



Five decades of declining methylmercury concentrations in boreal foodwebs suggest pivotal role for sulphate deposition

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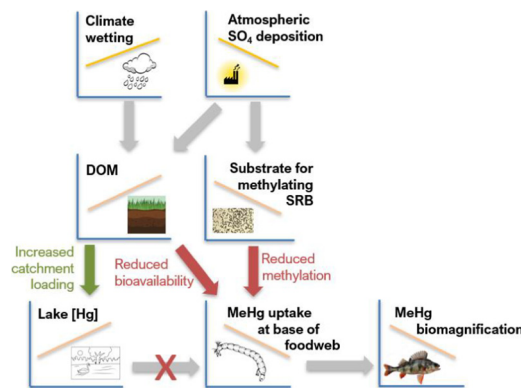
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HIGHLIGHTS

- [MeHg] in boreal lake Chironomids declined five-fold since 1970s.
- Water chemistry demonstrates lake recovery from acid deposition.
- Fish [Hg] reduced by 20–50% in boreal Fennoscandia.
- Declining SO₄-deposition is a driver of reduced MeHg contamination.

GRAPHICAL ABSTRACT



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ABSTRACT

Widespread declines in mercury (Hg) in fish in pristine lakes in Fennoscandia since the 1970s are unexplained. Interactions between climate, atmospheric deposition, and elemental cycling of carbon (C), sulphur (S) and Hg are complex and affect Hg bioaccumulation. A parallel significant decline in methyl-Hg (MeHg) concentrations in aquatic macroinvertebrates (Chironomidae) was found between 1976–78 and 2004–15 in an intensely studied, pristine boreal lake (Langtjern, boreal Fennoscandia). Monitoring at Langtjern demonstrated a four-fold decrease in aqueous sulphate concentrations (SO₄, 50-year record), significant lake browning (30-year records), increasing sediment Hg concentrations (50-year record), warming (45-year record) and increased runoff (40-year record). Contrasting Hg trends in biota (downward) and sediment (upward) indicated a disconnect between lake Hg loading and foodweb Hg bioaccumulation. We suggest that reduced SO₄-deposition has 1) constrained substrate availability for SO₄-reducing methylating bacteria (causing reduced foodweb MeHg exposure despite increased Hg loading to the lake), and 2), increased the binding affinity between aqueous organic matter and Hg species (leading to reduced MeHg bioavailability). The downward MeHg trend at the base of the foodweb at Langtjern is mirrored at higher trophic levels by strong declines in perch (*Perca fluviatilis*) and pike (*Esox lucius*) Hg concentrations in boreal Fennoscandia. A plausible explanation is that declining SO₄-deposition, rather than climate change or reduced atmospheric Hg, is currently driving reduced MeHg contamination in northern freshwater foodwebs.

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1. Introduction

International concerns about the toxic threat of mercury (Hg) have led to *The Minamata Convention on Mercury* (hereafter The Minamata Convention), which aims to protect human health and the environment from adverse effects of Hg at a global scale (UNEP, 2014). Fulfilment of the Convention necessitates adequate methods for assessing time trends of Hg concentrations in biota. Although concentrations of Hg in freshwater fish still often exceed limits for protection of human health (0.5 ppm) (FAO/WHO, 1995) and ecosystems (0.02 ppm) (WFD, 2014), recent studies show declines over the last half century, an indication of improved environmental status of some freshwater aquatic ecosystems (Åkerblom et al., 2014; Braaten et al., 2019). The reason for the decline, however, is not clear, because there are few comprehensive environmental records on Hg cycling and food chain exposure over time that allow for testing of hypotheses. Temporal Hg trends in aquatic biota often do not agree with trends in atmospheric Hg concentrations, probably because of legacy Hg and biogeochemical processing of Hg in the environment (Wang et al., 2019). Archived biological material constitutes a potential data source for investigations of long-term change in environmental pollutants (Green and Scharlemann, 2003), including Hg (Poulopoulos, 2013), but there are few examples of such studies. Aquatic macroinvertebrates have long been sampled from many European watercourses, and archived samples can potentially offer substantial information on the historical trends in bioaccumulation of Hg in lower trophic levels of the foodweb.

Whereas bioaccumulation at higher trophic levels in freshwater ecosystems can be relatively well described by community composition (Stemberger and Chen, 1998) and feeding relationships (Vander Zanden and Rasmussen, 1996), factors controlling the exposure to, and transfer of, MeHg into the base of the foodweb remain poorly understood (Rolffhus et al., 2011). Bioaccumulation of MeHg is often found to be promoted by aqueous organic matter (OM) (Chasar et al., 2009), measured as total or dissolved organic carbon (TOC/DOC), but its actual pathways remain unclear and concealed by additional factors affecting food web exposure to Hg. For instance, Hg dynamics in boreal soils and lakes is intertwined with sulphur (S) dynamics. In northern Europe and eastern North America declining sulphate (SO₄) deposition in recent decades has led to increased concentrations of OM (i.e. browning) in surface waters (de Wit et al., 2007; Monteith et al., 2007). Reduced SO₄ deposition could lead to a decline in MeHg levels (Åkerblom et al., 2013) through reduced activity of methylation by SO₄ reducing bacteria (SRB) (Gilmour et al., 1992; Morel et al., 1998). Aqueous OM could also influence MeHg cycling through changes in chemical complexation (Ravichandran, 2004), especially given the increase in charge density of dissolved OM (DOM) and thus potentially increased ion-binding affinity under less acidified and low ionic-strength conditions (de Wit et al., 2007; Tipping, 2007; Tipping et al., 1991). Further, high aqueous OM protects MeHg from photochemical degradation (Poste et al., 2015). High concentrations of aqueous MeHg are often associated with high TOC (Braaten et al., 2014a; Chasar et al., 2009), but Hg bioaccumulation factors can nonetheless decline while TOC increases (Braaten et al., 2018), possibly reflecting lower bioavailability of MeHg (French et al., 2014).

Long-term, widespread environmental change such as declines in S deposition, surface water browning and climate warming may thus, in concert, affect large-scale patterns in foodweb accumulation of Hg such as those observed in Fennoscandian lakes (Braaten et al., 2019). Unravelling the role of interacting controls of MeHg in aquatic foodwebs is challenging, however, and limited by lack of comprehensive environmental datasets. Because of the strong correlation between Hg in top predators and Hg at lower trophic levels (Chasar et al., 2009), we argue that exploration of factors explaining MeHg at lower trophic levels from an intensively studied site that represents wide-spread environmental change, including lake browning, wetting and recovery from acidification, can be used to shed light on poorly-explained

regional patterns in fish Hg from lakes with limited site-specific information.

Here, we present five decades of environmental records of Hg, including data on invertebrates (Chironomids), water chemistry, sediment chemistry, and climate data from an intensely studied boreal, undisturbed lake and its catchment in southeast Norway. Chironomid larvae (non-biting midges, family *Chironomidae*), common primary consumers in freshwaters, were chosen for analyses of MeHg concentrations, as this functional group constitutes an important energy source for fish (Pothoven et al., 2000). The Chironomids were obtained from archived samples. Additionally, we present long-term fish Hg records of perch (*Perca fluviatilis*) and pike (*Esox lucius*) from other remote lakes with undisturbed catchments across southern Fennoscandia – an area that includes the intensive study site Langtjern – that has experienced similar environmental change. The study will be valuable for risk assessment of Hg levels in fish under future scenarios of climate change and S deposition.

2. Experimental

2.1. Study site

Lake Langtjern is a 0.227 km² humic headwater lake situated at 518 m.a.s.l. in southern Norway (60° 37' N, 9° 73' E), in a 4.8 km² natural catchment dominated by pine forest and peatlands. Inlet streams (south inlet LAE02 and east inlet LAE03), the outlet (LAE01) and the lake have been monitored for acid deposition impacts on water chemistry and biota since the early 1970s (Lund et al., 2018) and for Hg processes since 2004 (Larsen et al., 2008). Mean pH, TOC, total phosphorous (P), and total nitrogen (N) (2011–2015) were 5.0, 10.9 mg C L⁻¹, 4.9 µg P L⁻¹, and 268 µg N L⁻¹, respectively. In the 1960s, the original trout (*Salmo trutta*) population in Langtjern was driven to extinction by acid deposition (Lund et al., 2018). In recent years an artificially stocked trout community has been re-established in the lake. Archived samples of fish from Langtjern are not available, but a survey from 2011 documented a mean (± one standard deviation, STD) trout Hg concentration at Langtjern of 0.29 ± 0.14 mg kg⁻¹ (n = 3).

2.2. Field sampling

Littoral macroinvertebrates were sampled in October of the years 1976 to 1978, and then again yearly in the period 2004 to 2015 as part of national monitoring programmes. All samples were fixed on ethanol at the sample site and kept cold in accordance with established conservation routines at the University of Bergen. The samples were archived at the University of Bergen and analysed here for Hg. In all cases a standardised kick-sampling method with a hand net was used, from the shoreline down to 1.5 m depth on bottom substrates comprised of patchy mosaics of periphyton, particulate detritus and accumulated flocculated peaty DOC between stones and large rocks.

Sediment data come from analyses of samples cut from a 22-cm long sediment core collected in April 2016 at the deepest point of the northern basin of Langtjern (9 m) using a gravity corer. The sediment core was split in 1-cm slices (n = 22) and analysed here for Hg. de Wit et al. (2018) give details on storage, dating and chemical analysis of the sediment samples.

Water chemistry samples have been collected regularly since the early 1970s as part of the Norwegian national monitoring programme (Garmo et al., 2013). Here we use data from weekly samples of the lake outlet. Autumn (August–October) lake water grab samples for analyses of total Hg (THg) and MeHg have been collected since 2004, using 250 mL fluorinated polyethylene (FLPE) bottles and following ultra-clean handling procedures (Braaten et al., 2014b; USEPA, 1996).

2.3. Storage solution test

Possible effects over time of storage on MeHg concentrations in invertebrates were tested by use of two aquatic macroinvertebrates comprising distinct different life history patterns, the holometabolic caddisfly *Hydropsyche siltalai* (Insecta; Tricoptera), and the aquatic crustacean *Asellus aquaticus* (Crustacea; Isopoda). Samples were collected in 2015 in Tista (59° 7' N, 11° 24' E), a humic river sited in Østfold county, southeast Norway. The samples were fixed on ethanol together with litter (mostly dead leaves and pine needles) in glass vials and stored cold (+5 °C). From these vials, individuals from each species were sampled weekly during a month to quantify the effect of ethanol on MeHg concentration. After further 12 months, a final analysis was conducted (see Supplementary information (SI) for details). The archived samples were corrected for loss of lipids related to ethanol-storage (Vander Zanden and Rasmussen, 1996). In an earlier study, lipid content in fresh Chironomids from lake Langtjern amounted to 8% of total body weight (Lindholm et al., 2014), and this value was used to correct the samples from the 1970s.

2.4. Fish Hg database

Fish Hg records from 212 boreal lakes between latitudes 58° 00' N and 63° 00' N (located from 7° 92' E in Norway to 29° 38' E in Finland) were selected from a Fennoscandian fish Hg database for the period between 1975 and 2015 (for details, see Braaten et al., 2019). It was previously established that these lakes are mainly influenced by long-range atmospheric transported Hg and not by local industrial sources of Hg (Braaten et al., 2019). We focused on small perch (*Perca fluviatilis*, n = 163 lakes, n = 814 specimens, 65–95 g) as their trophic level may connect directly to Chironomids (Ahonen et al., 2018; Braaten et al., 2014c) and pike (*Esox lucius*, n = 86 lakes, n = 2142 specimens) as pike typically represents the highest trophic level in the aqueous food webs in these boreal lakes (Sandheinrich and Drevnick, 2016; Vøllestad et al., 1986).

Because fish Hg concentration covaries with fish size (length and weight, Sonesten, 2003) and age (Braaten et al., 2014c) a standardization is required to allow for further investigation of temporal trends of Hg concentrations. Here, we followed procedures described by Braaten et al. (2019). In short, individual fish weight and Hg concentration were used in combination with fish species information and sampling year to find the modelled (i.e. expected) Hg concentration for fish at a standard weight. A linear regression model was applied to describe the log[Hg] concentrations, where explanatory variables included fish weight, fish species, sampling year, and the interaction terms year × species and weight × species. Explanatory variables were chosen, evaluated, and included in the model based on significance and the Akaike information criterion (AIC). The standardised fish Hg data were used to calculate annual lake-specific medians (ALMs) for the two species. For further details, see SI.

2.5. Analytical methods

2.5.1. Invertebrate samples

For all samples of invertebrates, MeHg was extracted using an acid extraction method utilised in several previous studies (Hammerschmidt and Fitzgerald, 2005; Hintelmann and Nguyen, 2005). Here, we follow the nitric acid procedure described in Braaten et al. (2014d). Extracts were ethylated before purge/trap and gas chromatography – cold vapor atomic fluorescence spectrometry (GC-CVAFS) analysis and detection. For every batch of MeHg analysis (n = 20 samples) quality assurance and quality control (QA/QC) measures typically included method blanks (n = 3), sample duplicates (n = 2), matrix spikes (n = 2) and certified reference materials (CRMs, n = 2). The certified MeHg concentrations of the CRMs used were 152 ± 13 µg kg⁻¹ (TORT-2 lobster hepatopancreas) and 28.09 ±

0.31 µg kg⁻¹ (SRM-2976 mussel tissue). Samples that were analysed in duplicates were also used for matrix spike samples. Samples chosen for matrix spikes were added 1000 pg (0.1 mL of 10.0 ng/mL MeHg hydroxide, MeHgOH). Concentrations of MeHg in blank solutions correspond to a method detection limit (MDL, 3 standard deviations of blank concentrations) of 1 ng g⁻¹ or better. The actual MDL will vary depending on the weight of sample available for analysis but are typically in the range of 0.2–1.0 ng g⁻¹ for sample weights included in this study. MeHg recovery of matrix spikes (75–125%) and CRM (90–110%) were within expected ranges. The relative percent difference (RPD) between duplicate samples was found to be satisfactory (<20%).

2.5.2. Sediment samples

For sediment total Hg determination, we refer to details described in Lindholm et al. (2014). In short, samples were freeze dried prior to analysis. Analysis was conducted by thermal decomposition and direct atomic absorption spectrophotometry (AAS, DMA-80). For every 10 samples of Hg analysis, QA/QC measures included method blanks sample duplicates (n = 2) and CRM (MESS-3 marine sediment, certified concentration 91 ± 9 µg kg⁻¹; n = 2). The RPD of sample duplicates was always <10% and recovery of CRM within 90–110%.

2.5.3. Aqueous samples

Aqueous THg and MeHg was analysed following USEPA method 1631 (USEPA, 2002) and method 1630 (USEPA, 1998) as described in Braaten et al. (2014b), including oxidation (for THg) and distillation and ethylation (for MeHg) followed by purge/trap and CVAFS detection. All water samples were analysed unfiltered because DOC in Langtjern is ca 95% of TOC, implying low concentrations of particles (de Wit et al., 2018). Method detection levels (MDLs) were 0.02 ng L⁻¹ and 0.1 ng L⁻¹ for MeHg and total Hg, respectively (3 standard deviations of method blanks). For both aqueous Hg species, automated systems were used for analysis (Brooks Rand Instruments MERX). RSD of sample duplicates was <10% and <20% for total Hg and MeHg, respectively. Recoveries of matrix spikes were 80–120% for MeHg and 90–110% for total Hg.

Determination of TOC, SO₄ and pH was done by infrared spectrophotometry (NS-EN1484), liquid chromatography (NS-EN-ISO10304-1), and potentiometry (NS-EN-ISO10523), respectively, with limits of quantification (LOQ) of 0.1 mg L⁻¹ and 0.04 mg L⁻¹ for TOC and SO₄. Analyses were performed at the accredited laboratory at the Norwegian Institute for Water research (NIVA).

2.6. Statistical analysis

Data on MeHg in Chironomids were grouped in five 3-year periods (1976–78, 2004–06, 2007–09, 2010–12 and 2013–15), and statistical differences between group means were tested using Analysis of Variance (ANOVA). For the fish data, standardised Hg concentrations were used to calculate annual lake-specific medians (ALMs) for each fish species as described in Braaten et al. (2019). Long-term temporal trends in fish Hg concentrations were investigated through linear regression models of the ALMs. A significance level of p = 0.05 was used unless noted otherwise.

3. Results and discussion

3.1. MeHg concentrations in macroinvertebrates

Concentrations of MeHg in archived, ethanol-stored littoral Chironomid larvae from lake Langtjern show a significant decrease over time (Fig. 1). The mean concentration (± one STD) of MeHg during the period 1976 to 1978 was 45.0 ± 21.6 µg kg⁻¹, significantly higher (p < 0.005) than the four 3-year means from the period between 2004 and 2015, which ranged between 4.5 ± 5.7 µg kg⁻¹ (2013–15) and 13.7 ± 13.1 µg kg⁻¹ (2004–06). The mean for 2004–2015 was 8.5 ±

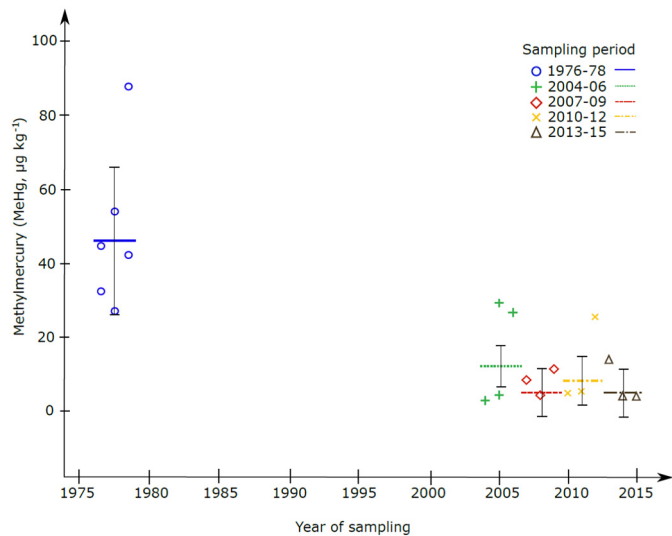


Fig. 1. Concentrations of methylmercury (MeHg) ($\mu\text{g kg}^{-1}$ dry weight) in the littoral Chironomid fauna of lake Langtjern for the periods 1976–1978 and 2004–2015. Values from the 1970s were corrected for 8% loss of body weight related to ethanol-associated loss of lipids. Mean concentrations for 3-year periods are given as horizontal lines, with vertical lines representing \pm one standard deviation of MeHg concentrations for the period.

$9.4 \mu\text{g kg}^{-1}$ and the individual group means in this period were not significantly different. A laboratory test was undertaken to evaluate potential effects of long-term storage on MeHg invertebrate concentrations. The test demonstrated that storage in ethanol had no effect (details in SI).

An uncertainty for the interpretation of long-term trends of MeHg in Chironomids is a possible alteration of species composition in the lake associated with altered environmental conditions such as the acidification and recovery at Lake Langtjern during the past 50 years, with implications for trophic position. Chironomid communities often display considerable variation in the stable N isotope (Grey et al., 2004; Jones et al., 2008), possibly related to changes in trophic position and thus

for bioaccumulation of MeHg (Post, 2002). However, change in stable isotope signals are solely observed among certain species adapted to profundal of eutrophic lakes (Saether, 1979). Our taxonomic resolution did not allow for determination of species shifts over this time, but the species composition of littoral Chironomid communities in humic lakes exposed to acidification is generally stable. Hynynen and Merilainen (2005) compared Chironomid diversity in 29 Finnish lakes before, during and after the post-war decades of acidification, and reported only weak responses along the pH gradient, and found high structural similarities between present and past Chironomid assemblages. Lake Langtjern is nutrient-poor as it is located on base cation poor geological deposits typical for large parts of southern Norway. Further, there has been no catchment disturbance since the 1950s, which implies that catchment inputs of N and P have been low and that aquatic biota in the lake have not experienced major changes in diet. pH has increased from 4.8 to 5.1 (Fig. 2), illustrating limited chemical recovery (Lund et al., 2018), as observed elsewhere in southern Fennoscandia (Garmo et al., 2014). The observed increase falls within the pH gradient of the 29 Finnish lakes referenced above, implying that major shifts in the Chironomid community related to pH changes are unlikely to have occurred. We conclude that the observed decline in MeHg in Chironomids (Fig. 1) is unlikely to be related to changes in species composition.

To our knowledge, this is the first long-term record of MeHg in aquatic organisms at low trophic levels from an undisturbed, boreal lake. Because of the lack of local Hg sources – atmospheric long-range transportation is the main source of Hg at Langtjern – and absence of local factors that can explain the long-term decline of MeHg in Chironomids we observe here, we hypothesize that the observed decline is related to changing 1) catchment loading of Hg; 2) MeHg production; and/or 3) MeHg bioavailability.

3.2. Sediment and catchment loading

Concentrations of Hg and Hg-to-C ratios in sediment at Langtjern show little variation in the historical period between approximately year 1300 and 1900 (Fig. 3). After the pre-industrial period, both Hg and Hg-to-C ratios rise distinctly from $98 \pm 11 \mu\text{g kg}^{-1}$ (pre-1900 mean \pm one STD) to $322 \pm 18 \mu\text{g kg}^{-1}$ (post-2000 mean \pm one STD),

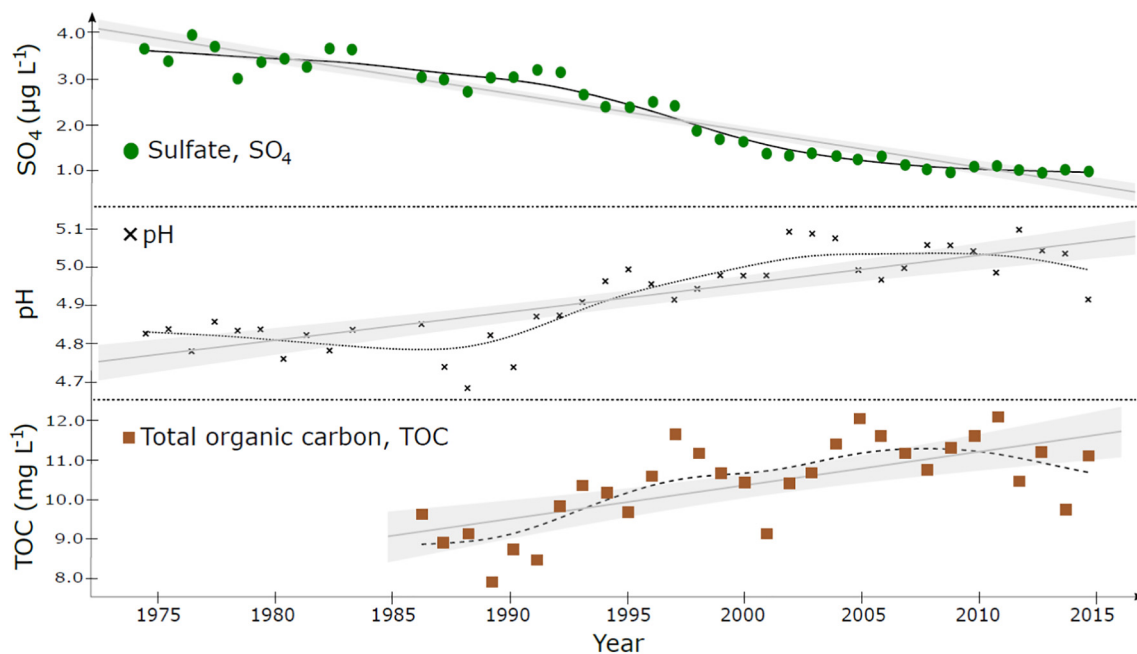


Fig. 2. Mean annual aqueous concentrations of (from top) sulphate (SO_4 , green circles, $\mu\text{g L}^{-1}$), pH (black crosses), and total organic carbon (TOC, brown squares, mg L^{-1}) from lake Langtjern. For the aqueous concentrations are shown the linear regression for the full period of data available (grey lines with 95% confidence intervals) and smoother lines as unbroken (SO_4), dotted (pH), and broken (TOC) lines.

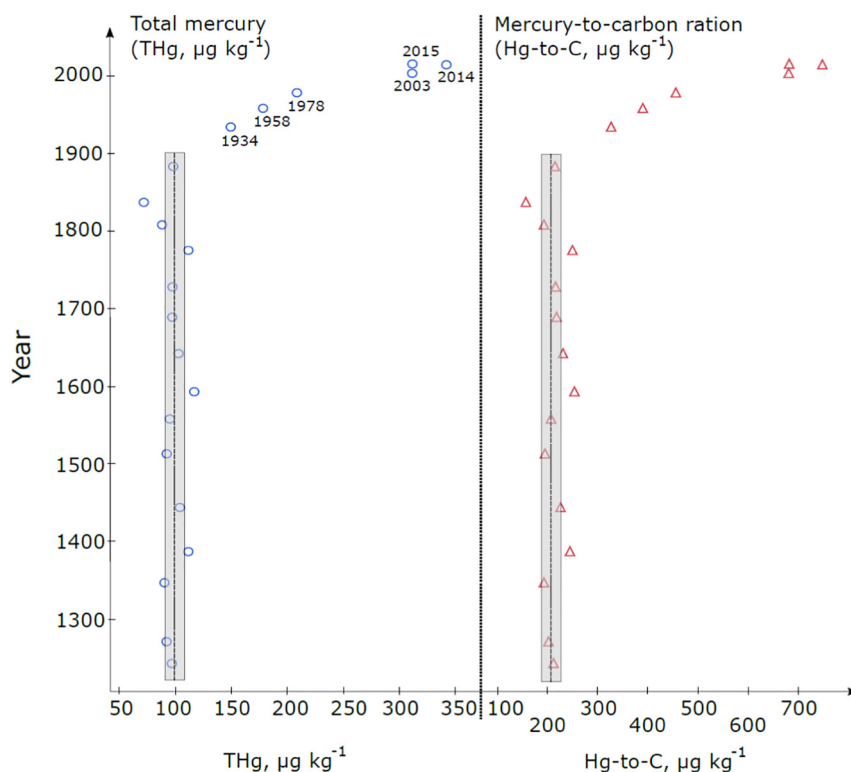


Fig. 3. Total mercury (THg, $\mu\text{g kg}^{-1}$, blue circles, left panel) concentrations and mercury-to-carbon ratio (Hg-to-C, $\mu\text{g kg}^{-1}$, red triangles, right panel) in a Langtjern sediment core. Shown on the y-axis is years, while numbers indicated on the THg core is determined sediment age for the top 6 samples (>year 1900) (the total depth of the collected core was 21 cm). Indicated as dotted vertical lines are the mean \pm one standard deviation (in shaded grey) levels in sediment from before year 1900: $98 \pm 11 \mu\text{g kg}^{-1}$ and $214 \pm 25 \mu\text{g kg}^{-1}$ for THg and Hg-to-C ratio, respectively.

and from $214 \pm 25 \mu\text{g Hg kg}^{-1} \text{ C}$ to $704 \pm 38 \mu\text{g Hg kg}^{-1} \text{ C}$, respectively (Fig. 3). Such temporal patterns in sediment Hg, and close correlations between Hg and C, in Fennoscandian lakes have been documented previously (Munthe et al., 2007). The Hg increases in Fennoscandian lake sediments were attributed to increased atmospheric deposition of Hg. Note that the increase in sediment Hg contrasts with the decline in MeHg in biota at Langtjern, and with observed declines in Hg in Fennoscandian fish populations.

Increased atmospheric deposition of Hg may not be the only possible explanation for the increased sediment Hg, especially in a headwater lake with a high catchment-to-lake ratio where element loading is typically strongly controlled by catchment inputs. Annual runoff at Langtjern increased significantly since the start of the record in 1974 (linear regression, $p < 0.05$; data in SI). The increase in annual runoff was 38% when comparing the period 2011–2015 ($798 \pm 86 \text{ mm}$, mean \pm one STD) with 1974–1978 ($577 \pm 164 \text{ mm}$) and fits regional patterns of trends in annual runoff in eastern Norway (Hanssen-Bauer et al., 2017).

Catchment element loading and discharge are highly correlated. At Langtjern, TOC concentrations (Fig. 2), TOC export and discharge all had positive trends (de Wit et al., 2018; flux and discharge data shown in SI). The trend in TOC export was mostly driven by the upward trend in TOC concentration. The 25% increase in TOC concentrations (Fig. 2) agrees with widespread observations of lake browning in northern Europe (Monteith et al., 2007) and Fennoscandia (de Wit et al., 2016), and is primarily a consequence of the decline in S deposition (de Wit et al., 2007), and secondarily in response to increased precipitation (de Wit et al., 2018), associated with climate change. The decline in S deposition has driven the four-fold decline in SO_4 concentrations from 3.5 ± 0.4 (annual mean \pm one STD, 1974–1978) to $0.8 \pm 0.1 \text{ mg S L}^{-1}$ (2011–2015) found in the lake outlet (Lund et al., 2018) (Fig. 2). The Langtjern data are an example of typical patterns in surface water chemistry in acid-sensitive catchments in Fennoscandia and eastern

North America (Garmo et al., 2014; Driscoll et al., 2016) related to chemical recovery from acid deposition.

Because DOM is the most important transport vector of Hg from catchment soils to lakes (Ravichandran, 2004), it is likely that the increase in TOC concentrations and export has increased the Hg loading to lake Langtjern since the beginning of the 1970s. This is substantiated by the strong correlations between THg and TOC in both inlet streams ($r^2 = 0.41$, $n = 90$, and $r^2 = 0.40$, $n = 119$, both $p < 0.0001$, monthly data from 2008 to 2015) (Fig. 4, Table 1). The annual catchment export record in THg and MeHg (2004–2015) show primarily variation related to discharge and is too short to contribute to the explanation of the long-term sediment records (data shown in SI).

3.3. Interactions between Hg and DOM

While all evidence suggests that Hg and TOC transport are strongly related, the increase in sediment Hg-to-C since the 1900s (Fig. 3) is a strong indicator that, relatively, the increase in Hg loading to the lake exceeded the TOC loading. Regular monitoring of aqueous Hg started in 2008 and concentrations of THg and MeHg in the lake outlet showed no significant trends (Fig. 5). However, a weakly significant increase in the THg-to-TOC ratio ($p < 0.1$, Fig. 5) was found, consistent with the directional change in the Hg-to-C ratio in the sediments, albeit for a much shorter time period. There is no evidence to support increases in atmospheric loading of Hg to northern Europe, rather the contrary (Tørseth et al., 2012). Thus, the increase in Hg-to-C ratio in the sediments (Fig. 3) must have another explanation. Possibly, the Hg binding affinity by DOM has increased, as a result of a change in DOM character (Fakhraei and Driscoll, 2015). de Wit et al. (2007) demonstrated an increase in charge density of the DOM over time, as a consequence of gradual deprotonation of carboxylic groups from a combined effect of pH increases and ionic strength decreases, which is in agreement with physical-chemical models of metal binding by humic acids. Theoretically, it is especially hydrophobic, large-

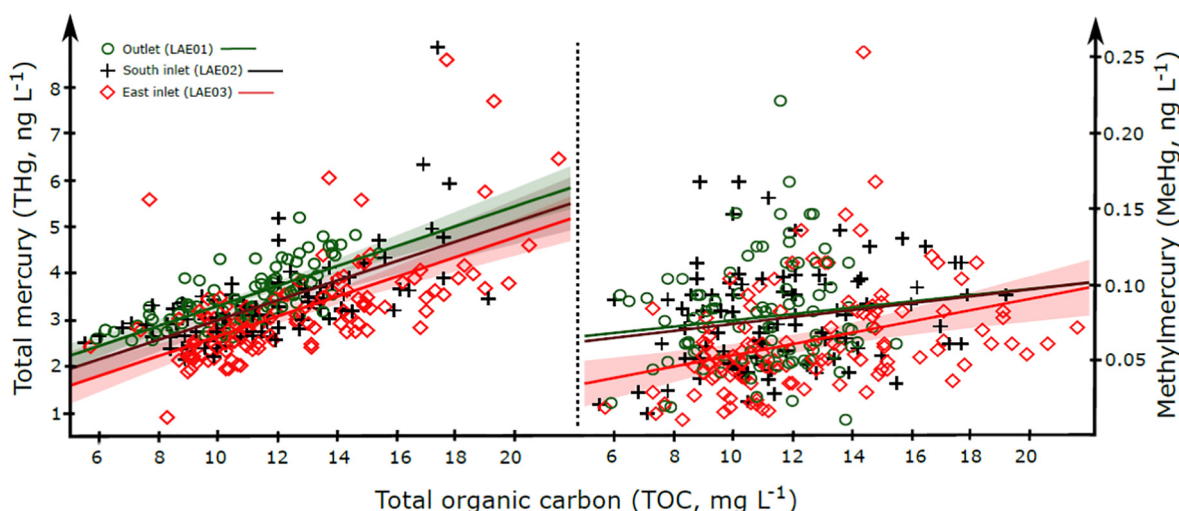


Fig. 4. Scatter plots showing the aqueous concentrations of total mercury (THg, left panel, ng L^{-1}) and methylmercury (MeHg, right panel, ng L^{-1}) versus aqueous concentrations of total organic carbon (TOC, x-axes, mg L^{-1}) for the lake Langtjern outlet (LAE01, green circles) and the two inlets (south inlet LAE02, black plus symbols and east inlet LAE03, red diamonds). The linear regressions are shown as continuous lines in green (LAE01), black (LAE02) and red (LAE03) with the 95% confidence intervals as shaded areas for the significant relationships ($p < 0.05$, Table 1). Data includes monthly or more frequently measurements between 2008 and 2015, and a summary of regression statistics is shown in Table 1.

molecular weight DOM (humic acids) which is responsible for the change in charge density because more hydrophilic, low-molecular weight DOM (fulvic acids) are expected to have been fully deprotonated at the reigning chemical conditions during the 1970s. The reactive groups discussed in de Wit et al. (2007) are carboxylic groups, which are not primarily responsible for binding of Hg. However, thiol-groups are subject to the same protonation-deprotonation interactions as carboxylic groups. Thus, a case can be made for enhanced Hg-complexation by DOM since the 1970s.

Supporting evidence for a change in DOM character since the 1970s can be found in data from drinking water plants in southeast Norway, where the colour-to-DOC ratio increased over time for the period 1983–2001 (Hongve et al., 2004). This suggests that DOM character has changed in addition to the change in DOM quantity, including at Langtjern where long-term colour data are not available. The drinking water reservoirs included in Hongve et al. (2004) are located in forested, undisturbed catchments in southeast Norway ($\sim 59^\circ \text{N}$, 10°E) and have been exposed to S deposition and climate change, and their browning records fit regional patterns of browning (de Wit et al., 2007; Monteith et al., 2007), suggesting that a widespread change in DOM character may have occurred alongside the widespread increases in TOC.

Table 1

Summary of regression statistics for the aqueous mercury (total, THg, and methylmercury, MeHg) concentrations versus total organic carbon for the Langtjern monitoring stations LAE01 (outlet), LAE02 (south inlet) and LAE03 (east inlet). Scatter plots are shown for concentrations of THg and MeHg versus concentrations of TOC in Fig. 2. Data includes monthly or more frequent measurements between 2008 and 2015.

Station	r^2	p	n
[THg] versus [TOC]			
LAE01	0.53	<0.0001	95
LAE02	0.41	<0.0001	90
LAE03	0.40	<0.0001	119
[MeHg] versus [TOC]			
LAE01	0.02	0.24	95
LAE02	0.04	<0.06	90
LAE03	0.12	<0.001	119
[MeHg] versus [THg]			
LAE01	<0.01	0.90	95
LAE02	<0.01	0.82	90
LAE03	0.02	0.13	119

3.4. Environmental controls of MeHg production

Several experimental studies have shown that addition of SO_4 increases methylation rates and MeHg concentrations in wetlands (Bergman et al., 2012; Coleman Wasik et al., 2015; Jeremiason et al., 2006), and that SO_4 concentration is a more important control of production of MeHg than Hg concentrations (Bergman et al., 2012). Branfireun et al. (2001) documented a six-fold increase in MeHg concentrations in peat pore-water during a three-year study in which additions of SO_4 were equivalent to 1980s levels in southern Sweden. Bergman et al. (2012) found a doubling of MeHg concentrations in pore water from $0.6 \pm 0.02 \text{ ng L}^{-1}$ to $1.3 \pm 0.08 \text{ ng L}^{-1}$ between areas with low ($3 \text{ kg ha}^{-1} \text{ year}^{-1}$) and high ($17 \text{ kg ha}^{-1} \text{ year}^{-1}$) S deposition. Previous work from Langtjern sub-catchments demonstrated an inversely correlated relationship between MeHg and SO_4 in porewater ($r^2 = 0.26$, $p = 0.0017$, unpublished, see data in SI) indicating substrate-limited MeHg production. At the Langtjern outlet, the MeHg-to-THg ratio, a proxy for methylation potential (i.e. an indicator of the environment's capability to produce MeHg (McClain et al., 2003; Mitchell et al., 2008)), show a weakly significant decrease ($p < 0.1$, Fig. 5). Higher MeHg production at Langtjern during the 1970s is consistent with higher SO_4 availability during that time (Fig. 2) and would provide an explanation for the elevated MeHg in Chironomids in the 1970s (Fig. 1).

The production of MeHg occurs primarily through methylation by SRB (Morel et al., 1998), which is affected by the availability of SO_4 , inorganic Hg and labile OM, as well as temperature (T) and pH (Ullrich et al., 2001). Experimentally, it has been shown that redox states play a less important role for methylation than DOC-to-Hg ratios (Frohne et al., 2012). As summarised by Paranjape and Hall (2017), the effects of pH on methylation is unclear. Examples from literature demonstrate both that the highest levels of methylation are associated with low pH (e.g. Ullrich et al., 2001) and that MeHg-to-THg ratios are positively correlated to pH (Pennanen et al., 1998; Braaten et al., 2014a, 2014b, 2014c, 2014d). Given that pH-impacts on methylation are unresolved, it is difficult to evaluate which effect the small increase in pH may have had on methylation in the Langtjern catchment.

A moderate warming trend has occurred at Langtjern, where the T has increased 1.25°C between 1971 and 2015 (Couture et al., 2015). The increase in T has led to an 8-day extension of the ice-free season. Application of a process-based lake model suggests that higher T and

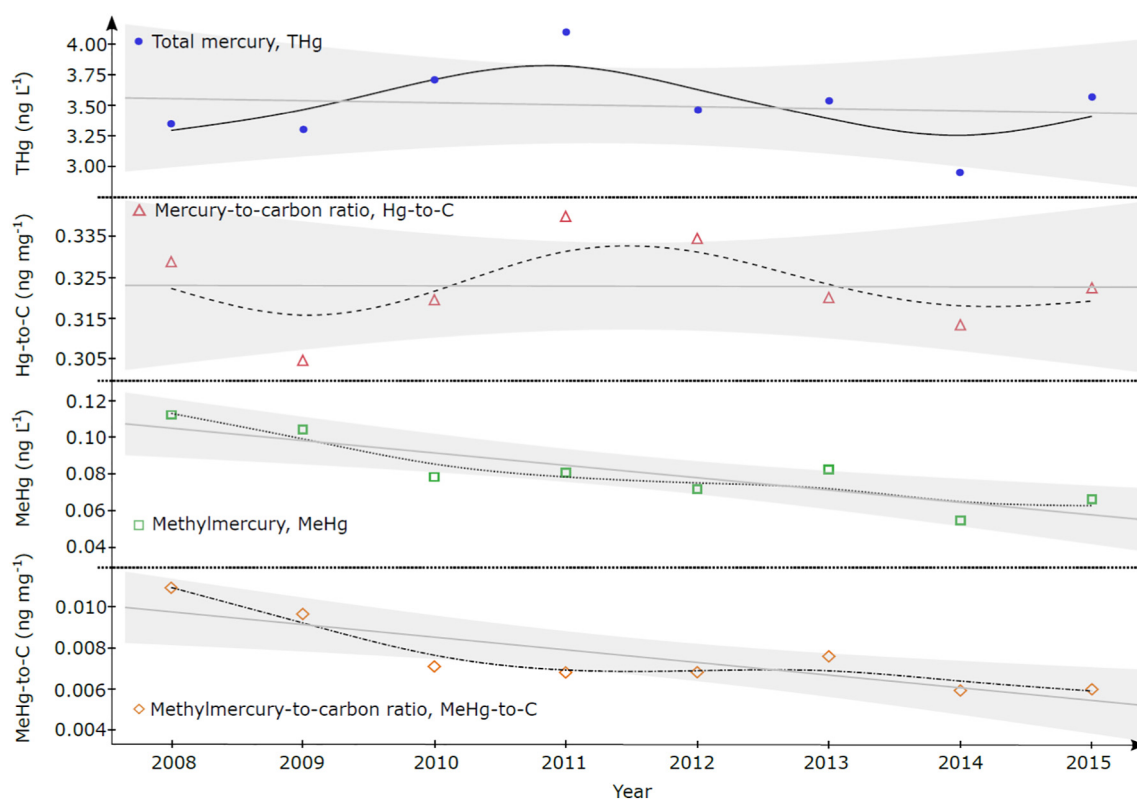


Fig. 5. Mean annual aqueous concentrations of (from top) total mercury (THg, blue circles, ng L^{-1}), Hg-to-carbon ratio (Hg-to-C, red triangles, ng mg^{-1}), methyl-Hg (MeHg, green squares, ng L^{-1}), and MeHg-to-C ratio (MeHg-to-C, orange diamonds, ng mg^{-1}) from the lake Langtjern outlet. Shown are mean annual concentrations from monthly measurements between 2008 and 2015. For the aqueous concentrations are shown the linear regression for the full period of data (grey lines with 95% confidence intervals) and smoother lines as unbroken (THg), broken (Hg-to-C ratio), dotted (MeHg), and broken dotted (MeHg-to-C ratio) lines.

higher TOC have led to a 10% longer period with hypolimnetic anoxia (Couture et al., 2015), possibly leading to enhanced bacterial metabolism in lake sediments and associated increased methylation (Ullrich et al., 2001). However, both methylation and de-methylation are microbial, T-dependent processes (Creswell et al., 2017) suggesting that a T increase may not automatically lead to increases in net production of MeHg. In a multifactorial field experiment, the stimulating effect of SO_4 addition on methylation was found to be counteracted by warming (Åkerblom et al., 2013). Considering the environmental trends at Langtjern, the Åkerblom et al. (2013) study would imply that the effect of reduced SO_4 on methylation would be strengthened by warming.

We suggest that the response, i.e. the decline of MeHg in the aquatic foodweb, is likely to be proportional to the size of the changes in the environmental drivers. Thus, the 80% decline in SO_4 concentrations – directly controlling methylation rates through substrate availability – appears to be a more likely factor than the more moderate changes in temperature and ice cover – which could increase both methylation and de-methylation rates.

3.5. MeHg bioavailability in relation to TOC

Changes in DOM character may have contributed to the increased sediment Hg found at Langtjern (Fig. 3) through an increase in binding affinity for Hg. Recent studies show that increased concentrations of aqueous TOC (or DOC) may inhibit bioaccumulation of MeHg in both lower trophic level biota (amphipods, French et al., 2014, Chironomidae, Chaves-Ulloa et al., 2016) and fish (perch (*Perca fluviatilis*), Braaten et al., 2018, brook trout (*Salvelinus fontinalis*), yellow perch (*Perca flavescens*), creek chub (*Semotilus atromaculatus*), Broadley et al., 2019, and yellow perch, Driscoll et al., 1994) through reduced Hg availability for uptake, which would be consistent with a higher binding affinity

for Hg by DOM. French et al. (2014), Chaves-Ulloa et al. (2016), Braaten et al. (2018), Broadley et al. (2019) and Driscoll et al. (1994) suggest thresholds at 8.6, ~5, 5.8, ~10 and ~8 mg C L^{-1} , respectively, where increased accumulation occurs below this limit and reduced accumulation above. The decline in bioaccumulation (measured as MeHg concentrations in biota divided by MeHg concentrations in water) with increasing TOC suggest that increased OM is associated with higher aqueous Hg concentrations, but lowers relative MeHg bioaccumulation because more OM is available to bind MeHg and more OM is present as larger less bioavailable molecules (Braaten et al., 2018). In lake Langtjern, aqueous TOC concentrations have increased from $8.8 \pm 0.6 \text{ mg C L}^{-1}$ (mean \pm one STD) to $10.9 \pm 0.9 \text{ mg C L}^{-1}$ from 1986–1990 to 2011–2015 (Fig. 2), which implies a net negative effect on Hg bioaccumulation provided that the threshold TOC concentration is around 8 mg C L^{-1} . Thus, browning has the potential to reduce MeHg uptake at the bottom of the foodweb.

3.6. Large-scale environmental drivers affecting MeHg bioaccumulation

Declining S deposition leading to reduced MeHg concentrations in littoral invertebrates at Langtjern, an oligotrophic, undisturbed lake typical of boreal catchments in Fennoscandia is relevant also at a larger regional scale to explain the widespread decline in concentrations of Hg in fish in Fennoscandia the past 50 years (Åkerblom et al., 2014; Braaten et al., 2019). The perch and pike records for 1975–2015 in undisturbed lakes in the southern part of Norway, Sweden and Finland (strongly impacted by S deposition and its decline) showed significant declines of almost 50% (perch) and 20% (pike) in Hg concentrations (Fig. 6), similar to the declines for the whole of Fennoscandia (Braaten et al., 2019). Thus, there is a synchronous long-term decline of Hg in in low (Fig. 1), intermediate and high (Fig. 6) trophic level aquatic organisms of

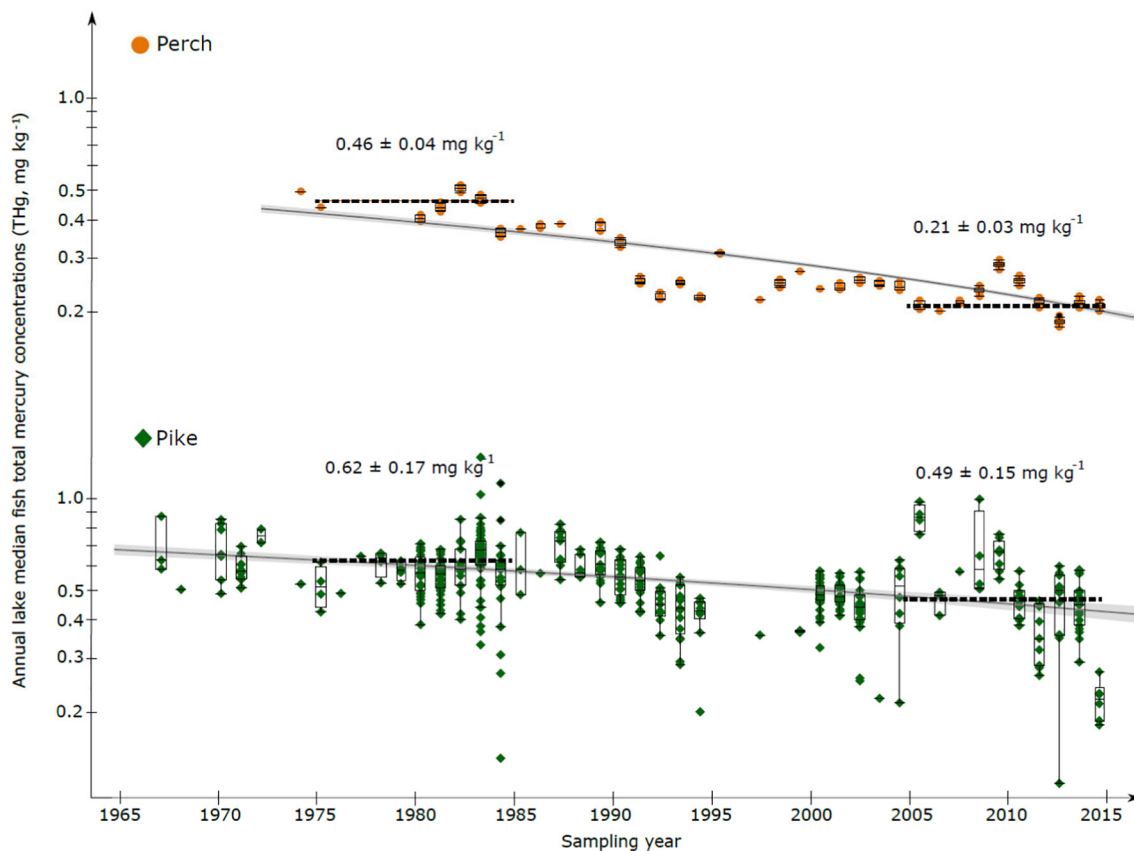


Fig. 6. Annual lake median (ALM) concentrations of mercury (Hg) (wet weight, ww) in perch and pike from lakes mainly influenced by long-range atmospheric transport of Hg. Box plots show median value, 25 and 75% quartiles, and minimum and maximum value each year. Individual lakes are shown as orange circles and green triangles for perch (top panel) and pike (lower panel). The overall trends (1965–2015) are presented as a linear regression (solid black line) with 95% confidence intervals (in grey). For the separated periods 1975–85 and 2005–15, the mean concentrations for the periods (dotted horizontal lines) are shown.

pristine boreal lakes. We are not aware of other documentation of long-term trends in lower foodweb organisms in similar ecosystems.

Long-term fish records from individual-lake studies are scarce and the ones that exist do not include five decades of data. The strength in the fish records presented here is the number of specimens per lake per year and the large number of lakes ($n = 163$ lakes with perch, $n = 86$ lakes with pike), providing a robust result. The strength in the Chironomid record is that these organisms originate from the same lake and have been sampled according to the same routines over time. As macroinvertebrates are an important energy source for fish (Pothoven et al., 2000), these records suggest a mechanistic link between changes in the abiotic environment (Figs. 2–5) and the decline in fish Hg the last decades (Fig. 6). The consistent trends at different trophic levels is conspicuous and in line with the widely accepted notion that Hg at higher trophic levels is strongly determined by MeHg uptake at the base of the food web (Chasar et al., 2009).

Other support for the control of SO_4 deposition on MeHg is found outside of Fennoscandia, presenting data of sediments and fish but lacking the base of the food web (Drevnick et al., 2007). In a study of pike (*Esox lucius*) populations from freshwater lakes on an island in Lake Superior in North America, Drevnick et al. (2007) documented significantly decreasing Hg concentrations between the mid-1990s and 2004–2006. As the authors could find no change in lake productivity or water quality, pike trophic position or growth rates, climate, landscape or Hg deposition in this time period, they hypothesized that declining Hg concentrations in fish were related to reduced rates of SO_4 deposition (Drevnick et al., 2007). Although the study did not link Hg concentrations in fish to lower trophic levels as we have done here, the authors showed that sediment concentrations of chromium-

reducible SO_4 (the end product of sulphide produced from reduction of SO_4) were significantly positively related to pike Hg concentrations ($r^2 = 0.79$) (Drevnick et al., 2007).

The strength of the present study lies in combining local in-depth data from the well-studied Langtjern with large-scale eco-regional trends, in the search for a better mechanistic understanding for the latter. We argue that the undisturbed, boreal lake Langtjern and its catchment can be used as a model to explain the regional fish Hg trends observed in the Fennoscandian dataset because it represents widespread environmental change, including lake browning (Garmo et al., 2014), wetting (de Wit et al., 2018) and recovery from acidification (Lund et al., 2018), and is data-rich, which allows for a detailed investigation of environmental drivers and determinants observed across climate regions. To bridge the gap between intensively studied sites and synoptic sampling campaigns for understanding of Hg in the environment, future fish surveys would benefit from additional collection of water chemistry and lower foodweb organisms. For intensively studied sites with long-term data records, sediment collection should include dating and Hg speciation. Also, more focus is needed on impacts of acidification on DOM quality and binding affinity, and the relation between DOM binding affinity and methylation rates.

4. Conclusions

The decline in MeHg at the base of the aquatic food web (Chironomids) contrasts with the increased concentrations of Hg found in the Langtjern sediments. Our findings support the hypothesis that methylation by SRB today is far more substrate-limited than previously, as a consequence of a significant decline in SO_4 deposition. Substrate

limitation implies that hotspots of Hg methylation (wetlands and lake sediments) now produce far less MeHg and that consequently, the base of the foodweb is exposed to lower MeHg than during the 1970s, resulting in a decline of Hg in fish. An additional factor may be the reduced bioavailability of Hg because of enhanced complexation between OM and Hg. Interestingly, browning and wetting have in concert led to increased Hg loading to lakes – even with constant Hg deposition – but not to higher Hg in foodwebs. Our conclusions imply that an unintended effect of the clean air policies which reduced SO₄ emissions has been to lower bioaccumulation of Hg. If factors impacting net MeHg production are more crucial for aquatic foodweb Hg levels than loading of Hg itself, the Minamata Convention may be less effective than hoped for in efforts to reduce Hg in fish, at least in the short term. The potential for further reductions in SO₄ emissions to the atmosphere is limited in Europe and North America, suggesting that the importance of SO₄ for Hg in foodwebs will decrease in the future. For future levels of Hg in aquatic biota, policy controls such as the Minamata Convention and the role of legacy Hg in the environment will be important.

Declaration of competing interest

We declare no conflict of interest.

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Appendix A. Supplementary data

Additional information referenced in the main text includes a detailed summary of the ethanol storage test, details of analytical methods for sediment and water, background information on the Fennoscandian fish Hg database, Langtjern outlet TOC and Hg chemistry, and peatland porewater MeHg and SO₄ concentrations. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.136774>.

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