

Mercury in soil, sediment, and lake water in upland headwater catchments in Ireland

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Abstract

Mercury concentrations in the atmosphere, surface waters, and soils have increased beyond natural levels as a result of human activities, which poses a risk to human and environmental health. Ireland is situated on the western periphery of Europe, and it is generally assumed that environmental mercury is low but there is limited information on mercury within natural environments. In this study the interlinkages in the concentration of mercury in soils, lake sediment, and lake water were investigated in remote upland acid-sensitive catchments influenced by low deposition of atmospheric mercury. Thirty-one upland lake catchments were sampled for topsoil, lake sediment, and lake water during 2017–2018. Total mercury (THg) concentrations in water (median 5.4 ng/L) and sediment (median 30 ng/g) were low, owing to the remote location of the lakes. In contrast, THg in catchment soil was relatively high for a background region (median: 240 ng/g), which was attributed to the high organic matter content of the soil (median 87%). The results suggest catchment soils are the dominant driver of variation in THg in lake water and sediment in upland regions in Ireland. Further, given that highly organic soils can obscure interlinkages within catchments, this study demonstrated the value of exploring mercury independent of the influence of organic matter, i.e., THg normalized by organic carbon. As global action (such as the Minamata Convention) decreases mercury emissions, legacy soil mercury may become a more important input to aquatic systems than atmospheric deposition, which makes the relationships between terrestrial catchments and their water bodies vital for our understanding of mercury cycling.

Introduction

Mercury is a metal found in the earth's crust that is emitted into the atmosphere through natural (e.g., volcanic eruptions) or anthropogenic (e.g., burning fossil fuels) means. Globally, human activities have caused mercury concentrations to increase beyond natural levels in the atmosphere, surface waters, and soils (AMAP and UNEP 2019). This is a concern because mercury is a neurotoxin, and it can also cause damage to the digestive and immune systems; the World Health Organization named mercury as one of the top ten chemicals of concern due to its extreme effects on human health (WHO 2017). Mercury can occur in elemental, inorganic, and organic forms based on its binding to other elements. Historically, mercury has been of greatest concern within aquatic environments where it can be methylated by anaerobic sulphate reducing bacteria, allowing mercury to bioaccumulate in organisms, and biomagnify up the food chain (Hsu-Kim et al. 2013; Ruus et al. 2015). The increase in environmental mercury concentrations have prompted global concern, notably leading to the United Nation's Minamata Convention on Mercury, which entered into force on August 16, 2017 (UNEP 2019).

One goal of the Minamata Convention is to improve understanding of the cycling, transport, and fate of mercury in natural environments (UNEP 2019). This reflects a shifting paradigm in the study of natural resources, where interconnections are emphasized. For example, the Resource Nexus encourages an approach that considers the many interlinkages between natural resources (e.g., air, water, soils) in contrast to the past when they were considered independently (EEA, 2022; Bleischwitz et al., 2018). One part of the resource nexus that is particularly relevant for mercury is the interlinkages between the

atmosphere, hydrosphere, and pedosphere. It is well-established that atmospheric deposition of mercury can introduce anthropogenic mercury pollution to aquatic and terrestrial ecosystems globally, no matter how remote (e.g., Zdanowicz et al. 2016; Aslam et al. 2019; Yang et al. 2010). Further, the movement of mercury from soils into aquatic systems through natural processes, such as soil erosion and leaching, can increase mercury concentrations in surface waters and sediments (Rose et al. 2012; Stoken et al. 2016).

The cycling of mercury is impacted by a variety of factors, organic matter content being the most notable within aquatic and terrestrial ecosystems (Watras et al. 1995; Tipping et al. 2011). Mercury binds to organic matter (Ravichandran 2004; Lavoie et al. 2019), and therefore the movement of terrestrial organic matter into an aquatic system (i.e., erosion or leaching) also has implications for mercury cycling (Yang and Smyntek 2014; Rose et al. 2012). This mechanism may become increasingly important as atmospheric mercury emissions are reduced globally, and terrestrial mercury (built up in catchment soils from decades of pollution) becomes the dominant controlling input of mercury to aquatic systems (Yang et al., 2016; Rose et al., 2012). Measuring the bulk concentration of mercury in all forms (elemental, inorganic, organic) is generally referred to as total mercury (denoted as THg). The positive relationship between THg and organic matter in surface waters, often measured as dissolved organic carbon (DOC), is well established (Lavoie et al. 2019), and has been widely observed (Watras et al. 1995; Burton and Aherne 2012; Braaten et al. 2014).

The Republic of Ireland is a signatory of the Minamata Convention, but there is limited data or knowledge of mercury concentrations or cycling within natural environments. It is generally assumed that environmental mercury concentrations are low and below detection for routine monitoring. Ireland sits on the western periphery of Europe and is considered a background region for atmospheric pollution (Leinert et al., 2008; Custodio et al., 2020). The prevailing wind direction is south-westerly, which brings in relatively clean air masses from the Atlantic Ocean, so atmospheric concentrations of mercury in Ireland are generally low ($\approx 1.3 \text{ ng/m}^3$ 2013–2018; Custodio et al. 2020).

The few studies that have measured environmental mercury in Ireland have primarily focused on a small number of study sites (e.g., Coggins et al. 2006; O'Halloran et al. 2003) or the measurement of air concentrations at Mace Head atmospheric research station (e.g., Weigelt et al. 2015; Custodio et al. 2020). An exception is a study of 54 lakes (Burton et al. 2013), with a subset of five sampled for catchment soil (Scott and Aherne 2013), which suggested associations between water and soil variables, but the exploration was limited owing to the small sample size. The objectives of this study were to investigate the interlinkages of mercury in soils, lake sediment, and lake water in upland acid-sensitive catchments in Ireland ($n = 31$) impacted by long-range atmospheric mercury pollution, and to contribute to the limited data on mercury in Irish natural environments, fulfilling some of the goals of the Minamata Convention.

Materials And Method

Study Sites

Ireland has a relatively mild climate due to the influence of the Atlantic Ocean, with inland daytime temperatures generally ranging from 8°C in the winter to around 20°C in the summer (Met Éireann 2020). The prevailing wind direction is south-west, leading to greater annual rainfall in the west, which receives 1000–1400 mm, compared to 750–1000 mm in the east. In the mountainous regions of Ireland, rainfall tends to be greater, with some areas receiving 2000 mm or more per year (Met Éireann 2020).

During April–July 2017 and 2018, 31 upland acid-sensitive lakes in Ireland were sampled to determine the concentrations of THg in lake water, lake sediment, and catchment topsoil (Fig. 1). Irish uplands are generally undeveloped areas at elevations greater than 150 m above sea level (masl) along the coast margins, comprising habitats such as heaths, semi-natural grasslands, and bogs, and predominately used for rough grazing (Perrin et al. 2014). Soils within the upland catchments are shallow and tend to be highly organic with greater exposed rock in the southern catchments (Supplementary Information Fig. SI-1). The dominant soil type is peat or peaty podzols (Teagasc and EPA 2015), which is generally underlain by slowly weathering base-poor geologies, such as granite, quartzite, schist, and gneiss (Bowman 1991; Aherne et al. 2002).

Ireland is home to more than 12 000 lakes; in the upland areas these lakes tend to be small precipitation-fed headwaters. Upland lake catchments are relatively un-impacted by development or local pollution owing to the rough landscape. The 31 study lakes were selected from a set of lakes sampled in 1997 to assess the impacts of long-range transboundary air pollution (Aherne et al. 2002) and re-sampled in 2007 and 2008 (Burton and Aherne 2012; Scott and Aherne 2013); the dominant inputs of mercury pollution to the study lakes are from long-range atmospheric transport. The lakes in the 1997 study were selected using stratified random sampling, with greater weighting on high elevation lakes in acid sensitive regions (Aherne et al. 2002). In the present study, the lakes were selected to ensure spatial coverage of all sampled regions, with preference for higher elevation sites (median elevation 476 masl), to limit the effects of local disturbance (Nelson and Aherne 2020). The study lakes are small (median: 1.6 ha) in small catchments (median: 11 ha) and were assumed to be representative of the ‘average lake’, as 88% of all lakes in Ireland are less than five hectares (EPA 2006).

Field Sampling

Lake water samples were collected from the shore, approximately 15 cm below the surface in an area free from emergent vegetation. The lakes are small, shallow, and well-mixed by wind; therefore, shore samples were assumed to be representative of the entire lake. Prior to collection, the sample container was rinsed three times with lake water, and rinse water was poured onto the shore to avoid disturbance of sediment. At each lake, two 30 mL water samples were collected in 40 mL glass I-Chem vials and acidified with 0.5% HCl for THg analysis. Precautions were taken to limit potential contamination during sampling; vials were individually double bagged, and gloves were worn when handling the vial and inner bag during sampling. Field blanks were used to test for contamination during sample collection or from the vials

themselves. A 250 mL unfiltered bulk water sample was also collected for all remaining chemical tests (e.g., DOC, pH, conductivity).

Lake sediment was also sampled from shore, using a stainless-steel trowel. The top 5–10 cm of sediment was collected at three randomly selected locations along the lake edge, mixed, and stored in a 250 mL glass jar as a composite of the three locations. Sampling of sediment was attempted at all 31 sites, however rocky lake bottoms prevented sediment collection at three of the lakes.

Soil was collected at three randomly selected locations around the perimeter of the lake, within 10 m of the shore. Vegetation was removed, and the top 5–10 cm of soil was collected. A composite of the three locations was stored in a 250 mL glass jar, consistent with the sediment. At each of the three locations a bulk density core (radius 5 cm, height 5 cm) was also collected and stored in individual Ziploc bags.

Samples were kept cool and transported to Trent University for analysis. Prior to sampling, vials for THg (Glass I-Chem with Teflon-lined caps) were cleaned in 10% BrCl/HCl bath (v/v) for 48 hours, triple rinsed with reverse osmosis water, once with b-pure water, and oven dried (> 100°C). All other sample containers were soaked in a 10% HCl bath for 24 hours, triple rinsed with reverse osmosis water, once with b-pure water, and then air dried.

Laboratory analysis

The water samples were analyzed for THg on a Tekran 2600 mercury analyzer, using US EPA method 1631. The samples for DOC were filtered using 0.45 µm disposable nylon syringe filters and measured on a Shimadzu TOC Analyzer. Conductivity and pH were determined on unfiltered samples using a Mantech PC-titrate.

The composite sediment and topsoil samples were oven dried for 72 hours at 40–50°C (to avoid volatilization of mercury). The dried samples were ground and sieved (< 2 mm). The fine material was used to determine THg, pH, percent organic matter (%OM), and particle size analysis (PSA); THg was determined using a DMA 80 (Direct Mercury Analyzer). Percent organic matter was calculated by loss-on-ignition (LOI) using a muffle furnace at 400°C for 10 hours. The residual ignited sample was used for PSA on a Horiba Particle Size Analyzer. Prior to PSA, samples were soaked in Calgon solution (30 g/L) for 12 hours to promote separation of particles during analysis. Bulk density samples were oven dried at 105°C for 24 hours and the dry mass was used for bulk density calculations.

Data Analysis

In this study mercury was quantified as THg concentration (ng/L for water, ng/g for sediment and soil), THg normalized by organic carbon (THg/OC mg/kg), and THg pool (µg/m²) in the catchment soil (see Supplementary Information A for calculations). The use of THg/OC allowed comparison of THg concentrations between the three environmental media (water, soil, and sediment), and the examination

of interlinkages that were hidden by organic carbon. Total Hg and THg/OC were used as dependent variables in statistical tests.

The number of times each lake was sampled during April–July 2017 and 2018 varied; most lakes were sampled once or twice, though a small number had additional observations. To allow for comparison between lakes the data were averaged to one value per variable per lake to represent the 2017–2018 data. All variables were tested for normality using the Shapiro-Wilk test ($p < 0.05$); due to the non-normal distribution of the data, non-parametric tests were used. All statistical tests were performed using the statistical software PAST version 4.03 (Hammer et al. 2001).

Variability between lakes was calculated as normalized median absolute deviation (NMAD) to best represent the non-normally distributed data (see Supplementary Information A). To assess regional variation across the north–south and east–west gradients, all variables were tested for significant Spearman Rank Correlations ($p < 0.05$) with easting and northing as an indicator of spatial autocorrelation. Significant differences ($p < 0.05$) between THg/OC in water, sediment, and soil, and between THg and organic matter in sediment and soil were assessed using Wilcoxon signed rank tests.

The associations between water, and sediment and soil were explored using Spearman rank correlations ($p < 0.05$). Spurious correlations were excluded from this analysis, e.g., for THg/OC in lake water, correlation with THg and DOC were omitted; similarly, for sediment and soil, associations between THg/OC, %OM, and THg, or between THg in soil and THg soil pool, were excluded.

The influence of catchment soil and lake sediment on THg and THg/OC in lake water was assessed using Redundancy Analysis (RDA). Further, a second RDA was run with sediment THg and THg/OC as the dependent variables to determine the influence of soil on sediment. The biplots for RDA were scaled to allow easier visual interpretation, using scaling type 2 as determined by Legendre and Legendre (1998). The correlation strength of the individual axes (THg and THg/OC) with their dominant drivers is indicated as an r value within-text. The strength of the overall RDA (both THg and THg/OC axes) is noted in the RDA biplot figure caption as R^2 and R^2_{adj} .

Results

Lake water

The upland lakes tended to be dilute and acidic systems, with median conductivity of 38.4 $\mu\text{S}/\text{cm}$ and pH of 5.6 (Table 1). The pH was highly spatially variable (NMAD 96%) and ranged from pH 4.5 to 7.2, but only two lakes were above pH 7. Dissolved organic carbon ranged from 0.8 to 13.7 mg/L (NMAD 44%), with a median of 3.9 mg/L (Table 1). The upper limit of DOC (13.7 mg/L) was driven by a single lake (peatland pool); every other lake had a DOC less than 10 mg/L. Total mercury (THg) in the study lakes ranged from 2.0–19.7 ng/L (NMAD 28%), with a median of 5.4 ng/L (Table 1). The central 50% of the data fell between 4.0 and 8.1 ng/L (Fig. 2). The upper range of the data was driven by a small number of lakes with higher THg; only three lakes ($\approx 10\%$) had a concentration greater than 11 ng/L (Fig. 2). The

corresponding DOC concentrations for those three lakes were all greater than 7 mg/L and were some of the highest DOC values (Fig. 2), highlighting the well-established relationship between DOC and THg (Lavoie et al. 2019).

Sediment and soil

Lake sediment ranged from coarse texture (sandy) with low organic matter content, to fine organic sediment (Table 1). In contrast, catchment soil varied little, with the vast majority of samples being highly organic (peatland) soils with few exceptions (Fig. 2). Organic matter (%OM) in sediment and soil had similar ranges (Table 1), but %OM was significantly lower in sediment ($p < 0.05$). In general sediment %OM was very low, with a median of 3%, while catchment soils were primarily organic, with a median of 87% and only three catchments had soil OM less than 30% (Fig. 2). Total Hg in sediment was also significantly lower than in soil (Fig. 2). The median THg concentration was 30 ng/g in sediment and 240 ng/g in soil. Sediment THg had a much smaller range than soil THg, and the middle 50% of the data fell between 7 and 63 ng/g for sediment, compared with between 176 and 276 ng/g for soil (Fig. 2). When THg was normalized by organic carbon (THg/OC), the difference between THg in soil and sediment was small and not significantly different, with a median of 0.5 and 0.8 mg/kg respectively (Table 1).

Table 1

Statistical summary of physiochemical variables for upland lake water (n = 31), sediment (n = 28), and catchment topsoil (n = 31); sampled in the Republic of Ireland during April–July 2017 and 2018. Note: NMAD = normalized median absolute deviation, THg = total mercury, DOC = dissolved organic carbon, THg/OC = total mercury normalized by organic carbon.

	Units	Min–Max	Median	NMAD (%)
Lake Water				
THg	ng/L	2.0–19.7	5.4	28
THg/OC	mg/kg	0.3–6.2	1.3	31
DOC	mg/L	0.8–13.7	3.9	44
pH		4.5–7.2	5.6	96
Conductivity	µS/cm	24.3–108.3	38.4	25
Lake Sediment				
THg	ng/g	2.2–189	30	77
THg/OC	mg/kg	0.2–2.2	0.8	66
Organic Matter	%	1–93	3	72
pH		3.4–6.5	4.9	83
Particle Size *	µm	18–826	250	70
Sand	%	22–98	86	9
Silt	%	1–74	13	77
Clay	%	0–4	0.1	100
Catchment Soil				
THg	ng/g	36.6–502	240	21
THg/OC	mg/kg	0.2–1.8	0.5	32
THg Pool	µg m ⁻²	1378–11 535	3561	39
Organic Matter	%	7–98	87	11
pH		3.2–5.9	4.0	57
Particle Size *	µm	14–296	30	39
Sand	%	13–83	39	35
* geometric mean				

	Units	Min–Max	Median	NMAD (%)
Silt	%	16–84	59	26
Clay	%	0.2–7	1	46
* geometric mean				

Lake water THg/OC (median 1.3 mg/kg OC) was significantly higher than THg/OC for sediment and soil (Fig. 3); of the three media, THg in sediment had the greatest variability, with an NMAD of 67% (water: 31%; soil: 32%).

Relationship of THg between soil, sediment, and water

Total Hg in lake sediment and lake water was strongly associated with catchment soil (Table 2 and Fig. 4). Variation in sediment THg was best explained by positive relationships with soil moisture and organic matter, and negative relationships with soil pH and coarse fragments ($r = 0.68$; Fig. 4), suggesting a positive association with catchments containing wet organic soils.

THg/OC in sediment was positively correlated to THg/OC in soil ($r_s=0.40$) and also correlated to THg soil pool; however, the connection between soil mercury and sediment could only be seen when THg was organic carbon normalized (Table 2). Redundancy Analysis also highlighted these variables as best explaining the variation in THg/OC in sediment, and THg pool had the strongest relationship ($r = 0.68$; Fig. 4).

The positive relationship between mercury and organic matter in the environment is well-established (Ravichandran 2004; Lavoie et al. 2019); in the current study, THg in water had a significant positive correlation to DOC ($r_s=0.66$) and THg in sediment had a significant positive correlation to %OM ($r_s=0.88$); however, THg in soil did not have a significant correlation with organic matter. The lack of correlation between THg and %OM in catchment soil was likely due to the fact that nearly all catchment soils were classified as highly organic (median 87%) with low spatial variability (11%), making THg the limiting factor rather than organic matter. While THg in soil did not have a significant correlation with %OM, it was positively correlated to moisture content, and negatively correlated to coarse fragments and pH, indicating that THg was greater in more organic (peaty) soils, though this relationship was not very strong (Supplementary Information Fig. SI-2).

Table 2

Significant spearman rank correlations (r_s , $p < 0.05$) with total mercury (THg) and total mercury normalized by organic carbon (THg/OC) in lake sediment and water, sampled during April–July 2017 and 2018 in the Republic of Ireland ($n = 31$). Water THg/OC was not presented as it had no significant correlations. Note: %w = moisture content; %CF = coarse fragment; %OM = organic matter; BD = bulk density; PS = particle size; %sand = sand content; subscript 'se'=sediment; 's'=soil.

Water THg	r_s	Sediment THg	r_s	Sediment THg/OC	r_s
Northing	+ 0.47	%OM _{se}	+ 0.88	Northing	- 0.65
DOC _w	+ 0.66	%W _{se}	+ 0.68	%W _{se}	- 0.58
pH _w	- 0.59	%CF _{se}	- 0.42	%CF _{se}	+ 0.52
THg/OC _s	- 0.36	PS _{se}	- 0.78	%W _s	- 0.44
THg soil pool	- 0.43	%sand _{se}	- 0.81	THg/OC _s	+ 0.40
PS _s	- 0.44			Soil THg pool	+ 0.48
%sand _s	- 0.48			%OM _s	- 0.57
				pH _s	+ 0.39
				BD	+ 0.56

Water THg/OC ($r = 0.95$; Fig. 5) was best explained by positive relationships with soil pH and soil THg/OC, and negative relationships with soil moisture content and sand content in sediment. The positive relationship with soil THg/OC is notable; the highly organic catchment soils obscure interlinkages between soil THg and other variables, but when THg was normalized by organic carbon, the connection between soil and water was evident (Table 2 and Fig. 5).

Lake water THg was negatively correlated to THg/OC in soil, soil THg pool, and soil texture (Table 2). Redundancy analysis also showed these soil variables best explained variation in THg in lake water, albeit with two differences; firstly, the addition of THg/OC in sediment in the RDA, and secondly, soil THg pool was the variable that best explained THg in water ($r = 0.82$; Fig. 5). There were a couple commonalities between the results for THg in water and THg/OC in sediment. First was their correlation with THg/OC in soil rather than with THg in soil (Table 2), which further suggests that the association was only apparent when total mercury was normalized for organic carbon. Secondly, the THg soil pool best explained variation in THg in water and THg/OC in sediment (see Figs. 4 and 5).

The connection between THg in lake water and THg/OC in sediment to THg soil pool was also seen when regional variation was evaluated. The three variables had significant correlations to northing, indicative of regional spatial autocorrelation (Table 2). The northern sites were dominated by peatland, while the southern sites were rocky and had higher proportions of inorganic soil (Supplementary Information Fig.

SI-1), with greater bulk density ($r_s=-0.40$) and consequently a larger THg soil pool ($r_s=-0.38$) since THg in soil did not vary by region (Supplementary Information Fig. SI-2). Accordingly, THg in water was higher in the north ($r_s=0.47$) where peatlands dominated, and THg/OC in sediment was higher in the south ($r_s=-0.65$) where there was a greater soil THg pool (see Supplementary Information Fig. SI-3).

Discussion

Total mercury concentrations in lake water, lake sediment, and catchment soil. While THg concentrations in the upland lake waters (median 5.4 ng/L, range 2.0–19.7 ng/L) were high compared with a previous survey of Irish lakes in 2008, which included 13 lakes from this study (median 2.78 ng/L, $n = 54$ [Burton et al. 2013]), they were generally within the range of pristine lakes in Norway (0.5–6.6 ng/L, $n = 51$ [Braaten et al. 2014]; 1.7–5.1 ng/L, $n = 4$ [Poste et al. 2015]), and mountain lakes in the UK (mean 14 ng/L, $n = 1$ [Yang et al. 2002]) and in the US (mean 1.73 ng/L, $n = 44$; [Yu et al. 2011]; mean 1.5 ng/L, $n = 1$ [Gerson and Driscoll 2016]). Further, the study lakes with higher THg concentrations (> 10 ng/L) were consistent with streams and lakes influenced by peatlands (e.g., 4.6–25 ng/L, $n = 1$ [Woerndle et al. 2018]; inflow 26 ng/L, $n = 1$ [Yang et al. 2002]).

Total Hg in sediment for the study lakes (median 30 ng/L, range 2.2–189 ng/L) was generally consistent with pristine remote lakes, e.g., arctic lakes (mean 22.2 ng/g, $n = 3$ [Gopikrishna et al. 2020]; 9.4–164 ng/g, $n = 6$ [Korosi et al. 2018]) but lower than observations from high elevation lakes in two national parks in the US (92–288 ng/g, $n = 9$ [Mast et al. 2010]). In contrast to lake water and sediment, THg concentration in catchment topsoil (median 240 ng/g) was higher than topsoil from other background regions (e.g., Svalbard: median 107 ng/g, $n = 57$ [Halbach et al. 2017]; Himalayas: 3.82–106 ng/g, $n = 5$ [Tripathy et al. 2018]), owing to their high organic content (87%). Total Hg in the study soils was more than twice as high as rural topsoil in the UK (median 95 ng/g, $n = 898$), however when normalised by organic matter content they were lower (median 0.5 mg/kg OC versus 0.63 mg/kg OM in the UK [Tipping et al. 2011]).

The low variation in soil THg and THg/OC across the study sites (21–32%) suggests a consistent Hg source, i.e., atmospheric deposition dominated by long-range transport, which is low in Ireland (e.g., Custodio et al. 2020). The influence of atmospheric mercury deposition on Irish environments has been previously demonstrated by analysis of peat cores, which reflect historical atmospheric mercury concentrations (Scott & Aherne, 2013; Coggins et al., 2006), including suspected long-range pollution from North America (Coggins et al., 2006). The lakes in this study are headwater lakes originally selected to study the impacts of long-range atmospheric pollution (Aherne et al., 2002) and therefore the only anthropogenic source of mercury to these catchments are low levels of atmospheric deposition.

Interlinkages between soil, sediment, and water

The results suggest that catchment topsoils drive variation in Hg concentrations in lake water and sediment in the upland regions of Ireland. The soil THg pool best explained the variation in sediment THg

($r = 0.68$) and especially water THg ($r = 0.82$), but THg concentration was also highly correlated to organic matter (sediment THg and %OM: $r_s=0.88$; water THg and DOC: $r_s=0.66$). The relationship between organic matter and THg has been widely reported for aquatic (e.g., Watras et al. 1995; Lavoie et al. 2019) and terrestrial (e.g., Tipping et al. 2011; Eklöf et al. 2012) systems. Further, it is well established that soil processes that affect the transport of DOC from terrestrial catchments to surface waters also strongly influence the concentration of THg (e.g., Stoken et al. 2016). However, in the current study the highly organic soils obscured this relationship. Stoken et al. (2016) similarly found that soils with high carbon content could 'dilute' THg, owing to limited Hg supply for adsorption to soils with relatively large carbon pools. This highlights the need to normalize THg by organic carbon to evaluate the interlinkages within lake catchments.

The interlinkages between lakes and their catchments may become increasingly important for aquatic mercury concentrations as decreasing anthropogenic emissions lead to legacy mercury pollution from atmospheric deposition stored in soils becoming the dominant source to aquatic systems, which has been observed for trace metals (Yang et al., 2018; Yang et al., 2016). In the study lakes, the source of mercury is still atmospheric, but with a shift away from direct atmospheric deposition towards the delayed inputs of legacy atmospheric mercury stored in the catchment soils. Since the study lakes are headwater systems, the movement of mercury from the soils to the lake is largely from erosion and seepage.

Conclusions

Total Hg concentrations in water and sediment in upland Irish lakes were low, consistent with pristine (background) regions. In contrast, topsoil THg concentrations were relatively high, with little variation, owing to the organic soils that dominate the study sites. This emphasizes the value of exploring mercury independent of the influence of organic matter, i.e., THg normalized by organic carbon. This study suggests that catchment soils are the dominant driver of variation in Hg concentrations in lake water and sediment in the upland regions of Ireland. Further, the low variation in topsoil THg across the study sites suggests that (long-range) atmospheric inputs were the dominant source. As global action (such as the Minamata Convention) decreases mercury emissions, soil mercury inputs to aquatic systems may become more important than atmospheric deposition, which makes the relationships between terrestrial catchments and their water bodies vital for our understanding of mercury cycling.

Declarations

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STATEMENTS AND DECLARATIONS

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The authors have no relevant conflicts of interest to disclose.

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Figures

Figure 1

Location of study lakes (n=31) in the Republic of Ireland, sampled during April–July 2017 and 2018. Sampling sites are indicated by green circles, major cities in Ireland are indicated by black squares. Note: the circles overlap in some regions owing to the proximity between lakes. The inset shows the location of Ireland on the western periphery of Europe.

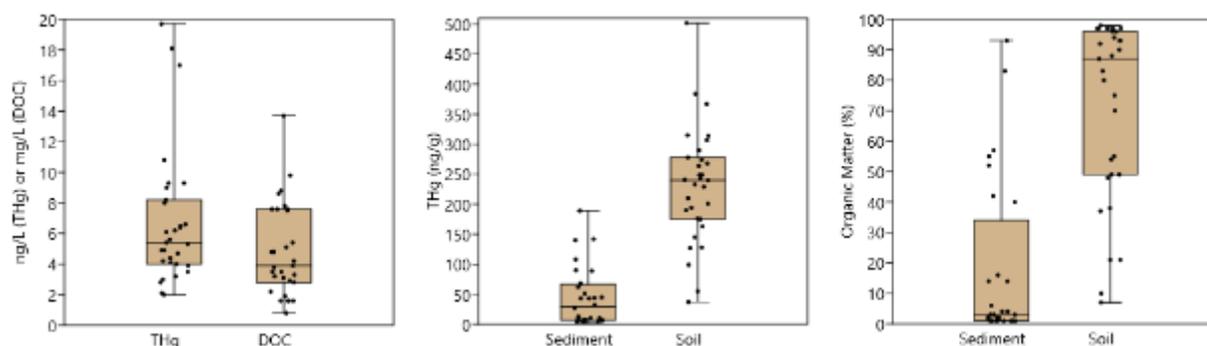


Figure 2

Left: Total mercury (THg) and dissolved organic carbon (DOC) in lake water (n=31); Middle: THg in lake sediment (n=28) and catchment topsoil (n=31); Right: Organic matter content in lake sediment (n=28) and catchment topsoil (n=31). Lake catchments sampled in the Republic of Ireland during April–July 2017 and 2018.

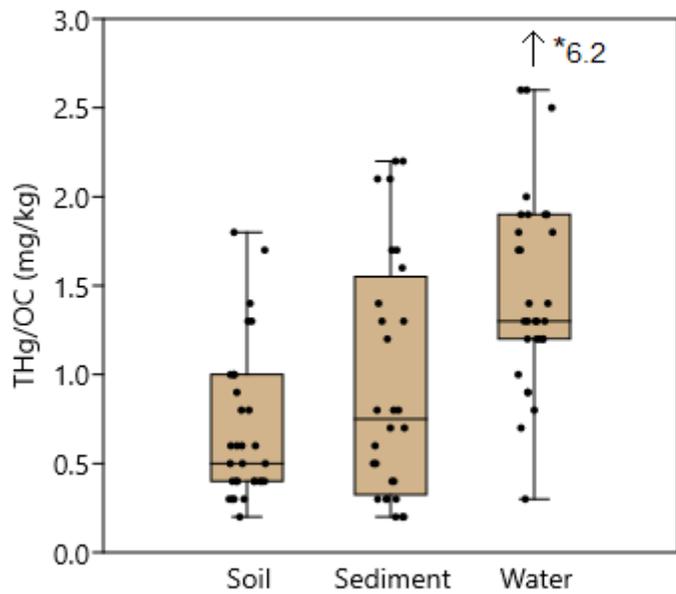


Figure 3

Total mercury concentration normalized by organic carbon (THg/OC) in catchment topsoil (n=31), lake sediment (n=28), and lake water (n=31). Samples collected during April–July 2017 and 2018, in the Republic of Ireland. Outlier indicated by arrow and asterisk ().*

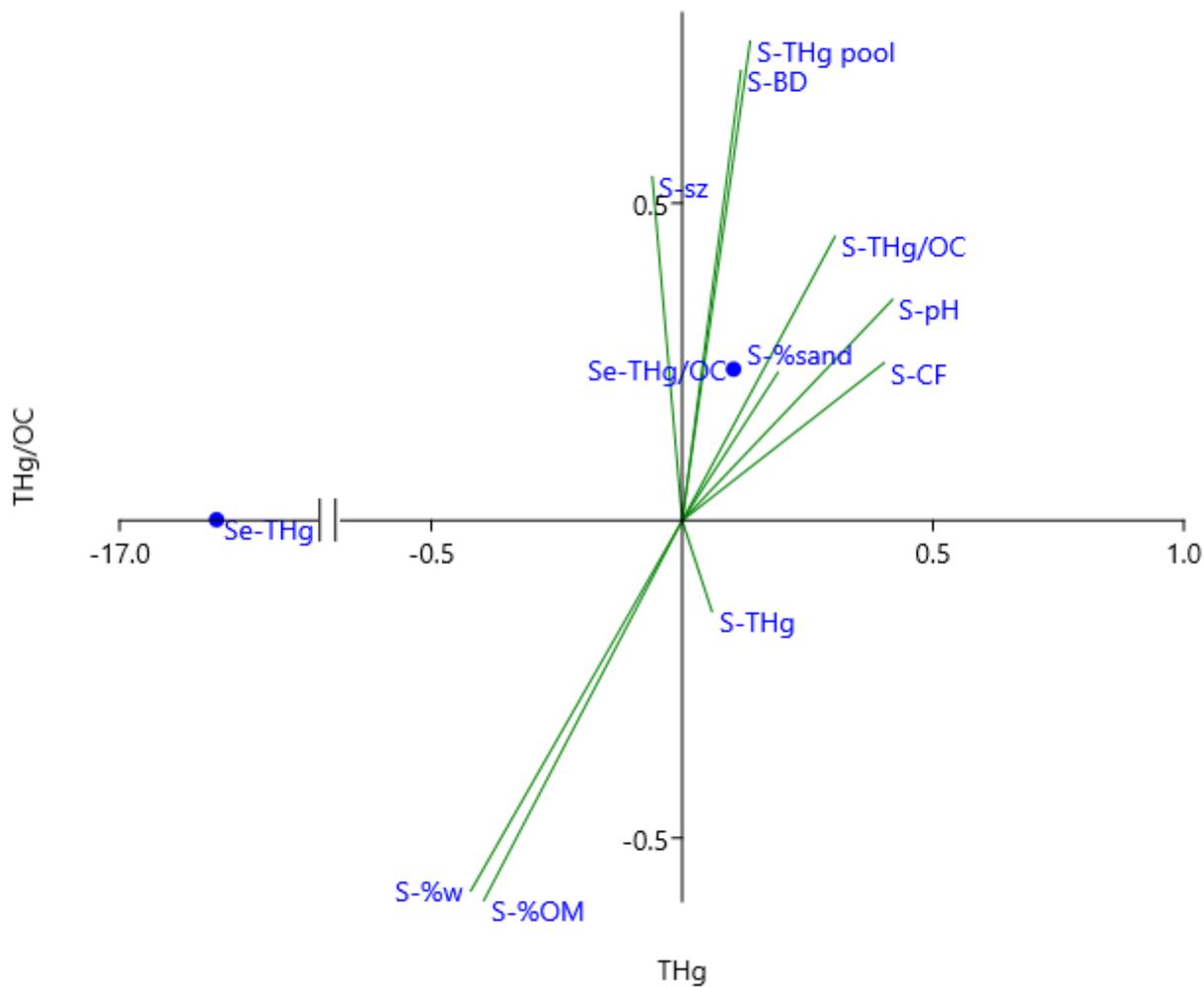


Figure 4

Biplot of Redundancy Analysis (RDA) for total mercury (THg) and total mercury normalized by organic carbon (THg/OC) in Irish sediment (n=31), sampled during April–July 2017 and 2018, with topsoil parameters as explanatory variables ($R^2=0.46$; R^2 adj=0.14). Column amplitude set to 0.5 to allow easier visual interpretation. Variables starting with ‘S’ or ‘Se’ indicate soil and sediment respectively. Note: %w=sample moisture, %OM=organic matter, CF=coarse fragment, sz=particle size.

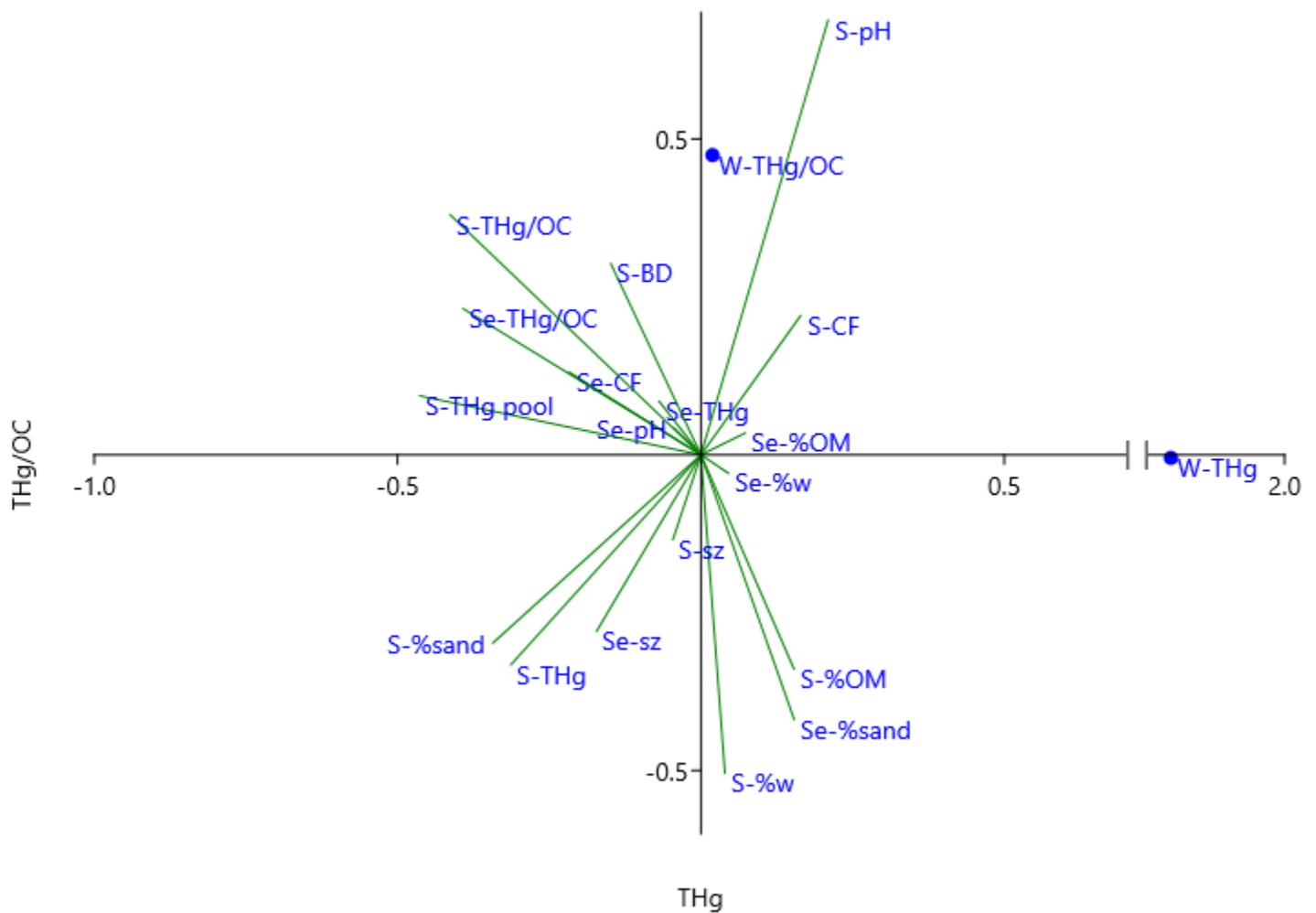


Figure 5

Biplot of Redundancy Analysis (RDA) for total mercury (THg) and total mercury normalized by organic carbon (THg/OC) in Irish lake water (n=31), sampled during April–July 2017 and 2018, with topsoil and sediment as explanatory variables ($R^2=0.68$; R^2 adj=0.20). Column amplitude set to 0.5 to allow easier visual interpretation. Variables starting with 'W', 'S' or 'Se' indicate water, soil, and sediment respectively. Note: %w=sample moisture, %OM=organic matter, %CF=coarse fragment, sz=particle size.

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