Mercury pollution in the lake sediments and catchment soils of anthropogenically-disturbed sites across England

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Abstract

Sediment cores and soil samples were taken from nine lakes and their catchments across England with varying degrees of direct human disturbance. Mercury (Hg) analysis demonstrated a range of impacts, many from local sources, resulting from differing historical and contemporary site usage and management. Lakes located in industrially important areas showed clear evidence for early Hg pollution with concentrations in sediments reaching 400 - 1600 ng g^{-1} prior to the mid-19th century. Control of inputs resulting from local management practices and a greater than 90% reduction in UK Hg emissions since 1970 were reflected by reduced Hg pollution in some lakes. However, having been a sink for Hg deposition for centuries, polluted catchment soils are now the major Hg source for most lakes and consequently recovery from reduced Hg deposition is being delayed.

Capsule abstract

Urban and suburban lake sediments across England reveal mercury pollution by local industry and urbanisation, while catchment inputs have become the major source of Hg for most lakes.

Keywords: Urban and suburban lakes; Mercury; Catchment inputs; Lake restoration.

1. Introduction

Although the emission of mercury from anthropogenic sources has a very long history (Hylander and Meili, 2003), the Industrial Revolution, principally through massive consumption of coal, greatly elevated Hg atmospheric emission. Globally, a rapid increase in Hg release into the environment occurred from the 1850s onwards, not only through coal burning, but also via other anthropogenic processes such as ore refining and, more recently, waste incineration (Hylander and Meili, 2003; Nriagu and Pacyna, 1988). It is estimated that Hg emissions to the atmosphere have increased by around three times over this period (Lindberg et al., 2007).

Following release to the atmosphere, Hg returns to the Earth's surfaces by both wet and dry depositional processes and lake sediments and their catchment soils are two important sinks. Soil, which acts as both sink and source of Hg and other trace metals, is an important reservoir (Gillis and

Miller, 2000; Yang et al., 2001) and contaminated catchment soils can have a long-term impact on freshwater ecosystems (Yang et al., 2002; Yang, 2010) with transfer via soil erosion being an important process (Rothwell et al., 2005; 2007; Rose et al., 2012). However, erosion itself is controlled by many factors including catchment slope, vegetation coverage, catchment hydrology and climate (Morgan et al., 1998; Dearing, 1991), while land-use and other direct human disturbance in catchments can also enhance soil movement (Bakker et al., 2008). Therefore, these processes potentially have a large influence on the rate and scale of Hg transfer to aquatic systems and can be recorded in sediment archives.

Lake sediments have been widely used to reconstruct pollution histories, but most published Hg records are derived from remote lakes, where atmospheric deposition is the sole input for anthropogenic Hg, and these can provide information on depositional trends over relatively large regions (e.g. Bindler et al., 2001; Fitzgerald et al., 2005; Yang et al., 2010). However, Hg sources for lakes that have been directly disturbed by human activities, e.g. lakes in urban or suburban areas, are more complicated (Bookman et al., 2008; Yang, 2010; Van Metre, 2012; Li et al., 2013), but their records may be equally important, especially considering the recent, and predicted, expansion of urban areas across the globe. Cooper et al. (2007) summarise three reasons why the study of human-dominated systems is important. First, because anthropogenic influences are so dominant they need to be included in ecological modelling. Second, including these influences in a realistic way raises the chances of solving existed problems, and third, ecosystem studies within human-dominated environments are relatively sparse and hence knowledge of them is limited. Data from this study addresses the second and third of these points and additionally provides data for future, spatially-resolved Hg modelling.

The first increase in Hg contamination above background in many remote lake sediment records is typically observed in the 1850s and 1860s (Johansson, 1985; Engstrom and Swain, 1997; Fitzgerald et al., 2005), and records from relatively remote areas across the UK show a similar trend (Yang and Rose, 2003). However, the UK was one of the pioneering nations in the Industrial Revolution and so industrialisation, and the environmental consequences of it, including urban expansion and population change, began much earlier than the mid-19th century. For example, rapid industrial expansion occurred in Birmingham from the 1770s due to the application of the steam engine driven by coal combustion (Skipp, 1997) while in Manchester coal consumption for domestic use was already considerable in the early-17th century and expanded in the late-18th and early-19th centuries with the rapid development of the cotton industry (Mosley, 2001). Since then, many lakes and their catchments, especially in urban and suburban settings, have been disturbed to varying degrees, mobilising industrial Hg deposition from catchments to lakes (e.g. Yang, 2010) but how reliably these enhanced Hg inputs are recorded in lake sediments is not well known.

This study uses lake sediment records and catchment soil analyses from variably disturbed, urban to rural lakes across England to explore how local inputs of Hg have affected these systems and how faithfully the sediment archive records these changes. We also assess the extent to which these lake systems have responded to the dramatic (>90%) reduction in UK Hg emissions since 1970 (NAEI, 2014) or whether this has been negated by an increased transfer of contamination from disturbed catchments. The responses of these lakes provide a useful reference for other regions, especially where urban and industrial development continues to expand.

2. Sites and methods

2.1. Study sites

Open Air Laboratories (OPAL), is a community-driven research programme in England (Davies et al., 2011) designed to promote a greater understanding of the state of the natural environment. As part of this, a national water survey was developed to encourage the public to explore local lakes and ponds. A second strand involving detailed monitoring at a lake in each of nine designated regions of England was also undertaken (Turner et al., 2013). These lakes were selected by regionally based OPAL Community Scientists and represented sites where there was a particular local interest. The monitoring programme provided these groups with useful information and they were able participate in, and support, the research. As a consequence, the selected lakes were a diverse group including urban lakes and ponds as well as those in more rural settings. These lakes have been subject to a variety of local disturbances illustrative of the range of histories, impacts and multiple stressors that have determined their current status. The locations of these lakes are shown in Figure 1 while basic geographical information is provided in Table 1. A brief description of the nature of the sites is provided in Supplementary Information (SI).

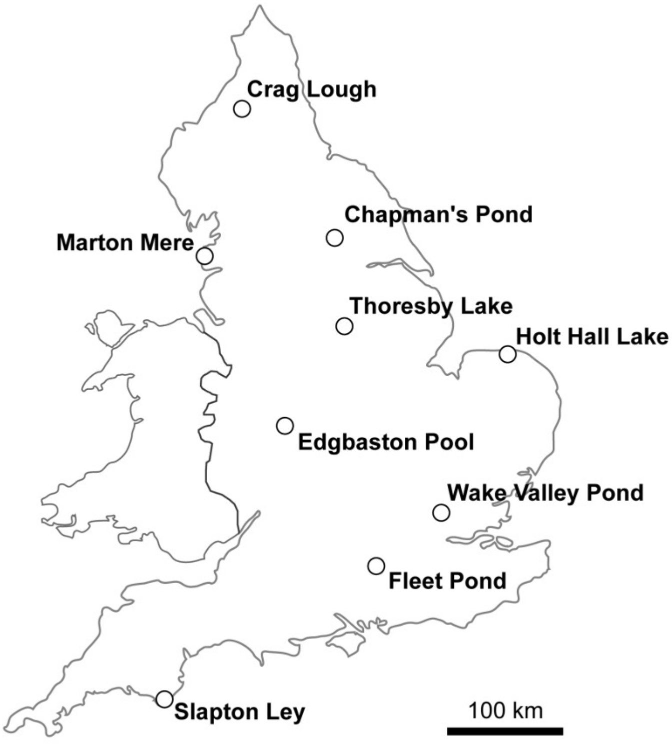

Figure 1. Location of study sites in England.

Table 1. Lake and catchment information

				Lake		Catchment
Site name [code]	Latitude	Longitude	Altitude (m a. s. l)	Water area (ha)	Max depth (m)	Area (ha)
Chapman's Pond [CHAP]	53.93423	-1.12023	16	0.6	4.5	< 10
Crag Lough [CRAZ]	55.005853	-2.365318	244	10.1	2.0	182
Edgbaston Pool [EDGB]	52.453901	-1.920802	127	7.2	2.5	644
Holt Hall Lake [HOLTU]	52.915543	1.087271	47	0.7	1.0	65
Marton Mere [MARM]	53.809337	-2.999984	7	10.8	4.5	1015
Fleet Pond [PFLE]	51.287473	-0.825006	68	26.4	1.0	1230
Slapton Ley [SLT]	50.283843	-3.650164	3	65.9	2.5	1774
Thoresby Lake [THOP]	53.226564	-1.058643	37	30.4	3.5	9615
Wake Valley Pond [WAKE]	51.669496	0.053029	96	1.0	4.0	32

2.2. Sediment and soil sampling

A sediment core was collected from the deepest part of each lake in 2008 using a wide-diameter piston corer. These cores were sliced at 1-cm intervals. Two surface soil (0-5 cm) samples and one soil profile were collected from representative areas of each lake catchment in 2011 (except Crag Lough and Marton Mere, where only the soil profile was collected) using a standard soil auger. Soil samples were collected as 5 cm vertical sections. Standard lithostratigraphic analyses (bulk wet density, water content and loss-on-ignition at 550°C) (Dean, 1974) were undertaken on each sediment sample. All sediment and soil samples were freeze-dried prior to chemical analysis.

2.3. Sample analyses and calculation of Hg fluxes in the sediments

Sediment cores were radiometrically-dated using ^{210}Pb, ^{137}Cs and ^{241}Am (see Supplementary Information) and chronologies calculated using the constant rate of supply (CRS) model (Appleby, 2001). For Hg analysis, 0.2 g of dried sample was weighed into a 50 mL polypropylene DigiTUBE (SCP Science). 8 mL aqua regia were added to each tube and gradually heated on a hotplate to 100 °C to avoid violent reaction. After reaching 100 °C, the sample was digested for another 1.5 h and then allowed to cool. The digested solution was diluted to 50 mL using distilled deionised water. Standard reference stream sediment (GBW07305; certified Hg value 100 ± 10 ng g^{-1}; our measured mean value 100.3 ng g^{-1}; RSD 4.5 ng g^{-1}; N=15) and sample blanks were digested with every 20 samples.

Mercury concentrations in digested solutions were measured by ASP cold vapour-atomic fluorescence spectrometry following reduction with $SnCl_2$. Standard solutions and quality control blanks were measured after every five samples to monitor measurement stability. Geochemical element concentrations were measured using X-ray fluorescence (XRF) spectrometry techniques described in Supplementary Information. Mercury fluxes in the sediments were derived from Hg concentrations and sedimentation rates calculated from the radiometric chronologies.

2.4. Anthropogenic Hg calculation

In a sediment sample, the natural contribution of an element is given by LR_s/LR_b, where LR_s and LR_b are the concentrations of a selected lithogenic reference element in the sample and the background (no anthropogenic impact), respectively. Therefore, the natural contribution to Hg concentration in a sample (Hg_{bc}) is:

$$Hg_{bc} = (LR_s/LR_b) \text{ x } Hg_b \qquad (1)$$

where Hg_b is the Hg concentration in background sediments. The anthropogenic concentration (Hg_{ac}) is therefore:

$$Hg_{ac} = Hg_t - (LR_s/LR_b) \text{ x } Hg_b \qquad (2)$$

where Hg_t is the total Hg concentration in the sample. Anthropogenic Hg flux to the sediments (Hg_{af}) is:

$$Hg_{af} = Hg_{ac} \text{ x } SR \qquad (3)$$

where SR is sedimentation rate. This method is simpler than calculations of metal enrichment factors but provides the same results (cf: Perry et al., 2006; Boes et al., 2011; Hermanns and Biester 2013). In most sediment cores, temporal changes in Ti provide a better representation of lithogenic inputs than other elements (cf. Yang and Smyntek, 2014), and so was chosen for the natural contribution calculations.

Some cores such as THOP and WAKE show high Hg contamination even in basal samples and so cannot be used for natural Hg contribution calculations. Therefore, as Hg and Ti concentrations in uncontaminated deep soils are close to those in uncontaminated sediments, especially in urban sites with high sedimentation rates, these were used to determine the natural Hg contribution, although it is possible that Hg may be transported deeper into soils by complexation with dissolved organic carbon (DOC) (Schuster et al., 2008).

3. Results

3.1. Sediment Chronologies and sedimentation rates

The unsupported ^{210}Pb profiles of all nine sediment cores show non-monotonic features, i.e. unsupported ^{210}Pb activities do not show an exponential decline with depth in individual cores. This implies changes in sedimentation rates at all sites. Equilibrium depths of total ^{210}Pb with the supported ^{210}Pb activity (corresponding to the last c. 150 years sedimentation period) in the sediment cores vary (Table 2). In general, they are considerably deeper than those in sediments taken from remote regions (cf., Appleby, 2000; Appleby, 2004; Yang et al., 2010) indicating higher sediment accumulation rates. Most of the cores have well-resolved 1963 ^{137}Cs peaks derived from the maximum fallout from nuclear weapons testing. This indicates that the sediments in these sites have been relatively unmixed since at least the 1960s, and that these cores might provide historically reliable records of pollutant inputs. However, the 1963 ^{137}Cs peaks in the cores from Holt Hall (HOLTU), Slapton Ley (SLT) and Thoresby Lake (THOP) are relatively poor, although still distinct, suggesting that these sediments may have been subjected to limited mixing.

Table 2. Radiometric dating features for the sediment cores.

Site name [code]	Equilibrium depth (cm) of total and supported ^{210}Pb	^{210}Pb flux (Bq m^{-2} yr^{-1}) to the core location	Sedimentation rate range (g cm^{-2} yr^{-1})	^{137}Cs 1963 peak
				Depth (cm)
Chapman's Pond [CHAP]	38±3	115±10	0.04-0.79	30±2
Crag Lough [CRAZ]	105±5	117±7	0.03-1.86	13.5±1
Edgbaston Pool [EDGB]	53±3	240±12	0.02-0.17	27.5±1.5
Holt Hall Lake [HOLTU]	64±4	176±11	0.04-1.18	42±2
Marton Mere [MARM]	63±4	193±20	0.02-0.40	45.5±2
Fleet Pond [PFLE]	45±3	177±13	0.03-0.16	21±1.5
Slapton Ley [SLT]	24±2	82±5	0.006-0.05	15.5±1
Thoresby Lake [THOP]	75±4	211±51	0.10-0.50	28±2
Wake Valley Pond [WAKE]	57±3	224±16	0.03-0.24	30.5±2

Sedimentation rates cover a large range (Figure S1) from 0.006 g cm^{-2} yr^{-1} before 1900 in Slapton Ley (SLT) to 1.86 g cm^{-2} yr^{-1} in the 1950s at Crag Lough (CRAZ). As the organic content and geochemical element concentrations were constant at Crag Lough through this brief period of extraordinarily high sediment accumulation, it appears that the sediment source did not change. This 'event' is probably due to a rock-fall from the cliffs above the lake causing a redistribution of contemporary sediments to the coring site (Turner et al., 2013).

In general, changes in sedimentation rates within individual cores are not smooth, and probably reflect human disturbance in the catchments (Figure S1). For example, the sedimentation rate in the core from Edgbaston Pool (EDGB) reached 0.17 g cm^{-2} yr^{-1} before the 1900s, implying enhanced catchment input, followed by declining rates through the 20th century. Similarly, there are sharp peaks in sedimentation rate in Chapman's Pond (CHAP) in the early-1980s and at Marton Mere (MARM) in the 1950s probably derived from waste disposal at these sites.

3.2. Hg in soils and sediments

Mercury concentrations in catchment soils vary from site to site, but also show considerable within-site variation (Figure S2) with differences in Hg concentrations in the surface soils varying by a factor of 2 to 10. Mercury concentrations in the top 0-15 cm are almost all higher than the median concentration (95 ng g-1) for UK rural topsoils (0-15 cm) sampled between 1998 and 2008 (Tipping et al., 2011), indicating a higher level of contamination. The exception is Marton Mere, where the surface soils have lower Hg concentrations, but are higher at depth, probably indicating burial of contaminated soils during an earlier period of catchment disturbance.

Sediment records show clear increases in Hg concentrations at, or before, the 1850s. In Edgbaston Pool and Marton Mere, Hg concentrations exceeded the consensus Probable effects Concentration (PEC) for freshwater sediments (1060 ng g^{-1}) (MacDonald et al., 2000) before the 1850s, the Hg concentration at which adverse biological effects on benthic aquatic organisms are commonly seen (e.g. US National Oceanic and Atmospheric Administration, 1999; CCME, 1999; MacDonald et al., 2000). The industrialisation of the city of Birmingham, in which Edgbaston Pool lies, started much earlier than some other regions of England (Allen, 2001) as it was active in the Industrial Revolution before the mid-19th century (Stobart and Raven, 2005). Economic expansion started in the 16th century (Allen, 2011) and by 1650 Birmingham had a population of around 5000, with iron-working named as the employment for one in every six households (Skipp, 1997). Industry expanded rapidly from the 1770s due to application of the steam engine driven by coal combustion, a source of Hg emissions. The city's population also expanded through this period from approximately 23,000 in 1731 to 170,000 in 1831 (Skipp, 1997), also due to this economic expansion and development of industrialisation (Allen, 2001).

Marton Mere is also located in an area of early factory-based industrialisation and urbanisation and was greatly affected by historical coal burning and by waste from local metal production and manufacturing entering the drainage system to which it was connected (Stobart, 2004). Therefore, the start of the Hg increase in the lake may reflect regional industrial development of factory-based industry, trade and transport systems produced by a locally integrated economy between 1700 and 1760 (Stobart, 2004). Hg concentrations in the sediments of Thoresby Lake show little temporal pattern but remain high (approximately 500 ng g^{-1}) throughout, even before the 1850s. This concentration is around 20 times higher than the Hg concentration in the deep soils taken from the catchment. Coal production has a long history around the site with seams from the Thoresby Colliery extending below the site (see Supplementary Information). The catchment area of Thoresby Lake is 316 times its lake area, high Hg concentrations in the pre-1850 sediments and significantly elevated catchment background concentrations suggest contamination possibly derived from early industrial activity in the area.

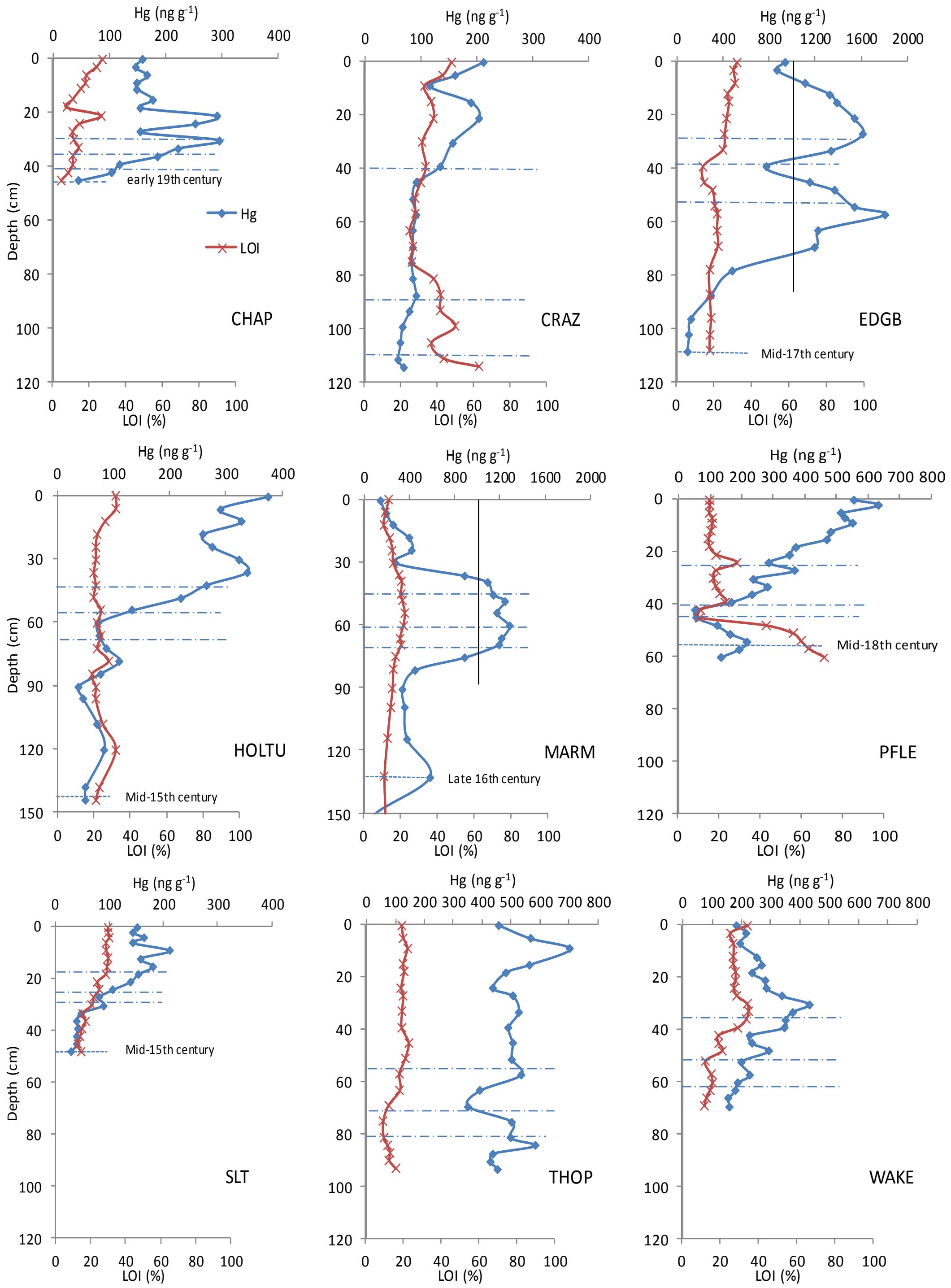

Figure 2. Mercury concentration profiles and loss-on-ignition (LOI) profiles for the lake sediment cores plotted on depths. Note differences in depth and concentration scales. Horizontal dashed lines (—·—·—) correspond to 1850, 1900, and 1950. Dates prior to the ^{210}Pb dated sections were extrapolated and are for guidance only (see text). Vertical lines indicate consensus Probable Effect concentration (PEC).

The differing historical influences to which the lakes have been subjected result in a variety of temporal patterns in both the Hg concentration and flux profiles (Figures 2 and 3) since the 1850s. Chapman's Pond was impacted by waste disposal from the early-1970s to the early-1980s resulting in high sedimentation rates and a period of very high Hg fluxes (exceeding 1200 μg m^{-2} yr^{-1}) (Figure 3). Sediment organic content and geochemical element (e.g. Zr, Ti, Ca, K) concentrations also show sharp concentration changes in the 1980s (see Turner et al., 2013) indicating a change in sediment sources, and could be due to material brought from outside of the catchment for disposal. Since waste disposal stopped, Hg concentrations in the sediments have reduced to a constant value. In Marton Mere, wetlands adjoining the lake were gradually drained through to 1850 (Clarke, 1969), and also subsequently used for disposal of urban waste. This stopped in 1972 after a reform of lake management in the 1960s, resulting in a sharp decline in sediment Hg concentrations from approximately 1000 ng g^{-1} to 400 ng g^{-1}. This implies that the material disposed at the site may have contained high levels of Hg. Nearly all the sediment Hg in Marton Mere is from anthropogenic sources (Figure 3) and this has remained the dominant source over the last ca. 140 years. Anthropogenic Hg follows trends to sedimentation rates, although relative scales have varied suggesting changes to Hg concentrations in inputs.

In Upper Holt Hall Lake, Hg concentrations increased rapidly from the 1900s (Figure 2) and may at least partially have been derived from inputs of domestic effluent and waste water from the surrounding area. These inputs are also likely to have increased the sedimentation rates as well as total and anthropogenic Hg fluxes, but this is not the case in all sites. The high sedimentation rate in the 1950s in Crag Lough possibly caused by a rock fall resulted in a brief period of very high Hg fluxes (800 μg m^{-2} yr^{-1}) (Figure 3) but does not indicate elevated contamination. Here, anthropogenic Hg fluxes were relatively constant before the 1940s while total Hg fluxes increased, following the same trend as sedimentation rate, indicating an increase in catchment inputs of less contaminated materials into the lake.

In recent decades, while some sites have shown constant Hg concentrations or a decline, others have shown an increase. Decreases may be due to improved catchment management or reduced atmospheric deposition. However, some decreases in Hg concentration may also be due to dilution by an increased sedimentation rate (e.g. WAKE core, see Figure S3), and in these cases concomitant Hg fluxes continue to follow the increasing trend in sediment accumulation (Figure 3). In Crag Lough, increasing trends in total and anthropogenic Hg concentrations and sediment fluxes over the last decade suggest an increase in atmospherically-contaminated soil input, possibly via an increase in catchment soil erosion or agricultural activity.

At Fleet Pond, there has been a rapid increase in Hg sediment concentrations since the 1970s (Figure 2), which is in direct contrast to the dramatic reduction in UK Hg emissions (emissions reduced from 63 tonnes yr^{-1} in 1970 to their current level of c. 6.3 tonnes yr^{-1}; NAEI, 2012). This increase in Hg concentration at Fleet Pond is therefore likely to be due to local contamination. Similar rates of change in sedimentation and Hg fluxes before 1970 (Figure 3), indicate catchment inputs. As Hg concentrations in the catchment soils are considerably lower than those in surface sediments, the high sediment Hg concentrations are likely to be derived from local, recently emitted Hg rather than Hg released from catchment soil storage. The delayed increase in sedimentation rates compared with the increase in Hg fluxes after 1970, also suggests a recent local Hg source.

In most sites, anthropogenic Hg has been the dominant source especially over the last hundred years, and changes in total and anthropogenic fluxes to the sediments are strongly linked with sedimentation rates (Figure 3).

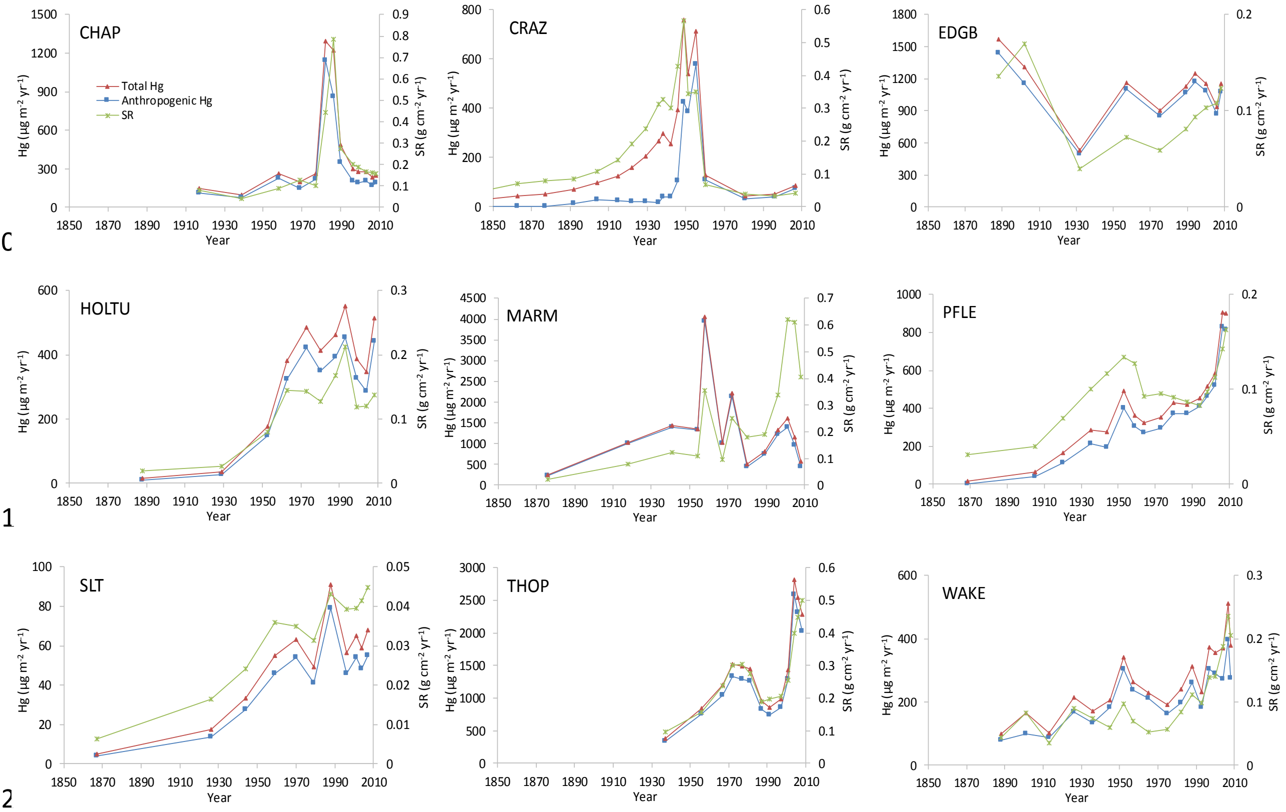

Figure 3. The total and anthropogenic Hg flux profiles and sedimentation rate changes for the sediment cores. Note the differences in the flux and rate scales.

4. **Discussion**

4.1. Historical Hg trends

Organic content of the sediments is relatively high with loss-on-ignition reaching 30% or more in the surface sediments of half of the cores (Figure 2). Variation in Hg concentrations might be related with the organic content of the pre-1850 sediments in Slapton Ley, pre-1900 sediments in Holt Hall Lake and pre-1950 sediments in Wake Valley Pond, as they follow similar trends. However, in most cases, changes in Hg concentrations in the sediments have only a weak relationship with sediment organic content (Figure 2). High organic content in lake sediments may cause considerable redox changes (Davison, 1993). Rapid changes of Mn concentrations in the surface sediments of Crag Lough, Edgbaston Pond and Slapton Ley (Figure S4) suggest a redox effect, as Mn is sensitive to redox change. However, the Hg concentration profiles of Edgbaston Pond and Slapton Ley do not follow the Mn trends, and Hg changes in the surface sediments of Crag Lough are more likely due to catchment inputs and suggesting only limit impact of redox on Hg profiles. As the ^{137}Cs records suggest that sediment mixing is also limited, then Hg profiles of the cores are likely to reliably represent historical Hg trends.

In lake sediment cores taken from many remote regions around the world, the first significant increase in Hg concentration is typically observed from the mid-19th century (Johansson, 1985; Verta et al., 1989; Engstrom and Swain, 1997; Lamborg et al., 2002; Fitzgerald et al., 2005; Muir et al., 2009) and an increase in Hg concentration observed prior to this time can usually be linked to small and local sources (e.g. Balogh et al., 1999; Bindler et al., 2001; Yang et al., 2010). Mid-19th century increases are usually attributed to the escalation in Hg emissions resulting from coal combustion during the Industrial Revolution (Hylander and Meili, 2003), and sediment and peat cores taken from relatively remote areas across the UK reflect this (Yang and Rose, 2003, Farmer et al., 2009). By contrast, the temporal records of Hg observed in this study are very different both from each other and from the larger-scale pattern of historical deposition. Instead, they record the local pollution history of disturbances and it is only with a more detailed knowledge of the lake histories, their catchments and the immediate area that the Hg records can be unravelled.

The Industrial Revolution started from the mid-19th century at a global scale, but was not the abrupt discontinuity that its name suggests, more the result of an economic expansion that started in the 16th century (Allen, 2011). In Britain, especially in regions such as the Midlands and north-west England, industrial development began much earlier and significant Hg concentration increases prior to the mid-19th century record evidence for early environmental impact resulting from it. In this study there are considerable increases in Hg concentrations in five of the nine lake sediment cores before the 1850s (Chapman's Pond; Edgbaston Pool; Marton Mere; Slapton Ley; Wake Valley Pond). While comparison of basal sediments with bottom soil samples in two others, Fleet Pond and Thoresby Lake, indicate that Hg concentrations had already increased to around 200 and 500 ng g^{-1} respectively, by this time. The most contaminated sites during the mid-19th century were Edgbaston Pool and Thoresby Lake in the Midlands and Marton Mere in north-west England, with Hg concentrations reaching 1200, 585 and 1800 ng g^{-1}, respectively. At Edgbaston and Marton Mere these mid-19th century concentrations exceed the sediment consensus-PEC for Hg, highlighting the severity of contamination that had already occurred by this time. Away from the Midlands and north-west, increases in pre-1850 Hg concentrations are substantially lower, in agreement with the intensity of industrial activities at the time, and showing similar spatial trend of industrial impacts on the lakes in the US (Van Metre, 2012).

After the mid-19th century, Hg concentrations continue to follow increasing trends at Chapman's Pond, Slapton Ley and Wake Valley Pond, while at Holt Hall Pond and Fleet Pond, a new phase of rapidly increasing contamination commenced. It is quite likely that local sources of Hg contamination to all these sites resulted from a combination of historical factors including ignorance of the impacts of waste inputs, lack of knowledge of the contamination burden within the waste, and lack of a realistic and pragmatic alternative to waste disposal (e.g. Yang, 2010). Hence, Chapman's Pond and Marton Mere were used to dump urban waste and Upper Holt Hall Lake received local effluent and waste water. However, contamination was not only directly received by release in the catchment but also via atmospheric deposition which was stored in both lake sediments and catchment soils. Our data indicate substantial catchment soil contamination and that these soils have been a source of Hg to the lakes to some degree.

4.2. Catchment Hg inputs to the lakes and sedimentation impacts

Increased awareness of the effects of metal contaminants in aquatic systems has resulted in improved lake management and a reduction of direct release to surface waters at local scales (Burniston et al., 2011). In this study, we observe this as a decline in Hg concentrations in Edgbaston Pool, Marton Mere and Wake Valley Pond since the 1960s. At other sites however, the scale of Hg contamination has not declined significantly despite a 90% reduction in UK Hg emissions from anthropogenic sources since the 1970s (NAEI, 2012).

Previous studies at upland UK lakes (e.g. Yang et al., 2002; Rose et al., 2012) have demonstrated that Hg stored in catchment soils could be a major source of contamination, obscuring the signal of reduction in atmospheric Hg deposition in the sediment record. Despite its potentially long atmospheric life-time (Lindberg et al., 2007) Hg deposition tends to be higher, closer to emission sources (Chen et al., 2010; Chen et al., 2012; Van Metre, 2012; Drevnick et al, 2012) and so we might expect catchment soils near urban lakes to exceed those in more remote locations. We see that this is the case as urban catchment surface soil Hg concentrations exceed the median concentration for UK rural topsoils (95 ng g^{-1}) (Tipping et al., 2011), except at Marton Mere. As catchment soil erosion is an important source of lake sediment material (Dearing, 1991), the transfer of Hg from catchment soils to lakes cannot be ignored, and will delay the response of the lake system to the reduction in emissions and deposition of contaminants (Rose et al., 2012), including Hg (Yang, 2015).

Change in sedimentation rate may be due to changes in productivity especially in the urban lakes (Turner et al, 2013). However, this should not increase the amount of Hg in the lake. In all the cores, total Hg fluxes follow the same trends as sedimentation rates (Figure 3). Their considerable changes in relative level indicate that catchment inputs are the most important source for these lakes. When anthropogenic Hg fluxes follow the same trends as total Hg fluxes, it suggests that anthropogenic Hg is mainly from catchment inputs. This is the case in all cores except CRAZ, where sedimentation rates and total Hg fluxes increase rapidly from the 1850s to the 1940s, while anthropogenic Hg fluxes change only slowly, indicating an increase in less contaminated material entering the lake.

The temporal distribution of some geochemical elements in the sediment cores suggests that sedimentation processes have gone through dramatic changes in the past (Figure S3). For Ca, concentrations have changed considerably in most cores and may be due to hydrological change (Dean, 1999) (e.g. Slapton Ley), or changes within the catchment (e.g. Crag Lough) and these processes could also affect Hg input to the sediments. However, direct human impact in urban or suburban sites has played a more important role in Hg input to the lakes. For example, waste inputs to Chapman’s Pond changed sediment Ca and Zr concentrations, and increased Hg fluxes to the sediments. Mercury concentrations reach or exceed consensus-PECs in two cores (Edgbaston Pool and Marton Mere), and 500 ng g^{-1} at a further two (Thoresby Lake and Fleet Pond), all of which have clear evidence for local human direct impacts. This shows similar results to increases in Hg loading from local source discharge in other urban, suburban or industrial areas (e.g. Yang, 2010; Van Metre, 2012; Li et al., 2013; Drevnick et al., 2016). Furthermore, human activities that disturb catchment soils such as agricultural and forestry processes raise the likelihood of increased Hg transfer from contaminated soils, so catchment management practices are therefore also an important consideration in controlling erosion and hence Hg burden in lakes (Lyons et al., 2006; Porvari et al., 2009).

Mercury accumulation rates (fluxes) are derived from the product of Hg sediment concentration and bulk sediment accumulation rate and hence an increase in one, or both, of these parameters can lead to an observed Hg flux increase. If both Hg concentration and sedimentation rate are high, then the combination can result in very high Hg fluxes. For example, the highest Hg flux measurement in this study was in the 1950s at Marton Mere where a sedimentation rate of over 0.35 g cm^{-2} yr^{-1} occurred with a Hg concentration of 1142 ng g^{-1} to produce a Hg flux of over 4000 μg m^{-2} yr^{-1}. Mercury fluxes reach or exceed 1000 μg m^{-2} yr^{-1} in four cores. Three (Edgbaston Pool, Thoresby Lake and Marton Mere) are in the Midlands and north-west England, and here, the high Hg fluxes are mainly derived from the high concentrations in the sediments. In Edgbaston Pool, Hg concentrations are over 1000 ng g^{-1} in most sediments deposited since the beginning of the 19th century, while sediments in Marton Mere have Hg concentrations over 1000 ng g^{-1} from the mid-19th century to the 1960s. While the high fluxes at Thoresby Lake are also due to high Hg concentrations, changes in flux through the core are driven by changing sediment accumulation rate as concentrations remain relatively constant (Figure S3). The high Hg flux in the fourth site, Chapmans Pond in York, was due to high sedimentation rates in the early-1980s (see Figure S3) probably due to the impact of waste disposal at the site. In the last decade, Hg fluxes in five sediment cores (Edgbaston Pool; Thoresby Lake; Marton Mere, Fleet Pond; Holt Hall Lake) have remained above 500 μg m^{-2} yr^{-1}, while those in Chapman’s Pond and Wake Valley Pond exceed 250 μg m^{-2} yr^{-1}, and those of Crag Lough and Slapton Ley are lower, at 87 and 68 μg m^{-2} yr^{-1}, respectively (Figure 3). These are all considerably higher than the limited Hg depositional flux data available for other sites in the UK for the same period (Table 3) (Yang et al., 2002; 2009).

Table 3. Hg sediment and soil concentrations and fluxes compared with Lochnagar (Yang et al, 2001) and London sites (Yang et al, 2009). Italic numbers in parentheses are measured atmospheric Hg deposition fluxes

Site	Soil surface Hg concentrations (ng g^{-1})	Sediment surface Hg concentrations (ng g^{-1})	Sediment fluxes (*atmospheric deposition fluxes*) (μg m^{-2} yr^{-1})
This study			
Chapman’s Pond	237, 416, 806	159	249
Crag Lough	111	212	87
Edgbaston Pool	242, 386, 569	939	1155
Upper Holt Hall Lake	81, 100, 255	376	515
Marton Mere	65	141	570
Fleet Pond	181, 219, 306	556	903
Slapton Ley	101, 224, 459	152	68
Thoresby Lake	93, 257, 270	458	2287
Wake Valley Pond	161, 1438, 1551	185	379
Other UK data			
Lochnagar, Scotland	132-277 (n=10)	111- 228 (n=17)	17.6 (*35.9*)
Central London		100-1718 (mean 491, n=30)	(*15 – 52.5*)

High Hg fluxes can also be derived from sediment focussing (where sediments from littoral areas are resuspended and transported to deeper areas where cores are usually taken), the scale of which can be assessed by comparing unsupported ^{210}Pb fluxes in the sediment cores with those from modelled atmospheric ^{210}Pb deposition (Appleby, 2001) . For the lakes in this study, sediment ^{210}Pb fluxes are only 1-3 times higher than depositional fluxes suggesting that the contribution of focussing to high sediment Hg fluxes is limited. Sediment focussing corrected Hg accumulation rates for the 2000s have a relatively good linear relationship with the ratio of catchment area to lake area in these sites (Figure 4). The intercept of regression line (107.64 µg m^{-2} yr^{-1}, see Figure 4, the 2000s) which should provide an indication of atmospheric depositional Hg flux in the sampling region may not be correct as some lakes (e.g. Fleet Pond, see SI) have received local, direct or point source inputs during this time, which are likely to increase the intercept level. The considerably higher predicted depositional flux than that for monitored Hg fluxes in Central London (Table 3) might also show evidence for direct, local anthropogenic Hg inputs. The proportion of atmospheric Hg that has been transported from catchments to the lakes in the 2000s has changed considerably when compared with the 1850s, 1900s, and 1950s (Figure 4), suggesting that these sites cannot be used to reconstruct the history of atmospheric Hg deposition (Swain et al 1992, Yang 2015). The poor linear relationship of Hg accumulation rates with the catchment to lake ratios in the 1850s, 1900s, and 1950s (Figure 4) imply complexity of Hg sources, and that atmospheric deposition is not the major source of Hg during the time.

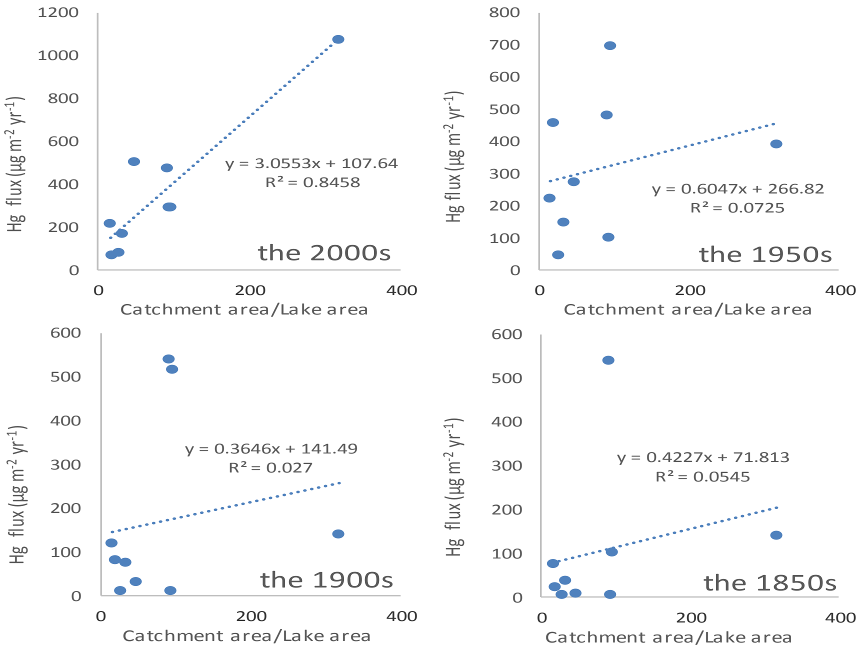

Figure 4. Sediment focussing corrected Hg accumulation rates as linear functions of the ratio of terrestrial catchment area to lake area in the 1850s, 1900s, 1950s and the 2000s.

Parallel changes in sedimentation rates and Hg fluxes (Figure 3) and high soil and sediment Hg concentrations and sediment Hg fluxes (Table 3) indicate the importance of catchment sources for Hg inputs to a range of aquatic environments. However, it is likely that this will only become further exacerbated in future decades as Hg emissions and deposition remain low and remobilisation of Hg stored within catchment soils remains elevated or increases as a result of climate-enhanced soil erosion (e.g. Rose et al., 2012). This has two consequences. First, inputs of Hg and other contaminants previously stored in catchment soils are transferred to aquatic systems at an increased rate and, second, sediment accumulation rates increase. In general, sedimentation rates at all these sites have increased within the ^{210}Pb dated period (excepting major changes from high magnitude, low frequency events such as at Crag Lough) and are in agreement with the pattern observed for many lake types across Europe (Rose et al., 2011). As described above, the combination of increased Hg inputs and elevated sedimentation rates results in significantly increased Hg fluxes and therefore these could remain high for some considerable time to come.

5. **Conclusions**

The use of lake sediment archives from urban and sub-urban lakes has been very limited, until recently, although there is now an increasing ecological and societal interest in them. While they are less likely to reveal the internationally important patterns of contaminant pathways that are commonly identified from remote lakes, they can faithfully record local disturbances and provide an historical archive of local environmental change, if the sediments have not been too disturbed. They may, therefore, be an under-used resource that, with local knowledge, can provide useful temporal data on contaminant inputs.

The sediment records from most of the lakes in this study, particular those in urban areas, show considerable Hg contamination earlier than the mid-19th century probably derived from local industrial and urban development. The data show that at a number of these lakes, Hg concentrations exceeded sediment quality guidelines for the protection of benthic aquatic organisms, before the mid-19th century, and remained high for a considerable period.

While UK Hg emissions have declined by over 90% since the 1970s, this has not brought a significant recovery in Hg concentrations and inputs to most of these lakes and mercury fluxes continue to increase in more than half during the period. While this is partially due to local direct inputs and urban development, our data show that this is also due to the reservoir of Hg stored in catchment soils as a result of contamination by centuries of atmospheric Hg deposition and direct release. Hence, Hg inputs to the sediments are mainly derived from catchment inputs reflected by the changes in sedimentation rates. Heavily contaminated soils usually exist at the soil surface but may be buried by catchment disturbance. The remobilisation of this contaminated soil, and the transfer of Hg to aquatic systems, increases both Hg inputs and sediment accumulation rates. Given the massive store of Hg within many catchments and the impact of climate change likely to enhance catchment soil erosion, Hg transfer and inputs to aquatic systems from these sources are likely to remain elevated for many decades to come.

Acknowledgments

This study formed part of the research work of the OPAL Water Centre, part of the Open Air Laboratories (OPAL) project funded by the Big Lottery Fund. We thank OPAL Community scientists for site selection and facilitating initial contacts and access, all the site owners who provided us with access and permissions to carry out these studies, and local people who provided advice and information. We also thank colleagues from the Environmental Change Research Centre, University College London for their help in the field and the laboratory.

References

Allen,R. C., 2011. Why the industrial revolution was British: commerce, induced invention, and the scientific revolution. Economic History Review, 64: 357–384

Appleby, P.G., 2000. Radiometric dating of sediment records in European mountain lakes. Limnol. 59 (Suppl. 1): 1-14.

Appleby, P G, 2001. Chronostratigraphic techniques in recent sediments. In W M Last and J P Smol (eds.) Tracking Environmental Change Using Lake Sediments. Vol. 1: Basin Analysis, Coring, and Chronological Techniques. Kluwer Academic Publishers, Dordrecht. Pp171-203.

Appleby, P.G., 2004. Environmental change and atmospheric contamination on Svalbard: sediment chronology. J Paleolimnol. 31: 433-443.

Bakker, M.M., Govers, G., van Doom, A., Quetier, F., Chouvardas, D., Rounsevell, M., 2008. The response of soil erosion and sediment export to land-use change in four areas of Europe: The importance of landscape pattern. Geomorphology, 98: 213-226.

Balogh, S.J., Engstrom, D.R., Almendinger, J.E., Meyer, M.L., Johnson, D.K., 1999. History of mercury loading in the Upper Mississippi River reconstructed from the sediments of Lake Pepin. Environ. Sci. Technol. 33: 3297-3302.

Bindler, R., Renberg, I., Appleby, P.G., Anderson, N.J., Rose, N.L., 2001. Mercury accumulation rates and spatial patterns in lake sediments from west Greenland: A coast to ice margin transect. Environ. Sci. Technol. 35: 1736-1741.

Bindler, R., Rydberg, J., Renberg, I., 2011. Establishing natural sediment reference conditions fro metals and the legacy of long-range and local pollution on lakes in Europe. J Paleolimnol. 45: 519-531.

Boes, X., Rydberg, J., Martinez-Cortizas, A., Bindler, R., Renberg, I. 2011. Evaluation of conservative lithogenic elements (Ti Zr, Al and Rb) to study anthropogenic element enrichments in lake sediment. J Paleolimnol. 46: 75-87.

Bookman, R., Driscoll, C.T., Engstrom, D.R., Effler, S.W., 2008. Local to regional emission sources affecting mercury fluxes to New York lakes. Atoms. Environ. 42: 6088-6097.

Burniston, D., Klawunn, P., Backus, S., Hill, B., Dove, A., Waltho, J., 2011. Spatial distributions and temporal trends in pollutants in the Great Lakes 1968-2008. Water Quality Research J Canada 46: 269-289.

CCME, 1999. Canadian Environmental Quality Guidelines. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, Mercury.

Chen, X., Xia, X., Wu, S., Wang, F., Guo, X., 2010 Mercury in urban soils various types of land use in Beijing, China. Environ. Pollut. 158: 48-54.

Chen, L., Xu, Z., Ding, X., Zhang, W., 2012. Spatial trend and pollution assessment of total mercury and methylmercury pollution in the Pearl River Delta soil, South China. Chemosphere 88: 612-619.

Cooper, C.B., Dickinson,J., Phillips,T., Bonney, R., 2007. Citizen science as a tool for conservation in residential ecosystems. Ecology and Society. 12(2): 11 [online].

Davies, L., Bell, J. N. B., Bone, J. J., Head, M ., Hill, L., 2011. Open Air Laboratories (OPAL): A community-driven research programme. Environ Pollu. 159: 2203-2210.

Davison, W., 1993. Iron and manganese in lakes. Earth-Sci. Reviews, 34: 119-163.

Dean, W.E., 1974. Determination of carbonate and organic-matter in careous sediments and sedimentary-rocks by loss on ignition – comparison with other methods. Journal of Sedimentary Petrology, 44: 242-248.

Dean, W. E., 1999. The carbon cycle and biogeochemical dynamics in lake sediments. J. Paleolimno. 21: 375-393.

Dearing, J. A., 1991. Lake sediment records of erosional processes. Hydrobiologia, 214, 99-106

Deelstra, J., Oygarden, L., Blankenberg, A.B., Eggestad, H.O., 2011. Climate change and runoff from agricultural catchments in Norway. International Journal of Climate Change Strategies and Management. 3: 345-360.

Drevnick, P.E., Cooke, C. A., Barraza, D., Blais, J. M., Coale, K. H., Cumming, B. T., 2016. Spatiotemporal patterns of mercury accumulation in lake sediments of western North America. Sci. Total Environ. (In press).

Engstrom, D.R., Swain, E.B., 1997. Recent declines in atmospheric mercury deposition in the upper Midwest. Environ. Sci. Technol. 31: 960-967.

Farmer, J.G., Anderson, P., Cloy, J.M., Graham, M.C., Mackenzie, A.B., Cook, G.T., 2009. Historical accumulation rates of mercury in four Scottish ombrotrophic peat bogs over the past 2000 years. Sci. Total Environ. 407: 5578-5588.

Fitzgerald, W.F., Engstrom, D.R., Lamborg, C.H., Tseng, C.M., Balcom, P.H., Hammerschmidt, C.R., 2005. Modern and historic atmospheric mercury fluxes in northern Alaska: Global sources and Arctic depletion. Environ. Sci. Technol. 39: 557-568.

Gillis, A.A., Miller, D.R., 2000. Some local environmental effects on mercury emission and absorption at a soil surface. Sci. Total Environ. 260: 191-200.

Hermanns, Y.-M., Biester, H., 2013. Anthropegenic mercury signals in lake sediments from southernmost Patagonia, Chile. *Sci Total Environ*. **445-446**, 126-135.

Hylander, L.D., Meil,i M., 2003. 500 years of mercury production: global annual inventory by region until 2000 and associated emissions. Sci. Total Environ. 304: 13-27.

Li,H.B., Yu,S., Li,G.L., Deng,H., Xu,B., Ding,J., Gao,J.B., Hong,Y.W., Wong,M.H., 2013. Spatial distribution and historical records of mercury sedimentation in urban lakes under urbanization impacts. Sci. Total Environ. 445/6: 117-125.

Lyons, W., Berry); Fitzgibbon, T. O., Welch, K. A., Carey, A. E., 2006. Mercury geochemistry of the Scioto River, Ohio: Impact of agriculture and urbanization. Appl Geochem. 21: 1880-1888.

Johansson, K., 1985. Mercury in sediment in Swedish forest lakes. Verh. Internat. Verein. Limnol. 22: 2359-2363.

Lamborg, C.H., Fitzgerald, W.F., Damman, A.W.H., Benoit, J.M., Balcom, P.H., Engstrom, D.R., 2002. Modern and historic atmospheric mercury fluxes in both hemispheres: Global and regional mercury cycling implications. Glob. Biogeochem. Cycles 16:1104.

Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W ., Pirrone, N., Prestbo, E ., Seigneur, C., 2007. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. Ambio 36: 19-32.

Lubchenco, J; Karl, TR. 2012. Predicting and managing extreme weather events. Physics Today, 65(3): 37.

MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39: 20-31.

Morgan, R., Quinton, J.N., Smith, R., Govers, G., Poesen, J., Auerswald, K., Chisci, G, 1998. The European Soil Erosion Model (EUROSEM): A dynamic approach for predicting sediment transport from fields and small catchments. Earth Surface Processes and Landforms , 23: 527-544.

Mosley, S., 2001. The chimney of the world. A history of smoke pollution in Victorian and Edwardian Manchester. Routledge, Abingdon. 271 pp.

Muir, D.C.G., Wang, X., Yang, F., Nguyen, N., Jackson, T.A., Evans, M.S., Douglas, M., Kock, G., Lamoureux, S., Pienitz, R., Smol, J.P., Vincent, W.F., Dastoor, A., 2009. Spatial trends and historical deposition of mercury in eastern and northern Canada inferred from lake sediment cores. Environ. Sci. Technol. 43: 4802-4809.

NAEI, 2014. http://naei.defra.gov.uk/data/data-selector-results?q=601 (accessed on 03/06/2014).

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature, 333: 134-139.

Perry, E., Norton, S. A., Kamman, N. C., Lorey, P. M., Driscoll, C. T., 2005. Deconstruction of historical mercury accumulation in lake sediments, Northeastern United State. *Ecotoxicol*. **14**: 85-99.

Porvari, P., Verta, M., Munthe, J., Haapanen, M., 2003. Forestry practices increase mercury and methyl mercury output from boreal forest catchments. Environ. Sci. Technol. 23: 2389-2393.

Rose, N.L., Yang, H., Turner, S.D., Simpson, G.L., 2012. An assessment of the mechanisms for the transfer of lead and mercury from atmospherically contaminated organic soils to lake sediments with particular reference to Scotland, UK. Geochimica et Cosmochimica Acta, 82:113-135.

Rose, N.L., Morley, D., Appleby, P.G., Battarbee, R. W., Alliksaar, T., Guilizzoni, P., Jeppesen, E., Korhola, A., Punning, J.M., 2011. Sediment accumulation rates in European lakes since AD 1850: trends, reference conditions and exceedence. J. Paleaolimnol. 45:447-468.

Rothwell, J.J., Robinson, S.G., Evans, M.G., Yang, J., Allott, T.E.H., 2005. Heavy metal release by peat erosion in the Peak District, southern Pennines, UK. Hydrological Processes, 19:2973-2989.

Rothwell, J.J., Evans, M.G., Allott, T.E.H., 2007. Lead contamination of fluvial sediments in an eroding blanket peat catchment. Applied Geochemistry, 22: 446-459.

Schuster P. E., Shanley, J. B., Marvin-Dipasquale, M., Reddy, M. M., Aiken, G. R., Roth, D. A., 2008. Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed. Water Air Soil Pollut. 187: 89-108.

Skipp, V., 1997. A history of Greater Birmingham – down to 1830. Studley: Brewin Books, Birmingham, pp96.

Stobart, J., 2004. The first industrial region. Manchester University Press, Manchester and New York, pp259.

Stobart, J., Raven, N., 2005. Towns, regions and industries, urban and industrial change in the Midlands, c. 1700 – 1840. Manchester University Press, Manchester and New York, pp272.

Tipping, E., P., Poskitt, J.M., Lawlor, A.J., Wadsworth, R.A., Norris, D.A., Hall, J.R., 2011. Mercury in United Kingdom topsoils; concentrations, pools, and Critical Limit exceedances. Environ. Pollut. 159: 3721-3729.

Turner, S., Rose, N., Goldsmith, B., Harrad, S., Davidson, T., 2013. OPAL Water Centre Monitoring Report, 2008-2012. ECRC Report.

US National Oceanic and Atmospheric Administration, 1999. Screening Quick Reference Tables. http://response.restoration.noaa.gov/sites/default/files/SQuiRTs.pdf (accessed on 03/06/2014).

Van Metre, P.C., 2012. Increased atmospheric deposition of mercury in reference lakes near major urban areas. Environ. Pollut. 162: 209-215.

Yang, H., Rose, N.L., Boyle, J.F., Battarbee, R.W., 2001. Storage and distribution of trace metals and spheroidal carbonaceous particles (SCPs) from atmospheric deposition in the catchment peats of Lochnagar, Scotland. Environ. Pollut. 115: 231-238.

Yang, H., Rose, N.L., Battarbee, R.W., Boyle, J.F., 2002. Mercury and lead budgets for Lochnagar, a Scottish mountain lake and its catchment. Environ. Sci. Technol. 36: 1383-1388.

Yang, H., Rose, N.L., 2003. Distribution of mercury in six lake sediment cores across the UK. Sci. Total Environ. 304: 391-404.

Yang, H., Berry, A., Rose, N.L., Berg, T., 2009. Decline in atmospheric mercury deposition in London. J. Environ. Monit. 11: 1518-1522.

Yang, H., Battarbee, R., Turner, S., Rose, N., Derwent, R., Wu, G., Yang, R., 2010. Historical reconstruction of mercury pollution across the Tibetan Plateau using lake sediment. Environ. Sci. Technol. 44: 2918-2924.

Yang, H., 2010. Historical mercury contamination in sediments and catchment soils of Diss Mere, UK. Environ. Pollut. 158: 2504-2510.

Yang, H., Smyntek, P., 2014. Use of mercury record in Red Tarn sediments to reveal air pollution and the implications of catchment erosion. Environ Sci: Processes impacts, **16**: 2554-1563.

Yang, H., 2015. Lake sediments may not faithfully record decline of atmospheric pollution deposition. Environ. Sci. Technol. 49: 12607-12608.