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Environmental factors influencing mercury speciation in Subarctic and Boreal lakes

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Abstract

Environmental drivers of total mercury (TotHg) concentrations, methylmercury (MeHg) concentrations, and MeHg fractions (a proxy for methylation potential, expressed as %MeHg) were assessed in a synoptic study of 51 lakes in southeast (Boreal) and northeast (Subarctic) Norway. Concentrations of TotHg and MeHg ranged between 0.5 – 6.6 ng/L and < 0.02 – 0.70 ng/L, respectively. The lakes span wide ranges of explanatory environmental variables, including water chemistry, catchment characteristics, climate conditions, and atmospheric deposition of Hg, sulphur and nitrogen (N). Dissolved organic matter (DOM), measured as total organic carbon (TOC), was the variable most strongly correlated with TotHg ($r^2 = 0.76$) and MeHg ($r^2 = 0.64$) concentrations. Lakes in the Subarctic region had significantly lower TotHg and MeHg concentrations, and %MeHg than lakes in the Boreal region ($p < 0.01$), implying a lower aquatic food web exposure of aqueous Hg species in Subarctic Norway than in the Boreal lakes. Statistical modelling (partial least squares) using data from the Boreal lakes produced models explaining 82%, 75% and 50% of the spatial variation of TotHg and MeHg concentrations and %MeHg, respectively. After TOC, the most significant explanatory variables were N availability, base cation status, and lake and catchment size. We conclude that a key process driving TotHg concentrations is DOM as a transport vector, while the role of DOM for MeHg and %MeHg is likely related to a combination of transport and DOM as a substrate for methylation. Also, negative correlations between MeHg and catchment and lake size are consistent with in-lake and in-stream de-methylation processes. The statistical relationship suggests that N availability exerts a positive contribution on concentrations of MeHg and %MeHg.

Key words

Total mercury, methylmercury, methylation potential, environmental drivers, lakes, Boreal, Subarctic

Highlights

- TotHg, MeHg and %MeHg were determined in 51 Subarctic and Boreal lakes in Norway
- Data indicate food webs in Subarctic lakes are exposed to Hg than Boreal lakes
- The key environmental factor explaining TotHg and MeHg concentrations was DOM
- N availability, base cation status, lake/catchment size also explained Hg variation

1. Introduction

Surface waters of Boreal lakes usually show low concentrations (ng/L) of mercury (Hg). In such systems, long-range transported atmospheric Hg is the main source of Hg contamination and has led to long-term accumulation of Hg in catchment soils (Fitzgerald et al., 1998). In catchment soils, inorganic Hg can be methylated into toxic and bioaccumulative methylmercury (MeHg; Bloom, 1992) and MeHg is accumulated in the aquatic food chain with potential harmful effects on organisms (WHO, 1991). Improving the understanding of the fate of Hg in pristine catchments and exposure of aquatic biota and other wildlife to inorganic Hg and MeHg is the primary concern for studying Hg species in lake water in areas affected by Hg deposition.

Organic matter (OM) as dissolved organic carbon (DOC) is the main transport vector for Hg and MeHg from catchment soils to surface waters (Grigal, 2002). Concentrations of total organic carbon (TOC) and DOC correlate strongly with concentrations of Hg in lake surface water in Scandinavia (Meili et al., 1991, Skyllberg et al., 2003, Eklof et al., 2012a) and North America (Driscoll et al., 1995, Benoit et al., 2003, Shanley et al., 2008). Fluxes of Hg in lake outlets relative to the catchment storage of Hg are usually small (Grigal, 2002, Grigal, 2003, Larssen et al., 2008), suggesting that leaching of deposited Hg from soils to surface waters is likely to continue for decades to centuries.

Processes of methylation and de-methylation in the catchment and lake determine the surface water MeHg concentrations. Production of MeHg occurs primarily through methylation of inorganic Hg by sulphur reducing bacteria (SRB) under anoxic conditions (Morel et al., 1998), but is also shown to occur through other mechanisms (Gilmour et al., 2013). The production of MeHg can hence take place in the catchment wetlands (St. Louis et al., 1994, Tjerngren et al., 2012a), the sediments (Benoit et al., 2003, Gilmour et al., 1998), or the water phase itself (Xun et al., 1987). Parameters thought to influence MeHg production mechanisms in lake systems include sulphur (S) chemistry, availability of inorganic Hg and organic material, temperature and pH (Ullrich et al., 2001). In addition, new studies show the importance of nutrient status on MeHg production rates in Boreal wetlands (Tjerngren et al., 2012a, Tjerngren et al., 2012b). The dominant MeHg degradation process in a lake system is thought to be photo de-methylation (Lehnher and St. Louis, 2009).

Existing studies of Hg species in surface waters of natural Boreal catchments have mainly focused on either a limited number of lakes (Larssen et al., 2008, Munthe et al., 1995, Fjeld et al., 2010), or only measured total Hg (TotHg; Meili et al., 1991, Eklof et al., 2012a, Munthe et al., 1995). Others have only used water chemistry (Meili et al., 1991) or physical factors (Shanley et al., 2005) as explanatory variables for the Hg species. In this study we focus only on natural and semi-natural lakes, i.e., lakes in catchments without local point sources of Hg from agriculture, human settlements or industry. We include several environmental parameters to determine, describe and statistically test the factors significantly controlling spatial variation of TotHg and MeHg concentrations in addition to the MeHg fractions (as MeHg-to-TotHg ratios and presented as %MeHg) in lakes in Boreal (southeast) and Subarctic (northeast) Norway (Figure 1). We use %MeHg as an indicator of the environment's capability to produce MeHg (cf. methylation potential; McClain et al., 2003, Mitchell et al., 2008a). The 51 chosen lakes were selected because they represent areas where previous investigations indicate substantial concentrations of Hg in fish (Fjeld et al., 2008, Fjeld et al., 2010), in some cases exceeding Norwegian fish advisory limits (0.5 mg/kg, Norwegian Food Safety Authority, 2013).

Our main hypothesis was that TotHg concentrations in the surface waters are largely driven by dissolved OM (DOM) as a transport vector and dependent on accumulated atmospheric deposition of Hg stored in the catchments. To test and determine the environmental factors that strongly influence MeHg concentrations, and %MeHg, we assessed lake chemistry, catchment characteristics, climate conditions, and atmospheric deposition of Hg, S and nitrogen (N).

2. Materials and methods

2.1. Study area

The 51 lakes are located in southeast and northeast Norway (Figure 1). The northern lakes (n = 5; ID 39 – 43) are located at a Subarctic tundra plain with little topographical differences. The area is dominated by birch forest and wetlands, with average yearly air temperatures below zero (from -0.8 to -3.2 °C). The lakes in the southeast are located within generally forested catchments, dominated by coniferous tree species, with presence of wetland, and in the Boreal ecotone. The mean yearly air temperature is above zero for all lakes (n = 46; ID 1 - 38; 44 - 51) in this area (from 1.3 to 5.8 °C).

The lakes represent a wide range of physical catchment characteristics (included are elevation, lake and catchment area, lake-to-catchment ratio, wetland area and wetland-to-catchment ratio). The surface areas of the studied lakes range from $< 0.01 \text{ km}^2$ to 16.6 km^2 and the size of the catchment areas span 4 orders of magnitude from 0.02 km^2 to 268.8 km^2 (Table 2). The lakes also represent a wide elevation range, running from 56 m.a.s.l to 610 m.a.s.l. Seven of the southern lakes are located in close proximity, i.e. within 5 km^2 (Figure 1 inset; ID 32 - 38). Six of these (ID 33 - 38) are small ($< 0.02 \text{ km}^2$) and are located upstream of number seven (ID 32; area 0.23 km^2). The surface area of the individual water bodies, and total wetland area, covers from less than 1 % to 32 %, and from 2 % to 29 % of the total catchment area, respectively.

2.2. Sampling

All sampling was conducted between March 2011 and June 2012, and each lake was sampled once. Most lakes ($n = 36$) were sampled during the ice-covered winter period (between November and April) with a water sampler (*Ruttner*, 1 L) at an approximate depth 1 m below ice cover. The water sampler was cleaned with acid (1 % trace level grade hydrochloric acid, HCl) followed by rinses with deionized water (DI). Concentrations of TotHg and MeHg were measured in DI water added to the sampler after cleaning and the concentrations were found satisfactory (TotHg $<$ method detection limit (MDL), MeHg $<$ MDL). We chose to collect most samples during the ice-covered winter period (March, April) as conditions are shown to be stagnant between autumn and spring circulation, and water chemistry are relatively constant (Henriksen and Wright, 1977). However, it was not practically feasible to sample all lakes during winter, and water samples in northern Norway ($n = 5$) were collected in September and 10 lakes in southeast Norway were collected after snowmelt in June. These samples were collected 1 m below surface. Samples were collected using 250 mL fluoropolymer (FLPE) bottles, following ultraclean sampling procedures to avoid contamination (USEPA, 1996). All samples were collected at the centre of the lake.

All bottles were previously unused and pre-tested for traces of TotHg (quality tested by Brooks Rand Labs; mean TotHg concentrations = 0.02 ng/L). TotHg and MeHg were sampled in individual bottles to avoid errors caused by loss of Hg during preservation (Parker and Bloom, 2005,

Braaten et al., 2013). Samples were stored cold and kept in double plastic bags. Preservation techniques are based on United States Environmental Protection Agency (USEPA) method 1630 for MeHg (USEPA, 1998) and method 1631 for TotHg (USEPA, 2002). Hydrochloric acid (concentrated trace level grade, 1 mL) was added to yield a 0.4 % solution for the MeHg samples. All samples used for TotHg analysis were oxidized with bromine monochloride (BrCl) within 48 hours after sampling. Samples collected for general water chemistry were collected at the same time and depths as the Hg samples, but in individual bottles (500 – 1000 mL).

2.3. Chemical analysis

The analytical method for MeHg was based on USEPA Method 1630 (USEPA, 1998) for determining MeHg in water by distillation, aqueous ethylation, purge and trap, and cold vapor atomic fluorescence spectrometry (CVAFS). The method for TotHg followed USEPA Method 1631 for determining Hg in water by oxidation, purge and trap and CVAFS (USEPA, 2002). The MDL is 0.02 ng/L and 0.1 ng/L (3 standard deviations of method blanks) for MeHg and TotHg, respectively. For both species automated systems were used for analysis (Brooks Rand Labs MERX automated systems with Model III AFS Detector). Due to low concentrations of particulate matter all samples were analysed unfiltered.

For every batch of Hg analysis (n = 24 individual samples) quality assurance and quality control measures included method blanks (n = 5), blank spikes (n = 5), sample duplicates (n = 3) and matrix spikes (n = 3). The relative difference of sample duplicates was < 10 % and < 20 % for TotHg and MeHg, respectively. Recovery of blank spikes and matrix spikes were 80 – 120 % for MeHg and 90 – 110 % for TotHg.

Samples for determination of general water chemistry were analysed according to Norwegian Standard (NS) and European Standard (EN-ISO). pH was measured by potentiometry (NS4720); conductivity was measured by electrometry (NS4721; ISO7888); alkalinity was measured by titration (NS-EN-ISO9963); total N (Tot-N; NS4743), total phosphorous (Tot-P; NS-EN1189) and nitrate (NS4745) was measured by spectrophotometry; chloride and sulphate was measured by liquid chromatography (NS-EN-ISO10304-1); and calcium, potassium, magnesium and sodium was

measured by liquid chromatography (NS-EN ISO 14911). TOC was measured by infrared spectrophotometry (NS-EN1484).

All chemical analysis was performed at the Norwegian Institute for Water research (NIVA).

2.4. Data sources

Catchment area and wetland area were determined using Geographical Information System (GIS) software (ESRI ArcMap 10.0). The GIS software was used in combination with Web Map Services (WMS) available from The Norwegian Geo Network. Background lake data (i.e. lake size, lake identification number and elevation) were gathered from the National Lake Database of The Norwegian Water Resources and Energy Directorate (NVE).

For 19 of 46 lakes in Boreal Norway, there was evidence of catchment disturbance by forest management (Figure 1; ID 10 - 15, 17 - 26, 28, 29, 31). Their disturbance history was assessed using historical aerial photographs (from the Hedmark County Governor, Forestry and Agricultural Department), i.e., when and how much of the forest in the catchment was logged (Rognerud et al., 2011). This resulted in three classes of catchment disturbance: logging in the last ten years (0 - 10), between 10 and 20 years ago (10 - 20) and more than 20 years ago (> 20). Also, % forest harvest was quantified. Data is not shown.

Deposition data for S and N were supplied by The Norwegian Institute for Air Research (NILU). The data set is based on interpolated data from the period 2007 to 2011 (Aas et al., 2012; samples collected on a daily or weekly basis). Top sediment (0 – 0.5 cm) TotHg concentrations were interpolated by kriging, based on measurement of sediment TotHg in Norway during 2006 – 2008 (Skjelkvåle et al., 2008). Investigations of lake sediments indicated considerable enrichment of Hg in top sediments compared with preindustrial sediments, and good correlations between contents of moss Hg and Hg in top sediments, indicate that the top sediment TotHg concentrations can be used as an proxy for TotHg deposition (Fjeld et al., 1994). No quantification of TOC content of the sediments was done.

Temperature and precipitation is presented as the yearly average value for each lake between 1961 and 1990, based on procedures described by World Meteorological Organisation (WMO, 1989).

We chose data from the last available standard reference period in climatology as it represents the “normal” climate conditions in a specific area. The data is available from Norwegian Meteorological Institute (Eklima, 2013). Run-off was estimated for each lake based on models from NVE (Beldring et al., 2003) and show the annual average between 1961 and 1990 (NVE, 2013).

2.5. Statistical analysis

To avoid influence from non-normality and reduce heteroscedasticity in the statistical analysis, all data variables were tested by the Shapiro-Wilks test. Variables that showed non-normality (MeHg, %MeHg, pH, alkalinity, total P, chloride, sulphate, calcium, potassium, magnesium, lake area, catchment area, lake-to-catchment ratio, wetland area, wetland ratio, S deposition) were transformed to a logarithmic scale and again tested for normality.

For variables that did not show normality after a logarithmic transformation (conductivity, nitrate, sodium, elevation, N deposition, Hg deposition, run-off, temperature and precipitation) the Box and Cox transformation were used to find a power transformation that fitted the response best. Because of the clear north-south gradient in the material, the variables top sediment Hg concentrations, N deposition, sulphate, temperature and precipitation did not show normality after Box and Cox transformations. These variables were however, normally distributed when the Subarctic lakes were removed, and hence, included in the statistical analysis.

Multivariate correlations between selected variables (predictors) and responses (MeHg concentrations, TotHg concentrations and %MeHg) were explored by Pearson’s correlation coefficient, r . To avoid over-fitted models due to multi co-linearity between our predictors we chose partial least squares (PLS) analysis to model and show the predictors that best can describe the spatial variations of our responses in the studied lakes. The PLS method is designed to include co-linear predictors by constructing new variables underlying the observed predictors. By doing this, most variance in the observed predictors is concentrated in the first new variables and the number of dimensions is effectively reduced (Dormann et al., 2013). We follow the notation of previous literature (Wold et al., 2001). To avoid influence from different units of measurements and for numerical stability in the PLS, both predictors and responses were centred and scaled to have mean 0 and

standard deviation 1. The predictors initially included in the PLS analysis are those presented in the correlation matrix (Table 3; only variables with normal distribution). The variable influence on projection (VIP) was used to evaluate the importance of the predictors in the model. Based on previous procedures predictors with $VIP > 1.0$ were chosen (Eklof et al., 2012a, Sonesten, 2003) and utilized in the final models, and are presented with coefficients of regression. The regression coefficients give the direction and strength of the predictor influence. The number of extracted factors was chosen on the basis of minimizing the prediction error (root mean square error; RMSE). The final models are represented by the goodness of fit (r^2) and the RMSE of the linear regression, in addition to individual model coefficients for the selected predictors.

To test for differences in lake characteristics between Subarctic and Boreal catchments, Student's t-tests were used. All t-tests shown in this study were two-tailed and homogeneity of variance was tested by F-tests.

All statistical analysis and calculations were done in JMP 9.0 (SAS) with a significance level $\alpha = 0.05$, unless otherwise mentioned.

3. Results

3.1 Effects of season and catchment disturbance on water chemistry

We tested, where we could, if the seasonality of our sampling design (i.e. winter and summer sampling events) had any influence on the interpretation of the lake chemistry. Three lakes (ID 1, ID 11 and ID 32) had temporal Hg chemistry data (seasonal sampling from August 2010 to June 2012) available. The three lakes showed a minimal and not significant variation throughout the year of TotHg (ID 1; 2.7 – 4.5 ng/L) and MeHg (ID 1; 0.06 – 0.09 ng/L) concentrations. For comparison, the PLS regression modelling was tested with the lakes sampled in the summer season excluded (data not shown). This modelling showed similar trends to the presented results with no significant differences. Thus, we conclude that we can use lake samples from both seasons in our analysis.

Although we found no indications of influences from traditionally seasonally changing explanatory variables (e.g. temperature and run-off), we acknowledge the fact that temporal variability may influence Hg speciation in Boreal lake systems. However, based on the significant relationships

found for Hg speciation with particularly water chemistry parameters in the present study, we find this spatial data set to be of importance when considering mechanisms responsible for changing Hg species concentrations in surface waters of Boreal catchment systems.

We investigated potential effects of forest management on water chemistry and Hg speciation (data not shown). No relation was found between chemical water parameters (included TOC, nutrients, TotHg concentrations, MeHg concentrations and %MeHg) and % catchment cover harvested or with time period of harvesting. We concluded that forest management effect did not significantly affect water chemistry and therefore this catchment characteristic was disregarded in the statistical analysis.

3.2. Spatial variations of Hg species

Distributions of TotHg and MeHg concentrations in the studied lakes ranged over more than an order of magnitude (Table 1; Figure 2), with mean concentrations of 3.4 ± 1.6 ng/L (mean \pm 1 standard deviation) and 0.16 ± 0.13 ng/L, respectively (all lakes included). All samples had TotHg above the MDL (0.1 ng/L), while one sample had a MeHg concentration below MDL (0.02 ng/L). The highest concentrations of both TotHg (maximum of 6.6 ng/L) and MeHg (maximum of 0.70 ng/L) were found among the forested catchments close to the Swedish border in southeast Norway. The lowest concentrations were found among the five lakes in the Subarctic region, with minimum concentrations of 0.5 ng/L (TotHg) and < 0.02 ng/L (MeHg). The mean concentrations of TotHg and MeHg in the Subarctic lakes were significantly lower than the mean concentrations in the southern lakes located in the Boreal Ecoregion ($p < 0.05$).

Based on data collected in 2006-2008 there was a strong decline in top lake sediment Hg concentrations from south to north in the studied lakes. The concentrations were below 0.21 $\mu\text{g/g}$ for all lakes in the Subarctic north, while the lakes in the Boreal southeast varied between 0.30 and 0.46 $\mu\text{g/g}$ (Table 2). The difference in top sediment concentrations between Subarctic lakes and Boreal lakes was significant ($p < 0.05$). To avoid influence from the non-normality of some Subarctic lake properties (top sediment Hg concentrations, N deposition, sulphate, temperature and precipitation), the five lakes in the north were treated separately in the correlation matrix and statistical analysis. The best

predictor for Hg species in the Subarctic lakes was TOC concentration; $r^2 = 0.97$, $r^2 = 0.99$ and $r^2 = 0.74$ (all $p < 0.01$) for TotHg concentrations, MeHg concentrations and %MeHg, respectively.

In general, the %MeHg levels were low, the mean being 4.8 ± 4.0 % (all lakes included). Thirty-seven of the studied lakes had %MeHg less than 5 %. There were two outliers shown as lakes having %MeHg higher than 10 % (outside the 1.5*interquartile range); 14.7 and 27.1 % respectively. The two lakes are both located in southeast Norway (Figure 1; ID 21 and 36). Mean %MeHg was lower in the Subarctic lakes (3.1 ± 0.7 %) compared to the Boreal lakes in the south (5.0 ± 4.1 %), but not significantly ($p = 0.29$).

The correlation between TotHg and MeHg (Table 3; $r = 0.52$, $p < 0.01$), and MeHg and %MeHg was significant and positive ($r = 0.74$, $p < 0.01$). There was no significant correlation between TotHg and %MeHg ($r = -0.17$, $p > 0.05$).

3.3. Hg and OM

The mean TOC concentration in the Boreal and Subarctic lakes was 10.7 ± 4.5 mg/L, with a minimum and maximum of 2.8 mg/L and 20.1 mg/L, respectively (Table 1; Figure 2). The TOC concentrations were significantly ($p < 0.01$) negatively correlated to pH, alkalinity and sulphate concentrations, while there was a significant positive correlation between TOC and Tot-P (Table 3). Both TotHg and MeHg were significantly correlated to TOC ($r = 0.83$, $r^2 = 0.76$ and $r = 0.73$, $r^2 = 0.64$, respectively, $p < 0.01$; Table 3; Figure 2; Figure 3). Total Organic Carbon concentrations were not significantly correlated with %MeHg ($r = 0.20$, $p > 0.05$). Ratios of TotHg-to-TOC and MeHg-to-TOC showed little variation (Table 1), in agreement with the strong correlations shown above.

3.4. Explanatory variables for Hg species in Boreal Norway

The PLS analysis and modelling explained the spatial variations of the responses TotHg concentrations, MeHg concentrations and %MeHg in the lakes in southeast (Boreal) Norway (Figure 3 and Figure 4) from the parameters of water chemistry, catchment characteristics, deposition patterns and climate variables included in Table 1 and 2.

The PLS model had three significant components that explained the variation of the response variables. The first component explained 41 % of the variation, while 62 % and 69 % was explained by the model that included two and three components. The loading plots (Figure 3; presented are the loadings, i.e. the relative influence, of each environmental variable on the three components) and individual model coefficients (Figure 4) showed that TOC (Figure 2) and Tot-P concentrations had strong positive correlations with TotHg concentrations, while pH and alkalinity had a negative influence. Total organic carbon and Tot-P had the strongest influence on the TotHg concentrations, and the two parameters were strongly inter-correlated (Table 3; $r = 0.60$, $p < 0.01$). Additionally, lake size and catchment area were weakly correlated to TotHg concentrations. The linear regression explained 82 % of the spatial variation of TotHg concentrations (RMSE = 0.63).

For MeHg concentrations, the loading plots showed that in addition to TOC (Figure 2) and Tot-P concentrations, also Tot-N had a strong positive influence. In addition, there was a negative correlation with lake size and catchment area. The two catchment characteristics, lake size and catchment area, were strongly positively correlated ($r = 0.88$, Table 3, Figure 3). Total organic carbon and Tot-N had the strongest influence on the MeHg concentrations, but were not internally correlated (Table 3; $r = 0.03$, $p > 0.05$). The linear regression explained 75 % of the spatial variation of MeHg concentrations (RMSE = 0.33).

Similar to MeHg concentrations, TOC and Tot-N had a strong positive correlation with %MeHg. Tot-N was the variable with the strongest influence for %MeHg in the PLS analysis (Figure 4). Lake size and catchment area had a negative influence on the %MeHg, while alkalinity and pH were positively correlated. The linear regression explained 50 % of the spatial variation in %MeHg (RMSE = 0.42).

The PLS modelling also indicated that Tot-N was a significant variable in describing variations of both MeHg concentrations and %MeHg. For %MeHg, Tot-N was in fact the variable with the strongest influence (Figure 4). The two lakes with %MeHg outside the 1.5*interquartile range both showed intermediate concentrations of Tot-N (415 and 455 $\mu\text{g/L}$, respectively).

4. Discussion

4.1. Spatial variations of Hg species

Concentrations of TotHg represent what is previously documented for natural lake catchment systems, minimally disturbed by direct anthropogenic influences. The range of TotHg concentrations in our study is within the range previously reported for lakes in Scandinavia (2 – 10 ng/L (Meili et al., 1991); 0.9 – 5.8 ng/L (Verta et al., 2010); 0.5 – 4.5 ng/L (Eklof et al., 2012a)) and North America (2 – 8 ng/L (Driscoll et al., 1995); 0.2 – 4.8 ng/L (Watras et al., 1995)). In our study, the Subarctic lakes had lowest TotHg concentrations compared with the Boreal lakes, and the same was true for TOC concentrations and sediment concentrations of Hg (Figure 2). Similar declines in environmental Hg along a north-south gradient in Norway are substantiated by studies of Hg in mosses (Berg et al., 2006) and monitoring studies of Hg in freshwater fish (perch; Fjeld et al., 2010).

The differences between Subarctic and Boreal Norway were most striking for Hg in fish (Fjeld et al., 2010) and in water (this study), suggesting that not only accumulated deposition (and thereby ecosystem pools of Hg) is driving the lower Hg concentrations in Subarctic lakes but also transport of Hg from soils to waters. This is substantiated by the low concentrations of TOC in Subarctic lakes (Figure 2), as DOM is the main transport vector of Hg (Grigal, 2002). The fish and water Hg concentrations are both consistent with the idea that exposure to Hg in Subarctic freshwater environments is lower than in Boreal ecosystems. From this we conclude that lower Hg deposition and lower TOC in Subarctic Norway are likely drivers of low Hg contamination in waters and aquatic food webs.

MeHg concentrations were below 0.70 ng/L in all the lakes. Previous studies in Scandinavia show similar concentration ranges; i.e. 0.04 – 0.58 ng/L (Rask et al., 2010) and 0.14 – 1.01 ng/L (Verta et al., 2010). Other studies of Scandinavian stream and waters directly related to wetlands show higher MeHg concentrations (Tjerngren et al., 2012a, Eklof et al., 2012b, Porvari and Verta, 2003). Similar to TotHg concentrations, also the lowest MeHg concentrations are found in Subarctic Norway (Table 1; Figure 2). As shown above, concentrations of inorganic Hg are lower in the Subarctic region, which limits production of MeHg. Additionally, MeHg production is a microbial process and temperature dependent (Ullrich et al., 2001). Probably, both climatic factors and deposition lead to conditions less favourable for MeHg production in Subarctic lake catchment systems. With lower

concentrations of Hg in fish in the Subarctic regions compared to the southern areas of Norway (Fjeld et al., 2010) this confirms previous studies where exposure to aqueous MeHg is assumed to be a controlling factor for bioaccumulation of MeHg in aquatic food webs (Chasar et al., 2009).

A biogeochemical MeHg hotspot is in the literature defined as an area with high reaction rates of MeHg production compared to the surrounding areas (McClain et al., 2003, Mitchell et al., 2008a). We follow these ideas here, suggesting that %MeHg can be used as an indirect measure of the environment's capability to produce MeHg. Percent MeHg in our study showed little variation (1.3 – 9.6 %) compared to a North American study (Watras et al., 1995; 2 – 48 %), but similar to other Scandinavian surface water values (Rask et al., 2010; 4 – 15 %). But two lakes had %MeHg values outside the 1.5*interquartile range. The two lakes had %MeHg of 14.7 (ID 36) and 27.1 % (ID 21). These lakes are located in southern Norway; one in the forested south east (ID 21) and the other in a mountainous region (ID 36). Because net production of MeHg is the difference between Hg methylation and MeHg de-methylation, %MeHg of these two lakes indicates elevated net MeHg production. A possible explanation for the elevated net MeHg production is provided further on.

4.2. Hg and OM

The variation of TOC concentrations (2.8 – 20.1 mg/L) in the lakes included in this study reflects the west-to-east gradient of increasing TOC throughout Scandinavia (Henriksen et al., 1998). Concentrations are similar to what is found in recent Swedish studies (Eklof et al., 2012a, Akerblom et al., 2012). The range of TotHg-to-TOC ratios found in this study (0.12 – 0.53 ng Hg/mg C) was slightly larger than what is seen in a recent study of Swedish Boreal lakes (0.20 – 0.43 ng Hg/mg C; Eklof et al., 2012a). This is linked to the smaller range of both TotHg and TOC concentrations (1.3 – 14.9 mg/L) in the Swedish study. The mean values of TotHg-to-TOC ratios in the present study (0.31 ng Hg/mg C), and in the Swedish study (0.33 ng Hg/mg C; n = 19; Eklof et al., 2012a), were similar.

In most Boreal lakes, DOC is shown to be the largest pool of organic C (TOC consists of > 90 % DOC; Wetzel, 2001, Hessen, 2005, Kortelainen et al., 2006, de Wit et al., 2012) and TOC is in the present study used as a measure of the concentrations of organic matter in the lake systems. Additionally, the supply of allochthonous DOC in humic lakes is many times higher than the

production of autochthonous DOC (Hessen, 1992, Jonsson et al., 2001). The major part originates from terrestrial catchment primary production (Jansson et al., 2008, Wilkinson et al., 2013). In the present study, TotHg and MeHg concentrations both showed a strong positive relation with TOC (Table 3; Figure 2). This relationship has also been shown elsewhere; both in Scandinavia (Meili et al., 1991, Skyllberg et al., 2003, Eklof et al., 2012a) and North America (Driscoll et al., 1995, Benoit et al., 2003, Shanley et al., 2003). The importance of this correlation is also shown by the PLS analysis (Figure 3 and Figure 4), where TOC was the strongest positive explanatory variable for both species in combination with Tot-P (for TotHg) and Tot-N (for MeHg). The significant relationship ($p < 0.05$) between TOC concentrations and the Hg species ($r^2 = 0.76$ and $r^2 = 0.64$ for TotHg and MeHg, respectively; Figure 2) when the complete data set was used (included the five Subarctic lakes), indicates that the relationship exists independently of the other explanatory variables included in this study. In other words; no matter the location (i.e. climate), deposition patterns and size of the lake-catchment system, Hg species will be transported by DOM from the catchment soil to the surface water of the receiving lake.

The simple linear regression revealed no significant correlation between %MeHg and TOC concentrations (Table 3; $r = 0.20$, $p > 0.05$). The PLS analysis did however show that TOC had a significant positive influence on the %MeHg, but the relationship was weaker than for both TotHg and MeHg concentrations (Figure 4). The significant positive correlation for both TotHg and MeHg concentrations and TOC concentrations is likely to be related to OM as a transport vector for Hg species from the catchment to the surface water. However, OM is also a necessary factor in the production of MeHg as a substrate for methylation (Ullrich et al., 2001). Possibly, this explains the weaker, but still positive, influence of TOC concentrations on %MeHg.

Concentrations of DOC in surface waters are usually correlated positively with wetland-to-catchment ratio (Watras et al., 1995, Eckhardt and Moore, 1990) and negatively with lake size (Rasmussen et al., 1989). In the present study, a significant negative relationship was seen between TOC and lake size, but the positive correlation between TOC and wetland-to-catchment ratio was not significant (Table 3). This might be due to large areas of wetlands being located relatively far from the lakes, thereby less effective in influencing lake water chemistry. With production of MeHg assumed to

occur primarily in catchment wetlands (St. Louis et al., 1994, Tjerngren et al., 2012a), we suggest that the variations in wetland proximity to the lakes is an important reason for the weak correlation found between MeHg concentrations and wetland-to-catchment ratio ($r = 0.31$, $p < 0.05$).

4.3. Explanatory variables for Hg species in Boreal Norway

In addition to TOC, both pH and alkalinity were shown to be significant explanatory variables for TotHg concentrations, MeHg concentrations, and %MeHg in the PLS analysis (Figure 4). Total organic carbon, pH, and alkalinity are strongly internally correlated (Table 3). Such internal correlations could hamper an interpretation of independent effects of these variables on TotHg concentrations, because they have opposite effects on TotHg (consistent with the sign of their internal correlation). However, for MeHg and %MeHg, the correlations with TOC, pH and alkalinity are all positive, which could imply that TOC and pH/alkalinity are separate controls for MeHg and %MeHg. With lake water pH and alkalinity, and catchment base cation status being correlated (Pennanen, et al., 1998), a possible interpretation is that microbial activity is stimulated in soils with lower acidity and higher base cation status (Mulder et al., 2001, Oulehle et al., 2006). Higher MeHg production is a possible side effect of this stimulation.

Together with TOC, Tot-P concentrations were the strongest explanatory variable of TotHg concentrations. Tot-P concentrations were also positively correlated with MeHg concentrations, but not with %MeHg. In humic oligotrophic lakes in Scandinavia, P is usually present only in its organic form (Vidal et al., 2011) which is substantiated in our study by the significant positive correlation between TOC and Tot-P concentrations (Table 3; $r = 0.60$, $p < 0.01$). The relation between Tot-P and TotHg is most likely due to inter-correlation of Tot-P and TOC, and demonstrates the strong link between Hg and DOM.

Concentrations of TotHg were related significantly to neither lake size nor catchment area ($p > 0.05$; Table 3). However, there is a significant negative relationship between TotHg and lake-catchment ratio ($r = -0.41$, $p < 0.01$). This is consistent with the idea that catchment loading of Hg dominates over direct on-lake Hg deposition (Lee et al., 1998, Lee et al., 2000). The larger the catchment compared to the lake area, the larger this effect is. MeHg concentrations and %MeHg were

significantly negatively influenced by both lake size and catchment area (Table 3 and Figure 4), but not by the lake-to-catchment ratio (Table 3). We suggest that the effect of lake size and catchment area could be related to the amount of surface water in the catchment, both streamwater and lakes, where loss of MeHg by photo de-methylation (Lehnherr and St. Louis, 2009) contributes to decrease MeHg leached from catchment soils and wetlands.

The main difference between significant explanatory variables for TotHg and MeHg concentrations was Tot-N. Tot-N concentration was strongly positively correlated with both concentrations of MeHg ($r = 0.34$, $p < 0.01$) and %MeHg ($r = 0.40$, $p < 0.01$), but not with TotHg. We tested other indicators of lake nutrient status (i.e. nitrate concentrations, nitrate-to-Tot-N ratios and nitrate-to-Tot-P ratios; Bergstrom et al., 2008, in addition to C/N ratios) without finding similar relations with MeHg and %MeHg. Still, Tot-N is an indicator of total N availability, and therefore we suggest that methylation is stimulated by N availability. To our knowledge, no previous study has shown a similar influence of N on methylation of Hg in Boreal lakes.

A recent study of Hg methylation in wetlands from Sweden (Tjerngren et al., 2012a) indicated that intermediate levels of nutrient status (measured as C/N ratios in the soil and nitrate in outlet stream waters) give the highest MeHg production rates. This is consistent with the two lakes that had ratios of %MeHg outside the 1.5*interquartile range (14.7 and 27.1 %) in the present study. Both lakes had intermediate concentrations of Tot-N (415 and 455 $\mu\text{g/L}$) and nitrate (43 and 57 $\mu\text{g/L}$). We did not find support for a relation between concentrations of nitrate and MeHg elsewhere in our dataset, however.

Opposite to our study, negative relations were found between nitrate and MeHg concentrations in studies of the water column (Todorova et al., 2009) and the sediments (Matthews et al., 2013) of a seasonally stratified, but contaminated lake in North America. The authors show that high concentrations of nitrate suppress MeHg accumulation and interpret this as an effect of nitrate outcompeting sulphate as electron acceptor for nitrate-reducing microorganisms. Further, the authors hypothesize that a negative nitrate control of MeHg production could occur in remote areas impacted by atmospheric Hg and N deposition.

In a study from the marine environment, nutrient loading (of mainly N) affected Hg contamination by reducing bioavailability and trophic transfer (Driscoll et al., 2012). The authors conclude that a better understanding of the linkages between nutrient loading and Hg contamination is needed. Another marine study (Zhang et al., 2013) indicates significant relationships of both N and P with MeHg and TotHg concentrations in surface sediments. The authors do not however, provide an explanation other than a link to the OM of the sediments.

5. Conclusions

Based on present data of humic lake TotHg and MeHg concentrations we conclude that DOM drives TotHg concentrations as a transport vector, while the role of DOM for MeHg and %MeHg is likely to be related to a combination of transport and DOM as a substrate for methylation. Low TotHg and MeHg water concentrations in combination with low top sediment Hg concentrations demonstrate that exposure to Hg in Subarctic freshwater environments is lower than in Boreal ecosystems. From this we conclude that lower deposition and low DOM in Subarctic Norway are likely drivers of low Hg contamination in waters and aquatic food webs.

Our statistical modelling suggest that factors determining variation in lake TotHg and MeHg concentration, and %MeHg are, in addition to DOM, N availability, base cation status and lake and catchment size. The statistical relations indicate that N availability exerts a positive contribution on concentrations of MeHg and %MeHg. Relationships between methylation and nutrient status are poorly understood and deserve more attention.

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Tables and figures

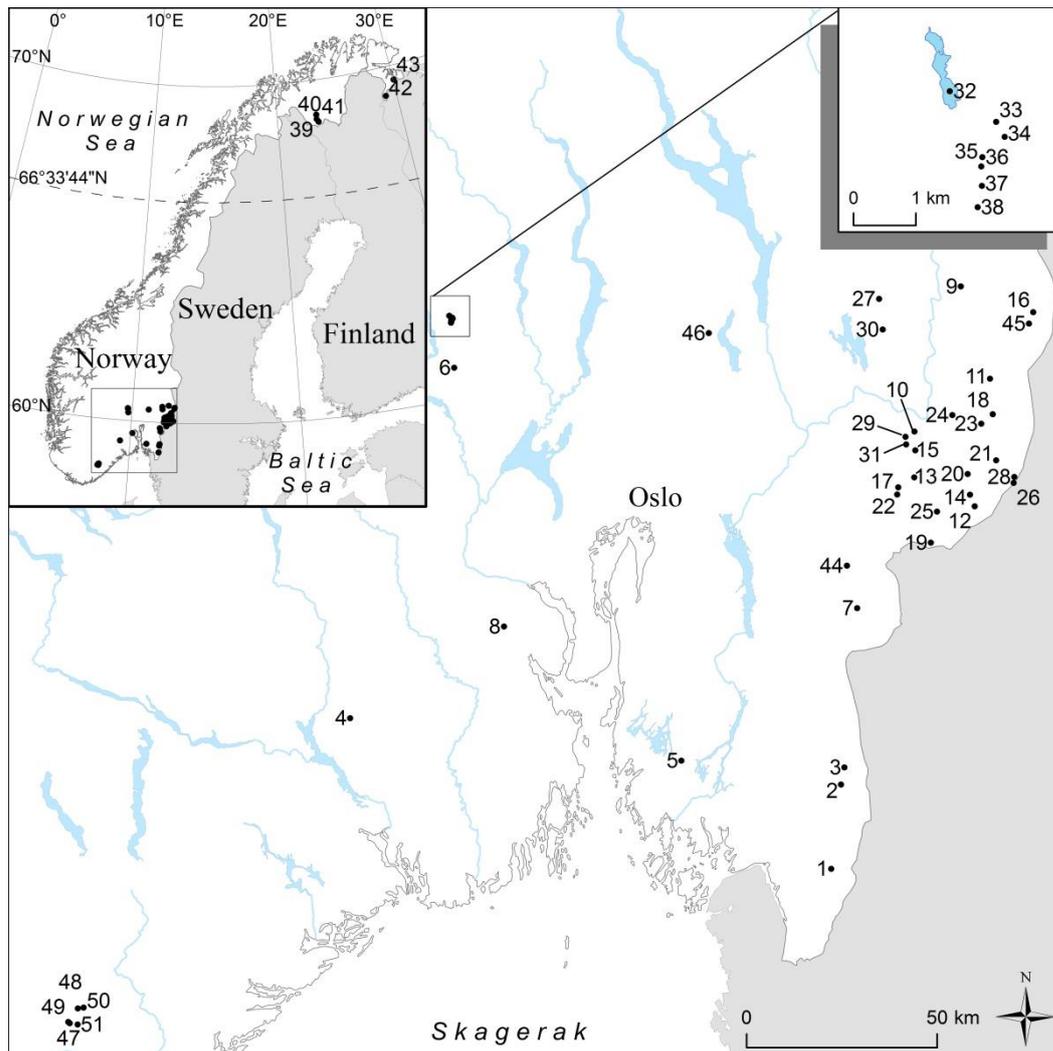


Figure 1. Geographical location of the 51 lakes included in the present study. Numbers on the map refers to lake ID used throughout the study.

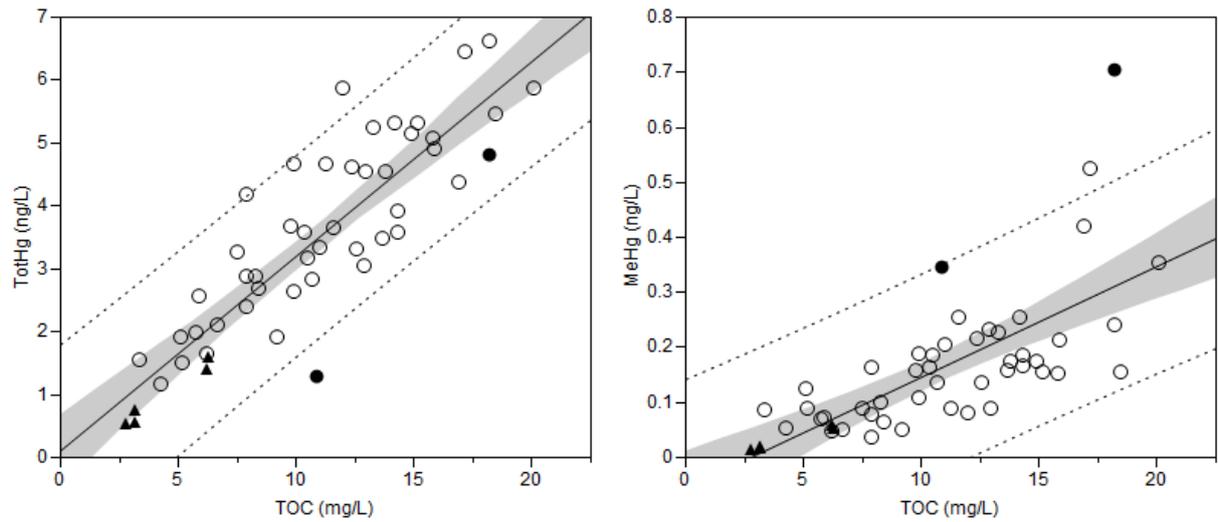


Figure 2. Scatter plots of TotHg (left) and MeHg (right) versus TOC. Solid lines represent the linear regression models ($\text{TotHg} = 0.11 + 0.31 \cdot \text{TOC}$, $r^2 = 0.76$; $\text{MeHg} = -0.06 + 0.02 \cdot \text{TOC}$, $r^2 = 0.50$). The shaded area represent the confidence curve for the linear line and the broken lines the confidence curve for the individual values. All data is included ($n = 51$ lakes). Lakes from the Subarctic are shown as triangles; lakes from the Boreal Ecoregion as circles; and filled data points indicate lakes with $> 10\%$ MeHg.

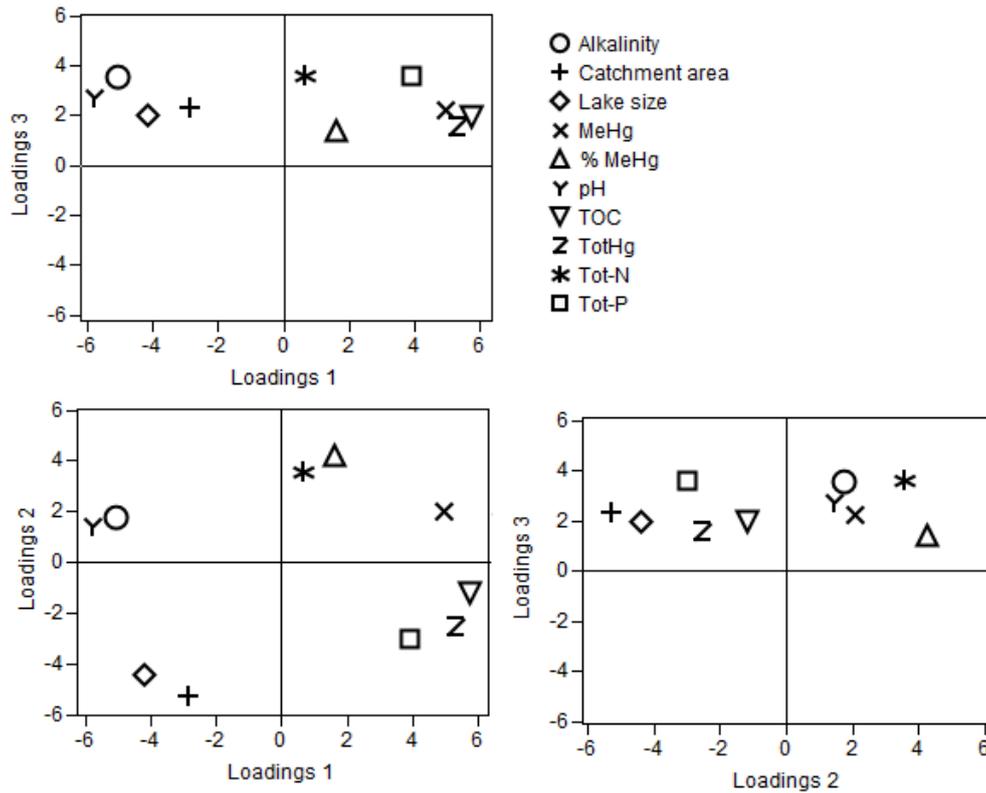


Figure 3. Loadings plots shown for the three significant factors in the PLS analysis. The loadings show the relative influence of each environmental predictor on the three components. The variable influence on projection (VIP) indicates the importance of the predictors in the model and the predictors shown have $VIP > 1.0$; alkalinity ($VIP = 1.3$), catchment area (1.6), lake size (1.8), pH (1.4), TOC (2.1), Tot-N (1.8) and Tot-P (1.7).

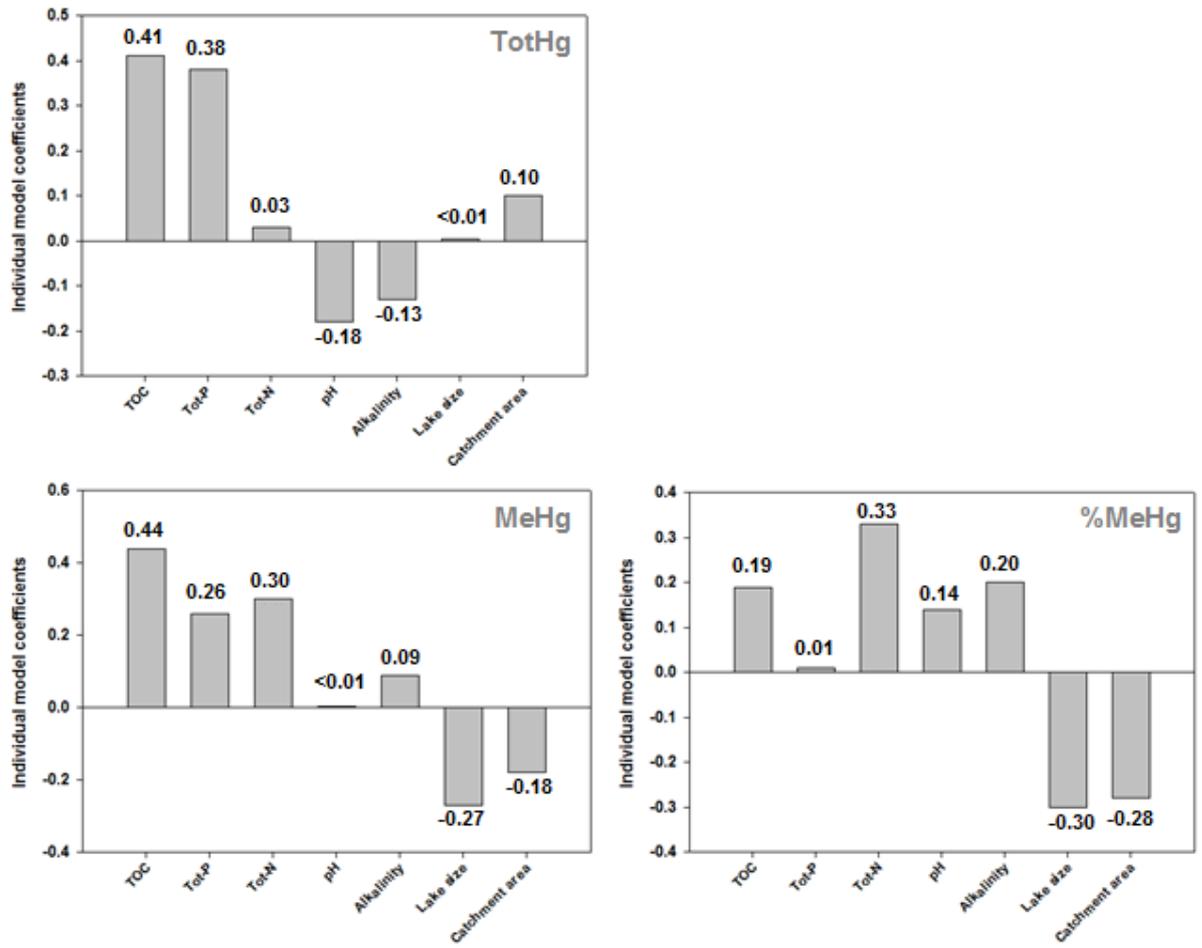


Figure 4. Individual model coefficients for each selected predictor for the responses: TotHg concentrations (top left), MeHg concentrations (left) and %MeHg (right).

Table 1. Minimum, mean and maximum concentrations for all water chemistry parameters included in the study. Data from all lakes (n = 51) are included and separated into lakes located in the north (n = 5) and located in the south (n = 46).

Specification	Unit	Mean value (minimum, maximum)	
		Subarctic lakes (n = 5)	Boreal lakes (n = 46)
Water chemistry			
TotHg	ng/L	1.0 (0.5, 1.6)	3.7 (1.2, 6.6)
MeHg	ng/L	0.03 (< MDL, 0.06)	0.17 (0.04, 0.70)
MeHg-to-TotHg ratio	%	3.1 (2.5, 4.2)	5.0 (1.3, 27.1)
TotHg-to-TOC ratio	ng/mg	0.22 (0.18, 0.25)	0.33 (0.12, 0.53)
MeHg-to-TOC ratio	ng/mg	0.007 (0.005, 0.009)	0.015 (0.005, 0.039)
pH	-	7.4 (7.0, 7.8)	5.6 (4.7, 6.8)
Alkalinity	mmol/L	0.41 (0.17, 0.74)	0.06 (0.01, 0.21)
TOC	mg/L	4.3 (2.8, 6.3)	11.4 (3.4, 20.1)
Total P	µg/L	6 (2, 12)	8 (3, 21)
Total N	µg/L	221 (155, 290)	404 (245, 620)
Sulphate	µg/L	3.3 (2.0, 5.5)	1.7 (0.9, 4.1)
Nitrate	µg/L	7.1 (0.5, 24)	72.4 (9.0, 235.0)

Table 2. Minimum, mean and maximum levels for all catchment characteristics, deposition patterns and climate variables included in the study. Data from all lakes (n = 51) are included and separated into lakes located in the north (n = 5) and located in the south (n = 46).

Specification	Unit	Mean value (minimum, maximum)	
		Subarctic lakes (n = 5)	Boreal lakes (n = 46)
Catchment characteristics			
Lake size	km ²	0.93 (0.20, 3.37)	0.88 (<0.01, 16.56)
Catchment size	km ²	26.67 (0.93, 60.51)	15.42 (0.02, 268.84)
Lake-to-catchment ratio	%	8.3 (0.5, 21.5)	7.4 (0.7, 31.6)
Wetland area	km ²	4.50 (0.03, 15.30)	1.14 (<0.01, 18.37)
Wetland-to-catchment ratio	%	11.4 (3.0, 25.3)	12.0 (1.7, 28.9)
Elevation	m.a.s.l	246 (56, 371)	307 (60, 610)
Deposition patterns			
Top sediment Hg	µg/g	0.16 (0.14, 0.21)	0.36 (0.30, 0.46)
N deposition	mEq/m ² /yr	10.5 (9.9, 11.9)	43.2 (33.7, 63.4)
S deposition	mEq/m ² /yr	8.0 (6.2, 10.7)	13.0 (10.3, 20.8)
Climate variables			
Run-off	mm/yr	316 (312, 324)	489 (230, 944)
Mean annual temperature	°C	-2.3 (-3.2, -0.8)	3.6 (1.3, 5.8)
Precipitation	mm/yr	372 (329, 453)	816 (653, 1182)

Table 3. Pearson's correlation matrix with the linear correlation coefficient r given for selected variables. Nominal significance levels are: $p_{0.05} = 0.29$; $p_{0.01} = 0.37$ ($n = 46$; data from the Subarctic lakes ($n = 5$) is excluded). Variables transformed for normality are shown in bold.

	TotHg	MeHg	MeHg-to-TotHg ratio	TotHg-to-TOC ratio	MeHg-to-TOC ratio	pH	Alkalinity	TOC	Tot-P	Tot-N	Sulphate	Nitrate	Lake size	Catchment area	Lake-to-catchment ratio	Wetland-to-catchment ratio	N deposition	S deposition	Hg deposition	Run-off	Temperature	Precipitation	
TotHg	1																						
MeHg	0.52	1																					
MeHg-to-TotHg ratio	-0.17	0.74	1																				
TotHg-to-TOC ratio	0.34	-0.28	-0.58	1																			
MeHg-to-TOC ratio	0.00	0.77	0.90	-0.19	1																		
pH	-0.66	-0.40	0.04	-0.14	-0.05	1																	
Alkalinity	-0.56	-0.28	0.11	-0.16	0.01	0.92	1																
TOC	0.83	0.73	0.20	-0.21	0.16	-0.62	-0.51	1															
Tot-P	0.74	0.43	-0.07	0.27	0.07	-0.37	-0.24	0.60	1														
Tot-N	-0.03	0.34	0.40	-0.06	0.46	0.15	0.19	0.03	0.07	1													
Sulphate	-0.31	-0.23	-0.01	-0.07	-0.09	0.62	0.64	-0.30	-0.03	0.43	1												
Nitrate	-0.05	-0.10	-0.14	0.21	-0.09	0.51	0.46	-0.14	0.14	0.33	0.62	1											
Lake size	-0.17	-0.58	-0.54	0.24	-0.55	0.49	0.40	-0.34	0.07	-0.12	0.41	0.51	1										
Catchment area	0.03	-0.44	-0.51	0.22	-0.52	0.30	0.26	-0.12	0.23	-0.16	0.29	0.32	0.88	1									
Lake-to-catchment ratio	-0.41	-0.24	-0.01	0.03	-0.01	-0.37	0.26	-0.43	-0.35	0.09	0.23	0.35	0.17	-0.32	1								
Wetland-to-catchment ratio	0.19	0.31	0.18	-0.14	0.17	-0.59	-0.53	0.27	0.00	-0.18	-0.66	-0.61	-0.58	-0.46	-0.21	1							
N deposition	-0.29	-0.30	-0.06	0.10	-0.03	0.06	0.08	-0.40	-0.18	0.35	0.38	-0.20	0.04	0.05	-0.02	-0.09	1						
S deposition	-0.34	-0.29	-0.02	0.06	0.01	0.08	0.10	-0.44	-0.24	0.37	0.32	-0.26	-0.01	-0.01	0.00	-0.04	0.98	1					
Hg deposition	-0.22	-0.12	0.06	0.03	0.10	-0.10	-0.07	-0.27	-0.35	-0.04	-0.32	-0.46	-0.30	-0.22	-0.14	0.25	0.36	0.45	1				
Run-off	0.00	0.13	0.19	0.03	0.25	-0.32	-0.27	-0.04	-0.16	0.00	-0.38	-0.53	-0.59	-0.54	-0.07	0.43	0.35	0.42	0.63	1			
Temperature	-0.18	-0.28	-0.14	0.12	-0.12	0.28	0.31	-0.31	0.08	0.42	0.64	0.16	0.39	0.35	0.05	-0.41	0.81	0.76	0.05	-0.11	1		
Precipitation	-0.45	-0.29	0.05	0.02	0.08	0.11	0.10	-0.51	-0.38	0.26	0.02	-0.38	-0.12	-0.10	-0.02	0.11	0.74	0.84	0.65	0.62	0.41	1	

