas atmospheric deposition of MeHg[32] and DOC onto the central wetland were considered small enough to have negligible effect on the overall budgets. In our budget calculations we used 7 and 10 ng/L as the concentration of $Hg_{inorg}$ in wet deposition at the northern and southern sites, respectively. Dry deposition is notoriously difficult to determine.[33,34] It was accounted for by multiplying concentrations of $Hg_{inorg}$ in wet deposition by a factor 2.0 at SKM (where the central wetland was covered by Norway spruce) and a factor of 1.4 at site ETH (the Alder swamp, dominated by deciduous trees), based on deposition rates onto different types of forest canopies.[34] The uncertainty in atmospheric deposition of $Hg_{inorg}$ was evaluated by a sensitivity analyses in which the concentration of $Hg_{inorg}$ (which was multiplied by the total volume of precipitation to yield the atmospheric input) was varied (Table S19, SI). Contribution from shallow groundwater was included in the budgets at sites SRD, KSN, and GDL, as indirectly determined by the Cl input−output budget (as

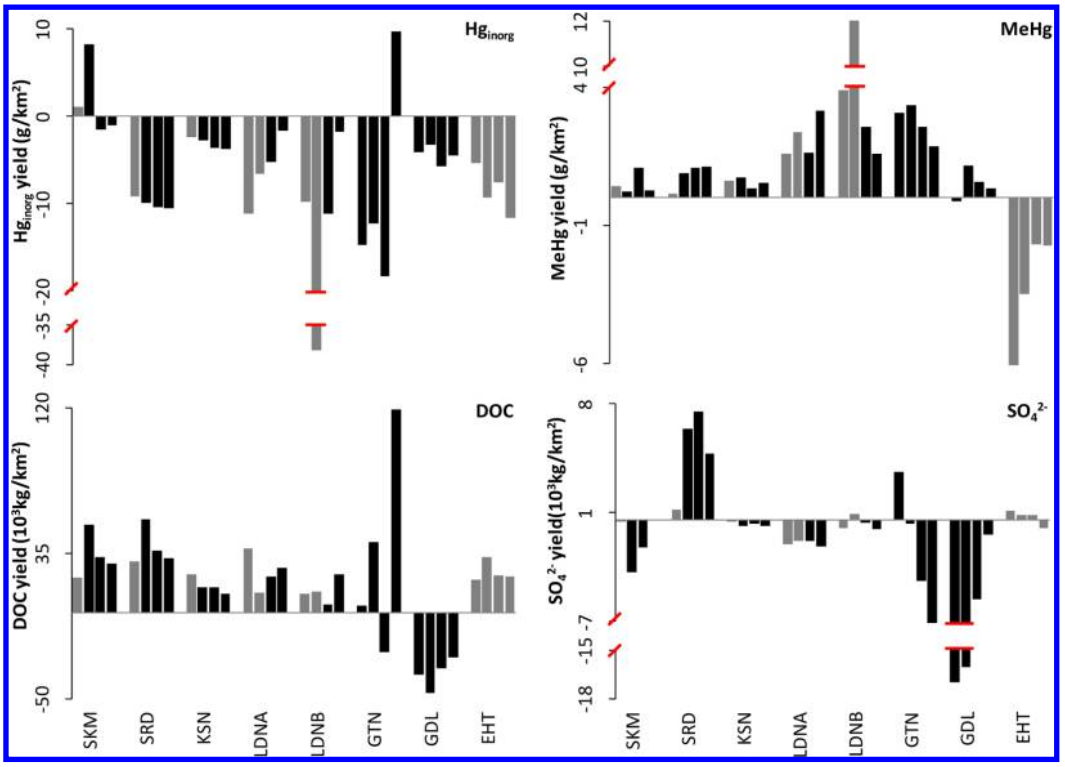


**Figure 1.** Annual wetland yields 2007–2010 of $Hg_{inorg}$, MeHg, DOC and sulfate before (gray bar) and after restoration measures (black bar). Site order follows largely a decrease in acidity and an increase in nutrient status from left to right (Table 1). Positive values indicate a source, and negative values indicate a sink.

described on page S4, SI).[35] The central wetland mass yield of a certain element was calculated by eq 3.

$$Yield = Output - \sum Input \quad (3)$$

A positive yield indicates that the wetland is a net source. Yields as percentage of input were calculated using eq 4.

$$\%Yield = 100 \times \frac{Output - \sum Input}{\sum Input} \quad (4)$$

To account for differences in area, masses of catchment exports and wetland yields were divided by the total catchment area and central wetland area, respectively, and are reported as g/km$^2$.

**Budget Uncertainties.** Because the central wetland areas were small in relation to the total catchment area (range 3–9% for all sites except KSN, Table 1), the difference in water flux in and out from the central wetland was small. As a consequence, the calculated wetland yield is mainly controlled by differences in concentrations of element/compound in the inlet and outlet streams (Figure S15, Table S16, SI), and the main source of uncertainty in the budgets is likely due to the limited intensity of streamwater sampling. As reported in the Supporting Information (pages S27–S28), the limited sampling intensity may give rise to an uncertainty of ±10–30% of % MeHg wetland yields. Estimates of errors, sensitivity analyses, and further discussion of uncertainties associated with specific runoff data, chemical analyses, atmospheric deposition data, shallow groundwater contribution, and delineation of catchment and subcatchment boundaries are reported in the Supporting Information.

## RESULTS AND DISCUSSION

**Catchment Exports.** Annual $Hg_{inorg}$ and MeHg exports from the catchments in this study (0.51–6.1 g/km$^2$ and 40–647 mg/km$^2$, respectively) are in range of results reported for northern forested catchments with wetlands (0.17–34 and 0.007–6.8 g/km$^2$ for $Hg_{inorg}$ and MeHg, respectively).[1,9,12,22,36] Catchment exports for individual sites and years are reported in Table S18 (SI).

**Wetland Yields.** Because of different proportions, relative positions, and connectivity of wetlands, upland soils, and streams, results of whole catchment exports are difficult to evaluate and compare. To isolate the effect of the central wetland object, mass balance budgets were therefore used to calculate wetland yields by subtracting all inputs from the output and normalizing to the wetland area. Both absolute yields (g/km$^2$) and yields in percent of input are reported. The former measure is sensitive to variations in absolute water flux, giving different yields wet and dry years, while the latter is sensitive to the landscape element composition (upland or wetland) determining the input to the wetland. Wetland yields are reported for individual sites and years in Table S17 (SI).

**$Hg_{inorg}$ Yields.** Seven of the wetlands were regular net $Hg_{inorg}$ sinks (retention of 1.5–18 g/km$^2$, Figure 1), with the exception that site GTN turned into a source 2010 (discussed below). The riparian wetland SKM appeared to be neither a sink or source (±10% yield). The $Hg_{inorg}$ wetland yield covered generally a range of −10 to −40% of the input. Because of the small percentage area contribution from the central wetlands to the whole catchment, the uncertainty associated with dry and wet $Hg_{inorg}$ atmospheric deposition onto the central wetland had a relatively small effect on the results. A change of ±40% in total deposition (corresponding to a change in precipitation


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**Table 2. Wetland MeHg Yields (And Percent Yield of Input) Reported from Boreal Freshwater Wetlands in Which Input and Output Has Been Determined at Least One Complete Calendar Year (Annual Budgets) and All Output Is Generated in the Wetland**

| wetland | %wetland area of catchment | MeHg yield g/km$^2$ | %MeHg yield (of input) | ref | wetland | %wetland area of catchment | MeHg yield g/km$^2$ | %MeHg yield (of input) | ref |
|---|---|---|---|---|---|---|---|---|---|
| SKM riparian | 4.2 | 0.21−1.1 | 6−50 | this study | valley-bottom 2 ELA | 14 | 0.13−0.49 | 192−447 | 13 |
| SRD open fen | 7.0 | 0.12−0.80 | 41−225 | this study | basin ELA | 11 | 0.58−2.0 | 242−614 | 13 |
| KSN dystrophic lake-peatland | 26 | 0.33−0.74 | 78−280 | this study | riverine ELA | 2.0 | 0.18−0.22 | 13−64 | 13 |
| LDNA bog | 8.6 | 1.6−3.1 | 113−564 | this study | riverine artificially flooded ELA | 2.0 | 1.4−7.0 | 200−630 | 3 |
| LDNB fen | 2.5 | 1.6−12.2 | 14−89 | this study | beaver meadow Adirondack | 1.5 | 3.2 | 623 | 15 |
| LDN bog-fen gradient | 9.6 | 1.9−4.9 | 198−676 | this study | riparian Adirondack | 0.4 | 0.13 | 8 | 15 |
| GTN mesotrophic lake-peatland | 2.5 | 1.9−3.3 | 39−134 | this study | beaver pond Adirondack | 18 | 0.45 | 18 | 20 |
| GDL artificial wetland | 8.4 | −0.11−1.2 | −10−84 | this study | | | | | |
| EHT *Alnus* swamp | 7.2 | −6.2 − −1.7 | −58− −29 | this study | | | | | |

[a]Data for the wetlands of this study cover all four years (2007−2010), i.e., including periods before and after small-scale flooding.

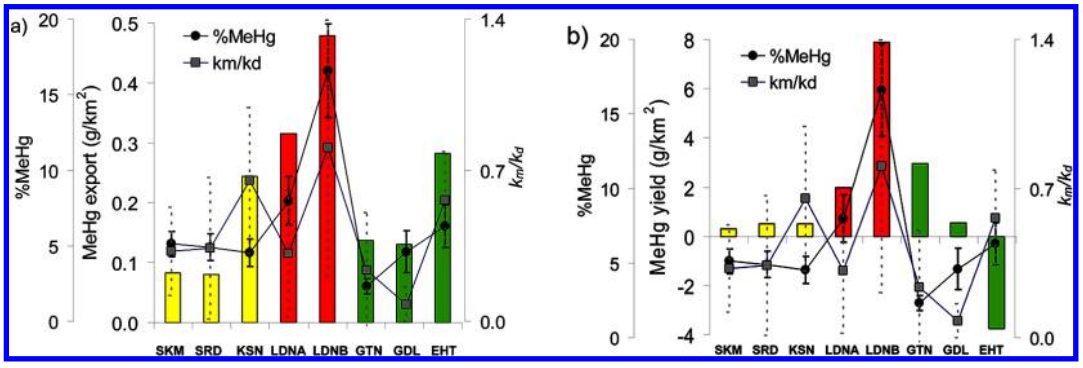


**Figure 2.** Catchment exports and wetland yields of MeHg (bars, g/km$^2$), compared to soil proxies for long-term (%MeHg of total Hg in soil, black circles) and short-term ($k_m/k_d$, white squares) net MeHg production. Bars represent average of years prior to small-scale flooding (SKM, SRD, KSN, LDNA, LDNB) or the period 2007−2009 (EHT, GTN, GDL). Soil data are from 2007 to 2009, reported in ref 15. Error bars represent ± SE for incubated soil samples. The sites from left to right follow the order: the three northern, nutrient poor sites (yellow bars), the bog-fen nutrient gradient (red bars), and southern nutrient rich sites (green bars).

concentration from 7 to 10 or from 10 to 14 ng/L) resulted in 3−9% change in $\%Hg_{inorg}$ yield for all wetlands except KSN, where a larger area contribution from the central wetland (26% of the catchment) resulted in a change of 8−12% (Table S19, SI).

In most previous studies, wetlands have been reported to be sinks for total Hg. In the Experimental Lakes Area (ELA), Ontario, the range of total Hg retention in four boreal forest catchments of 1.9−3.7 g/km$^2$ corresponds to a retention of 13.2−22.1 g/km$^2$ if recalculated to wetland areas only.[9] In Wisconsin, a groundwater-fed wetland was reported to be a small sink of total Hg corresponding to 0.8 g/km$^2$.[12] In contrast, a beaver meadow and a riparian wetland in Adirondack, New York, were major sources of total Hg, with annual yields of 77 and 28 g/km$^2$ wetland, respectively, corresponding to 211 and 6% of the input.[10]

**MeHg Yields.** With one exception (*Alnus* swamp, EHT), the wetlands in this study were net MeHg sources (Figure 1, Table 2). Notably, the variability in wetland yields among sites was larger for MeHg than for $Hg_{inorg}$. The site with intermediate pH and C/N ratio (LDN) was the largest MeHg source among the wetlands both in relative (198−676% yield of input) and absolute terms (1.9−4.9 g/km$^2$ wetland). The downstream fen part (LDNB) showed higher yield than the upstream bog part (LDNA) (1.6−12.2 and 1.6−3.1 g/km$^2$, respectively). Because of lower concentrations of MeHg in the input from the surrounding uplands, the percent yield was higher in LDNA (113−564%) than in LDNB (14−89%). The wetland yield at LDN is similar in magnitude to the largest MeHg source ("basin wetland", 0.6−2 g/km$^2$ and 242−614% wetland yield) reported from ELA, Canada[9] and the "beaver meadow" (3 g/km$^2$) in Adirondack, U.S.[10] (Table 2). At these three sites, the wetlands receive runoff mainly from uplands.

The three northern sites (SKM, SRD and KSN) were the most acidic and nutrient poor sites and had the lowest absolute MeHg yields (0.12−1.1 g/km$^2$). The yield from these three sites compares with the "valley-bottom2" and "riverine wetland" at ELA (0.13−0.49 g/km$^2$)[9], the "riparian" (0.13 g/km$^2$)[10], and the "beaver pond" at the Adirondack (0.45 g/km$^2$).[11] All these wetlands receive a mixed input from uplands and wetlands (and lake input to the "riverine wetland"). In particular riparian type of wetlands seems to be sites with relatively small MeHg yields.The two nutrient rich sites GTN and GDL showed slightly different trends over the study period, with absolute

yields in the range −0.11 to 3.3 g/km$^2$ (correspond ing to −10 to 134% yield of input). Differences between these two sites were likely affected by environmental conditions prior to restoration (GTN a mesotrophic, drained lake and GDL a clayey soil on former grassland), and consequences of the substantial flooding (see discussion below).

In contrast to the other sites, the *Alnus* swamp EHT was a net MeHg sink of 1.7−6.2 g/km$^2$. This is on the same order of magnitude as the greatest MeHg sources of our study. Figure S15 illustrates that MeHg concentrations were very high in inlet streams during summer, reflecting methylation in the upstream located bog. Processes responsible for the Alder swamp to be a sink are reported in a forthcoming related paper (Kronberg et al., in preparation). On a relative scale, 29−58% of the MeHg inputs were lost in the swamp. The total mass of MeHg degraded in the *Alnus* swamp (0.071−0.26 g/year) provides a significant sink at the landscape level.

**MeHg Budget Results and Wetland Nutrient Status.** A comparison of MeHg yields among wetlands in this study show a clear pattern with soil acidity and nutrient status. The highest catchment exports and wetland yields are reported for wetlands with intermediate pH and C/N ratio; i.e. the bog-fen site LDNA and LDNB. Also, the flooded, mesotrophic lake (GTN) showed high MeHg yields, similar to LDNA. Furthermore, similar patterns were observed for MeHg budgets (catchment exports and wetland yields) and proxies for net MeHg production determined in the wetland soils in this study[15] (Figure 2). The %MeHg of total Hg in soil may be used as a proxy for long-term net MeHg production,[37] and the quotient between potential Hg methylation and MeHg demethylation rate constants, $k_m$ and $k_d$, may be used as proxy for short-term net MeHg production, as these two parameters are determined during 48 h of laboratory incubations using isotopically enriched tracers.

Averages of whole catchment exports and wetland yields of MeHg were significantly, positively correlated with the average %MeHg of total Hg in wetland soil (Pearson correlations, $R$ = 0.83 and 0.86 for exports and yields, respectively, $p < 0.05$). Similarly, MeHg catchment exports and wetland yields followed the same pattern as the ratio of the potential methylation and demethylation rate constants ($k_m/k_d$) (Figure 2), even if the correlations were less significant (Pearson correlations, $R$ = 0.70, $p$ = 0.05 for MeHg exports, and $R$ = 0.51, $p$ = 0.19 for MeHg yields). The positive relationships between MeHg catchment exports, wetland yields, and soil proxies for net MeHg production rates in soil illustrate a link between wetland soil processes and streamwater exports. Furthermore, the link reported between acidity/nutrient status and net MeHg production in the wetland soils also seems to be relevant on a larger scale as reflected by a similar relationship with MeHg input−output budget results. Thus, results from process-oriented studies on the wetland soils and from larger-scale time and space integrated budgets point at boreal wetlands of intermediate acidity and nutrient status (pH ∼5 and C/N ratio ∼20) as sites with the highest net MeHg production. This observation is in line with interpretations of previous studies, suggesting that high net MeHg productions are promoted in "poor fen" types of wetlands.[16,17] The most extensive studies on MeHg net production in relation to nutrient status have been conducted in the subtropic wetlands of Florida Everglades, where %MeHg, $k_m$ and $k_d$ decreased from the pristine southern peatlands to the northern, highly eutrophic agricultural influenced sediments.[38,39] Despite major differences in vegetation and other environmental conditions, the pattern observed in the Everglades seemingly mirrors the decrease in % MeHg in the nutrient rich end of the boreal wetlands in this study. Also the fact that the five southern sites in this study are exposed to higher air temperatures (Table 1) than the three northern sites may play a role. A number of studies report an increased MeHg production with temperature.[20]

Molybdate inhibition experiments showed that sulfate-reducing bacteria were responsible for most of the mercury methylation in the wetland soils of this study.[15] If site SRD (which was undergoing several cycles of drainage−flooding) is disregarded, concentrations of the electron acceptor sulfate were highest at the three southern, nutrient rich sites (13−17 $\mu$M in pore water, 45−134 $\mu$M in wetland outlets), intermediate at sites LDNA and LDNB (6.8−7.5 $\mu$M and 23 $\mu$M), and lowest at the northern sites SKM and KSN (5.6−6.2 $\mu$M in pore water and 6.9−10 $\mu$M in stream outlets).[15] Thus, the concentration of the major electron acceptor for methylating bacteria showed a similar pattern among the three groups of wetlands as did acidity/nutrient status. Concentrations of iron varied less, but showed a pattern somewhat similar to sulfate,[15] whereas concentrations of nitrate were only significant at site EHT (4.1 $\mu$M, and less than 0.7 $\mu$M at the other sites). $SUVA_{254\ nm}$, a proxy for organic matter quality (and indirectly electron donor availability to bacteria), showed an inverse relationship with pH in the wetland outlet stream.[15] Thus, the availability of electron donors and acceptors for methylating and demethylating bacteria may play a role behind the link between acidity/nutrient status and net MeHg production and yield, by affecting the balance between production and degradation of MeHg, but the interrelations are clearly not simple.

Net production and export of MeHg is controlled by the balance among input, output, methylation, and demethylation reactions. Based on budget results from the eight wetlands (this study), and from incubation studies of the wetlands soils,[15] we hypothesize that an increase in nutrient status/trophy from low (dystrophic) to intermediate levels favors methylation over demethylation reactions, whereas a further increase in nutrient status/trophy to meso-/eutrophic levels primarily promotes demethylation reactions (Figure 3). In agreement with observations in mercury contaminated sediments,[43] we suggest that the increase in methylation rates with increasing nutrient

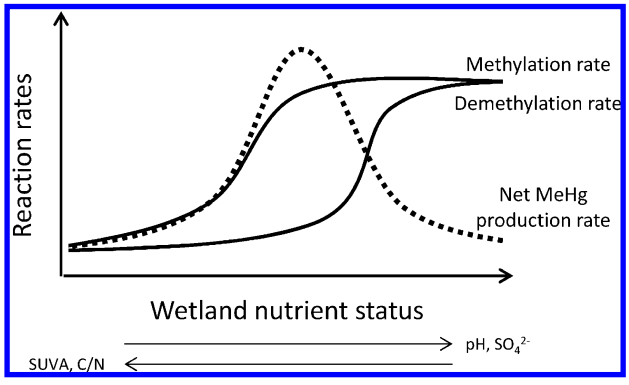


**Figure 3.** Hypothesized, conceptual model relating methylation and demethylation rates to nutrient status/trophy, as reflected by soil acidity (pH) and C/N ratio. Changes in availability of electron donors (SUVA) and acceptors (sulfate) may also contribute to the hypothesized shape of the net MeHg formation curve.

status is mainly driven by an increasing availability of organic electron donors (as reflected by increasing C/N ratio and decreasing SUVA). At a certain level of electron donor availability, other factors, e.g. electron acceptors, micronutrients, or the availability of Hg for microbial uptake, may limit the methylation process. In contrast, MeHg serves as an electron donor in the oxidative demethylation process, which is widespread among different types of bacteria as the predominant biotic MeHg degradation process in low contaminated environments.[21] Thus, it may be that MeHg degradation relates to bacterial activity in general, which in turn may be positively related to nutrient status also in wetlands with higher trophic levels. Abiotic demethylation processes should also be taken into consideration, and here differences in quality of DOC (including concentrations and types of chromphoric groups) in open waters of dystrophic, mesotrophic, and eutrophic wetlands may give rise to different conditions for photolysis of MeHg.

**Consequences of Flooding.** The southern sites GTN and GDL were subjected to flooding already from the beginning of the study, by raising the water table at the wetland outlet by approximately 1 m. This means that a pretreatment period is lacking and an analysis of the consequences is limited to the time trend during 2007−2010. The mesotrophic lake-peatland GTN was a net MeHg source (both in absolute and relative numbers) of a similar magnitude in years 1−2, followed by a decreased yield in years 3−4 (Figure 1). A roughly similar pattern was reported from large-scale experiments at ELA, Ontario, after flooding a riverine wetland,[3] as well as uplands.[4] Thus, although we lack a pretreatment year at site GTN, the pattern suggests that the increased water table of in average 1 m of the formerly drained mesotrophic lake resulted in a peak of increased methylation of Hg in years 1−2. At the artificial wetland GDL, the peak was observed year 2, after a small net degradation/retention of MeHg year 1 (Figure 2). It has been shown that both quantity and quality of soil organic matter control MeHg net production during flooding.[3,4] The MeHg yield of 3.3 g/km$^2$ year 1 and 2 at the mesotrophic site GTN, and 1.2 g/km$^2$ year 2 at the artificial wetland GDL, can be compared with an increase from 0.2 g/km$^2$ to 7.0 g/km$^2$ year one, and 5.4 g/km$^2$ two years after flooding a riverine wetland at ELA.[3] The relatively small production of MeHg and slow response at site GDL may be explained by the relatively nonproductive starting conditions, where a clayey soil with a low content of soil organic matter was flooded.

The substantial flooding at GTN and GDL resulted in a deviating pattern of the DOC budgets. While all other sites were quite steady sources of DOC all years, the net release increased dramatically in year 2 and 4 in the mesotrophic lake GTN, with year 3 serving as a sink (Figure 1). The artificial wetland GDL was a substantial sink for DOC all years. It is likely that the restoration measures created instability in the balance among import, internal production, and degradation of organic matter. At the artificial wetland GDL, the organic matter content in the soil prior to flooding was low and internal production obviously was not large enough to compensate for the increased DOC photodegradation in the artificially created open water body.[40] At site GTN the storage of organic matter in the several meter deep peat was large and cycles of accumulation and degradation of peat likely occurred. The extreme DOC yield of 120 × 10$^3$ kg/km$^2$ in 2010 (Table S17, SI) explains why GTN turned into an $Hg_{inorg}$ source that year (Figure 1). This DOC yield can be compared with an increase in DOC yield from 9.2−13.2 × 10$^3$ kg/km$^2$ prior to, and 29−34 × 10$^3$ kg/km$^2$ 1−3 years after flooding the riverine wetland at ELA. Similarly to what happened at site GTN, the release of DOC turned the wetland into a source of $Hg_{inorg}$ year 1 and 2 after restoration, until the DOC yield decreased.[3] Likely for the same reasons as for DOC, sulfate budgets were also less stable at GTN and GDL (Figure 1). Starting as a source in 2007, sulfate was increasingly retained at the mesotrophic site GTN 2008−2010, whereas an opposite trend with less retention over time was observed at the artificial wetland GDL. The instable character of site GDL was also reflected by the Cl budget, which was not in balance the first two years (Table S17, SI). We suggest previously accumulated Cl was washed out from the clayey soil.

The northern open fen (SRD) was subjected to 6-month intervals of drainage/damming cycles. The amplitude between minimum and maximum water tables was approximately 1 m. As a direct consequence of these measures, sulfate was exported from the wetland (Figure 1). The sulfate yield increased from 0.5 × 10$^3$ kg/km$^2$ in year 2007, to 3.2−5.2 × 10$^3$ kg/km$^2$ the last three years, presumably caused by oxidation of reduced sulfur stored in the peat. Whatever effect damming may have had on restoring the sulfate-reducing conditions, it was obviously counteracted by the oxidation effects during subsequent drainage. Parallel to sulfate, site SRD showed a substantial increase as a source for MeHg from 0.1 g/km$^2$ during the pretreatment year 2007, to 0.6−0.8 g/km$^2$ in 2008−2010 (Figure 1). It has been argued that dynamic redox cycles at which sulfate is transformed to sulfide, and vice versa, is beneficial for the activity of SRB, by providing a continuous source of sulfate as electron acceptor.[41]

In the remaining four wetlands (SKM, KSN, LDNA and LDNB), which all were subjected to small-scale flooding by raising the water table or groundwater table by less than 0.5 m at the outlet, the effect on MeHg yields was generally small and difficult to separate from interannual variability (Figure 1). At site LDN two wet years were followed by two much dryer years (Table S15, SI), making an evaluation of the effect of the small-scale flooding difficult. Overall, we attribute the small effects to the fact that the flooded area was not large enough to significantly affect previously nonflooded upland soils. Rather it reestablished the formerly drained basins. It is well-known that more easily degradable organic matter in well-drained upland surface soils give rise to higher MeHg net production after inundation, than more recalcitrant organic matter in peat.[3,4] Furthermore, in the dystrophic lake−wetland complex KSN, possible increases in MeHg production in flooded soils were likely counteracted by photodegradation of MeHg by the action of UV light in the increased volume of open clear water.[42] The lack of flooding effect in the riparian wetland SKM may be a consequence of the low pH and nutrient conditions, as demonstrated by low methylation rates and %MeHg determined in the soil.[15] At the bog−fen site LDN, two small flooded areas of about 0.5 ha each were created in May 2009, one in the bog and one in the fen part.

**Environmental Implications.** Based on input−output budgets for MeHg reported in this paper, previously reported rates on potential methylation and demethylation rates, and %MeHg determined in the wetland soils,[15] we conclude that the net MeHg production and export varies among different types of boreal wetlands. Factors such as bedrock mineralogy, climate, and hydrology, which in turn are in control of soil acidity, nutrient status, and type of vegetation, seem to be

important for the balance between methylation and demethylation processes. Our results suggest that a decrease in acidity, and increase in nutrient status from very poor to intermediate conditions, results in an increased net production of MeHg. On the other hand, a further increase in nutrient status, to meso- and eutrophic levels, tends to promote demethylation over methylation processes.

Previous large-scale manipulations of hydrology by artificial flooding of well-drained soils and wetlands have been shown to dramatically promote net methylation.[3,4] In this study, wetlands undergoing substantial flooding (GTN and GDL) or drainage/flooding cycles (SRD) either showed time patterns or clear absolute effects of increased net MeHg production 1−3 years after treatment. In contrast, small-scale flooding (on the level that is commonly adopted by forest companies in Sweden) used to restore previous water levels (prior to historical drainage) at five wetlands with low to intermediate nutrient status showed no or small effects. It can be concluded that factors in control of differences in MeHg yields among the different types of wetlands (presumably linked to nutrient conditions) were more important than the effect of small-scale flooding. In wetlands where the area of open water is increased by flooding, photodegradation of MeHg may become more important, and restoration measures may in fact result in a decreased net MeHg production. The finding that the *Alnus* swamp was a net MeHg sink on the same order of magnitude as the largest MeHg sources in this study is very important and warrants further research. If it can be shown that *Alnus* swamps in general are sinks for MeHg, restoration of formerly drained *Alnus* swamps can actively be used to mitigate the effect of net MeHg production in upstream located wetlands.

## ■ ASSOCIATED CONTENT

### Supporting Information

Maps and more detailed information on description of sites, small-scale flooding, sampling, chemical analyses, and discussion about assumptions and uncertainties in the mass balance calculation method. Tables and figures on annual water and element/compound budgets, hydrographs, sampling occasions, catchment size, land use, hydrological and meteorological data, annual average concentrations of $Hg_{inorg}$, MeHg, DOC, sulfate, and Cl in outlet stream waters, concentrations of MeHg in inlet and outlet streams, annual wetland yield and catchment export data, sensitivity analyses associated with $Hg_{inorg}$ deposition. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) St. Louis, V. L.; Rudd, J. W. M.; Kelly, C. A.; Beaty, K. G.; Bloom, N. S.; Flett, R. J. Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. *Can. J. Fish. Aquat. Sci.* **1994**, *51* (5), 1065−1076.

(2) Galloway, M. E.; Branfireun, B. A. Mercury dynamics of a temperate forested wetland. *Sci. Total Environ.* **2004**, *325* (1−3), 239−254.

(3) St. Louis, V. L.; Rudd, J. W. M.; Kelly, C. A.; Bodaly, R. A.; Paterson, M. J.; Beaty, K. G.; Hesslein, R. H.; Heyes, A.; Majewski, A. R. The rise and fall of mercury methylation in an experimental reservoir. *Environ. Sci. Technol.* **2004**, *38* (5), 1348−1358.

(4) Hall, B. D.; St Louis, V. L.; Rolfhus, K. R.; Bodaly, R. A.; Beaty, K. G.; Paterson, M. J.; Cherewyk, K. A. Impacts of reservoir creation on the biogeochemical cycling of methyl mercury and total mercury in Boreal Upland Forests. *Ecosystems* **2005**, *8* (3), 248−266.

(5) Zedler, J. B.; Kercher, S. Wetland resources: Status, trends, ecosystem services, and restorability. *Ann. Rev. Environ. Resour.* **2005**, *30*, 39−74.

(6) Selin, N. E. Global Biogeochemical Cycling of Mercury: A Review. *Ann. Rev. Environ. Res.* **2009**, *34*, 43−63.

(7) Swedish Environmental Protection Agency). *National Strategy for Thriving Wetlands [Online]*; 2005. Available from www.naturvardsverket.se/Documents/publikationer/620-1254-1.pdf. [Sept. 20, 2011].

(8) Lindqvist, O.; Johansson, K.; Aastrup, M.; Andersson, A.; Bringmark, L.; Hovsenius, G.; Håkanson, L.; Iverfeldt, A.; Meili, M.; Timm, B. Mercury in the Swedish Environment - Recent Research on Causes, Consequences and Corrective Methods. *Water, Air, Soil Pollut.* **1991**, *55*, 1−2.

(9) St. Louis, V. L.; Rudd, J. W. M.; Kelly, C. A.; Beaty, K. G.; Flett, R. J.; Roulet, N. T. Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. *Environ. Sci. Technol.* **1996**, *30*, 2719−2729.

(10) Selvendiran, P.; Driscoll, C. T.; Montesdeoca, M. R.; Bushey, J. T. Inputs, storage, and transport of total and methyl mercury in two temperate forest wetlands. *J. Geophys. Res.* **2008**, *113*, G00C01.

(11) Driscoll, C. T.; Holsapple, J.; Schofield, C. L.; Munson, R. The chemistry and transport of mercury in a small wetland in the Adirondack region of New York, USA. *Biogeochemistry* **1998**, *40*, 137−146.

(12) Krabbenhoft, D. P.; Benoit, J. M.; Babiarz, C. L.; Hurley, J. P.; Andren, A. W. Mercury cycling in the Allequash creek watershed, northern Wisconsin. *Water, Air, Soil Pollut.* **1995**, *80*, 425−433.

(13) Liu, G.; Cai, Y.; Kalla, P.; Scheidt, D.; Richards, J.; Scinto, L. J.; Gaiser, E.; Appleby, C. Mercury mass budget estimates and cycling seasonality in the Florida Everglades. *Environ. Sci. Technol.* **2008**, *42*, 1954−1960.

(14) Bergamashi, B. A.; Krabbenhoft, D. P.; Aiken, G. R.; Patino, E.; Rumbold, D. G.; Orem, W. H. Tidally driven export of dissolved organic carbon, total mercury and methylmercury from a mangrove-dominated estuary. *Environ. Sci. Technol.* **2012**, *46*, 1371−1378.

(15) Tjerngren, I.; Karlsson, T.; Björn, E.; Skyllberg, U. Potential Hg methylation and MeHg demethylation rates related to the nutrient status of different boreal wetlands. *Biogeochemistry* **2012**, *108*, 335−350.

(16) Branfireun, B. A.; Roulet, N. T. Controls on the fate and transport of methylmercury in a boreal headwater catchment, northwestern Ontario, Canada. *Hydrol. Earth Syst. Sci.* **2002**, *6* (4), 783−794.

(17) Mitchell, C. P. J.; Branfireun, B. A.; Kolka, R. K. Spatial characteristics of net methylmercury production hot spots in peatlands. *Environ. Sci. Technol.* **2008**, *42* (4), 1010−1016.
(18) Gilmour, C. C.; Henry, E. A.; Mitchel, R. Sulfate Stimulation of Mercury Methylation in Fresh-Water Sediments. *Environ. Sci. Technol.* **1992**, *26* (11), 2281−2287.
(19) Wasik, J. K. C.; Mitchell, C. P. J.; Engstrom, D. R.; Swain, E. B.; Monson, B. A.; Balogh, S. J.; Jeremiason, J. D.; Branfireun, B. A.; Eggert, S. L.; Kolka, R. K.; Almendinger, J. E. Methylmercury declines in a boreal peatland when experimental sulfate deposition decreases. *Environ. Sci. Technol.* **2012**, *46*, 6663−6667.
(20) Ullrich, S. M.; Tanton, T. W.; Abdrashitova, S. A. Mercury in the aquatic environment: A review of factors affecting methylation. *Crit. Rev. Environ. Sci. Technol.* **2001**, *31* (3), 241−293.
(21) Marvin-DiPasquale, M.; Agee, J.; McGowan, C.; Oremland, R. S.; Thomas, M.; Krabbenhoft, D.; Gilmour, C. C. Methyl-mercury degradation pathways: A comparison among three mercury-impacted ecosystems. *Environ. Sci. Technol.* **2000**, *34* (23), 4908−4916.
(22) Lee, Y. H.; Bishop, K. H.; Munthe, J.; Iverfeldt, Å.; Verta, M.; Parkman, H.; Hultberg, H. An examination of current Hg deposition and export in Fenno-Scandian catchments. *Biogeochemistry* **1998**, *40*, 125−135.
(23) Ravichandran, M. Interactions between mercury and dissolved organic matter - a review. *Chemosphere* **2004**, *55* (3), 319−331.
(24) Skyllberg, U. Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland soils and sediments under suboxic conditions: Illumination of controversies and implications for MeHg net production. *J. Geophys. Res.* **2008**, *113*, G00C03.
(25) Society of Ecological Restoration International, 2004. *The SER International Primer on Ecological Restoration*. http://www.ser.org/content/ecological_restoration_primer.asp.
(26) U. S. Environmental Protection Agency. *Method 1631, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*; 2002.
(27) Snell, J. P.; Stewart, II; Sturgeon, R. E.; Frech, W. Species specific isotope dilution calibration for determination of mercury species by gas chromatography coupled to inductively coupled plasma- or furnace atomisation plasma ionisation-mass spectrometry. *J. Anal. At. Spectrom.* **2000**, *15* (12), 1540−1545.
(28) Lambertsson, L.; Björn, E. Validation of a simplified field-adapted procedure for routine determinations of methyl mercury at trace levels in natural water samples using species-specific isotope dilution mass spectrometry. *Anal. Bioanal. Chem.* **2004**, *380* (7−8), 871−875.
(29) Lindström, G.; Pers, C.; Rosberg, J.; Strömqvist, J.; Arheimer, B. Development and testing of the HYPE (Hydrological Predictions for the Environment) water quality model for different spatial scales. *Hydrol. Res.* **2010**, *41* (3−4), 295−319.
(30) Sjögren, J.; Eklund, D.; Sehalic, B.; Andersson, C.; Jones, J.; Engdahls, A. *Oskarshamn site investigation, Hydrological and meteorological monitoring at Oskarshamn, September 2007-September 2008*; SKB P-08-86; Swedish Nuclear Fuel and Waste Management Co: Stockholm, 2008; p 58.
(31) Linacre, E. T. Data-sparse estimation of lake evaporation, using a simplified Penman equation. *Agric. Forest Meteorol.* **1993**, *64* (3−4), 237−256.
(32) Mowat, L. D.; St Louis, V. L.; Graydon, J. A.; Lehnherr, I. Influence of Forest Canopies on the Deposition of Methylmercury to Boreal Ecosystem Watersheds. *Environ. Sci. Technol.* **2011**, *45* (12), 5178−5185.
(33) Grigal, D. F. Inputs and Outputs of Mercury from Terrestrial Watersheds: a Review. *Environ. Rev.* **2002**, *10*, 1−39.
(34) Graydon, J. A.; Louis, V. L. S.; Hintelmann, H.; Lindberg, S. E.; Sandilands, K. A.; Rudd, J. W. M.; Kelly, C. A.; Hall, B. D.; Mowat, L. D. Long-Term Wet and Dry Deposition of Total and Methyl Mercury in the Remote Boreal Ecoregion of Canada. *Environ. Sci. Technol.* **2008**, *42* (22), 8345−8351.
(35) Wood, W. W.; Sanford, W. E. Chemical and isotopic methods for quantifying groundwater recharge in a regional, semiarid environment. *Ground Water* **1995**, *33* (3), 458−468.
(36) Shanley, J. B.; Mast, M. A.; Campbell, D. H.; Aiken, G. R.; Krabbenhoft, D. P.; Hunt, R. J.; Walker, J. F.; Schuster, P. F.; Chalmers, A.; Aulenbach, B. T.; Peters, N. E.; Marvin-DiPasquale, M.; Clow, D. W.; Shafer, M. M. Comparison of total mercury and methylmercury cycling at five sites using the small watershed approach. *Environ. Pollut.* **2008**, *154* (1), 143−154.
(37) Drott, A.; Lambertsson, L.; Bjoern, E.; Skyllberg, U. Do potential methylation rates reflect accumulated methyl mercury in contaminated sediments? *Environ. Sci. Technol.* **2008**, *42*, 153−158.
(38) Gilmour, C. C.; Riedel, G. S.; Ederington, M. C.; Bell, J. T.; Benoit, J. M.; Gill, G. A.; Stordal, M. C. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry* **1998**, *40*, 327−345.
(39) Marvin-DePasquale, M. C.; Oremland, R. S. Bacterial methylmercury degradation in Florida Everglades peat sediment. *Environ. Sci. Technol.* **1998**, *32*, 2556−2563.
(40) Bertilsson, S.; Tranvik, L. J. Photochemical transformation of dissolved organic matter in lakes. *Limnol. Oceanogr.* **2000**, *45* (4), 753−762.
(41) Branfireun, B. A.; Bishop, K.; Roulet, N. T.; Granberg, G.; Nilsson, M. Mercury cycling in boreal ecosystems: The long-term effect of acid rain constituents on peatland pore water methylmercury concentrations. *Geophys. Res. Lett.* **2001**, *28* (7), 1227−1230.
(42) Sellers, P.; Kelly, C. A.; Rudd, J. W. M.; MacHutchon, A. R. Photodegradation of methylmercury in lakes. *Nature* **1996**, *380* (6576), 694−697.
(43) Drott, A.; Lambertsson, L.; Bjoern, E.; Skyllberg, U. Importance of dissolved neutral mercury sulfides for methyl mercury production in contaminated sediments. *Environ. Sci. Technol.* **2007**, *41*, 2270−2276.