Organic Matter and Total Mercury in Acid-Sensitive Lakes in Ireland

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ABSTRACT

Organic Matter and Total Mercury in Acid-Sensitive Lakes in Ireland

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The following study measured dissolved organic carbon (DOC) and total mercury (THg) concentrations in acid sensitive lakes in the Republic of Ireland. Sixty-eight upland lakes and 48 lowland lakes were sampled for DOC; the upland lakes were additionally sampled for THg. Spatial variability of DOC was explained by regional precipitation and soil organic matter. A subset of lakes was tested for long-term trends and in contrast to reports of rising DOC in European surface waters, changes in DOC were minor. Spatial variability in THg was explained by DOC and organic matter aromaticity. Long-term THg concentrations increased, likely caused by inputs of terrestrial THg. A subset of lakes was sampled for sediment and soil and the results suggested soils drove THg variation in lake water and sediment. Lake water and sediment THg was low and consistent with background regions, while soil THg was relatively high due to high organic content.

KEYWORDS: Dissolved Organic Carbon, Organic Matter, Total Mercury, Lakes, Water, Soil

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DOC	Dissolved organic carbon
EPA	Environmental Protection Agency
EU	European Union
E2:E3	Absorbance ratio 254 nm by 365 nm
Hg	Mercury
ICP Waters	International Cooperative Programme for assessment and monitoring of the effects of air Pollution on rivers and lakes
Na:Cl	Sodium to chloride ratio
NMAD	Normalized median absolute deviation
OC	Organic carbon
OM	Organic matter content (%)
PCA	Principal component analysis
$SUVA_{254}$	Specific ultraviolet absorbance at 254 nm
THg	Total mercury
THg/OC	Total mercury normalized by organic carbon
RDA	Redundancy analysis
UK	United Kingdom
WFD	Water Framework Directive
285:254	Absorbance ratio 285 nm by 254 nm

CHAPTER ONE: Introduction

Water is vital for life and prominent in our cultural and recreational activities. Our reliance on water resources makes water quality a global concern. The two facets of water chemistry that were studied for this thesis are organic matter and mercury, which are independently important for water quality considerations but are also interconnected.

Aquatic organic matter

Aquatic organic matter is partially or entirely decomposed material from living things, either autochthonous or allochthonous in origin; autochthonous organic matter originates from sources within a water body (e.g., algae), while allochthonous organic matter is of terrestrial origin, washed in from the catchment (e.g., soil runoff or percolation). Since organic matter is carbon based, its concentration in water is quantified as total organic carbon (TOC) or dissolved organic carbon (DOC), where TOC quantifies all organically derived carbon in a water sample, both dissolved (<0.45 µm) and particulate (>0.45 µm) matter. Measuring TOC or DOC requires specialized equipment (e.g., Shimadzu TOC Analyzer) or laborious persulfate oxidation; less costly options to indirectly quantify organic matter include turbidity, secchi depth, absorbance, and water colour (Kaplan, 1992; Toming et al., 2016).

While organic matter can be quantified through a variety of methods, not all organic matter is the same; the differences in characteristics of organic matter is often called organic matter quality and is a product of the origin of the organic matter (e.g., autochthonous vs allochthonous), as well as alterations from system processing (e.g., biodegradation and abiotic reactions). Organic matter quality is generally defined by molecular weight, size, aromaticity, polarity, solubility, molar ratios (e.g., N/C), or biodegradability. These measures of quality are not independent, and several are closely linked. Organic matter quality can be measured directly (e.g., biodegradability experiments), but this again requires specialized equipment (e.g., PreSens SensorVials and SDR SensorDish Reader). An alternative is to approximate quality, using light absorbance to calculate organic matter quality indices, though this is only possible for certain facets of quality and only represents the photoactive fraction of organic matter. One common index is specific ultraviolet absorbance (SUVA in units of L mg^{-1} m-^{1}), which is calculated by dividing absorbance (1/m) at a given wavelength by DOC concentration (mg/L). SUVA is most commonly used for the wavelength 254 nm ($SUVA_{254}$), and indicates aromaticity (Weishaar et al., 2003). Absorbance ratios are also used as indices of organic matter quality, for example, the ratio of 250 nm by 365 nm (E2:E3), and the ratio 285 nm:254 nm, are associated with molecular weight (Peuravuori & Pihlaja, 1997) and polarity, respectively (Clarke et al., 2007). While there are several approaches to measure organic matter quality, their usage varies between studies and regions, with no general consensus or widespread systematic usage in water quality literature, in contrast to the widespread use of DOC to quantify organic matter.

Organic matter is influenced by the physical and chemical characteristics of the water body and the surrounding environment, which can impact the production and movement of autochthonous and allochthonous derived organic matter; it can be further influenced by climate and other factors impacting the region (e.g., oceanic influences). Organic matter plays a significant role in aquatic environments, existing at the center of natural water chemistry dynamics, from water clarity to nutrient and carbon cycling, but also plays a part in current water quality concerns, particularly in the contaminant cycling, as various pollutants bind or otherwise interact with organic matter. For example, DOC and mercury concentrations have a positive relationship (e.g., Ravichandran, 2004), but mercury concentrations have also been associated with hydrophobic fractions of organic matter (Dittman et al., 2010), and aromaticity (Lescord et al., 2018).

Due to the importance of organic matter in aquatic systems, and the positive relationship it has with many contaminants, there is concern over reported DOC increases in surface waters across North America and Europe (e.g., Monteith et al., 2007; Oni et al., 2013; Garmo et al., 2020). There have been several theories for the cause of this trend; as these increases in DOC have coincided with changes in acidic deposition, the trend has been most commonly linked to acidification recovery of aquatic ecosystems (e.g., Monteith et al., 2007). Another common theory posits that the increases in DOC are the result of climate change (e.g., Porcal et al., 2009). Studies of long-term changes of organic matter quality in surface water are less common than studies of changes in DOC, but available studies have also shown significant temporal trends attributed to the same mechanisms as changes in DOC (e.g., Dawson et al., 2009; Jane et al., 2017). While the cause remains disputed, confirmation of what is driving changes in DOC is important for determining whether DOC will continue to increase.

Total mercury (THg) in aquatic systems

Mercury is a metal that can be found in various environmental media (e.g., air, water, sediment, and soil) and can cycle between these facets of an ecosystem. For example, atmospheric deposition can transport mercury to surface soils (e.g., Aslam et al., 2019) and mercury in soil can enter aquatic environments through soil erosion, increasing mercury concentrations in sediment or water (e.g., Rose et al. 2012; Stoken et al. 2016). Mercury can occur in elemental, inorganic, and organic forms, and transformations naturally occur in the environment; for example, anaerobic sulphate reducing bacteria in aquatic or wetland environments can transform elemental mercury into methylmercury. Measuring the bulk concentration of mercury in all forms (elemental, inorganic, organic) is referred to as total mercury, and is generally denotated as THg. The equipment and methods used to analyze mercury vary depending on the forms of mercury being quantified (THg vs methylmercury) and the environmental media being analyzed (air, water, soil, sediment), but equipment specialized for mercury analysis (e.g., Tekran 2600) is commonly used, paired with methods designed to limit contamination or volatilization of mercury from the sample (e.g., EPA method 1631e; United States EPA, 2002).

Human activities impact the global mercury cycle in a variety of ways. Burning of fossil fuels releases stored mercury from the earth's crust, increasing atmospheric concentrations (AMAP & UN Environment, 2019), and localized inputs to terrestrial and aquatic environments can occur through mismanagement of mercury-containing industrial or mining waste (e.g., Kinghorn et al., 2007). In addition to increasing environmental concentrations of mercury, human activities have also caused disruptions to the ecosystem transfer and storage of mercury on a global scale; for example, rising temperatures are being shown to impact oceanic mercury (Zhang et al., 2021).

Human exposure to mercury is a global concern due to the severe impacts to human health; mercury is a neurotoxin and can also cause damage to the digestive and immune systems (WHO, 2017). The World Health Organization named mercury as one of the top ten chemicals of public health concern due to the extreme effects it has on human health (WHO, 2017). Global concern about mercury pollution has also prompted the adoption of the United Nation's Minamata Convention on Mercury, the goal of which is to reduce global mercury pollution and monitor mercury concentrations globally (UNEP, 2019). While there are many notable instances of localized industrial mercury pollution causing high levels of mercury exposure to a local population (e.g., Grassy Narrows, Ontario; Minamata, Japan) mercury pollution can reach even the most remote communities through transboundary air pollution (e.g., Steffen et al., 2014) and exposure through marine food webs (e.g., Kirk et al., 2012).

While reductions in mercury emissions should lead to reductions in the concentrations of mercury found in surface waters, the relationship between organic matter and mercury could complicate long term recovery. Firstly, soils are the largest sinks of mercury on earth, and catchment surface soils, particularly highly organic soils, are holding remnants of historic mercury pollution that may be released into surface waters over time, delaying the effects of pollution controls (Yang et al., 2016). Secondly, the widespread increases in surface water DOC may also have impacts on mercury trends, potentially driving increases in mercury concentrations in surface waters (Millard et al., 2018). Therefore, it is important to consider long term changes in organic matter when considering long term changes in aquatic mercury concentrations.

Ireland

Ireland sits on the western periphery of Europe and experiences a mild climate due to the influence of the Atlantic Ocean; inland daytime temperatures generally range from 8°C in the winter to around 20°C in the summer (Met Éireann, 2020). In addition to the mild temperatures, the oceanic influence causes high precipitation across the island, and especially in the west due to the prevailing wind direction. The western half of the Island usually receives 1000–1400 mm annual rainfall, compared with 750–1000 mm in the east (Met Éireann, 2020). In the mountainous regions of Ireland, rainfall tends to be greater, with some areas receiving 2000 mm or more per year (Met Éireann, 2020).

The topography of Ireland can be divided into upland and lowland areas. The uplands are undeveloped areas above 150 masl, usually composed of habitats such as heaths, semi-natural grasslands and bogs, predominately used for rough grazing, and mostly situated along the coast (Perrin et al., 2014). Comparatively, lowland areas are composed of a myriad of habitats and land uses, including developed areas, agriculture, semi-natural protected lands, and forestry. Ireland is home to more than 12 000 lakes. In the upland areas these lakes tend to be small and precipitation fed, while the lowland lakes are larger interconnected systems within larger catchment networks.

Many upland and lowland regions across Ireland are classified as acid-sensitive due to the underlying bedrock, resulting in lakes with naturally low pH and alkalinity which are at greater risk of acidification from anthropogenic acidic deposition. Controls on global acidic deposition have been in place for decades (e.g., UNECE Convention on Long-range Transboundary Air Pollution), and evidence of recovery has been observed in surface waters globally (e.g., Hesthagen et al., 2011; Driscoll et al., 2016), including in Ireland (Burton & Aherne, 2012) but the acid-sensitive status of Irish surface water is particularly relevant to this study as one of the most common theories for rising DOC concentrations in acid-sensitive surface waters is progressive recovery from acidification in response to decreased acidic deposition (e.g., Monteith et al., 2007). It’s hypothesized that the increased ionic strength and decreased pH caused by acidic deposition resulted in suppressed organic matter solubility in surface waters and soils, and recovery from these conditions has caused DOC concentrations to rise in the associated surface waters (Monteith et al., 2007; de Wit et al., 2021).

Study justification

Lakes in Ireland are surveyed through several monitoring programs (e.g., EU's Water Framework Directive; ICP Waters), nonetheless, there is limited knowledge with respect to organic matter and mercury. Few studies have focused on lake water organic matter in Ireland, and the literature that exists has small sample sizes (e.g., McCaul et al., 2011), or is limited to rivers and streams (e.g., Liu et al., 2014; Koehler et al., 2009). Similarly, studies in the UK tend to be more focused on rivers and streams (e.g., Evans et al., 2005; Worrall & Burt, 2004). There are other studies for both Ireland and UK that present DOC amongst their data, but these studies use DOC as a predictor for the variable of interest and do not explore or focus on DOC specifically (e.g., Robson et al., 2019); this includes published studies using past data from the lakes covered in this study (e.g., Burton et al., 2013). The above studies tend to focus solely on the concentration of organic matter, and do not examine quality; studies that characterize DOC in Ireland and the UK are limited (e.g., Turner et al., 2016; Yates et al., 2016).

Mercury data for Irish surface waters is far more limited than organic matter. It is generally assumed that mercury concentrations are low and below detection, making it a challenge for routine monitoring and leading to a lack of consistent mercury data for natural environments in Ireland. To the extent of the author's knowledge, the only published studies of mercury concentrations in lakes in the Republic of Ireland are those of the same sites used in this thesis (e.g., Scott & Aherne, 2013). In the UK there are a greater number of mercury studies in aquatic environments, but rather than studies of present concentrations of mercury in surface water they tend to be estimates of past concentrations based on sediment cores (e.g., Yang, 2010), or studies that are focused on concentrations in biota while presenting water concentrations as a secondary aspect of the paper (e.g., Edwards et al., 1999), however, there are exceptions (Rose et al., 2013).

Study sites

To meet the requirements of the European Union's Water Framework Directive (WFD), in 2006 the Irish EPA established a network of lakes to assess and monitor the quality of Ireland's water bodies. Under the WFD a set of predominately lowland lakes are regularly sampled by the EPA and analyzed for water chemistry. In 2010 the lakes were analyzed for DOC concentration for the first time. All lakes monitored under the WFD are greater than one hectare and used for water abstraction, which largely excludes upland lakes. Upland lakes are recognized as sentinels of change (Moser et al., 2019) however, despite their value as study lakes, the upland lakes in Ireland are more rarely sampled because of difficulty of access, with many being in remote areas with no road access. In 1997 the survey of upland acid-sensitive systems (SUAS) collected water samples from upland lakes across Ireland, followed by re-surveys in 2007–2008 and 2017–2018. In 2007, DOC concentration was directly measured for the first time, since the 1997 survey approximated DOC using absorbance. Unlike the WFD lakes, the SUAS lakes also have THg data; in 2008 the lakes were sampled for THg for the first time and during the 2017–2018 survey lake sediment and catchment soil was also collected and analyzed for THg for a subset of the lakes.

Objectives

The primary objective of this thesis was to determine what drives variation in DOC and THg between lakes in Ireland, while also testing for significant changes in either variable during the past decade. A secondary objective was to investigate the interlinkages in the concentration of THg in soils, lake sediment, and lake water. The study collected and analyzed lake water for DOC at 68 upland lakes over the course of 2017 & 2018 and utilized available lake chemistry at 48 lowland lakes sampled by the Irish EPA during the same period. Additional DOC data for a subset of upland (n=7) and lowland (n=14) lakes from the respective start of the data records for the two datasets (2007 & 2010) until the 2017–2018 survey were also used to test for temporal change in DOC. The upland lakes were additionally analyzed for THg concentrations in 2017–2018, and these data, as well as previous THg measurements starting in 2008, were used to determine associations with THg and test for significant changes in THg concentrations over the decade. Thirty-one of the upland lakes were also sampled for THg in lake sediment and catchment soil during the 2017–2018 survey.

This thesis was written in manuscript style, with three research chapters. The first manuscript chapter is focused on DOC in upland and lowland Irish lakes, while the second and third manuscripts are focused on THg in upland Irish lakes. The second manuscript explored THg in lake water while the third manuscript examined the link of THg concentrations between lake water, sediment, and catchment soil. Due to the upland dataset being used in all three chapters the methods will have repeated content.

The objectives of Chapter Two ‘Dissolved Organic Matter in Acid-Sensitive Lakes’ were to:

1. Determine DOC concentrations in 68 upland and 48 lowland acid-sensitive lakes and identify physical and chemical variables with the strongest associations to DOC
2. Test for significant changes in DOC over a decade in a subset of the study lakes (n=21)

3. Explore organic matter quality in the upland lakes using absorbance indices (e.g., $SUVA_{254}$)

The objectives of Chapter Three ‘Total Mercury in Upland Acid-Sensitive Lakes’ were to:

1. Determine THg concentrations in 68 upland acid-sensitive lakes and identify physical and chemical variables with the strongest associations to THg
2. Test for significant changes in THg over a decade in two subsets of the study lakes (n=24, n=7)

Chapter Four ‘Mercury in soil, sediment, and lake water in upland headwater catchments in Ireland’ has been accepted to the journal *Environmental Earth Sciences* for the thematic issue ‘Soil-Water-Atmosphere Nexus’ and has been through peer review. The objective was to:

1. Determine THg concentrations in lake water, lake sediment and catchment soil for 31 upland lakes (a subset of the 68 lakes from chapters 2 and 3) and test for connections in THg concentrations or other relevant variables (e.g., organic matter) between the three environmental media.

This research will address gaps in the published literature, such as an examination of recent DOC concentrations across Ireland in both upland and lowland systems, testing for changes in DOC to determine if they are consistent with reports of increasing DOC across Europe, and expanding on limited data for mercury in Irish environments.

CHAPTER TWO: Dissolved Organic Matter in Acid-Sensitive Lakes

2.1 ABSTRACT

Aquatic organic matter has a large influence on natural water chemistry (e.g., nutrient and carbon cycling) and plays a role in water quality concerns due to binding with pollutants. This study measured dissolved organic carbon (DOC) in 116 acid-sensitive Irish lakes and assessed the drivers of spatial variation. Sixty-eight upland lakes and 48 lowland lakes were sampled in 2017–2018; a subset of 21 lakes (7 upland, 14 lowland) had DOC measurements over the past decade and were tested for long-term changes in DOC. Despite physical, chemical, and climatic differences between the upland and lowland lakes, variability in DOC between lakes was best explained by the effects of regional precipitation levels and organic matter in the catchment soils for both upland and lowland systems. Organic matter quality data for the upland lakes suggested a dominance of allochthonous organic matter, further emphasizing the influence of terrestrial organic matter on the lakes. Lastly, in contrast to reported DOC increases elsewhere in Europe, changes in organic matter concentration and quality over the decade were very minor; this was likely due to the relatively short, recent time period of the study since it occurred during a time when the rate of DOC change was slowing, as well as during a period of unprecedented rainfall and storm activity in Ireland.

2.2 INTRODUCTION

Organic matter influences natural water chemistry in a variety of ways, from water clarity to nutrient and carbon cycling, but it also plays a role in water quality concerns, as pollutants can bind to organic matter (e.g., Ravichandran, 2004). Organic matter is quantified as total organic carbon (TOC) or dissolved organic carbon (DOC), where DOC quantifies dissolved (<0.45 µm) organically derived carbon in a water sample, and TOC quantifies both dissolved and particulate matter (>0.45 µm). The concentration of DOC in surface waters can vary widely across a region (e.g., Gavin et al., 2018; Braaten et al., 2018), which can be attributed to a combination of factors such as precipitation, sunlight, and the amount of organic matter in the catchment soils or wetlands in the catchment (e.g., Larsen et al., 2011; Monteith et al., 2015; Sobek et al., 2007).

There have been reports of increases in DOC in surface waters across North America and Europe (e.g., de Wit et al., 2021; Monteith et al., 2007; Oni et al., 2013), which presents a concern for water quality. For acid-sensitive surface waters, recovery from acidification has been one of the most popular theories for the cause of this trend (e.g., Monteith et al., 2007) but there have been other theories, such as altered precipitation patterns and increased temperatures due to climate change (e.g., Porcal et al., 2009).

The concentration of organic matter is commonly considered in studies of water chemistry, but less often considered are the characteristics, or ‘quality’, of organic matter. The quality of organic matter is impacted by its origin (e.g., autochthonous vs allochthonous), as well as alterations from system processing (e.g., biodegradation). Some aspects of organic matter quality can be approximated using ratios of light absorbance and DOC, though they represent only the photoactive fractions of organic matter. One example is $SUVA_{254}$which represents aromaticity and has been widely incorporated into water quality studies (e.g., Jane et al., 2017; Dittman et al., 2010; Lavoie et al., 2019; Lescord et al., 2018). The evaluation of long-term changes of organic matter quality in surface waters is less common than studies of changes in DOC concentration, but available studies have shown some significant temporal trends (e.g., Dawson et al., 2009; Jane et al., 2017).

Ireland is home to more than 12 000 lakes, dominated by small upland lakes (EPA, 2006). The uplands are undeveloped areas above 150 masl composed of habitats such as heaths, semi-natural grasslands and bogs, which are predominately used for rough grazing (Perrin et al., 2014). In contrast, lowland areas are composed of a myriad of habitats and land uses, including developed areas, agriculture, semi-natural protected lands, and forestry. Upland lakes tend to be small, located in small catchments, and are almost entirely precipitation fed. In contrast, lowland lakes are larger interconnected water bodies in larger catchments. Despite these differences, both upland and lowland areas are home to acid-sensitive environments, with poor buffering capacity in the soils resulting in lakes that are more vulnerable to acidification (Aherne et al., 2002).

Lakes in Ireland are surveyed through several monitoring programs (e.g., EU’s Water Framework Directive; ICP Waters), nonetheless, few studies have focused on organic matter; the literature that exists is limited to small sample sizes (e.g., McCaul et al., 2011) or focused on rivers and streams (e.g., Liu et al., 2014; Koehler et al., 2009). Similarly, studies in the UK tend to be more focused on rivers and streams (e.g., Evans et al., 2005; Worrall & Burt, 2004). Further, some studies have used DOC as a predictor of their variable of interest but do not explore or focus on

DOC specifically (e.g., Robson et al., 2019). The above studies also tend to focus solely on concentration of organic matter, and do not examine quality; studies that characterize DOC in Ireland and the UK are limited (e.g., Turner et al., 2016; Yates et al., 2016). The objectives of this study were to determine what drives spatial variation in DOC in acid-sensitive Irish lakes in both upland and lowland environments, and to test for significant changes in DOC during the past decade in a subset of the lakes. A secondary objective was to explore organic matter quality in the upland lakes, and test for significant changes.

The chemistry of upland (n=68) and lowland (n=48) acid-sensitive lakes was summarized and compared for the period April–July 2017–2018 and used to determine the association between DOC and other physico-chemical and climatic variables. A subset of upland lakes (n=7) sampled during 2007–2018 and lowland lakes (n=14) sampled during 2010–2018 were further tested for significant temporal changes in DOC. Lastly, organic matter quality data for the 68 upland lakes was approximated using absorbance and tested for significant changes using the subset of seven upland lakes. This study presents a representative summary of DOC in acid sensitive lakes across Ireland, due to its large sample size (n=116) and geographical coverage of Ireland.

2.3 METHODS

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 rainfall in the west, which usually receives 1000–1400 mm annual rainfall, compared to 750–1000 mm in the east (Met Éireann, 2020). In the mountainous regions, rainfall tends to be greater, with some areas receiving 2000 mm or more per year (Met Éireann, 2020).

During April–July 2017 and 2018, 116 lakes in acid-sensitive regions in the Republic of Ireland were sampled for water chemistry including DOC; 68 were upland, and 48 were lowland lakes (Figure 2.1).

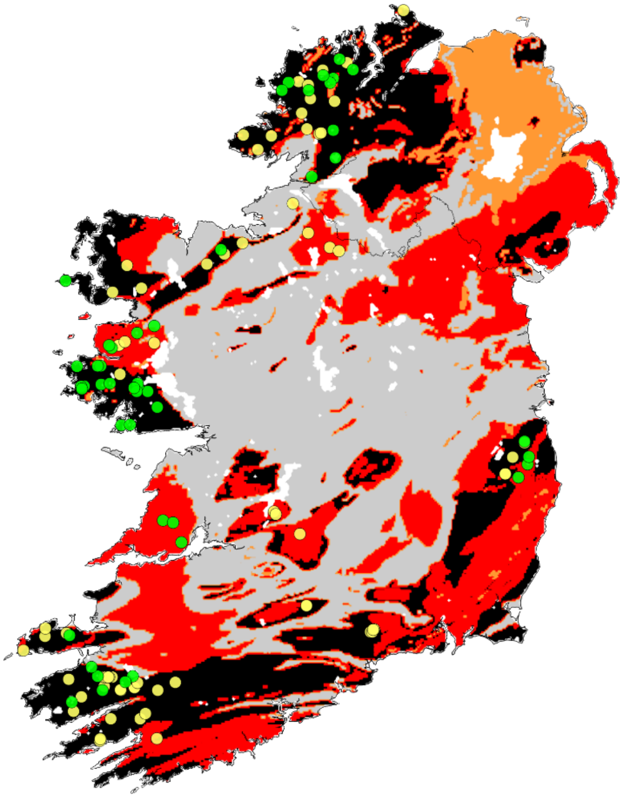

Figure 2.1: *Location of study lakes (n=116) and acid sensitive bedrock in Ireland. Black=high acid sensitivity, red=medium acid sensitivity, orange=low acid sensitivity, grey=not acid sensitive. Yellow circles indicate upland lakes (n=68) and green circles indicate lowland lakes (n=48), sampled April–July 2017 & 2018.*

Upland acid-sensitive lakes (n=68)

The 68 upland lakes were selected from a larger set 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 & Aherne, 2012; Whitfield et al., 2011). The lakes in the 1997 study were selected using stratified random sampling, with greater weighting on higher elevation lakes in acid sensitive regions (Aherne et al., 2002). In the present study, the sub-set of lakes were selected to ensure spatial coverage of all sampling regions, with preference for higher elevation sites, to limit the effects of local disturbance. The 68 study lakes were primarily situated along the mountainous and hilly Western coast (Figure 2.2), had a median elevation of 437 masl and median size of 1.7 ha (Table 2.1). While the upland study lakes were very small (81% < 5 ha), they represent the average sized lake for Ireland (88% < 5 ha [EPA, 2006]). The lakes were sampled at least once during the period of April–July in 2017 & 2018. A subset of seven lakes (Figure 2.2) were sampled approximately once per year between 2007–2018 and were tested for significant temporal changes in DOC and organic matter quality.

Lowland acid-sensitive lakes (n=48)

The lowland lakes used in this study were monitored by the Irish EPA for water quality under the EU's Water Framework Directive (WFD). The WFD lakes were selected to represent a range in lake types, risk categories, and environmental pressures, informed by the National Characterisation Report (EPA, 2006). The WFD is not focused specifically on lowland lakes, but on sources used for water abstraction and with a minimum size of one hectare, which largely excludes smaller upland lakes (Table 2.1). During the period of April–July 2017 & 2018, 48 acid-sensitive lakes were sampled under the WFD's Lake Monitoring Programme. A subset of 14 WFD lakes are also included under the International Cooperation Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters). DOC was first measured in the WFD lakes in 2010, and the 14 ICP Waters lakes were sampled a minimum of six times per year between 2010 and 2018; these data were used to test for temporal changes in DOC in lowland lakes (Figure 2.2).

For simplicity, the WFD lakes are referred to as lowland lakes in this study; a few of the 48 lakes had elevations greater than 150 masl but were still physically distinct from the 68 upland lakes due to their greater lake and catchment sizes (Table 2.1). The upland lakes were also headwater systems, whereas the lakes in the lowland subset had both inlets and outlets, connecting them to other water bodies in the region. Lastly, unlike the upland lake set, which are generally isolated, the WFD lakes experience more human interference as there is greater ease of access for the general public (roads and parking lots).

Physical characteristics and climate of upland and lowland lakes

The differences in elevation, lake area, catchment area, and lake to catchment ratio between the upland and lowland lakes were statistically significant ($p<0.05$; Mann-Whitney U). In general, the upland lakes were small and located in small catchments at higher elevation compared with the lowland lakes (Table 2.1). All upland lakes had elevations greater than 220 masl (median: 427 masl), whereas 77% of lowland lakes were below 120 (median: 39 masl). Most (93%) upland lakes were less than 10 ha in size (median: 1.7 ha) and most (90%) lowland lakes were greater than 10 ha (median: 64 ha); 69% of the upland lakes were smaller than the smallest lowland lake (3.1 ha). In general, upland catchments (median: 14 ha) were much smaller than lowland catchments (median: 764 ha), and the upland lakes had a greater lake to catchment ratio (median: 0.14) than the lowlands (median: 0.08).

The upland and lowland lakes also had significant differences in air temperature, precipitation, and percent peatland coverage (Table 2.1). The upland lakes had cooler air temperatures due to their higher elevations and received greater precipitation; median annual precipitation was 2.2 m for the upland lakes, and 1.8 m for the lowland lakes. Peatland coverage of the lake catchments was higher in the upland sites; thirty-five of the upland lakes (51%) had 100% coverage of peatland in their catchment and 13 (19%) had 0% coverage. The lowland sites had greater variation with half having > 50% coverage and half < 50% (Table 2.1).

Table 2.1: *Physical characteristics and climate averages for upland (n=68) and lowland (n=48) lakes in the Republic of Ireland.*

		Upland Lakes (n=68)			**Lowland Lakes (n=48)**		
	Units	**Range**	**Median**	**NMAD(%)**	**Range**	**Median**	**NMAD(%)**
Elevation[1]	masl	250 – 681	437	19	7 – 205	39	72
Lake Surface Area[1]	ha	0.3 – 12.6	1.7	68	8 – 264	64	61
Catchment Area[1]	ha	1.2 – 161	14	84	58 – 7537	764	76
Lake:Catchment[1]		0.03 – 0.3	0.14	53	0.02 – 0.3	0.08	55
Solar Radiation	kJ/m^2/d	8524 – 9500	9125	3	8587 – 9508	8992	3
Air Temperature[1]	°C	5.9 – 9.2	7.6	11	8.2 – 10.5	9.7	6
Precipitation[1]	m/yr	1.5 – 3.1	2.2	18	1.3 – 2.5	1.8	16
Soil Moisture	m^3/m^3	0.4 – 0.9	0.5	11	0.4 – 1.0	0.7	39
Peatland Coverage[1]	%	0 – 100	100	0[2]	0 – 97	49	61

NMAD: Normalized Median Absolute Deviation

[1] Significant difference (p<0.05) between upland and lowland lakes (Mann-Whitney U)

[2] Due to limited data variation, and half the upland lakes having a peatland coverage of 100%, NMAD (%) was 0.

The subset of upland (n=7) and lowland (n=14) lakes analyzed for significant ($p<0.05$) changes in DOC were generally physically representative of the full datasets. The seven upland lakes spatially represent the primary sampling regions for this study (Figure 2.2) however, they represent only very small lakes at higher elevations (Appendix 2.1) because they were originally selected to limit effects of local pollution or disturbance. The fourteen lowland lakes also spatially represent the primary sampling locations (Figure 2.2). The lowland lake subset tended toward higher elevations, and larger catchments in comparison to the full lowland dataset, but were still physically distinct from the upland lakes, with lower elevations and much larger catchment sizes (Appendix 2.1).

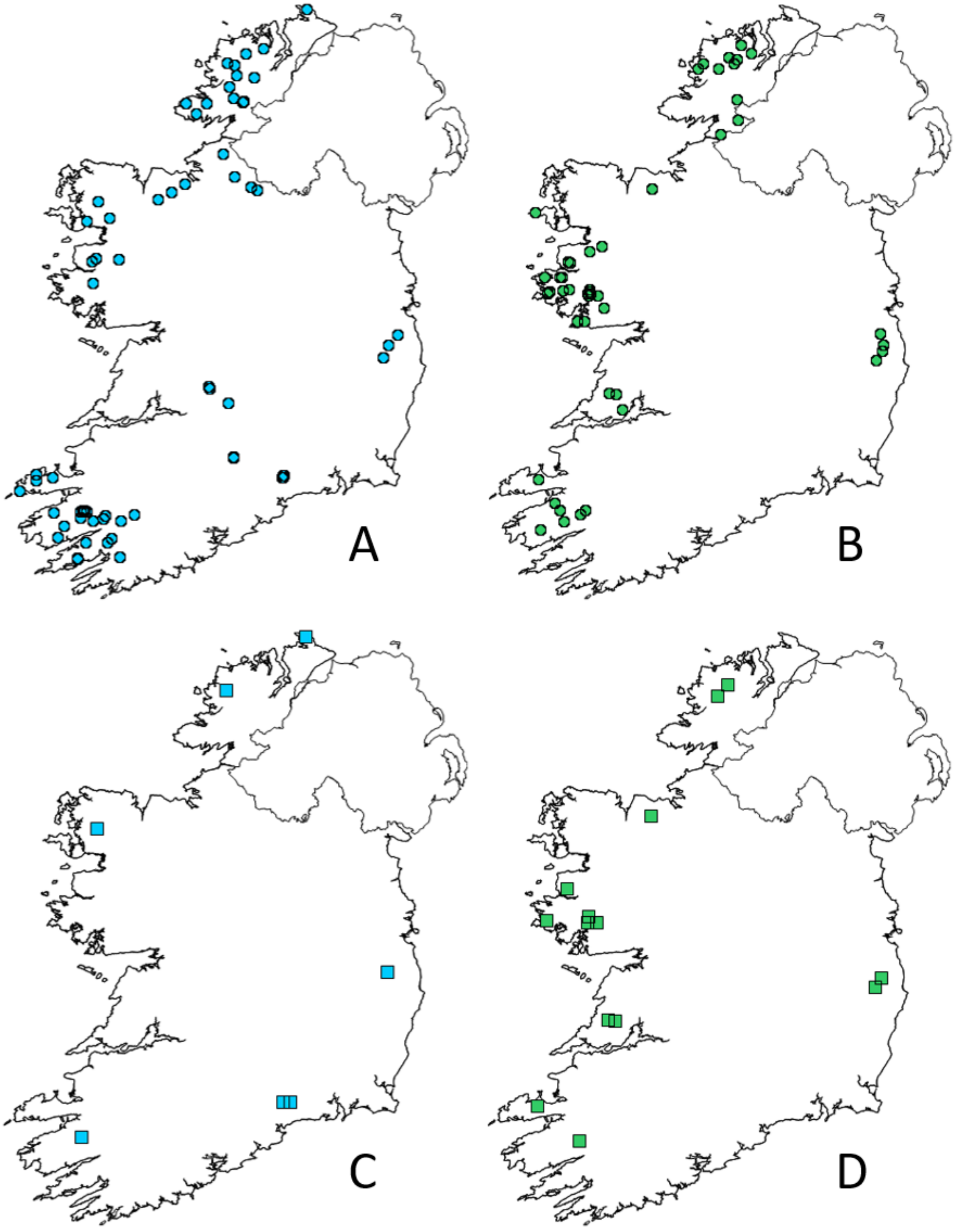

Figure 2.2: *Location of study lakes in the Republic of Ireland. (A) Upland lakes sampled April–July 2017 & 2018 (n=68); (B) Lowland lakes sampled April–July 2017 & 2018 (n=48); (C) Upland lakes sampled 2007 to 2018 (n=7); (D) Lowland lakes sampled 2010 to 2018 (n=14).*

Field & laboratory methodology

All upland lakes were sampled at least once during April–July in 2017 or 2018; 29 were sampled in both years (Appendix 2.1). The lowland lakes were sampled more frequently than the upland lakes as they are routinely sampled under the WFD, and during April–July 2017 and 2018 each lake was sampled at least twice per year, but sampling schedules varied between lakes. Due to the size of the lowland lakes, some of the lakes were sampled at a variety of locations from shore and sometimes by boat. In contrast, all upland lakes were sampled from the shore, but the upland lakes are small, shallow, and well-mixed by wind, so shore samples were assumed to be representative of the entire lake.

Upland lakes

All containers were soaked in a 10% HCl bath (v/v) for 24 hours, triple rinsed with reverse osmosis water, once with b-pure water, then air dried prior to sampling. Water samples were collected from the shore, approximately 15 cm below the surface in an area free of emergent vegetation. Prior to sample collection, the container was rinsed three times with lake water; rinse water was poured onto the shore to avoid disturbing the sediment. At each site a 250 mL unfiltered water sample was collected in a high-density polyethylene (HDPE) bottle and capped underwater. Samples were kept cool and were transported to Trent University for analysis.

All water samples were analyzed for DOC, absorbance, major ions, alkalinity, conductivity, and pH. The samples for DOC, absorbance, and major ions were filtered prior to analysis using 0.45 µm disposable nylon syringe filters. DOC was measured on a Shimadzu TOC Analyzer and quality control data are available in Appendix 2.2. Absorbance was determined at three wavelengths

(254, 285, and 365 nm) using a Lambda XLS+ UV-Vis Spectrometer. Anions (Cl^- and SO_4^{2-}) were measured on a Dionex 600 Ion Chromatograph, and cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) were analyzed using a Perkin-Elmer Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Alkalinity, conductivity, and pH were determined on unfiltered samples using a Mantech PC-titrate; the sample bottles remained sealed until immediately before each sample was analysed.

Lowland lakes

Sampling and analysis of the lowland lakes was conducted by the EPA regional inspectorates. The standard procedures for field sampling and laboratory analysis followed Irish Standard methods (I.S. EN), or alternatively European Standard Methods (EN) or International Standard Methods (ISO) where Irish Standard methods were not possible (EPA, 2006). The lowland lake water was analyzed for DOC, major ions, alkalinity, conductivity, and pH. The lowland lake water was not analyzed for absorbance, although true colour (Hazen) was measured.

In the lowland lakes, alkalinity data were limited; a subset of 20 lakes had gran alkalinity data, but only for less than half of 2018 sampling events for those lakes. Sulphate data was also limited for the lowland lakes because most sulphate measurements were reported as below detection. Available lowland alkalinity and sulphate data are presented here in the data summary results but were excluded from further statistical analysis.

Data analysis

Data sources

Climate data was used in the assessment of drivers of DOC (i.e., air temperature, global solar radiation, precipitation, and regional soil moisture). The data were obtained from the Irish Meteorological Service (Met Éireann) and were spatially modeled (kriging interpolation) using 30-year (1981–2010) climate averages from the Met Éireann monitoring stations (Walsh, 2012). The proportional peatland coverage of the lake catchments was determined using CORINE land cover inventories from 2018. CORINE uses satellite imagery to estimate land cover type, with a resolution of 25 ha (land.copernicus.eu/pan-european/corine-land-cover). The location of peatlands within a catchment relative to a lake's location may indicate how much influence the peatland may have on the lake (i.e., proximity to the lake and/or inlets, topography) and we acknowledge this is a limitation for our analyses.

The influence of catchment bedrock weathering and the soil exchange complex on lake chemistry was determined using the sodium to chloride ratio (Na:Cl), calculated as the concentration of sodium to chloride ions in lake water (eq/L). Catchment bedrock influence was indicated by a ratio greater than 0.859, which is the ratio of sodium to chloride in seawater (ICP Waters, 2010).

The influence of anthropogenic emissions of sulphur on lake chemistry was estimated by correcting the measured sulphate (SO_4^{2-}) concentrations in the lakes for the influence of sea salts. Non-marine sulphate was calculated using 0.140 (mg/kg : mg/kg) for the ratio of sulphate to chloride in sea water (De Vries et al., 2015):

$$[SO_4^{2-}]_{\text{non-marine}} = [SO_4^{2-}]_{\text{total}} - (0.140 \times [Cl^-])$$

Three organic matter quality indices were calculated for the upland lakes, using absorbance and DOC data. Absorbance was only measured for a few wavelengths so the indices were selected based on what was possible to calculate from the available data. Firstly, specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), which indicates aromaticity and molecular weight, was calculated by dividing absorbance by DOC and multiplying by 100 (Weishaar et al., 2003). Second, the absorbance ratio of 250 nm by 365 nm (E2:E3), which has a negative relationship with molecular weight (Peuravuori & Pihlaja, 1997). In this study the ratio was calculated using 254 nm since absorbance was not measured at 250 nm, but results were consistent with relevant studies. Lastly, the absorbance ratio 285 nm by 254 nm (285:254), which has a negative relationship with the polarity of aromatic organic matter (Clarke et al., 2007). Both E2:E3 and $SUVA_{254}$ are commonly used indices and these ratio notations are widely accepted and recognized; in contrast, the ratio 285 nm by 254 nm is not widely used and in this study the notation for the ratio will be 285:254.

Data treatment

Data analysis was separated into three stages: (1) analysis of current (2017–2018) DOC in upland and lowland lakes, (2) assessment of changes in DOC in upland and lowland lakes over time (2007 to 2018), and (3) exploration of organic matter quality in the upland lakes. Data was tested for normality using the Shapiro-Wilk test for normality ($p<0.05$). Due to the non-normal distribution of the water chemistry data, non-parametric tests were used. All statistical analysis was run separately for the upland and lowland datasets; statistical tests were performed using the statistical software PAST version 4.03 (Hammer et al., 2001).

Current lake chemistry

Because there was a range in the number of sampling events for each lake (Appendix 2.1), all water chemistry data were averaged to one value per variable per lake to represent current (2017–2018) lake chemistry. Lake chemistry was summarized for upland and lowland datasets and differences between upland and lowland lake chemistry were tested for significance ($p<0.05$) using a Mann-Whitney U test. The range for each variable was presented as 5th to 95th percentile, so outliers would not misrepresent the general extent of the data's range. Variability between lakes within each dataset was calculated as normalized median absolute deviation (NMAD) to best represent the non-normally distributed data (Appendix 2.2). Variability in pH was calculated using the concentration of H^+ because NMAD underestimated the variability of pH when using pH units, due to the logged scale and limited range of values in natural waters.

The distribution of upland and lowland DOC was visually presented using box and jitter plots and cumulative frequency graphs. Principal Component Analysis (PCA) was used to explore variability within the upland and lowland datasets and make comparisons between upland and lowland sites. The loadings for the first six components (eigenvalue >1) are included in the appendix (Appendix 2.3). To examine associations between DOC and other variables, Spearman Rank Correlation was used to determine which variables were significantly correlated with DOC ($p<0.05$) in the upland and lowland lakes. Spearman Rank Correlation was also used to test for significant ($p<0.05$) correlations between all study variables and easting and northing, to explore regional trends.

Redundancy Analysis (RDA) was used to test for significant drivers of DOC ($p<0.05$), and a biplot was used to visualise the relationships. RDA requires a minimum of two dependent variables;

conductivity was used as the second dependent variable in both the upland and lowland analysis because it is an important variable in the coastal study lakes, but in general it was not considered to be a significant driver of DOC spatial variability in this dataset ($p<0.05$). The RDA biplots were scaled to allow easier interpretation, using “scaling type 2” as determined by Legendre & Legendre (1998). The loadings are included in the appendix (Appendix 2.3).

Changes in DOC

Significant changes ($p<0.05$) in DOC and other chemical variables during the last decade were tested using Mann-Kendall tests. The seven upland lakes were sampled approximately annually between 2007 and 2018 (Appendix 2.1), but the sampling was not restricted to April–July. The fourteen lowland lakes were generally sampled once a month or once every two months from 2010 to 2018. The Mann-Kendall was run using all observations (all-seasons data) because the upland lakes had limited observations. If there were multiple observations in a single month, the data was averaged so there was a maximum of one observation per month.

An important consideration when examining long-term chemical trends in surface waters, is seasonality. Concentrations of DOC are known to fluctuate widely throughout a year, the scale of which depends on the location but DOC tends to be higher in the summer due to the influence of temperature on in-lake DOC production and terrestrial sources (e.g., Koehler et al., 2009; Liu et al., 2014). Seasonal fluctuations may cause false positive results for long-term trend tests (e.g., greater seasonal fluctuations in later years), or could make long-term trends more difficult to detect in systems with high seasonality. All temporal data was plotted and examined to confirm Mann-Kendall test results; there were no apparent issues with seasonality influencing the test results, but some lowland trends were found to be false positives due to issues with early year DOC analysis. Due to suspected quality control issues for early year lowland DOC measurements, true colour was used to support temporal trend analysis of lowland DOC; true colour was a more established measurement in the lowland lakes in contrast to DOC, which was not measured by the EPA until 2010.

One of the lowland lakes (Lough Veagh) experienced a catchment disturbance July 2018 that impacted DOC concentrations August–December 2018. Gorse fires in the catchment occurred July 2018 (McNulty, 2018); fires have been previously observed to cause increases in DOC and export of DOC from peatlands into surface waters (e.g., Yallop et al., 2010). The data for August–December 2018 indicate that DOC concentrations were impacted by this disturbance. These observations were excluded from the analysis of temporal changes in DOC.

Organic matter quality

The organic matter quality indices were averaged as described above for other water chemistry variables. Spearman Rank Correlation and RDA were used to explore associations between organic matter quality indices and other study variables. DOC and absorbance were excluded from these tests as the indices are derived from their values. Temporal change in organic matter quality was tested for the seven upland lakes using Mann-Kendall trend tests; absorbance data were unavailable for 2007 and 2008, so changes in organic matter quality was tested for the period of 2009–2018.

2.4 RESULTS

Lake chemistry in upland and lowland lakes

There was a statistically significant difference between the upland and lowland lake chemistry for all variables except the sodium to chloride ratio ($p<0.05$; Mann-Whitney U). While both the upland and lowland lakes were mostly acidic, the upland lakes had lower pH and alkalinity (Table 2.2). Further, the upland lakes were more dilute, with lower DOC, conductivity, and ion concentrations; chemical variability tended to be higher in the upland lakes (Table 2.2).

The upland lakes had a median pH of 5.8, and the lowland lakes had a median of 6.8 (Table 2.2). Only 10% of the upland lakes had a pH of 7 or higher, compared with 30% of the lowland. Median chloride concentrations were 7.8 mg/L in the upland lakes and 14.4 mg/L in the lowland lakes; despite the difference in ion concentrations, both the upland and lowland lakes had a median sodium to chloride ratio of 0.99. Nearly all lakes had a ratio greater than the sea salt ratio of 0.859, which suggests that bedrock weathering of sodium is a dominant process across all catchments; only six of the 116 study lakes (five upland lakes, one lowland lake) had a ratio below 0.859.

Sulphate had a median concentration of 1.5 mg/L in the upland lakes and 2.5 mg/L in the lowland lakes. Most of the sulphate in the study lakes was of marine origin; 72% of sulphate in upland lakes, and 97% of sulphate in lowland lakes. Additionally, ten of 68 upland lakes (15%) and seven of 34 lowland lakes (21%) had a non marine sulphate concentration of 0 mg/L. Despite having lower total sulphate concentrations, the upland lakes had higher non marine sulphate concentrations, with a median of 0.4 mg/L in the upland compared with 0.1 mg/L in the lowlands; this was expected since the upland lakes are headwaters and were originally selected to study the impacts of long-range air pollution (Aherne et al., 2002), and were assumed to be better reflections of atmospheric deposition than 'noisier' lowland lakes. Despite the significant differences in ion concentrations between the upland and lowland lakes, they were dilute in the same proportions (Appendix 2.4), suggesting similar sources and processes behind the relative contributions of ions in each lake.

Table 2.2: *Summary of chemical characteristics in upland (n=68) and lowland (n=48) lakes sampled in the Republic of Ireland during April–July 2017 & 2018.*

		Upland Lakes (n=68)			**Lowland Lakes (n=48)**		
	Units	**Range**	**Median**	**NMAD(%)**	**Range**	**Median**	**NMAD(%)**
DOC	mg/L	1.6 – 9.2	3.9	43	3.4 – 11.2	6.6	23
pH		4.6 – 7.2	5.8	89	5.4 – 7.7	6.8	52
Conductivity	µS/cm	27.5 – 79.1	42.7	22	34.0 – 152.5	59.7	24
Gran Alkalinity[1]	mg/L	-1.2 – 12.1	0.8	47	2.0 – 38.2	6.0	22
Ca^{2+}	mg/L	0.4 – 5.8	1.2	43	0.8 – 12.9	2.0	36
Mg^{2+}	mg/L	0.5 – 2.2	0.9	34	0.7 – 2.8	1.1	27
K^{+}	mg/L	0.1 – 0.7	0.3	32	0.2 – 1.4	0.4	31
Na^{+}	mg/L	3.3 – 9.9	5.5	22	4.9 – 20.7	9.5	21
Cl^{-}	mg/L	4.2 – 18.0	7.8	31	8.0 – 33.6	14.4	24
SO_4^{2-} *	mg/L	0.7 – 3.0	1.5	22	2.0 – 6.3	2.5	19
Na:Cl		0.85 – 2.35	0.99	9	0.90 – 1.21	0.99	3
Non-marine SO_4^{2-} *	mg/L	0.0 – 1.1	0.4	60	0.0 – 2.6	0.1	89

NMAD: Normalized Median Absolute Deviation

[1] For the lowland lakes, Gran Alkalinity is based on limited available data: 2018 data for a subset of 20 lakes

* For the lowland lakes most [SO_4^{2-}] was <DL, so values presented are all the available values (n=34)

The influence of the coastal setting was highlighted by the PCAs (Figure 2.3), with sea salts explaining most of the variance in the lake data for both upland (28.4%) and lowland lakes

(35.1%). This was also seen in the ion data – chloride and sodium were the dominant ions in both sets of lakes – and in the conductivity axes for the RDAs which were dominated by marine ions (Appendix 2.3). The second principal component was dominated by DOC and pH for both upland (17.5%) and lowland lakes (13.0%), with DOC and pH having a negative relationship due to organic acids.

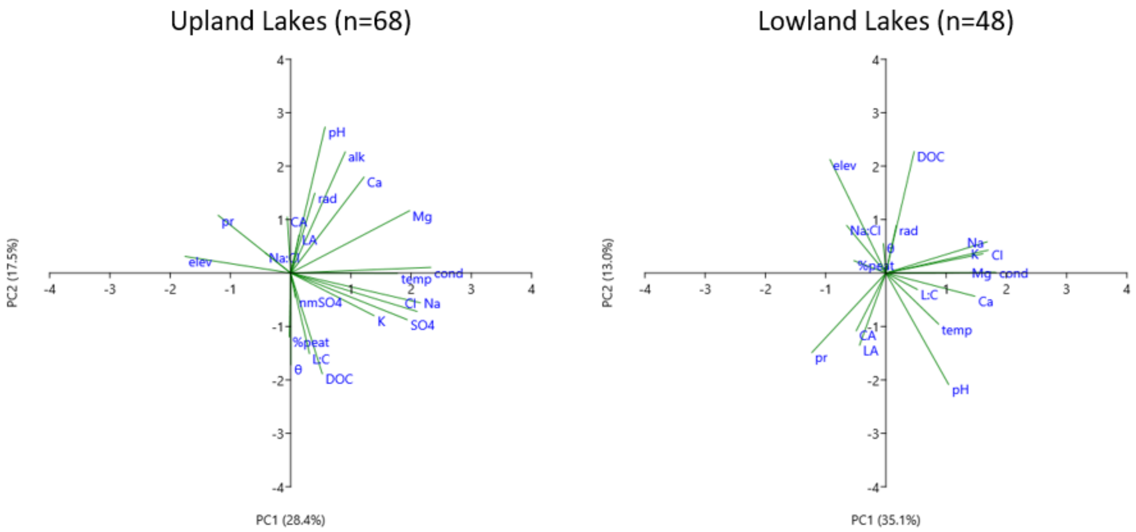

Figure 2.3: *Principal Component Analysis for upland (left) and lowland (right) lakes. Two most dominant components PC1 (sea salts) and PC2 (DOC, pH) plotted against each other; contribution toward data variance indicated in brackets on axis label. elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation, θ=soil moisture, %peat=peatland coverage, alk=gran alkalinity, cond=conductivity, DOC=dissolved organic carbon, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio; element concentrations use standard symbols.*

DOC in upland and lowland lakes

DOC in the upland lakes (median 3.9 mg/L) was significantly lower than DOC than the lowland lakes (median 6.6 mg/L). The central fifty percent of the DOC data ranged from 2.8–7.2 mg/L in the uplands, compared with 4.6–7.8 mg/L in the lowlands (Figure 2.4), as the upland lakes had greater inter-lake variability (43% vs 23%; Table 2.2).

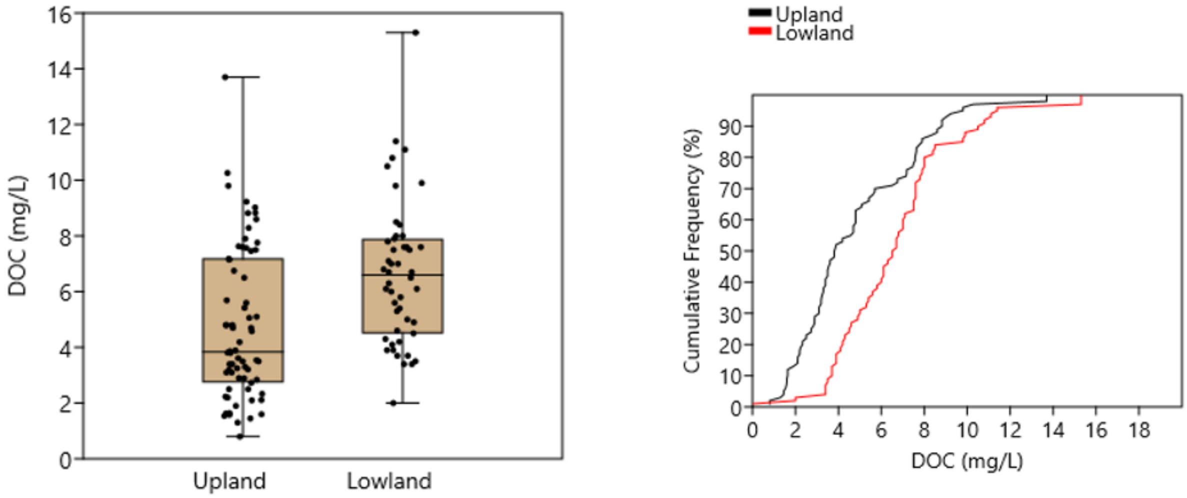

Figure 2.4: *Dissolved organic carbon (DOC) concentrations in upland (n=68) and lowland (n=48) lakes in the Republic of Ireland, sampled April–July 2017 & 2018.*

Despite the significant differences in chemistry, climate, and physical characteristics between the upland and lowland lakes, variability in DOC was driven by the same factors; a positive relationship with soil moisture, and negative relationships with pH and precipitation, in upland lakes (r=0.82; Figure 2.5) and lowland lakes (r=0.84; Figure 2.6). Soil moisture and precipitation were also the only variables that were significantly correlated to both upland and lowland DOC (Appendix 2.4). As soil moisture was based on 30-year climate averages, this parameter was assumed to be an indicator of soil organic matter rather than hydrology, with more organic soils having greater water holding capacity than inorganic soils (Hudson, 1994). Therefore, the results indicated that inputs of terrestrial organic matter from the catchment soil and dilution by regional precipitation could generally explain variation in DOC concentrations between lakes across Ireland. Upland DOC had the strongest association to soil moisture, while lowland DOC had the strongest association to precipitation, for both the RDA (Figures 5,6) and correlations (Appendix 2.4). The upland lakes are headwaters, primarily influenced by direct catchment and atmospheric inputs, while lowland lakes had inflows and therefore are influenced by inputs from other regions and soils along their hydrological network.

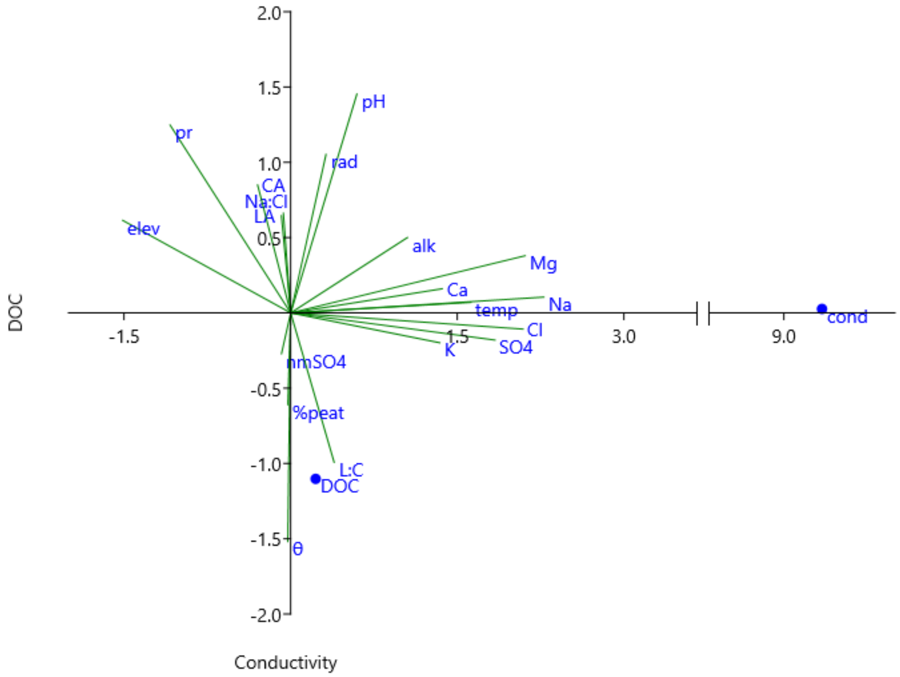

Figure 2.5: *Redundancy Analysis (RDA) for upland lake chemistry in the Republic of Ireland (n=68), sampled April–July 2017 & 2018. R2=0.98; R2adj=0.97. Amplitude of explanatory variables changed to 2.5 original size, and dependent variable amplitude decreased to 0.5 to allow easier figure interpretation. elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation, θ=soil moisture, %peat=peatland coverage, alk=gran alkalinity, cond=conductivity, DOC=dissolved organic carbon, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio; element concentrations use standard symbols.*

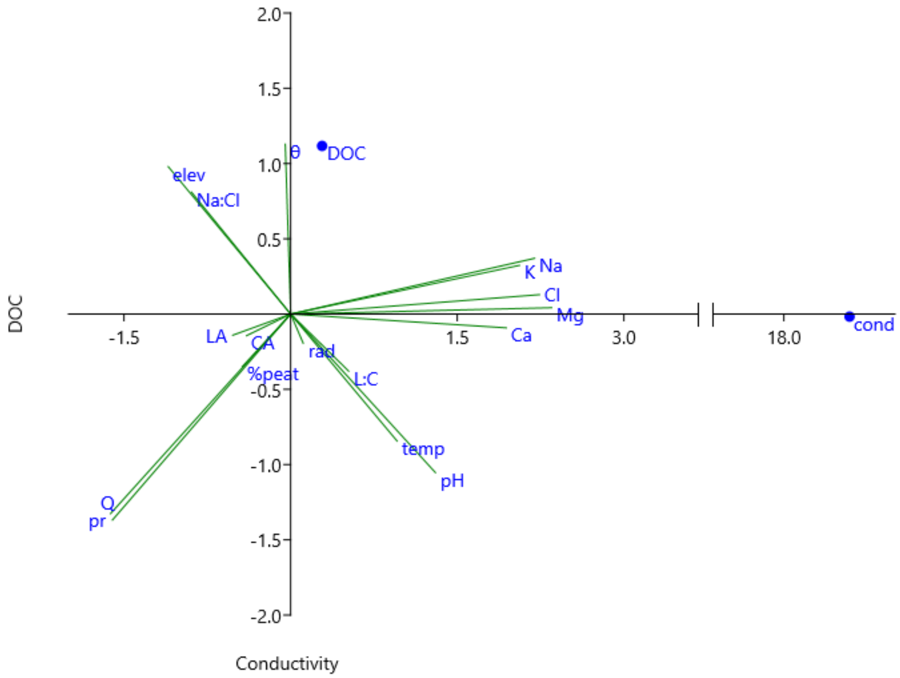

Figure 2.6: *Redundancy Analysis (RDA) for lowland lake chemistry in the Republic of Ireland (n=48), sampled April–July 2017 & 2018. R2=0.95; R2adj=0.92. Amplitude of explanatory variables changed to 2.5 original size, and dependent variable amplitude decreased to 0.5, to allow easier figure interpretation. elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation,* θ*=soil moisture, %peat=peatland coverage, cond=conductivity, DOC=dissolved organic carbon, Na:Cl=sodium to chloride ratio; element concentrations use standard symbols.*

Upland DOC tended to be highest in the most northern and eastern lakes (Figure 2.7) and had significant positive correlations to northing (r_s=0.45) and easting (r_s=0.50), consistent with the regional coverage of peatland (Appendix 2.1). The data used to represent peatland coverage was not significantly correlated to DOC concentrations in upland and lowland lakes since land cover data from CORINE is limited by resolution (25 ha), but the general regional pattern can be seen when the data is plotted on a map (Appendix 2.1). Variables indicative of peatland coverage (soil moisture, pH) were also significantly correlated to northing and easting for the upland lakes (Appendix 2.4), providing additional support that the regional patterns in upland DOC could be attributed to the influence of peatlands in their catchments. A secondary influence for upland DOC’s correlation with easting may be precipitation, as precipitation is lower in the east (Met Éireann, 2020) and upland precipitation was significantly correlated to easting (r_s=–0.58). The regional trends for lowland DOC were similar to the upland lakes; there was a difference between the southern-most and northern-most lowland sites, with DOC tending to be higher in the north (Figure 2.7), though it was not statistically significant. Lowland DOC was significantly correlated to easting (r_s=0.58); DOC was lower in the western lakes, likely because the west of Ireland experiences greater precipitation (Met Éireann, 2020), though lowland precipitation was not significantly correlated to easting.

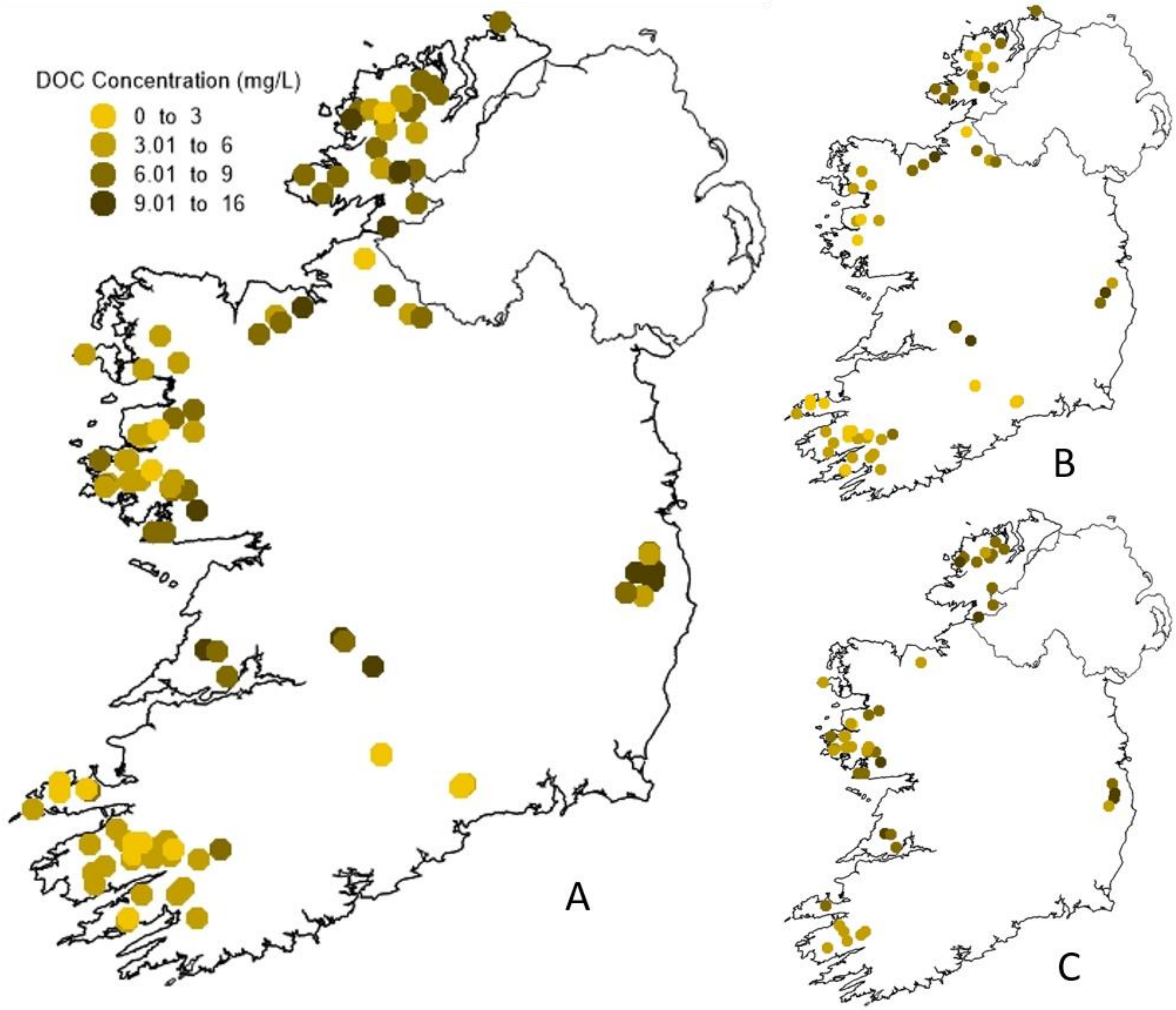

Figure 2.7: *Dissolved organic carbon (DOC) concentrations in upland and lowland lakes in the Republic of Ireland (n=116), sampled April–July 2017 & 2018. (A) DOC concentrations in the upland and lowland study lakes, (B) DOC concentrations in upland (n=68) lakes, and (C) DOC concentrations in lowland (n=48) lakes.*

Changes in DOC in upland and lowland lakes (2007–2018)

Eight (38%) of the 21 study lakes (one upland and seven lowland) tested for temporal changes in DOC showed a significant change ($p<0.05$) during the study period. However, the direction of change was not consistent; the upland lake and four of the lowland lakes decreased in DOC, while the other three lowland lakes increased in DOC (Appendix 2.5). The true colour trends and correlations between DOC and true colour supported the conclusions for three of the seven lowland lakes with significant changes in DOC (Dan, Maumwee, Veagh), all three of which had significant decreases (Appendix 2.5). The temporal trends for the four remaining lowland lakes were not supported by coinciding true colour trends and appeared to be driven by sporadic outlier values prior to 2014 rather than genuine long-term trends (e.g., 43 mg/L for a lake with a normal range of 10–15 mg/L). If the trends for those four lakes are excluded then most of the 21 study lakes (81%) did not significantly change in DOC concentration in the past decade, but those that did decreased in concentration. The lakes that had a significant decrease in DOC represented each of the four main sampling regions (north, south, east, and west coasts), indicating it was not a regionalized trend.

While long term changes in conductivity and DOC were not consistent (Appendix 2.5), acute temporal fluctuations in DOC appeared to be related to conductivity, suggesting the impact of sea salts on organic matter solubility. Coastal storms and hurricane force winds during the study period (e.g., Met Éireann, 2008; Met Éireann, 2012) corresponded to observed spikes in conductivity and corresponding drops in DOC for lakes in the affected regions (Appendix 2.5). However, this shift was temporary, and the DOC concentrations recovered rapidly when conductivity decreased (Appendix 2.5). Therefore, the decreasing trends in DOC were not attributed to rising sea salts, but DOC in these coastal lakes appeared to be influenced which may become increasingly significant in the face of climate change and increased storm events.

Upland organic matter quality

Observed $SUVA_{254}$ ranged from 1.8 to 4.5 L mg^{-1} m^{-1} with a median of 3.2 mg^{-1} m^{-1} (Table 2.3). The absorbance ratio E2:E3 had a range of 2.8–4.7, with a median of 3.9. The absorbance ratio

285:254 had a small range (0.57–0.75), with a median of 0.71. All three organic matter quality variables had lower variability than DOC (Table 2.3), which indicates a consistency in organic matter quality across the catchments, regardless of the concentration of organic matter.

Like DOC, $SUVA_{254}$ was correlated with soil moisture (r_s=0.47) and precipitation (r_s=–0.37) (Appendix 2.4); variation in $SUVA_{254}$ between lakes was also best explained by a negative relationship with precipitation and positive relationships with soil moisture and lake to catchment ratio (r=0.73; Figure 2.8). Further, correlations with easting and northing indicated greater aromaticity in the peatland dominated north and eastern sites (Appendix 2.1), where there is higher DOC, soil moisture and lake to catchment ratio, and lower precipitation (Appendix 2.4).

Table 2.3: *Summary of organic matter quality indices in upland lakes (n=68) in the Republic of Ireland during April–July 2017 & 2018.*

Index	**Units**	**Range**	**Median**	**NMAD(%)**
$SUVA_{254}$	L mg^{-1} m^{-1}	1.8 – 4.5	3.2	25
E2:E3		2.8 – 4.7	3.9	12
285:254		0.57 – 0.75	0.71	4
DOC	mg/L	1.6 – 9.2	3.9	43

Like DOC and $SUVA_{254}$, 285:254 had a significant positive correlation with soil moisture (r_s=0.40), and a negative one with precipitation (r_s=–0.28); a higher 285:254 ratio indicates lower polarity, so polarity was negatively correlated to soil moisture, and positively correlated to precipitation. This association with soil moisture was also seen in the RDA but 285:254 only explained 0.03% of the data's variance and was not plotted (see Appendix 2.3). Polarity's negative association with soil moisture may be due to a greater concentration of ions in more organic soils (Saxton et al., 2006) available to occupy soil OM binding sites, thereby decreasing the polarity, while precipitation diluted this effect. Correlations with easting and northing indicated lower polarity of aromatic substances in the peatland-dominated northern and eastern sites, explained by its relationships with soil moisture and precipitation (Appendix 2.4), consistent with SUVA and DOC. Unlike $SUVA_{254}$, however, 285:254 had a stronger relationship with easting (r_s=0.42) than with northing (r_s=0.28) and may suggest a greater influence of regional precipitation, which decreases west to east (Met Éireann, 2020).

Variability in E2:E3 between lakes was driven by a negative relationship with Na:Cl, and positive relationships with lake area and catchment area (r=0.65; Figure 2.8). The E2:E3 ratio has an inverse relationship with molecular weight, so greater catchment weathering (indicated by Na:Cl), and smaller lake and catchment sizes were associated with greater organic matter molecular weight. In contrast to $SUVA_{254}$ and 285:254, easting and northing were not significantly correlated to E2:E3, indicating no regional patterns in organic matter molecular weight. While there was no available information on water residence time for the upland lakes, larger lakes in larger catchments tend to have greater residence times, allowing more time for photodegradation and biodegradation of organic matter (e.g., Kothawala et al., 2014; Du et al., 2021). While less clear, the association with Na:Cl may be because the same mechanisms would facilitate both weathered sodium and terrestrial (high molecular weight) organic matter to enter the lake water from the catchment.

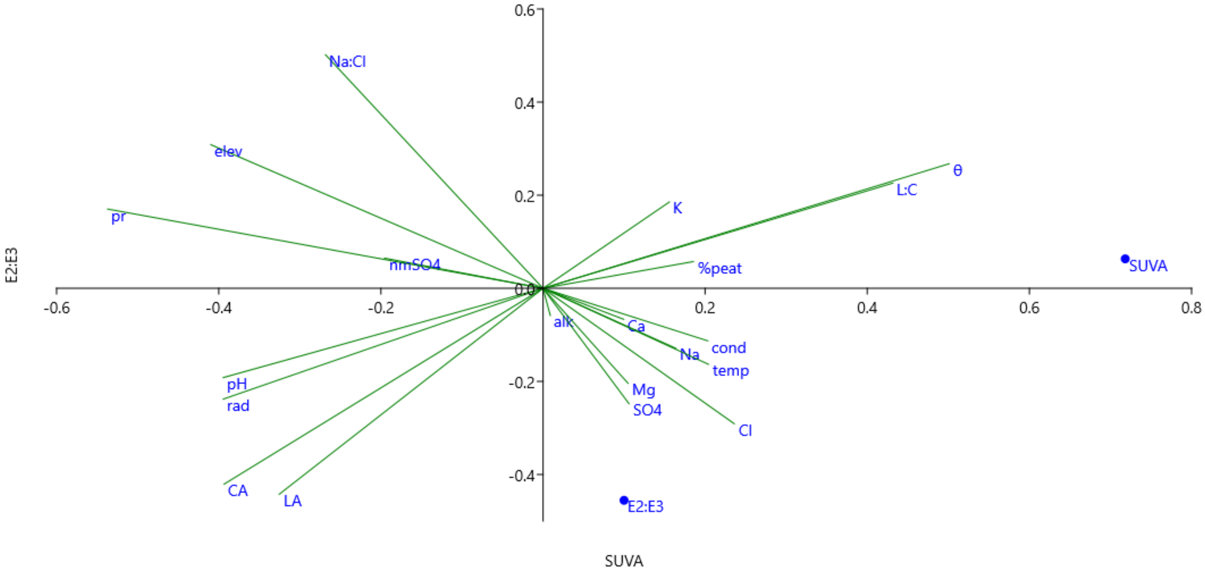

Figure 2.8: *Redundancy Analysis (RDA) for upland lake chemistry in the Republic of Ireland (n=68), sampled April–July 2017 & 2018. R2=0.49; R2adj=0.28. Axis 1 (x axis) was dominated by specific ultraviolet absorbance at 254 nm (SUVA). Axis 2 (y axis) was dominated by the absorbance ratio 254 nm by 265 nm (E2:E3). elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation, θ=soil moisture, %peat=peatland coverage, alk=gran alkalinity, cond=conductivity, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio; element concentrations use standard symbols.*

None of the seven lakes with long-term observations (2009–2018) had any statistically significant change in the three organic matter quality variables. Two of the lakes showed very weak, non-significant ($p > 0.05$) increases in $SUVA_{254}$ but no other lakes or organic matter variables had any semblance of a pattern of change.

2.5 DISCUSSION

DOC in Irish lakes

The range in DOC concentrations in the study lakes (upland: 0.8–13.7 mg/L; lowland: 2.0–15.3 mg/L) was comparable to lakes in the UK (1.6–13.9 mg/L, n=30 [Monteith et al., 2015]) and Norway (3.6–20.1 mg/L, n=34 [Braaten et al., 2018]) which are similarly situated in western Europe with large coastal influences on lake chemistry, and are dominated by acid sensitive surface waters (Austnes et al., 2018). DOC in the study lakes was also comparable to small high elevation acid-sensitive headwater lakes in Maine, USA, on the east coast of North America (0.1–15.5, n=29 [Gavin et al., 2018]).

The main drivers of spatial variation of DOC for upland and lowland lakes (soil moisture and precipitation) were consistent with other similar studies. Spatial variation of DOC for upland UK catchments (n=30) was largely explained (79% variance) by a positive effect of wetland soil cover, and negatively by precipitation and elevation (Monteith et al. 2015). Similarly, a study of 1000 Norwegian lakes also found spatial variability in DOC could be explained in part by catchment area fraction of bogs, which was the second-best predictor following vegetation density (Larsen et al., 2011). Lastly, a global study of 7500 lakes found that DOC was explained by several factors and included a positive relationship with soil carbon density, and a negative correlation to precipitation (Sobek et al., 2007). The reported relationship with wetland soils (Monteith et al., 2015; Larsen et al., 2011) is particularly relevant since our study results indicated an influence of regional peatland coverage on lake DOC.

Changes in DOC (2007–2018)

While temporal decreases of DOC concentrations in surface waters are not unprecedented (e.g., Jane et al., 2017; Garmo et al., 2020), the observed decrease in some of the study lakes and lack of significant trends for the rest is in contrast to widely reported DOC increases, including reports from the UK (e.g., Worrall et al., 2004; Monteith et al., 2007). This may be because the Irish lakes were examined for changes during the last decade, rather than longer term (since the 1990’s). One of the popular theories for rising DOC is a response to declining sulphate deposition (e.g., Monteith et al., 2007; Evans et al., 2005), but controls on global acidic deposition have been in place for decades (e.g., the 1999 Gothenburg protocol under UNECE Convention on Long-range Transboundary Air Pollution); a study of surface waters in Europe and eastern North America found that in the last decade DOC trends were being driven by climatic variables (i.e. precipitation, temperature) in addition to the previous atmospheric chemistry controls on DOC trends (de Wit et al., 2021). This supports other studies that have pointed to climate change for DOC trends (e.g., Oni et al., 2013), and which may not be detected in the relatively short term of this study. While DOC continues to increase in surface waters, the observed trends have been decelerating in Europe since the early 2000s (de Wit et al., 2021; Garmo et al., 2020) and our study period is at the end of this ‘slowing period’, suggesting that short term trends would be less detectable and changes over a decade would be minor. The rates of recent changes in DOC concentrations have been approximately 0–2% per year (de Wit et al., 2021), which is less than the average variation between replicates for the Irish study lakes (Appendix 2.2).

Further, the study lakes are particularly sensitive to seasonal variation since the systems are being directly impacted by the Atlantic Ocean, which could make significant long-term changes in chemistry more difficult to detect. A previous study of European lake chemistry noted that the influence of the Atlantic Ocean on Irish lakes meant that “the hydrochemical signal to noise ratio is often low” (Austnes et al., 2018). The lowland lakes had more consistent data than the upland lakes, with monthly or bi-monthly samplings throughout the study period, therefore taking seasonal fluctuations into account. While it can be acknowledged that the upland data is not consistent and does not take seasonality into account in temporal tests, the upland results were similar to lowland results, as 14% and 21% of upland and lowland lakes respectively had (verified) significant changes, which were decreases.

A final consideration for the lack of expected DOC increases is the high precipitation levels during the study period; the decade 2006–2015 was the wettest in Ireland in the past 300 years (Murphy et al., 2018), and there were several heavy precipitation events during the study period (Met Éireann, 2022). While increased precipitation can increase inputs of terrestrial organic matter to water bodies (e.g., de Wit et al., 2016), a diluting effect is possible in the Irish lakes. Peat and peat podzol soils dominate Ireland (Teagasc and EPA 2015) and organic saturated soils do not show a large change in export during increased flow from high precipitation events, and precipitation events can instead dilute DOC (Clark et al., 2008).

Upland organic matter quality

The range in $SUVA_{254}$ values for the upland lakes (1.8–4.5 L mg^{-1} m^{-1}) were comparable to lakes in Norway (means: 1.61, 4.93; n=2 [Poste et al., 2019]), upland peatland pools in the UK (2.81–3.53; n=66 [Turner et al., 2016]), and Adirondack Mountain lakes (1.62–3.95, n=16 [Wasswa et al., 2020]). $SUVA_{254}$ shared the same main drivers of DOC which suggests that organic matter in the study lakes was primarily allochthonous, as terrestrial organic matter tends to be more aromatic than aquatic derived organic matter (Malcolm, 1990). Further, peatland soils have a positive relationship with organic matter aromaticity (Sepp et al., 2019) and $SUVA_{254}$ was greater in the north and eastern sites where peatland coverage and DOC was greater. The ratio E2:E3 also supported that the organic matter in the lake was primarily allochthonous; the values (2.8 to 4.7, median 3.9) suggest a lack of low molecular weight organic matter in the upland lakes and a dominance of terrestrial organic matter (McCabe & Arnold, 2018). The values from this study were in the range observed for other peatland systems (3.25–3.91, n=2[1] [Peacock et al., 2014]; 2.07–5.17, n=1 [Xu et al., 2021]), and were generally lower than the ratios for lake water from non-peatland areas with more mineral soil (e.g., 5.03–9.32, n=16 [Wasswa et al., 2020]; 4.27–5.86, n=23 [O'Driscoll et al., 2006]). The range in values for the ratio 285:254 was consistent with Clarke et al. (2007). Most lakes had values on the upper end of the range, which suggests lower polarity of organic matter (Clarke et al., 2007). Polarity can indicate hydrophobic/hydrophilic organic matter fractions, with lower polarity indicating more hydrophobic organic matter, which is less soluble, and can impact trace metal binding, such as increased binding potential with mercury (Ravichandran, 2004).

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[1] Range in values represents 100 total samples between two peatlands

2.6 CONCLUSIONS

The upland and lowland lakes had significant differences in physical characteristics, chemistry, and climate averages. While the upland and lowland lakes had similar ranges in DOC, the upland lakes tended to be more dilute due to being precipitation-fed headwater systems. Despite their differences, for both datasets the variability in DOC between lakes was best explained by the effects of regional precipitation levels and organic matter in the catchment soils. The influence of terrestrial organic matter on lake DOC was further supported by organic matter quality for the upland lakes, which suggested a dominance of allochthonous organic matter. Finally, the changes in organic matter concentration and quality that occurred 2007–2018 were very minor, with few lakes having significant changes in DOC concentration and no significant changes in organic matter quality. While in contrast to reported increases in DOC concentration in Europe and North America, this was likely due to the relatively short, recent time period of the study since it occurred during a time when the rate of DOC change was slowing, as well as during a period of unprecedented rainfall in Ireland.

CHAPTER THREE: Decadal Increase of Total Mercury Concentrations in Irish Upland Lakes

3.1 ABSTRACT

Mercury concentrations in the atmosphere, soils, and surface waters have increased beyond pre-industrial levels as a result of human activities (e.g., coal burning). Ireland is situated on the western periphery of Europe and it is generally assumed that environmental concentrations of mercury are low but there is limited mercury data available. In this study, total mercury (THg) was measured in 68 remote upland acid-sensitive lakes during 2017–2018, which included a subset previously sampled for THg in 2008. As expected, total mercury concentrations in the lakes were low (median 5.4 ng/L), with the highest levels observed in peatland-dominated lake catchments where dissolved organic carbon (DOC) concentrations and aromaticity was greater. While THg concentrations in 2017–2018 were low, they were significantly higher than THg concentrations in 2008, despite decreasing atmospheric mercury concentrations in Ireland. The lower THg in 2008 can be partially attributed to the suppression of DOC following a major sea salt episode across Ireland during March 2008. Nonetheless, THg normalized by organic carbon was also significantly higher in 2017–2018 indicating that the observed increase in THg was beyond the influence of DOC concentrations. One possible cause is mobilization of legacy mercury stored in catchment soils.

3.2 INTRODUCTION

Mercury is listed as one of the top ten chemicals of major public health concern by the World Health Organization (WHO, 2017). Being ubiquitous in the environment, all people are exposed to some amount of mercury throughout their lives. However, exposure to high concentrations can have toxic effects on the nervous, digestive, and immune systems (WHO, 2017). Human activities, such as the burning of fossil fuels, have caused mercury concentrations in the atmosphere, soils, and surface waters to increase beyond natural levels worldwide (AMAP & UNEP, 2019). These increases have prompted global concern, notably leading to the United Nation’s Minamata Convention on Mercury, which aims to decrease anthropogenic mercury pollution, and to monitor mercury in the environment (UNEP, 2019).

Mercury has historically been of greatest concern in aquatic environments where it can be methylated by bacteria, allowing mercury to bioaccumulate in organisms, and biomagnify up the food chain (Hsu-Kim et al. 2013; Ruus et al. 2015). Cycling of mercury in aquatic environments is impacted by a variety of factors, the most notable being organic matter. Mercury binds to organic matter (Ravichandran, 2004; Lavoie et al., 2019), and therefore the cycling of organic matter in aquatic systems has implications for mercury cycling. Organic matter in water is generally quantified as dissolved organic carbon (DOC) and in recent decades there have been widespread reports of increasing DOC concentrations in surface waters (e.g., Monteith et al., 2007; Garmo et al., 2020). These increases in DOC may also drive increases in mercury concentrations (Millard et al., 2018). Mercury concentrations have also been associated with certain fractions or characteristics of organic matter – often called organic matter quality – such as aromaticity (Lavoie et al., 2019; Lescord et al., 2018). Organic matter quality is a product of the origin of the organic matter (e.g., autochthonous versus allochthonous), as well as alterations from system processing (e.g., biodegradation).

The Republic of Ireland is a signatory of the Minamata Convention, but there is limited data on mercury concentrations in natural environments. Ireland sits on the western periphery of Europe and receives relatively clean air masses from the Atlantic Ocean (Custodio et al., 2020) and the remote upland areas in Ireland are further isolated from local pollution, so it is generally assumed that mercury concentrations are low, making it a challenge for routine monitoring. 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). One exception to this was a study of upland acid-sensitive lakes in 2008 (Scott & Aherne, 2013; Burton et al., 2013). Many upland regions across Ireland are classified as acid-sensitive due to their underlying bedrock, resulting in lakes with naturally low pH and alkalinity that are at greater risk to acidification from anthropogenic acidic deposition (Aherne et al., 2002). The objectives of this study were (1) to assess concentrations of total mercury (THg) in acid-sensitive upland lakes across the Republic of Ireland and its relationship with chemical, physical, and climatic variables, including organic matter concentration (DOC) and quality (e.g., aromaticity), and (2) to assess changes in THg during the last decade, in light of on-going increases in surface water DOC in Europe (e.g., de Wit et al., 2021).

3.3 METHODS

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 rainfall in the west, which receives 1000–1400 mm annual rainfall compared with 750–1000 mm in the east (Met Éireann, 2020). 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, 68 upland acid-sensitive lakes in the Republic of Ireland were sampled to determine the concentrations of total mercury (THg) in lake water (Figure 3.1). Irish uplands are undeveloped areas at elevations greater than 150 meters above sea level (masl), comprising habitats such as bogs, heaths, and semi-natural grasslands (Perrin et al. 2014). Due to the rough landscape, upland lake catchments are relatively un-impacted by development or local pollution, with the dominant source of mercury to the lakes being long-range atmospheric transport. Further, these lakes are strongly influenced by atmospheric sea salt inputs owing to their proximity to the Atlantic Ocean, especially on the west coast (Aherne et al., 2002). The 68 study lakes were primarily situated along the mountainous and hilly Western coast and had a median elevation of 437 masl (Table 3.1).

The study lakes were selected from a set of lakes sampled in 1997. They were originally studied to assess the impacts of long-range transboundary air pollution (Aherne et al., 2002), and re-sampled in 2007 and 2008 (Burton & Aherne, 2012; Whitfield et al., 2011). 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 sampling regions, with preference for higher elevation sites, to limit the effects of local disturbance. During the 2008 survey, a subset of 54 lakes was sampled to establish THg baseline concentrations (Scott & Aherne, 2013; Burton et al., 2013); 24 of these lakes were re-sampled during the 2017–2018 survey (Figure 3.1). In addition, seven of the lakes were occasionally sampled for THg between 2008 and 2018.

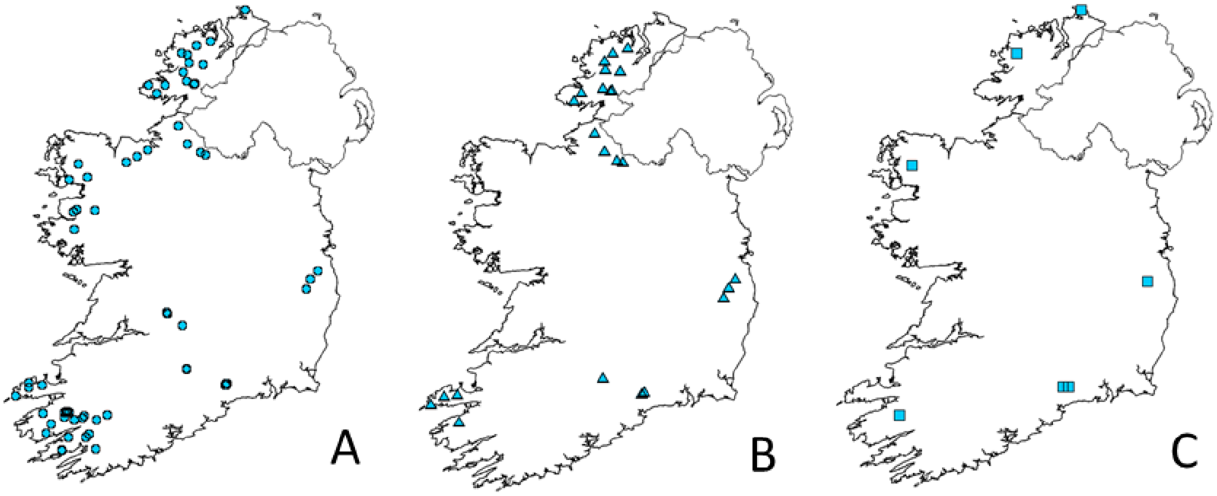

Figure 3.1: *Locations of study lakes in the Republic of Ireland. (A) Lakes sampled during April–July 2017–2018 (n=68); (B) Lakes sampled during 2008 and re-sampled 2017–2018 (n=24); and (C) Lakes sampled 2008 to 2018 (n=7).*

The study sites were small headwater lakes (median: 1.7 ha) in small peatland-dominated catchments (median: 14 ha). Despite their size (81% < 5 ha), the study lakes were assumed to be representative of the 'average lake' in Ireland, as 88% of all lakes in Ireland are less than 5 ha (EPA, 2006). The primary land use was rough grazing, nonetheless, the sites were generally undisturbed by extensive human activity due to their remoteness and rough terrain, though a few (≈ 5%) did have forestry operations within or in proximity to their catchments.

The 24 lakes that were sampled in 2008 and re-sampled in 2017–2018 were assumed to be a representative sub-set of the full dataset for the 2017–2018 survey (n=68) as there were no significant differences between physical or climate characteristics (Mann-Whitney U; $p>0.05$). In contrast, the seven lakes sampled during 2008–2018 (Figure 3.1) tended toward the smallest (median 1.4 ha) and highest elevation lakes (median 505 masl) in the dataset since they were originally selected for their higher elevations to limit effects of local pollution or disturbance (Appendix 3.1).

Table 3.1: *Site characteristics for Irish upland lakes sampled April–July 2017 and 2018 (n=68).*

	Units	**Min – Max**	**Mean**	**Median**	**NMAD (%)**
Elevation	masl	224 – 715	446	437	19
Lake Surface Area	ha	0.04 – 33	3.6	1.7	68
Catchment Area	ha	0.3 – 261	34.3	14.0	84
Lake to Catchment Ratio	–	0.03 – 0.5	0.15	0.14	53
Solar Radiation	kJ/m^2/d	8444 – 9771	9032	9125	3
Air Temperature	°C	5.0 – 10.6	7.6	7.6	11
Precipitation	m/yr	1.3 – 3.4	2.3	2.2	18
Regional Soil Moisture	m^3/m^3	0.4 – 0.9	0.6	0.5	11
Peatland Coverage	%	0 – 100	66	100	0[1]

NMAD: Normalized Median Absolute Deviation

[1] Due to limited data variation, and half the upland lakes having a peatland coverage of 100%, NMAD (%) was 0.

Field & laboratory methodology

Prior to sampling, vials for THg (Glass I-Chem with Teflon-lined caps) were cleaned in a 10% BrCl/HCl bath (v/v) for 48 hours, triple rinsed with reverse osmosis water, once with b-pure water, oven dried (> 100°C) and individually double bagged. 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.

Water samples were collected from shore, in an area free of emergent vegetation; shore samples were assumed to be representative of the entire lake as the lakes are small, shallow, and well-mixed by wind. Samples were collected approximately 15 cm below the surface of the water. Prior to collection, the sampling container was rinsed three times with lake water; rinse water was poured onto the shore to avoid disturbing the sediment.

At each lake two 30 mL water samples were collected in 40 mL glass I-Chem vials for THg analysis. Precautions were taken to limit potential contamination during sampling; gloves were worn when handling the vial and inner bag during sampling. Samples were preserved with HCl by the end of the day (0.5% v/v). Field blanks were used to test for contamination introduced during sample collection or contamination from the vials themselves. A 250 mL unfiltered bulk water sample was also collected for all remaining chemical analyses.

All water samples were analyzed for THg, DOC, absorbance, major ions, alkalinity, conductivity, and pH. Total Hg was measured on a Tekran 2600 mercury analyzer, using US EPA method 1631. The samples for DOC, absorbance, and major ions were filtered prior to analysis using 0.45 µm disposable nylon syringe filters. DOC was measured on a Shimadzu TOC Analyzer. Absorbance was determined at three wavelengths (254, 285, and 365 nm) using a Lambda XLS+ UV-Vis Spectrometer. Anions (Cl^- and SO_4^{2-}) were measured on a Dionex 600 Ion Chromatograph, and cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) were analyzed using a Perkin-Elmer Inductively Coupled Plasma

Optical Emission Spectrometer (ICP-OES). Alkalinity, conductivity, and pH were determined with unfiltered samples using a Mantech PC-titrate; the sample bottles remained sealed until immediately before each sample was analysed. Quality control data for THg and DOC analysis are in Appendix 3.1.

Data analysis

Data sources

Climate data (global solar radiation, air temperature, precipitation, and regional soil moisture) were obtained from the Irish Meteorological Service (Met Éireann). Data were spatially modeled (kriging interpolation) using 30-year (1981–2010) climate averages from Met Éireann monitoring stations (Walsh, 2012). Peatland coverage of the study catchments was determined using CORINE land cover inventories from 2018. CORINE uses satellite imagery to estimate land cover type, with a resolution of 25 ha (land.copernicus.eu/pan-european/corine-land-cover).

Calculated variables

(1) Total Hg in lake water was normalized by dissolved organic carbon (THg/OC) to examine trends potentially hidden by the influence of organic carbon. While THg and DOC generally have a positive linear relationship, the ratio does vary (Lavoie et al., 2019). THg/OC in water was expressed in mg Hg/kg DOC.

(2) Three organic matter quality indices were calculated using the available data. Firstly, specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), which indicates aromaticity and molecular weight, was calculated by dividing absorbance at 254 nm by DOC (mg/L) and multiplying by 100 (Weishaar et al., 2003). Second, the absorbance ratio of 250 nm by 365 nm (E2:E3), which has a

negative relationship with molecular weight (Peuravuori & Pihlaja, 1997); the ratio was calculated using 254 nm since absorbance was not measured at 250 nm, but results were consistent with relevant studies. Lastly, the absorbance ratio 285 nm by 254 nm, which has a negative relationship with the polarity of aromatic organic matter (Clarke et al., 2007). Both E2:E3 and $SUVA_{254}$ are commonly used indices and the ratio notations are widely accepted and recognized; in contrast, the ratio 285 nm by 254 nm is not widely used and in this study the notation for the ratio will be 285:254.

(3) The influence of bedrock weathering and the soil exchange complex on lake chemistry was determined using a sodium to chloride ratio (Na:Cl), calculated as a ratio of the concentration of sodium and chloride ions in lake water (eq/L). Catchment bedrock influence was indicated by a ratio greater than 0.859, which is the ratio of sodium to chloride in seawater (ICP Waters, 2010).

(4) The influence of anthropogenic emissions of sulphur on lake chemistry was estimated by correcting the measured sulphate (SO_4^{2-}) concentrations in the lakes for the influence of sea salts. Non-marine sulphate was calculated using 0.140 (mg/kg : mg/kg) for the ratio of sulphate to chloride in sea water (De Vries et al., 2015):

$$[SO_4^{2-}]_{\text{non-marine}} = [SO_4^{2-}]_{\text{total}} - (0.140 \times [Cl^-])$$

Lake chemistry in 2017–2018

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

Lake chemistry from 2017–2018 was summarized and presented, with variability between lakes calculated as normalized median absolute deviation (NMAD) to best represent the non-normally distributed data (Appendix 3.1). Variability in pH was calculated using the concentration of H^+ because NMAD underestimated the variability of pH, due to the logged scale and limited range of values in natural waters. The distribution of THg, DOC, and THg/OC data was visualized using box and jitter plots. To assess regional variation, all variables were tested for significant Spearman rank correlations ($p<0.05$) with easting and northing. Total Hg and DOC concentrations were mapped to observe regional differences in concentrations.

Spearman rank correlation was used to determine which variables were significantly associated with THg and THg/OC ($p<0.05$). For THg/OC, correlations with THg and DOC were not presented as THg/OC is a product of the two. Redundancy Analysis (RDA) was used to determine drivers of variation in THg between lakes ($p<0.05$) and visualized using a biplot; THg and THg/OC were both tested as dependent variables. Biplots for RDA were scaled to allow easier interpretation, using scaling type 2 as determined by Legendre & Legendre (1998). The correlation strength of the individual axes (THg and THg/OC) with their dominant drivers was indicated as an r value in-text. The strength of the overall RDA (both THg and THg/OC axes) was noted in the RDA figure caption as R^2 and R^2_{adj}. The RDA loadings are included in the Appendix (Appendix 3.2).

Long-term changes in THg

Significant ($p<0.05$) differences in THg and other lake chemistry variables (DOC, etc.) between the 2008 and 2017–2018 surveys (n=24) were tested using Wilcoxon signed rank tests. Significant ($p<0.05$) changes in THg and THg/OC for the subset of seven lakes sampled 2008 to 2018 were tested using a Mann-Kendall trend test. These lakes were sampled approximately annually between 2007 (prior to first THg measurements) and 2018, but THg analysis was not carried out for every sampling event. Mann-Kendall tests for pH, conductivity, DOC, and organic matter quality were run using all available data, rather than just the data corresponding to the THg sampling events, in order to provide a more accurate representation of changes over the decade. Changes in organic matter quality in the seven lakes were tested for the period of 2009–2018 since absorbance data were not available for 2007 or 2008. Since THg was not measured consistently over the decade, chemistry changes in the seven lakes were additionally tested using Wilcoxon signed rank tests, comparing the period 2008–2011 (n=45) to 2017–2018 (n=25).

An important consideration when examining long-term chemical trends in surface waters, is seasonality. Concentrations of DOC and THg are known to fluctuate throughout a year due to indirect weather influences on organic matter/mercury sources (precipitation/temperature shifts impacting runoff, primary production etc.) (e.g., Wang et al., 2013; Liu et al., 2014). While some 2017–2018 sampling occurred in July, generally the test comparing 2008 to 2017–2018 (n=24) was comparing two spring periods (April/May). In contrast, the tests for the intensive sampling subset (n=7) did not take seasonality into account due to the very limited data available and it is acknowledged that this is an unavoidable limitation to this study.

3.4 RESULTS

Total mercury in upland Irish lakes

The study lakes were generally acidic (median pH: 5.8) and dilute (median conductivity: 42.7 µS/cm). Chloride and sodium were the dominant ions as expected, due to the coastal environment (Table 3.2). The concentration of DOC ranged from 0.8 to 13.7 mg/L, with a median of 3.9 mg/L. Organic matter quality parameters (Table 3.2) suggested a dominance of allochthonous organic matter in the study lakes as evidenced by the aromaticity (median $SUVA_{254}$ = 3.2 L mg^{-1} m^{-1}) and lack of low molecular weight (median E2:E3 = 3.9) organic matter (McCabe & Arnold, 2018; Sepp et al., 2019).

Table 3.2: *Summary of chemical characteristics in upland lakes (n=68) sampled in the Republic of Ireland during April–July 2017 & 2018.*

	Units	**Min – Max**	**Median**	**NMAD (%)**
THg	ng/L	2.0 – 19.7	5.4	37
THg/OC	mg/kg	0.4 – 5.2	1.4	26
DOC	mg/L	0.8 – 13.7	3.9	43
pH		4.4 – 7.4	5.8	89
Conductivity	µS/cm	24.3 – 120.6	42.7	22
Gran Alkalinity	mg/L	-1.9 – 21.5	0.8	47
Ca^{2+}	mg/L	0.3 – 7.4	1.2	43
Mg^{2+}	mg/L	0.3 – 2.6	0.9	34
K^{+}	mg/L	0.04 – 0.9	0.3	32
Na^{+}	mg/L	2.4 – 17.3	5.5	22
Cl^{-}	mg/L	2.0 – 30.8	7.8	31
SO_4^{2-}	mg/L	0.4 – 4.3	1.5	22
Na:Cl		0.77 – 4.24	0.99	9
Non-marine SO_4^{2-}	mg/L	0.0 – 1.7	0.4	60
$SUVA_{254}$	L mg^{-1} m^{-1}	0.8 – 5.5	3.2	25
E2:E3		1.6 – 6.0	3.9	12
285:254		0.5 – 0.8	0.7	4

NMAD: Normalized median absolute deviation

Total Hg in the study lakes ranged from 2.0–19.7 ng/L, with a median of 5.4 ng/L (Table 3.2). The central 50% of the data fell between 3.9 and 8.2 ng/L (Figure 3.2). The upper range of the data (19.7 ng/L) was driven by a small number of lakes; six lakes (9%) had a concentration greater than 13 ng/L. The concentration of THg varied less between lakes (NMAD 37%) than DOC (NMAD 43%). When normalized by organic carbon, THg variability between lakes was lower (NMAD 26%); THg/OC ranged from 0.4–5.2 mg/kg, with a median of 1.4 mg/kg. The central 50% of the data fell between 1.1 and 1.8 mg/kg. Two lakes had much higher THg/OC, at around 5 mg/kg, while the remaining sites (97%) fell below 3 mg/kg (Figure 3.2).

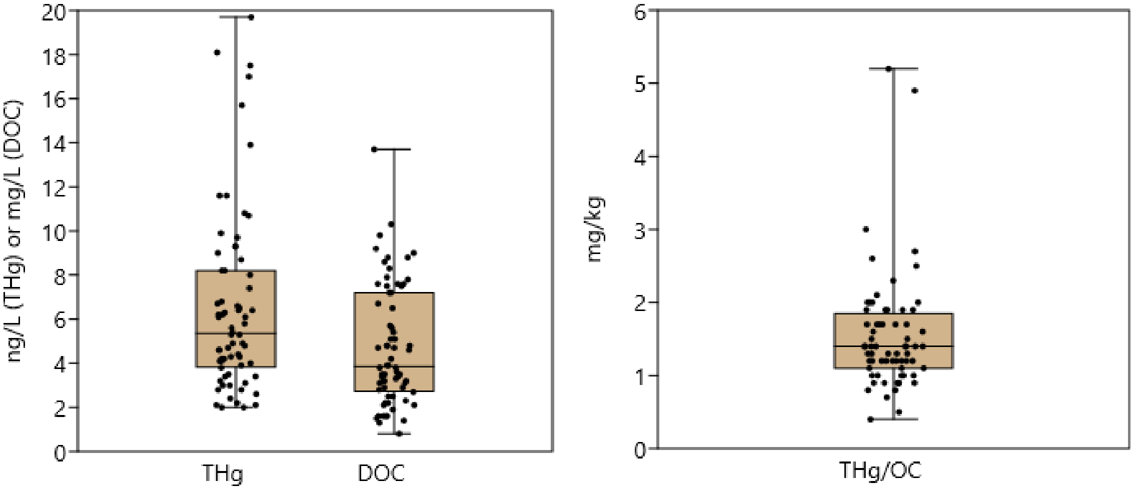

Figure 3.2: *Total mercury (THg) and dissolved organic carbon (DOC) concentrations (left) and THg concentrations normalized by organic carbon (right) in upland lakes (n=68) in the Republic of Ireland, April–July 2017 & 2018.*

Variability in THg between the lakes was primarily explained by positive relationships with DOC and SUVA$_{254}$, and a negative relationship with pH (r=0.83 RDA; Figure 3.3); these three variables also had the strongest correlations with THg (Table 3.3). The association with aromaticity, paired with positive correlations with regional soil moisture and peatland coverage (Table 3.3) suggests that variation in THg can be attributed to the influence of terrestrial organic matter, specifically peatlands.

Variability in THg/OC was explained by a positive relationship with precipitation, and negative relationships with calcium and alkalinity (r=0.73 RDA; Figure 3.3). The positive relationship between THg/OC and precipitation was likely due to dilution given the strong diluting effect of precipitation on DOC (Figure 3.3; Appendix 3.2). The associations with calcium and alkalinity were also seen in the correlation results for both THg/OC and THg (Table 3.3) and suggest an inverse relationship with catchment buffering. This relationship highlights the differences in the two distinct types of upland lakes in this study: poorly buffered peaty catchments and mineral catchments (Appendix 3.1). While there were no regional trends for THg/OC to confirm this, it indicates that the poorly buffered catchments have higher THg/OC.

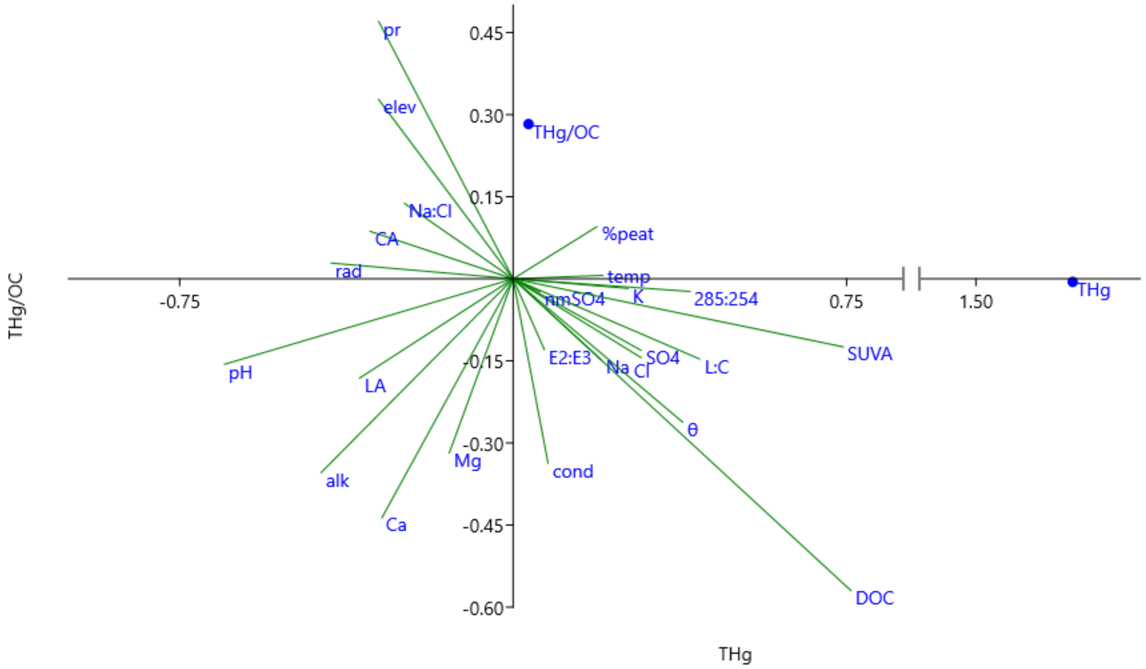

Figure 3.3: *Redundancy Analysis (RDA) for total mercury (THg) and total mercury normalized by organic carbon (THg/OC) in upland lakes in the Republic of Ireland (n=68), sampled April–July 2017 & 2018. R^2=0.69; R^2 adj=0.51. Dependent variable amplitude decreased to 0.5 to allow*

easier figure interpretation. elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation, θ=soil moisture, %peat=peatland coverage, alk=gran alkalinity, cond=conductivity, DOC=dissolved organic carbon, SUVA=specific ultraviolet absorbance, E2:E3=absorbance ratio 254/365, 285:254=absorbance ratio 285/254, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio; element concentrations use standard symbols.

Table 3.3: *Spearman Rank Correlation, variables significantly ($p<0.05$) correlated to THg in lakes in the Republic of Ireland ($n=68$) sampled April–July 2017 & 2018*

THg			**THg/OC**		
Variable	**+/-**	**r_s**	**Variable**	**+/-**	**r_s**
Alkalinity	–	–0.53	Alkalinity	–	–0.27
Ca^{2+}	–	–0.33	Ca^{2+}	–	–0.39
pH	–	–0.59	pH	–	–0.40
DOC	+	0.70			
$SUVA_{254}$	+	0.66			
285:254	+	0.37			
Precipitation	–	–0.33			
Regional soil moisture	+	0.46			
Peatland coverage	+	0.29			
Solar radiation	–	–0.37			
Elevation	–	–0.26			
Lake area	–	–0.29			
Catchment area	–	–0.41			
Lake to catchment ratio	+	0.31			

The concentrations of THg were highest in the northern sites, where DOC concentrations were also high (Figure 3.4); further THg and DOC had significant positive correlations with northing and easting ($p<0.05$; Appendix 3.2). The northern sites had greater peatland coverage than the rocky southern sites (Appendix 3.1). Aromaticity ($SUVA_{254}$) was also higher in the northern lakes, due to the positive relationship between peatland soils and aromaticity (Sepp et al., 2019). In contrast, THg/OC was not significantly correlated to northing or easting and had no discernible regional patterns (Figure 3.4).

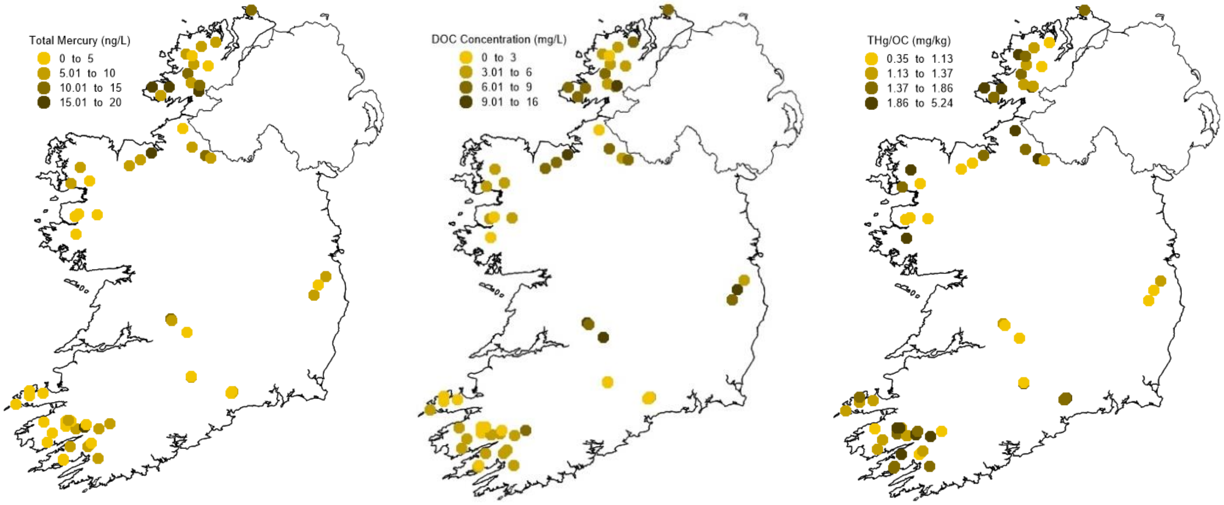

Figure 3.4: *Total mercury (left), dissolved organic carbon (DOC) concentrations (centre), and total mercury normalized by organic carbon (right) in upland lakes in the Republic of Ireland (n=68), sampled April–July 2017 & 2018.*

Changes in THg between 2008 and 2018

Median THg and DOC concentrations were 50% lower in 2008 than 2017–2018 (Table 3.4). All variables were significantly different between 2008 and 2017–2018 except calcium and non-marine sulphate concentrations ($p<0.05$; Appendix 3.2). The difference in sodium and chloride is particularly notable; the median concentrations were twice as high during the 2008 survey, as was conductivity (Table 3.4), showing the effects of a severe ocean storm that wracked Ireland in March 2008 (Met Éireann, 2008). It is well established that the study lakes are strongly influenced by atmospheric oceanic inputs (Aherne et al., 2002). The lower DOC concentrations in 2008 were due to suppression of organic matter solubility under elevated sea salts (Moldan et al., 2012), rather than dilution from precipitation given there was no significant difference in calcium between the two periods, which is primarily associated with catchment soil weathering. Further, pH was significantly lower in 2008, which can also be explained by the sea salt event (Farrell et al., 1998; Moldan et al., 2012). While the lower THg in 2008 can be attributed in part to the suppression of DOC from sea salts, THg/OC was significantly higher in 2017–2018, indicating that THg was higher in 2017–2018 beyond the influence of DOC concentrations (Figure 3.5). It should be noted there was a significant difference between THg in 2017 (median 4.5 ng/L) and 2018 (median 5.7 ng/L) but it was not enough to influence the observed increase in THg between 2008 and 2017–2018 and there was no significant difference in THg/OC.

Table 3.4: *Comparison of chemistry in upland lakes (n=24) sampled in the Republic of Ireland during May 2008 and April–July 2017 & 2018.*

		2008			2017–2018		
	Units	**Min – Max**	**Median**	**NMAD(%)**	**Min – Max**	**Median**	**NMAD(%)**
THg	ng/L	1.6 – 5.1	2.7	19	2.0 – 19.7	6.0	43
DOC	mg/L	0.8 – 9.2	3.1	32	1.6 – 9.8	4.9	44
THg/OC	mg/kg	0.5 – 2.1	0.9	23	0.3 – 2.7	1.3	20
pH		4.2 – 6.9	5.4	93	4.5 – 7.4	5.8	85
Conductivity	µS/cm	35.2 – 142.3	88.4	31	24.3 – 120.6	40.2	31
Gran Alkalinity	mg/L	-2.8 – 7.8	0.1	20	-1.5 – 8.3	0.8	40
Ca^{2+}	mg/L	0.7 – 3.8	1.5	35	0.3 – 4.4	1.1	52
Mg^{2+}	mg/L	0.4 – 2.8	1.4	28	0.3 – 2.6	0.9	35
K^+	mg/L	0.2 – 0.8	0.4	43	0.1 – 0.7	0.3	23
Na^+	mg/L	3.9 – 19.5	10.7	39	3.1 – 17.3	5.4	33
Cl^-	mg/L	6.2 – 47.3	20.0	35	2.0 – 30.8	7.3	42
SO_4^{2-}	mg/L	1.2 – 4.6	2.7	14	0.4 – 4.3	1.6	32
Na:Cl		0.64 – 1.01	0.81	6	0.86 – 4.24	1.02	9
Non-marine SO_4^{2-}	mg/L	0.0 – 1.8	0.1	93	0.0 – 1.2	0.6	48

NMAD: Normalized median absolute deviation

The effects of the 2008 sea salt event on lake chemistry were further seen in the intensive subset (n=7) which indicates that the effects were temporary (see Appendix 3.2 for further details). Only one of the seven intensive sampling lakes (Lake ID L2211x) had a significant increase in THg 2008–2018, though the other lakes had slight non-significant positive trends in THg. Lake L2211x was also the only lake with a significant increase in THg/OC. The general increasing THg was in contrast to DOC, which had no positive trends; one lake (Lake ID L0808) had a significant decrease in DOC. Organic matter quality indices had no significant changes. Therefore, while organic matter and THg have a very strong relationship that explained the spatial variation of the study lakes, the temporal changes in THg could not be attributed to changes in DOC or organic matter quality. The second temporal test for the seven intensive lakes, comparing 2008–2011 to 2017–2018, found THg in 2017–2018 was significantly higher (p<0.05) than THg in 2008–2011 (Appendix 3.2). Further, THg/OC in 2017–2018 was higher than THg/OC in 2008–2011, while there was no significant difference in DOC between 2008–2011 and 2017–2018 (see Appendix 3.2). Therefore, both temporal datasets support that THg concentrations in the study lakes were higher in 2017–2018 than earlier in the decade.

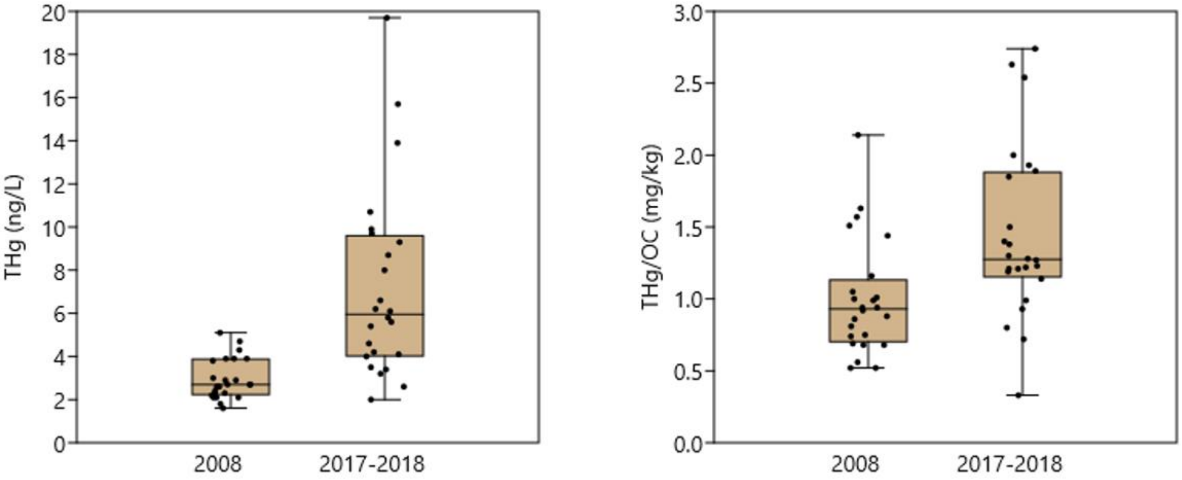

Figure 3.5: *Total mercury (THg) concentrations (left) and THg normalized by organic carbon (THg/OC) concentrations (right) in upland lakes (n=24) in the Republic of Ireland, sampled 2008 and 2017–2018.*

3.5 DISCUSSION

Total mercury in upland Irish lakes

Total Hg concentrations in the upland lake water were generally low (median 5.4 ng/L, range 2.0–19.7 ng/L), given their distance from direct pollution sources. The lakes with the highest concentrations (>10 ng/L) were peatland-dominated lake catchments with high DOC and were consistent with other streams and lakes influenced by peatlands (e.g., 4.6–25 ng/L, n=1 [Woerndle et al. 2018]; mean 14 ng/L, n=1 [Yang et al. 2002]). The bulk of the remaining lakes had concentrations similar to 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 north-eastern Canada (0.19–3.1, n=37 [Richardson et al., 2021]) as well as mountain lakes in the US (0.10–4.96 ng/L, n=44; [Yu et al. 2011]). The drivers of THg variability were consistent with previous studies; DOC, $SUVA_{254}$, and pH are commonly found to have strong relationships with THg (e.g., Lavoie et al., 2019; Watras et al., 1995). The strong relationship between mercury and DOC can be attributed to mercury's affinity for the reduced sulfur binding sites in organic matter (Ravichandran, 2004) and a global review of mercury and DOC in freshwater reported that the aromatic fraction of DOC is observed to have a stronger relationship with THg compared to bulk DOC due to the abundance of reduced sulfur binding sites in aromatic DOC (Lavoie et al., 2019). In contrast to Lavoie (2019), we found the THg-DOC relationship was slightly stronger than the THg-SUVA relationship, though it was very similar in strength for both correlation and RDA (Table 3.3; Appendix 3.2). This is likely because the organic matter in the lakes appeared to be largely terrestrially sourced – DOC was correlated to soil moisture and DOC concentrations were higher in peatland dominated areas – and terrestrial organic matter tends to be more aromatic than aquatic derived organic matter (Malcolm, 1990), particularly in peatland soils (Sepp et al., 2019).

In this study the THg/OC values ranged from 0.4 to 5.2 mg/kg, with a median of 1.4 mg/kg; in contrast several studies report all values < 1 mg/kg, which includes lake studies with comparable THg concentration in Norway (0.12–0.53, n=51 [Braaten et al., 2014]) and north-eastern Canada (n=37, Richardson et al., 2021). The THg/OC values in this study were also generally higher than freshwater stream and river studies in Sweden (mean range 0.20–0.43, n=19 [Eklöf et al., 2012]) and the US (mean 0.42, n=19 [Stoken et al., 2016]). One stream in the US was observed to have higher THg/OC than the study lakes (median 2.94 mg/kg), but this was an anomaly among the other headwater streams (0.24–0.37, n=3 [Shanley et al., 2008]) and other studies of rivers and streams elsewhere in the US (Stoken et al., 2016). A possible explanation for the Irish lakes having greater THg/OC would be because only the dissolved fraction was measured for organic carbon while THg included both the dissolved and particulate fractions. In contrast, other studies used total organic carbon (TOC) instead of DOC (Eklöf et al., 2012) or used dissolved THg (Stoken et al., 2016). While not covered by this study, mercury also has a strong relationship with particulate (>0.45 µm) organic matter which plays an important role in mercury cycling (e.g., Dittman et al., 2010; Shanley et al., 2008). While this may account for some of the difference, particulate organic carbon (POC) concentrations in the Irish lakes are low and it is generally accepted that TOC≈DOC. Available data indicates POC is 20% of TOC, but the difference between DOC replicates could be up to 10% (Appendix 3.1), making this influence relatively minor. Regardless, even if POC is accounted for by a 20% increase to DOC measurements, the THg/OC values remained notably higher than values in the literature (most >1 when literature reports <1; see Appendix 3.2).

In contrast to THg, studies that use THg/OC have found a variety of variables that explain variation, such as water retention time (Richardson et al., 2021), the catchment’s soil organic carbon content (Stoken et al., 2016), and degree of human disturbance (Lavoie et al., 2019). In this study, THg/OC variability was attributed to regional precipitation (DOC dilution), and poor catchment buffering (calcium, alkalinity). The negative association with catchment buffering was also shown for THg (Table 3.3) and suggests greater export of THg from the more acidic peatland catchment soils than from the mineral catchments (Appendix 3.1), driven by decreased pH inhibiting mercury adsorption to soils (Gabriel & Williamson, 2004).

Temporal variation in total mercury

The temporal data presented in this study provides insight on the effects of a sea salt event on THg concentrations; this is valuable as it shows how THg in the lakes may react to future ocean storm events which will likely increase in frequency in Ireland due to climate change (Nolan, 2015; Cámaro-García et al., 2021). However, while the difference in THg for the 24 lakes sampled in 2008 and 2017–2018 can be attributed to DOC suppression by sea salts (Moldan et al., 2012), it does not explain the increase in THg/OC, nor the increases in both THg and THg/OC for the subset of seven lakes sampled 2008–2018. While it cannot be determined conclusively, two possible mechanisms that could account for changes in THg without a matching change in DOC are (1) increased THg inputs to the lakes, and (2) a shift in organic matter quality.

Higher THg concentrations in 2017–2018, despite lower or unchanged DOC, could potentially be explained by increased mercury deposition but Ireland has low atmospheric mercury concentrations which decreased between 1996 and 2018 (Weigelt et al., 2015; Custodio et al., 2020). Given the lakes are headwater systems, and the lack of nearby anthropogenic mercury sources, the catchment soils would be the only other potential source of mercury to the lakes that could account for the increase in THg. There have been reports of legacy mercury pollution stored in catchment soils becoming the dominant source of mercury to lakes in light of decreasing atmospheric deposition (Sun et al., 2022; Rose et al., 2012; Yang et al., 2016) but what remains unclear is the timeline for this remobilization. Peat cores indicate that mercury deposition in Ireland peaked 1950–1970s and decreased since the 1980s (Coggins et al., 2006; Scott & Aherne, 2013), but without additional data it cannot be determined whether the observed increase in lake water THg is a recent phenomenon and the release of legacy mercury was delayed for decades, or if this is part of a continuous long-term re-mobilization trend.

A decoupling of THg and TOC (total organic carbon) temporal trends was observed in a study of 19 surface waters in Sweden; in contrast to our study, TOC increased but generally lacked an accompanying change in THg, resulting in a significant negative trend in THg/OC between 2000–2010 (Eklöf et al., 2012). It was hypothesized that while TOC was increasing, certain fractions of organic matter with stronger associations with THg were not increasing to the same extent, resulting in the lack of THg trends (Eklöf et al., 2012). While there were no significant changes in organic matter quality observed in the Irish study lakes, the available data was limited and we suggest that future research should consider the influence of organic matter quality on temporal THg trends in surface waters due to the relationships observed in this study (Table 3.3, Figure 3.3) and others (e.g., Lescord et al., 2018; Dittman et al., 2010).

3.6 CONCLUSIONS

In upland acid-sensitive lakes, higher concentrations of THg were associated with higher concentrations of DOC and greater aromaticity of organic matter. Further, the variability in THg concentrations across the study lakes was related to regional peatland coverage, with the highest THg concentrations in the northern lakes where the landscape was dominated by peatlands. In contrast, the concentration of THg/OC did not have a regional pattern, rather variability was explained by poor catchment buffering, which suggests leaching of mercury from organic soils into the lakes. Mercury leaching from soils may also be the cause of the observed temporal increase in lake THg. While the sea salt event in 2008 had a notable effect on both DOC and THg concentrations, DOC could not fully explain THg trends, evidenced by the significantly higher THg/OC in 2017–2018. Due to the lakes' isolation from other mercury sources, this may be related to the release of mercury stored in catchment soils. Mobilization of legacy mercury pollution from soils could delay observed effects of decreasing atmospheric mercury on Irish lakes.

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

4.1 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 atmospheric mercury. Thirty-one upland lake catchments were sampled for topsoil, lake sediment, and lake water during 2017–2018. Total mercury concentrations (THg) 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 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, 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.

4.2 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. Historically, mercury has been of greatest concern within aquatic environments where mercury 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 (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 et al. 2014; Rose et al. 2012). This mechanism may become increasingly important as 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 (Rose et al. 2012). Measuring the bulk concentration of mercury in all forms (elemental, inorganic, organic) is generally referred to as total mercury (denotated 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 (e.g., Watras et al. 1995; Scott and Aherne 2013; 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 (≈1.3 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.

4.3 METHODS

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 (Figure 4.1). 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 (Appendix 4.2). 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 input of mercury pollution to the study lakes is 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).

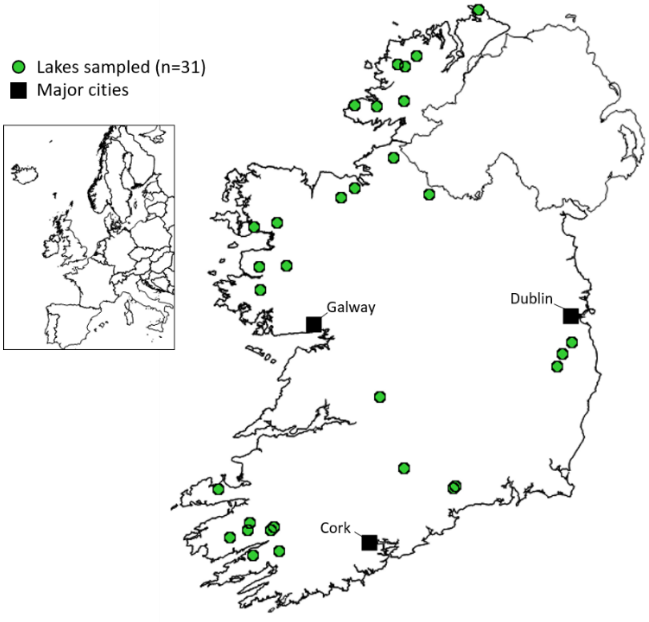

Figure 4.1: *Location of study lakes (n=31) in the Republic of Ireland, sampled during April–July 2017 and 2018. Sampling sites are indicated by green circles, major cities in Ireland are indicated by black squares. Note: the circles overlap in some regions owing to the proximity between lakes. The inset shows the location of Ireland on the western periphery of Europe.*

Field & laboratory methodology

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.

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. Quality control data for DOC and THg analysis are in Appendix 4.2.

The composite sediment and soil 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). Total Hg was determined using a DMA 80 (Direct Mercury Analyzer) and quality control data are in Appendix 4.2. 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/m^2) in the catchment soil (see Appendix 4.1 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 normalized by organic carbon (THg/OC) in water was calculated using THg and DOC concentration data. In sediment and soil, it was calculated using THg concentrations and percent organic matter data, with percent organic matter being first converted to organic carbon (see Appendix 4.1 for more details). 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 Appendix 4.1). 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}.

4.4 RESULTS

Lake water

The upland lakes tended to be dilute and acidic systems, with median conductivity of 38.4 µS/cm and pH of 5.6 (Table 4.1). 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 4.1). 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 4.1). The central 50% of the data fell between 4.0 and 8.1 ng/L (Figure 4.2). The upper range of the data was driven by a small number of lakes with higher THg; only three lakes (≈10%) had a concentration greater than 11 ng/L (Figure 4.2). The corresponding DOC concentrations for those three lakes were all greater than 7 mg/L and were some of the highest DOC values (Figure 4.2), 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 4.1). In contrast, catchment soil varied little, with the vast majority of samples being highly organic (peatland) soils with few exceptions (Figure 4.2). Organic matter (%OM) in sediment and soil had similar ranges (Table 4.1), 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% (Figure 4.2). Total Hg in sediment was also significantly lower than in soil

(Figure 4.2). 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 (Figure 4.2). 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 4.1).

Table 4.1: *Statistical summary of physiochemical variables for upland lake water (n=31), sediment (n=28), and catchment soil (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
Silt	%	16–84	59	26
Clay	%	0.2–7	1	46

* geometric mean

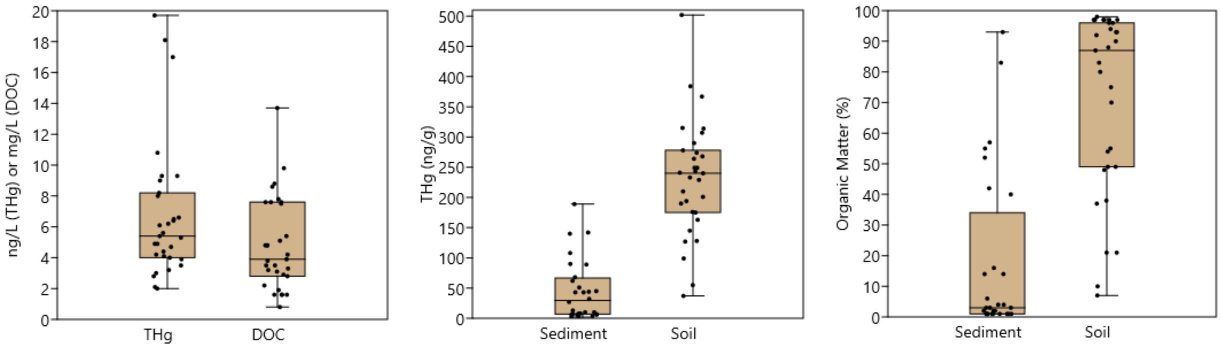

Figure 4.2: *Left: Total mercury (THg) and dissolved organic carbon (DOC) in lake water (n=31); Middle: THg in lake sediment (n=28) and catchment soil (n=31); Right: Organic matter content in lake sediment (n=28) and catchment soil (n=31). Lake catchments sampled in the Republic of Ireland during April–July 2017 and 2018.*

Lake water THg/OC (median 1.3 mg/kg OC) was significantly higher than THg/OC for sediment and soil (Figure 4.3); of the three media, THg in sediment had the greatest variability, with an NMAD of 67% (water: 31%; soil: 32%). A possible explanation for lake water having greater THg/OC than sediment and soil would be because only the dissolved fraction (<0.45 µm) was measured for organic carbon while THg included both the dissolved and particulate fractions. While not covered by this study, mercury also has a strong relationship with particulate (>0.45 µm) organic matter that plays an important role in mercury cycling (e.g., Dittman et al., 2010; Shanley et al., 2008). While this may account for some of the difference, particulate organic carbon (POC) concentrations in the Irish lakes are low and it is generally accepted that TOC≈DOC. Available data indicates POC is 20% of TOC, but the difference between DOC replicates could be up to 10% (Appendix 4.2), making this influence relatively minor. Regardless, even if POC is accounted for by a 20% increase to DOC measurements, there was still a significant difference ($p<0.05$) between THg/OC for lake water and THg/OC in soil and sediment.

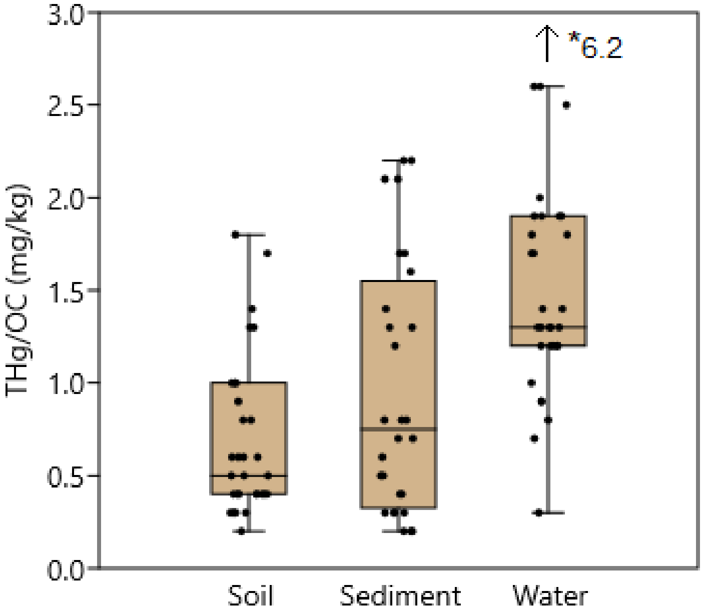

Figure 4.3: *Total mercury concentration normalized by organic carbon (THg/OC) in catchment soil (n=31), lake sediment (n=28), and lake water (n=31). Samples collected during April–July 2017 and 2018, in the Republic of Ireland. Outlier indicated by arrow and asterisk (*).*

Relationship of THg between soil, sediment, and water

Total Hg in lake sediment and lake water was strongly associated with catchment soil (Table 4.2 and Figure 4.4). 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; Figure 4.4), 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 4.2). 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; Figure 4.4).

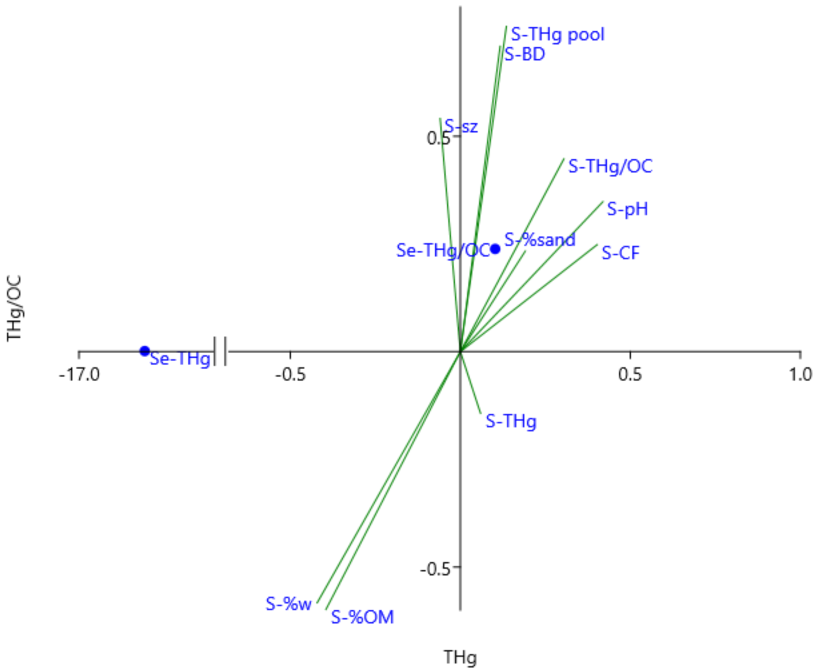

Figure 4.4: *Biplot of Redundancy Analysis (RDA) for total mercury (THg) and total mercury normalized by organic carbon (THg/OC) in Irish sediment (n=31), sampled during April–July 2017 and 2018, with soil parameters as explanatory variables (R^2=0.46; R^2 adj=0.14). Column amplitude set to 0.5 to allow 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.*

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 (Appendix 4.2).

Table 4.2 *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; Figure 4.5) 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 4.2 and Figure 4.5).

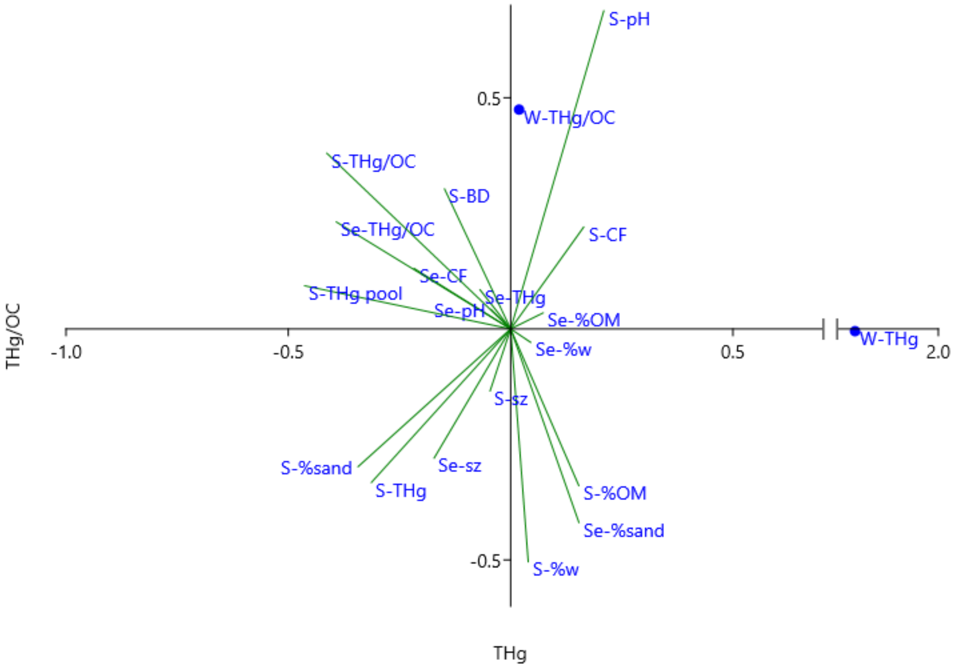

Figure 4.5: *Biplot of Redundancy Analysis (RDA) for total mercury (THg) and total mercury normalized by organic carbon (THg/OC) in Irish lake water (n=31), sampled during April–July 2017 and 2018, with soil and sediment as explanatory variables (R^2=0.68; R^2 adj=0.20). Column amplitude set to 0.5 to 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.*

Lake water THg was negatively correlated to THg/OC in soil, soil THg pool, and soil texture (Table 4.2). 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; Figure 4.5). 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 4.2), 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 Figures 4.4 and 4.5).

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 4.2). The northern sites were dominated by peatland, while the southern sites were rocky and had higher proportions of inorganic soil (Appendix 4.2), 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 (Appendix 4.2). 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 (Appendix 4.2).

4.5 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 (median 2.78 ng/L, n=54 [Burton et al. 2013]), most of the lakes were 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 US (0.10–4.96 ng/L, n=44; [Yu et al. 2011]). The 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]; mean 14 ng/L, n=1 [Yang et al. 2002]).

Total Hg in sediment for the study lakes (median 30 ng/g, range 2.2–189 ng/g) 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 topsoils (median 240 ng/g) was higher than topsoils 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 [Tripathee et al. 2018]), owing to their high organic content (87%). Total Hg in the study soils was more than twice as high as rural topsoils in the UK (median 95 ng/g, n=898), however when normalized 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 of low atmospheric deposition.

Interlinkages between soil, sediment, and water

The results suggest that catchment soils 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 past atmospheric deposition in soils becoming the dominant source to aquatic systems, which has been observed for trace metals in the UK (Yang et al., 2018; Yang et al., 2016). For the study lakes the origin of the mercury will still be atmospheric, with a shift away from direct atmospheric deposition and 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 would be largely from erosion or seepage.

4.6 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 dominated 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.

CHAPTER FIVE: Conclusion

General conclusions and observations

The primary objective of this thesis was to determine what drives variation in dissolved organic carbon (DOC) and total mercury (THg) between lakes in Ireland, while also testing for significant changes in either variable during the past decade. A secondary objective was to investigate the interlinkages in the concentration of THg in soils, lake sediment, and lake water. The thesis assessed lake water DOC for 68 upland lakes and 48 lowland lakes in 2017–2018, with a subset (7 upland and 14 lowland) tested for temporal change in DOC during the previous decade. The upland lakes were additionally analyzed for THg and at thirty-one of the upland sites lake sediment and catchment soil were sampled for THg.

The upland and lowland lakes were significantly different in their physical, climatic, and chemical characteristics, including DOC concentrations. The upland lakes tended to have lower DOC due to being dilute precipitation-fed headwater systems. Despite the numerous differences between the upland and lowland lakes, in both datasets the variability in DOC between lakes was best explained by the effects of regional precipitation levels (dilution) and organic matter in the catchment soils (terrestrial inputs). Organic matter quality data for the upland lakes further supported the terrestrial influence on the study lakes. In contrast to widespread reports of rising DOC in surface waters in Europe and North America, the study found that any temporal changes in DOC were very minor and tended to be decreases; this was likely due to the relatively short and recent time period of the study since it occurred during a time where the rate of DOC change was slowing, as well as during a period of unprecedented rainfall in Ireland.

Total mercury concentrations in upland lake water were low, consistent with other background regions. Variability in lake water THg concentrations was explained by DOC concentrations and organic matter aromaticity. The highest THg concentrations were in the northern lakes where the landscape is dominated by peatlands, resulting in higher DOC and greater aromaticity of organic matter. Despite decreasing atmospheric mercury concentrations in Ireland, THg in the lakes was significantly higher in 2017–2018 than a previous survey in 2008. This can partially be attributed to the suppression of DOC following a sea salt episode in March 2008, but the observed increase in THg was greater than the influence of DOC concentrations, as evidenced by a significant increase in THg normalized by organic carbon (THg/OC). Since the lakes are isolated from local mercury pollution sources, and atmospheric mercury is decreasing, this trend may be caused by the release of legacy mercury pollution stored in catchment soils.

The concentrations of THg in both lake water and lake sediment in the upland lakes were low and consistent with other background regions, but THg in catchment soils were relatively high due to the very high organic content of the soils. The low variation in soil THg and THg/OC suggested a consistent source of mercury pollution to the sites (i.e., long-range atmospheric mercury deposition). The results suggested catchment soils drive THg variation in both lake water and sediment in the upland lakes. These findings provide some support to the theory presented in chapter three, that legacy mercury from catchment soils may have been the source of the observed increase in lake water THg.

Research contributions

This thesis presented a representative summary of DOC in acid sensitive lakes across Ireland, due to its large sample size (n=116) and geographical coverage of Ireland. Few studies have focused on lake water organic matter in Ireland, and the literature that exists have small sample sizes (e.g., McCaul et al., 2011), or is limited to rivers and streams (e.g., Liu et al., 2014; Koehler et al., 2009). This thesis also examined organic matter quality in upland lakes; studies that characterize DOC in Ireland or the UK are limited (e.g., Turner et al., 2016; Yates et al., 2016).

Mercury data for Irish surface waters is very limited and to the extent of the author's knowledge the only published studies of mercury concentrations in lakes in the Republic of Ireland are those of the same sites used in this thesis (e.g., Scott & Aherne, 2013). This thesis contributes lake THg data for 68 lakes, representing upland acid-sensitive regions across Ireland; it was also the first large scale THg lake survey since the previous one in 2008. This thesis also examined temporal patterns for THg which is absent in the current literature for Ireland. The temporal data presented in this thesis is additionally useful as it includes a period following a sea salt event, allowing insight into how THg in the lakes may react to future storm events which will likely increase in Ireland due to climate change (Nolan, 2015; Cámaro-García et al., 2021).

Lastly, this thesis builds off the results of Scott & Aherne (2013) which suggested an association between soil and water THg by examining the interlinkages between lake water, lake sediment, and catchment soil. As atmospheric mercury in Ireland decreases (Weigelt et al., 2015; Custodio et al., 2020), the role of catchment soils as the source of mercury to the lakes can be expected to grow, as observed in the UK for mercury and lead pollution (Yang et al., 2018; Yang et al., 2016).

Future research

Future research should continue to measure DOC and THg in these lakes and add to the temporal datasets, particularly for THg, which is currently limited. Future temporal studies should also take seasonal fluctuations into account, which may shed more light onto the source of the THg increase observed. It is also notable that the DOC and THg trends in this study diverged, and therefore DOC alone is not sufficient to estimate THg trends in these lakes and THg should be measured directly. Further research on organic matter quality would also be recommended, including direct measurement or tests (e.g., TFF membrane fractionation, biodegradation tests) or molar ratios (e.g., N/C) to give insight into characteristics not represented by the three indices used in this thesis, such as biodegradation or photodegradation potential. However, even further exploration of $SUVA_{254}$ and building a long-term dataset would be valuable due to the strong relationship between mercury and aromaticity of organic matter (Lavoie et al., 2019).

In addition to the above, the following three research topics are recommended due to the very limited information on mercury in natural environments in Ireland: (1) THg in lowland lakes to provide a more diverse analysis of THg in Irish lakes, (2) further analysis of THg in soils on a larger scale, including at different depths, and (3) isotopic mercury analysis, which may help determine whether the increase in lake water THg can be attributed to legacy mercury inputs from the catchment.

Lastly, while not related to long term trends, the effect of the 2008 sea salt event on both DOC and THg was notable. This sort of event can be expected to become increasingly common in Ireland due to climate change (Nolan, 2015; Cámaro-García et al., 2021), therefore further study on the reaction of the lakes to sea salt events would be valuable. One possible focus may be how long the effects can be observed before the system recovers.

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APPENDICES

Chapter Two Appendices

Appendix 2.1:

Table A2-1: Site characteristics for upland (n=7) and lowland (n=14) lakes sampled approximately annually 2007–2018 for DOC

	Units	**Min – Max**	**Median**	**NMAD (%)**
Upland (n=7)				
Elevation	masl	247 – 711	505	9
Lake Surface Area	ha	0.35 – 2.4	1.4	28
Catchment Area	ha	3.9 – 64	13	66
Lake:Catchment		0.03 – 0.04	0.10	73
Lowland (n=14)				
Elevation	masl	14 – 209	67	64
Lake Surface Area	ha	8.0 – 260	55	66
Catchment Area	ha	89 – 8493	1099	75
Lake:Catchment		0.02 – 0.26	0.07	43

Table A2-2: Sample observations for upland (n=68) and lowland (n=48) lakes in the Republic of Ireland, April–July 2017 & 2018. For lakes with multiple observations within a single month, either due to multiple sampling events or due to sampling at multiple locations around the lakes during a single sampling, the data was first averaged by month, before being averaged by year so a sampling event was not over-represented. Lastly, values for 2017 and 2018 were averaged for lakes that were sampled during both years.

	2017				2018				
Lake ID	April	May	June	July	April	May	June	July	2017 & 2018
L0309						1			1
L0410						1			1
L0411x		1							1
L0508		1				1			2
L0510		1							1
L0606		1							1
L0607		1							1
L0704		1				1			2
L0705						1			1

L0707		1							1
L0708		1			1				2
L0806				1		1			2
L0807		1							1
L0807x		1							1
L0808	1			1				1	3
L0808x		1							1
L0808y					1				1
L0808z					1				1
L0825		1				1			2
L0826x		1							1
L0826y		1							1
L0829		1			1				2
L0906		1				1			2
L0907		1				1			2
L0907x		1							1
L0908		1				1			2
L0927						1			1
L0931	1			1					2
L1005		1							1
L1006		1				1			2
L1007		1				1			2
L1027		1							1
L1030		1				1			2
L1108		1				1			2
L1331		1							1
L1432		1							1
L1532		1				1			2
L1538				1					1
L1637				1					1
L1717		1							1
L1717x		1							1
L1738						1			1
L1816		1							1
L1834		1							1
L1839					1				1
L1841	1			1	1			1	4
L1912		1			1				2
L1912x		1			1				2
L1933				1	1				2
L1938				1					1
L1939		1							1
L1940						1		1	2

L1941		1							1
L2032				1	1				2
L2038				1					1
L2040						1			1
L2042						1			1
L2132		1			1				2
L2142						1			1
L2210		2			1				3
L2210x		1			1				2
L2211	1	2			1			1	5
L2211x	1	2			1			1	5
L2445						1			1
L3019		1			1				2
L3019x		1			1				2
L3020		1						1	2
L3121		1			1			1	3
Lowland	2017				2018				
Lake ID	April	May	June	July	April	May	June	July	2017 & 2018
Acorrymore	1			1	1			1	4
Aille	1			1	1			1	4
Akibbon	1		1		1		1		4
Ardderry	1			1	1			1	4
Ballynakill	1			1	1			1	4
Beaghcauneen	1			1	1			1	4
Bofin GY	1			1	1			1	4
Bray Lower	1			1	1			1	4
Derryclare	1			1	1			1	4
Enask	1			1	1			1	4
Fadda	1			1	1			1	4
Gortglass	1			1	1			1	4
Illauntrasna	1			1	1			1	4
Loughanillaun Maam Cross	1			1	1			1	4
Loughaunwillan	1			1	1			1	4
Maumwee	1			1	1			1	4
Moher	1			1	1			1	4
Muckross		1		1	1		1		4
Nahasleam	1			1	1			1	4
Naminna	1			1	1			1	4
Pollacappul	1			1	1			1	4
Seecon	1			1	1			1	4
Unshin	1		1		1		1		4

Upper Glendalough	1			1	1			1	4
Easky	1	1	1	1		1	1		6
Glencullin	1	1		2	1			1	6
Tay*	1			1	1	1	1	1	6
Barra	1	1		1	1	1	1	1	7
Dunglow	1	1		1	1	1	1	1	7
Ballynahinch	2			2	2			2	8
Cloonaghlin	2	2			2	2			8
Derg DL	2		2		2		2		8
Gartan	2		2		2		2		8
Kylemore	2			2	2			2	8
Mourne DL	1	1	1	1		2	1	1	8
Shindilla	2			2	2			2	8
Brin	2	2	2	2	2		2		12
Cam KY	2	2	2	2		2		2	12
Dan	2			2	2	2	2	2	12
Doo CE		2	2	2		2	2	2	12
Doo MO	2	2		4	2			2	12
Anure	2	2		2	2	2	2	2	14
Fern	2	2		2	2	2	2	2	14
Glen DL	2	2		2	2	2	2	2	14
Veagh	2	2		2	2	2	2	2	14
Acoose	3	3	3	3	3		3		18
Caragh	4	4	4	4		4		3	23
Upper KY	7	7	7	7	7		7	7	49

* Lough Tay overlapped between the upland and lowland datasets but in this study it was used only in the lowland lake dataset and was not included in upland lake analysis. The large surface area (50 ha) and catchment size (1993 ha) made it more physically similar to the lowland lake dataset, despite its high elevation (242 masl). Further, as a WFD lake it was sampled multiple times during 2017/2018, whereas it was only sampled once as part of the upland lake survey during the same period.

Table A2-3: Sample observations of upland (n=7) and lowland (n=14) lakes in the Republic of Ireland, sampled 2007–2018.

Upland	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**
L0808	1	1	2	4	3	2	2	1		3	4	2
L0931	2	1	2	4	3						2	
L1841	2	1	2	4	4	2	2	1		4	4	3
L2211	1	1	3	5	3	2	3	1		3	4	3
L2211x	1		3	5	3	2	2	1		3	4	3
L2445	1		3	3	1					1	1	1
L3020	1	1	3	4	3	2	2	1		1	2	2
Lowland	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**

Barra				6	6	11	6	6	12	6	6	12
Bofin GY				5	6	5	6	6	5	6	6	6
Cam KY					11	12	6	11	10	6	12	6
Dan				7	6	11	6	6	12	6	6	12
Doo CE				8	8	8	8	8	8	7	8	8
Easky				6	8	7	6	12	7	6	12	5
Fadda				6	5	6	6	6	6	6	6	6
Glencullin				6	10	6	6	11	6	6	11	6
Maumwee				12	6	7	12	6	6	12	6	6
Nahasleam				5	6	5	6	6	5	5	6	6
Naminna				6	6	6	7	6	6	5	6	6
Upper Glendalough				6	6	6	6	6	6	6	5	5
Upper KY					10	12	6	10	9	6	12	6
Veagh				7	6	12	6	6	12	6	6	12

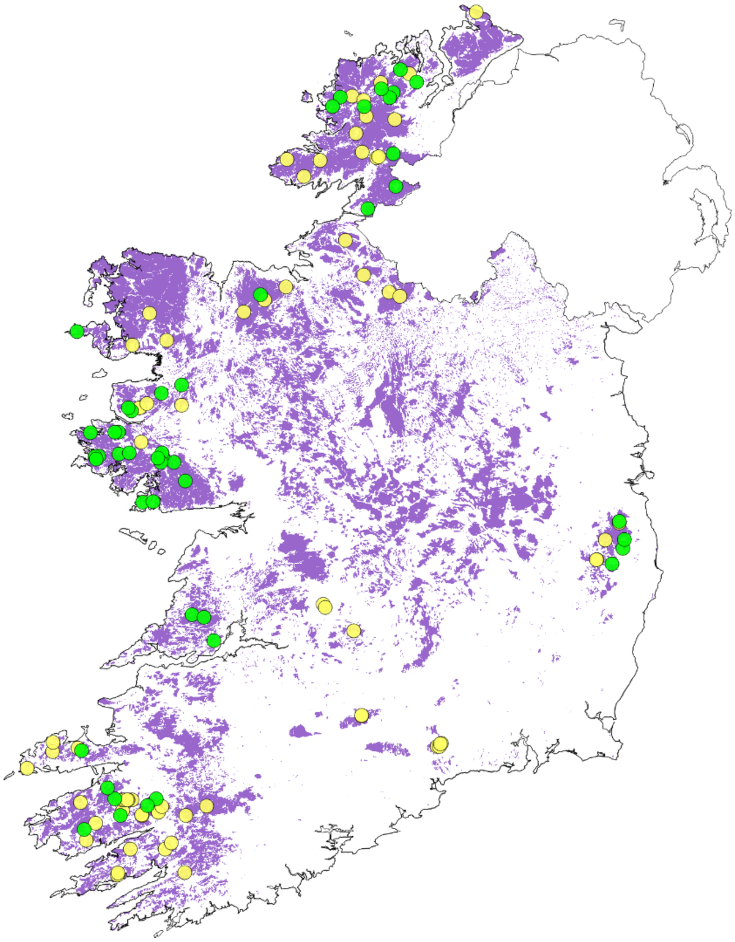

Fig. A2-1: Map of peatland areas (purple) in the Republic of Ireland. Yellow circles indicate upland lakes (n=68), green circles indicate lowland lakes (n=48) sampled April–July 2017 & 2018.

Appendix 2.2

Table A2-4: Quality control information for dissolved organic carbon analysis of upland lake water samples, sampled in Republic of Ireland, 2017–2018.

	Detection Limit* (mg/L)	Lab Blanks (mg/L)	Variance between replicates (%CV)
n	6	20	9
Mean	0.177	0.490	7%
Median	0.171	0.352	5%
NMAD (%)	29	44	

* Detection limit = average of blanks + (3 x standard deviation)

Equation A2-1: Normalized Median Absolute Deviation (NMAD) calculation

$$Median\ [ABS(x_1 - y), ABS(x_2 - y) \ldots ABS(x_{29} - y)]\ \div y\ \times 100\%$$

ABS: absolute value
x: measurement for a given lake in 2017–2018 (e.g. x_1=lake 1; conductivity at upland lake #1)
y: median for all lakes in a dataset (e.g. median conductivity for all upland lakes)

Appendix 2.3

Table A2-5: PCA loadings for upland lakes (n=68) sampled in the Republic of Ireland, April–July 2017 & 2018. elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation, θ=soil moisture, %peat=peatland coverage, alk=gran alkalinity, cond=conductivity, DOC=dissolved organic carbon, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio; element concentrations use standard symbols.

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Eigenvalue	5.96857	3.66549	2.19335	1.90881	1.26134	1.11997
% variance	28.422	17.455	10.445	9.0896	6.0064	5.3332
cond	0.39283	0.017711	0.081252	-0.06889	0.027467	0.10239
alk	0.15327	0.38295	0.32328	0.12522	0.033046	-0.14343
Ca	0.20577	0.30318	0.36054	0.1402	-0.033011	-0.066451
Mg	0.3337	0.19706	0.12496	-0.0091665	0.055068	0.017322
K	0.23384	-0.13477	-0.11363	-0.21892	-0.05123	0.089231
Na	0.36359	-0.094103	-0.085345	-0.20534	0.031193	0.18172
Cl	0.3547	-0.12142	-0.16279	-0.17287	-0.13784	-0.067867
SO4	0.32674	-0.14736	-0.17884	0.041722	-0.33534	0.16901
DOC	0.088523	-0.31821	0.24892	0.19148	0.037249	-0.36968
Na:Cl	-0.070985	0.063443	0.20266	-0.062387	0.48402	0.63552
nmSO4	0.013309	-0.076969	-0.043001	0.39594	-0.3969	0.44111
pH	0.096564	0.46121	0.036623	0.087243	-0.023871	0.03703
temp	0.2996	-0.0015353	-0.099197	-0.064932	0.25948	0.0034025
pr	-0.20315	0.18232	-0.14678	-0.28425	-0.083804	0.14307
%peat	-0.0039008	-0.20188	-0.028524	-0.26291	0.36508	-0.19826
θ	0.0010111	-0.29001	0.1862	0.35237	0.0217	-0.039742
rad	0.067823	0.25229	-0.079342	-0.14219	-0.28277	-0.21481
elev	-0.29599	0.052399	0.12051	-0.25225	-0.31751	0.09282
LA	0.02338	0.11972	-0.41747	0.39829	0.19894	0.0367
CA	-0.0092752	0.17669	-0.49814	0.28647	0.19125	-0.13169
L:C	0.052809	-0.25461	0.21969	0.17417	-0.013908	0.13695

Table A2-6: PCA loadings for lowland lakes (n=48) sampled in the Republic of Ireland, April–July 2017 & 2018. elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation, θ=soil moisture, %peat=peatland coverage, cond=conductivity, DOC=dissolved organic carbon, Na:Cl=sodium to chloride ratio; element concentrations use standard symbols.

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Eigenvalue	6.31547	2.34203	1.94154	1.50339	1.24098	1.0994
% variance	35.086	13.011	10.786	8.3522	6.8943	6.1078
cond	0.38204	0.0020551	0.0405	-0.0034219	-0.018567	0.10881
Ca	0.30768	-0.090514	0.068803	-0.36842	-0.13253	0.15111
Mg	0.37763	0.0029229	-0.0044518	-0.092434	-0.10071	0.0082011
K	0.33601	0.075178	0.062334	-0.22361	-0.063361	0.22517
Na	0.35072	0.12177	-0.04438	0.23857	-0.025756	-0.11072
Cl	0.35391	0.08912	-0.043223	0.21843	0.07071	-0.029359
DOC	0.097743	0.47369	0.34828	0.022121	-0.085802	-0.1461
Na:Cl	-0.1356	0.18537	-0.032705	-0.017233	-0.33712	-0.21419
pH	0.21707	-0.43476	0.10981	-0.22944	0.0041983	-0.063609
temp	0.18253	-0.19937	-0.29424	0.49334	-0.012067	-0.027056
pr	-0.25611	-0.31008	-0.23318	-0.088091	-0.061669	-0.22309
%peat	-0.1105	0.048005	-0.046906	0.1224	0.28925	0.61383
θ	-0.0085414	0.11462	0.46404	0.36903	0.25758	-0.27254
rad	0.03583	0.18578	-0.43714	0.29699	-0.23489	0.22585
elev	-0.19347	0.44247	-0.038129	-0.23826	0.12376	0.2744
LA	-0.091275	-0.2814	0.39643	0.12318	0.076268	0.17908
CA	-0.10269	-0.22518	0.3579	0.29097	-0.37394	0.41233
L:C	0.10847	-0.063961	-0.12321	-0.023162	0.6864	-0.014466

Table A2-7: Redundancy Analysis (RDA) loadings for analysis of DOC and conductivity in upland (n=68) and lowland (n=48) lakes in the Republic of Ireland, sampled April–July 2017 & 2018. elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation, θ=soil moisture, %peat=peatland coverage, alk=gran alkalinity, cond=conductivity, DOC=dissolved organic carbon, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio; element concentrations use standard symbols.

Upland				
Axis	Eigenvalue	%	Cumulative %	XY corr. (R)
Canonical				
1	349.35	96.18	96.18	0.9906
2	4.8622	1.339	97.51	0.8216
Residual				
3	6.6963	1.843	99.36	
4	2.3334	0.6424	100	
	Axis 1	Axis 2	Axis 3	Axis 4
Response				
DOC	0.0240282	-0.999711	-0.0192338	0.999815

cond	0.999711	0.0240282	0.999815	0.0192338
Explanatory				
alk	0.420484	0.200245		
Ca	0.545622	0.0641237		
Mg	0.844576	0.151951		
K	0.537263	-0.0793281		
Na	0.911755	0.0418953		
Cl	0.836517	-0.0430067		
SO4	0.735967	-0.0722338		
Na:Cl	-0.0263025	0.264668		
nmSO4	-0.0330552	-0.108453		
pH	0.238386	0.581347		
temp	0.649054	0.027927		
pr	-0.43441	0.499079		
θ	-0.0105974	-0.607412		
rad	0.127312	0.420986		
elev	-0.604964	0.245917		
LA	-0.0333277	0.258233		
CA	-0.119196	0.339931		
L:C	0.156517	-0.397041		
%peat	-0.0101835	-0.243861		
Lowland				
Axis	Eigenvalue	%	Cumulative %	XY corr. (R)
Canonical				
1	1376	94.53	94.53	0.9744
2	4.4392	0.305	94.84	0.8396
Residual				
3	73.364	5.04	99.88	
4	1.8019	0.1238	100	
	Axis 1	Axis 2	Axis 3	Axis 4
Response				
cond	0.999862	-0.0166156	0.999933	0.0115579
DOC	0.0166156	0.999862	-0.0115579	0.999933
Explanatory				
Ca	0.778394	-0.0580585		
Mg	0.942425	-0.00550322		
K	0.826107	0.116828		
Na	0.880598	0.135366		
Cl	0.898217	0.0325354		
Na:Cl	-0.358363	0.352882		
pH	0.522649	-0.459988		
temp	0.38416	-0.367497		
pr	-0.64374	-0.564552		
θ	-0.0195112	0.4795		
rad	0.0451774	-0.0833134		

elev	-0.442084	0.426651		
LA	-0.209277	-0.0542928		
CA	-0.159794	-0.0570329		
L:C	0.209499	-0.166104		
%peat	-0.174979	-0.144099		

Table A2-8: Redundancy Analysis (RDA) loadings for analysis of SUVA$_{254}$, 285:254, and E2:E3 in upland (n=68) lakes in the Republic of Ireland, sampled April–July 2017 & 2018. elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation, θ=soil moisture, alk=gran alkalinity, cond=conductivity, DOC=dissolved organic carbon, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio, SUVA=specific ultraviolet absorbance, E2:E3=absorbance ratio of 254 and 365 nm, 285:254=absorbance ratio; element concentrations use standard symbols.

Axis	Eigenvalue	%	Cumulative %	XY corr. (R)		
Canonical						
1	0.52604	35.18	35.18	0.7281		
2	0.21144	14.14	49.33	0.6496		
3	0.00051895	0.03471	49.36	0.5421		
Residual						
4	0.49529	33.13	82.49			
5	0.26056	17.43	99.92			
6	0.0012381	0.08281	100			
	Axis 1	Axis 2	Axis 3	Axis 4	Axis 5	Axis 6
Response						
SUVA	0.990207	-0.137186	0.0258758	-0.878727	0.476417	0.0294227
E2:E3	0.137547	0.990413	-0.0127334	-0.476868	-0.878913	-0.0104566
285:254	0.0238809	-0.0161678	-0.999584	-0.0208783	0.0232192	-0.999512
Explanatory						
alk	0.00897768	0.0583352	-0.0453294			
Ca	0.0995186	0.0666801	0.0120369			
Mg	0.104887	0.204221	-0.0344875			
K	0.15591	-0.185369	**0.205227**			
Na	0.163907	0.129261	0.103652			
Cl	0.235816	0.291025	-0.0546687			
SO4	0.106035	0.247977	-0.06632			
Na:Cl	-0.268287	**-0.50182**	0.128397			
nmSO4	-0.195257	-0.0649096	-0.0510671			
pH	-0.394585	0.191603	-0.096096			
temp	0.203856	0.163529	**0.199919**			
pr	**-0.53715**	-0.170333	0.157851			
θ	**0.501184**	-0.267549	**-0.172892**			
rad	-0.394722	0.237911	0.129134			
elev	-0.409583	-0.308679	-0.050477			
LA	-0.325749	**0.442402**	0.0768708			

CA	-0.393685	**0.420558**	-0.00031971			
L:C	**0.431635**	-0.225821	0.0879351			
%peat	0.185481	-0.0572918	0.0903829			
cond	0.203269	0.11297	0.0236291			

Appendix 2.4

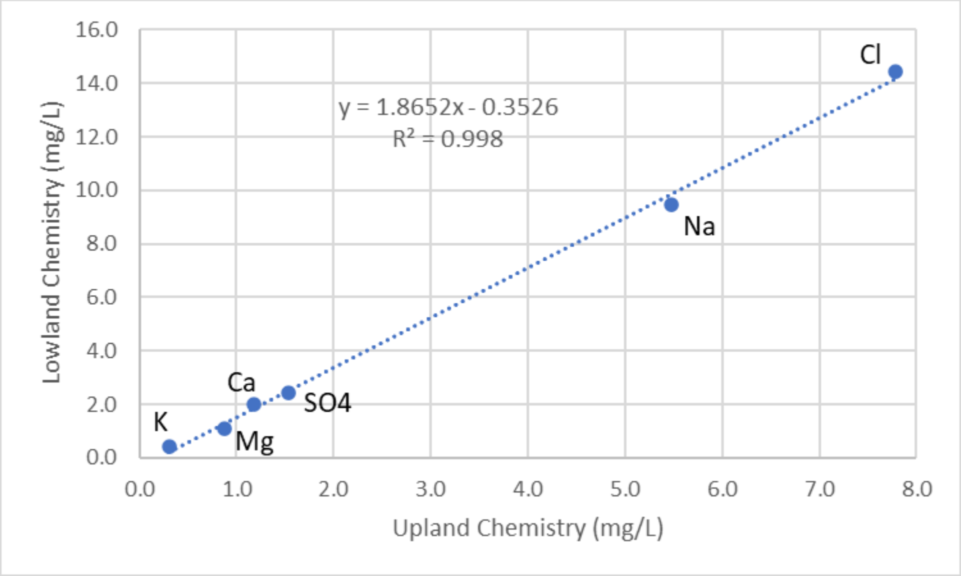

Fig. A2-2: Median ion concentrations (potassium, magnesium, calcium, sulphate, sodium, and chloride) in upland and lowland lake water in the Republic of Ireland, sampled April–July 2017 & 2018.

Table A2-9: Significant ($p<0.05$) Spearman Rank Correlations with dissolved organic carbon (DOC) in upland ($n=68$) and lowland ($n=48$) lakes sampled April–July 2017 & 2018 in the Republic of Ireland.

Upland (n=68)			Lowland (n=48)		
Variable	+/-	r_s	Variable	+/-	r_s
Precipitation	-	-0.44	Precipitation	-	-0.68
Soil Moisture	+	0.59	Soil Moisture	+	0.35
Gran Alkalinity	-	-0.31	Conductivity	+	0.39
pH	-	-0.39	Potassium	+	0.48
Elevation	-	-0.34	Sodium	+	0.42
Catchment Area	-	-0.38	Chloride	+	0.39
Lake:Catchment	+	0.34			
Solar Radiation	-	-0.34			

Table A2-10: Significant ($p<0.05$) Spearman Rank Correlations with northing and easting in upland ($n=68$) and lowland ($n=48$) lakes sampled April–July 2017 & 2018 in the Republic of Ireland. elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation, θ=soil moisture, alk=gran alkalinity, cond=conductivity, DOC=dissolved organic carbon, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio, Abs=absorbance (nm), SUVA=specific ultraviolet absorbance (nm), 285:254=absorbance ratio; element concentrations use standard symbols.

Northing		Easting	
Upland	Lowland	Upland	Lowland

Variable	r_s	Variable	r_s	Variable	r_s	Variable	r_s
alk	-0.33	cond	+0.39	alk	-0.30	DOC	+0.58
DOC	+0.45	K	+0.40	Ca	-0.26	temp	-0.72
pH	-0.38	Cl	+0.33	Na	-0.35	rad	-0.45
pr	-0.43	Na:Cl	-0.39	Cl	-0.29	elev	+0.41
θ	+0.38	pH	+0.31	DOC	+0.50	CA	+0.36
rad	-0.83	rad	-0.85	nmSO4	+0.24	Northing	+0.35
elev	-0.28	Easting	+0.35	pH	-0.35		
L:C	+0.34			temp	-0.31		
SUVA 254	+0.41			pr	-0.58		
285:254	+0.28			θ	+0.48		
Easting	+0.59			rad	-0.36		
				L:C	+0.26		
				SUVA 254	+0.42		
				285:254	+0.42		
				Northing	+0.59		

Table A2-11: Significant ($p<0.05$) Spearman Rank Correlations with organic matter quality parameters in upland (n=68) lakes sampled April–July 2017 & 2018 in the Republic of Ireland. elev=elevation, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, pr=precipitation, θ=soil moisture, SUVA=specific ultraviolet absorbance, E2:E3=absorbance ratio of 254 and 365 nm, 285:254=absorbance ratio.

SUVA 254			E2:E3			285:254		
Index	+/-	r_s	Index	+/-	r_s	Index	+/-	r_s
pH	-	-0.28				Pr	-	-0.28
Pr	-	-0.37				θ	+	0.40
θ	+	0.47						
rad	-	-0.32						
elev	-	-0.25						
CA	-	-0.27						
L:C	+	0.27						

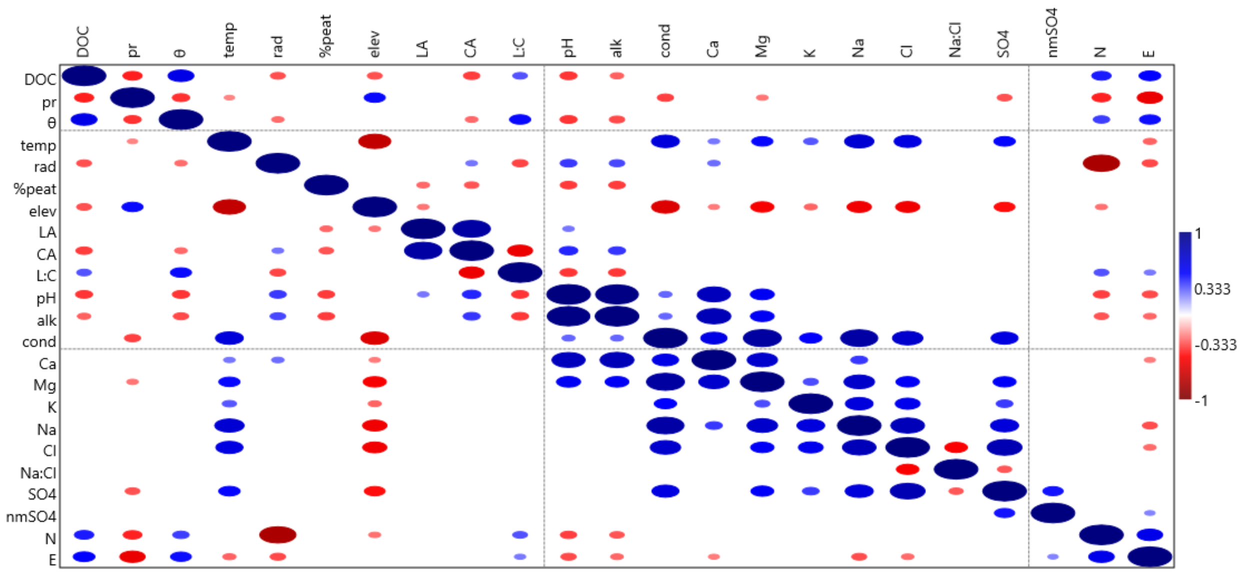

Fig. A2-3: Significant (p<0.05) Spearman Rank Correlations summary in upland (n=68) lakes sampled April–July 2017 & 2018 in the Republic of Ireland. DOC=dissolved organic carbon, pr=precipitation, θ=soil moisture, rad=solar radiation, temp=temperature (°C), %peat=peatland coverage, elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, alk=gran alkalinity, cond=conductivity, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio, N=northing, E=easting; element concentrations use standard symbols.

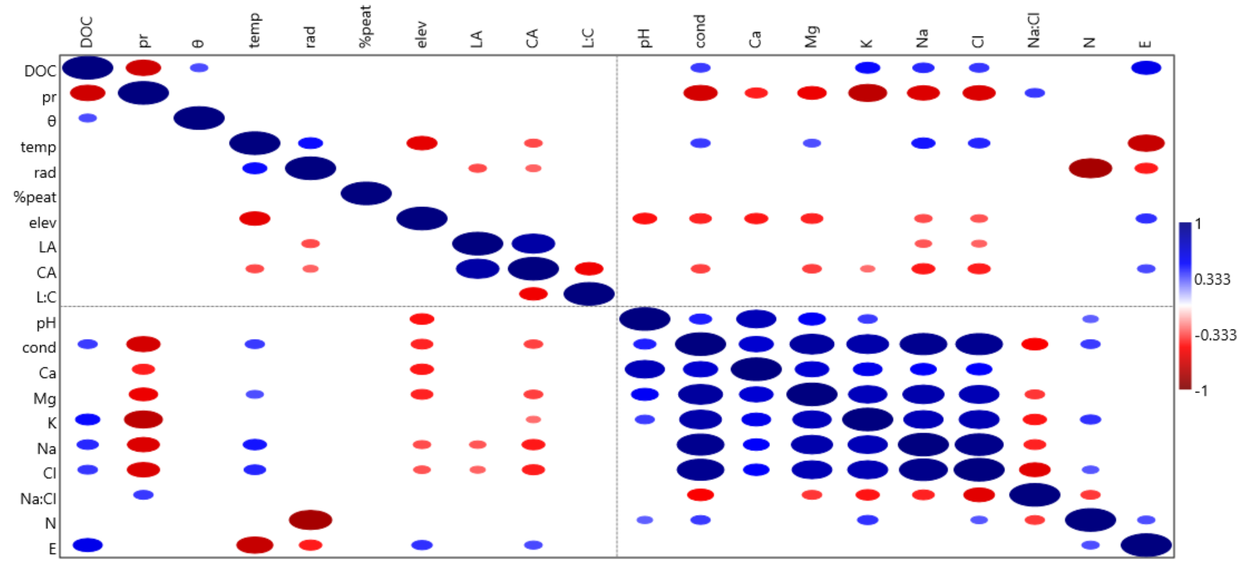

Fig. A2-4: Significant (p<0.05) Spearman Rank Correlations summary in lowland (n=48) lakes sampled April–July 2017 & 2018 in the Republic of Ireland. DOC=dissolved organic carbon, pr=precipitation, θ=soil moisture, rad=solar radiation, temp=temperature (°C), %peat=peatland coverage, elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, cond=conductivity, Na:Cl=sodium to chloride ratio, N=northing, E=easting; element concentrations use standard symbols.

Appendix 2.5

Table A2-12: Upland (n=1) and lowland (n=7) lakes with significant changes ($p<0.05$) in dissolved organic carbon (DOC) concentrations in the Republic of Ireland, between October 2007 and December 2018. DOC changes in lowland lakes that were supported by trends in true colour (TC) during the same time period are indicated as 'Y' in last column.

Upland/Lowland	Lake ID	# years	# observations	Change in DOC	Supported by TC
Upland	L0808	10	25	Decrease	N/A
Lowland	Cam	8	74	Increase	
Lowland	Dan	9	72	Decrease	Y
Lowland	Doo	9	71	Increase	
Lowland	Glencullin	9	68	Decrease	
Lowland	Maumwee	9	73	Decrease	Y
Lowland	Naminna	9	54	Increase	
Lowland	Veagh	9	68	Decrease	Y

Table A2-13: Significant changes ($p<0.05$) in conductivity and dissolved organic carbon (DOC) in upland and lowland lakes in the Republic of Ireland, between October 2007 and December 2018.

Upland Lake ID	# obs	Conductivity	DOC
L0808	25		Decrease
L0931	14	Decrease	
L1841	29		
L2211	29		
L2211x	27		
L2445	11		
L3020	22		
Lowland			
Barra	71		
Bofin	51		
Cam	74	Increase	Increase
Dan	72	Increase	Decrease
Doo	71	Increase	Increase
Easky	69		
Fadda	53		
Glencullin	68		Decrease
Maumwee	73		Decrease
Nahasleam	50		
Naminna	54		Increase
Upper Glendalough	52	Increase	
Upper KY	71		
Veagh	68		Decrease

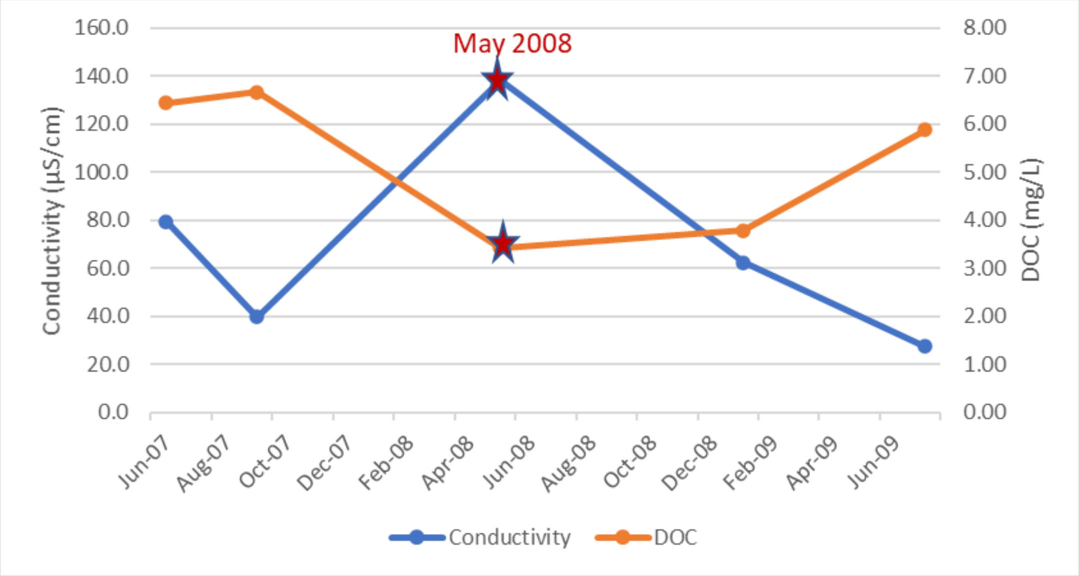

Fig. A2-5: Graph of conductivity and DOC in upland lake “L1841” to display the effect of the March 2008 coastal storms on lake chemistry during the lake sampling in May 2008 and the subsequent recovery.

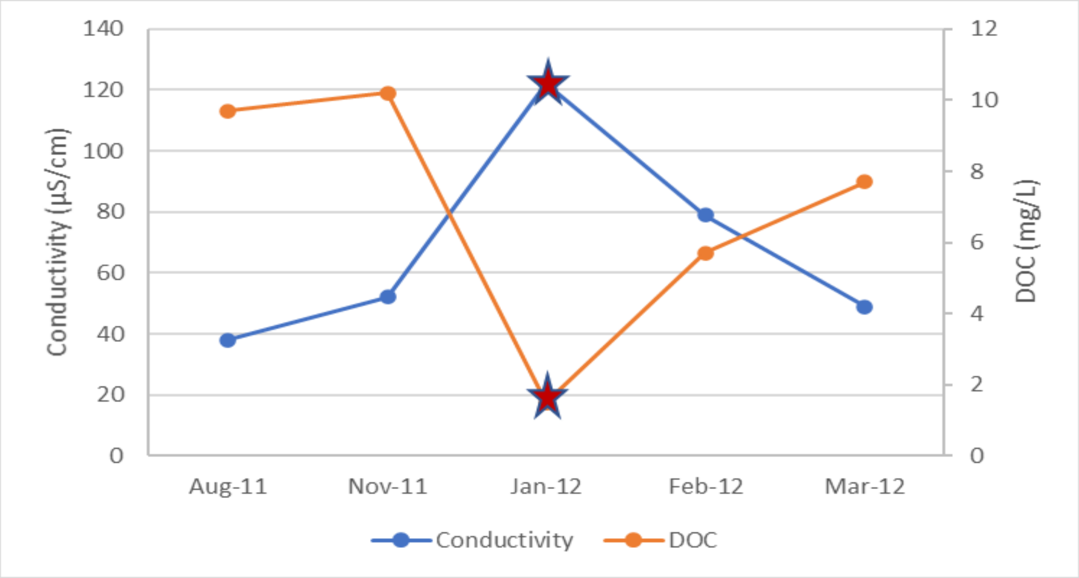

Fig. A2-6: Graph of conductivity and DOC in lowland lake “Barra” to display the effect of the January 2012 hurricane force wind gusts in the north-west (area around Malin Head) on lake chemistry and the subsequent recovery.

Chapter Three Appendices

Appendix 3.1:

Table A3-1: Site characteristics of upland lakes sampled for THg in 2008 and re-sampled in 2017–2018 (n=24), in the Republic of Ireland

	Units	Min – Max	Median	NMAD (%)
Elevation	masl	224 – 682	437	18
Lake Surface Area	ha	0.4 – 23.8	2.0	65
Catchment Area	ha	1.6 – 161.6	22.3	62
Lake:Catchment		0.03 – 0.31	0.13	51
Solar Radiation	kJ/m^2/d	8444 – 9771	8750	3
Air Temperature	°C	5.5 – 10.6	7.2	9
Precipitation	m/yr	1.5 – 2.8	2.1	13
Soil Moisture	m^3/m^3	0.4 – 0.9	0.6	29

Table A3-2: Site characteristics for upland lakes sampled 2008–2018 for THg (n=7), in the Republic of Ireland

	Units	Min – Max	Median	NMAD (%)
Elevation	masl	247 – 711	505	9
Lake Surface Area	ha	0.35 – 2.4	1.4	28
Catchment Area	ha	3.9 – 64	13	66
Lake:Catchment		0.03 – 0.04	0.10	73
Solar Radiation	kJ/m^2/d	8522 – 9385	9054	3
Air Temperature	°C	5.5 – 8.6	7.0	12
Precipitation	m/yr	1.3 – 3.4	2.1	15
Soil Moisture	m^3/m^3	0.4 – 0.8	0.5	7

Table A3-3: Quality control information for total mercury (THg) and dissolved organic carbon (DOC) analysis of upland lake water samples, sampled in Republic of Ireland, 2017–2018.

	Detection Limit*	Lab Blanks	Field Blanks	Variance between replicates (%CV)
Total Mercury (ng/L)				
n	8	47	9	99

Mean	1.9	0.7	1.8	17%
Median	1.1	0.4	1.3	10%
NMAD (%)	48	51	18	
Dissolved Organic Carbon (mg/L)				
n	6	20		9
Mean	0.177	0.490		7%
Median	0.171	0.352		5%
NMAD (%)	29	44		

* Detection limit = average of blanks + (3 x standard deviation)

Equation A3-1: Normalized Median Absolute Deviation (NMAD) calculation:

$$Median\ [ABS(x_1 - y), ABS(x_2 - y) \ldots ABS(x_{29} - y)]\ \div y\ \times 100\%$$

ABS: absolute value
x: value for a given lake in 2017–2018 (e.g., x_1=lake 1; conductivity at upland lake #1)
y: median value for all lakes in a dataset (e.g., median conductivity for all upland lakes)

Figure A3-1: Photograph of two of the 68 upland lakes sampled during April–July 2017 and 2018 in the Republic of Ireland. While the dominant soil type was peat or peaty podzols across all study sites, the size of the soil pool varied. The lake catchments varied between peat bog (upper) and rocky terrain (lower), with the southern sites tending to have more exposed rock and a greater soil bulk density.

Appendix 3.2:

Table A3-4: Significant spearman rank correlations ($p<0.05$) between easting & northing, and physical, climate, and water chemistry characteristics in upland lakes in the Republic of Ireland (n=68) sampled April–July 2017 & 2018. THg=total mercury, DOC=dissolved organic carbon, SUVA=specific ultraviolet absorbance, 285:254=absorbance ratio 285 nm/254 nm, L:C lake to catchment ratio.

Easting	r_s	Northing	r_s
THg	0.40	THg	0.41
DOC	0.50	DOC	0.45
SUVA$_{254}$	0.42	SUVA	0.40
285:254	0.42	285:254	0.29
pH	-0.35	pH	-0.38
Alkalinity	-0.29	Alkalinity	-0.34
Precipitation	-0.58	Precipitation	-0.44
Regional soil moisture	0.48	Regional soil moisture	0.38
Solar radiation	-0.36	Solar radiation	-0.83
L:C	0.26	L:C	0.34
Calcium	-0.25	Elevation	-0.29
Sodium	-0.35		
Chloride	-0.29		
Non-marine sulphate	0.24		
Air temperature	-0.31		

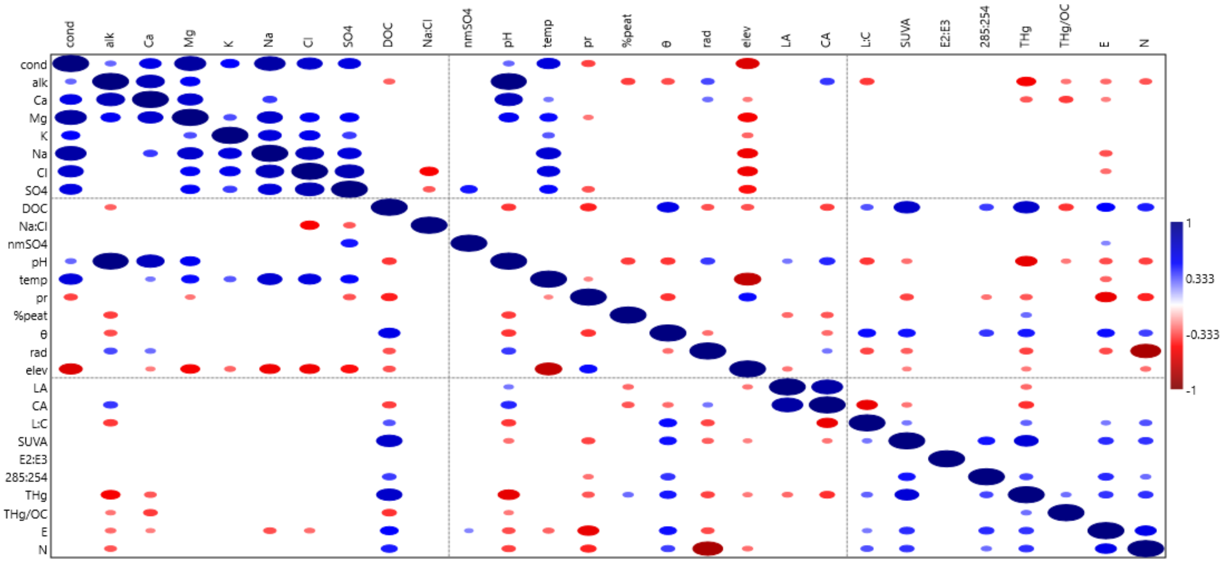

Figure A3-2: Significant spearman rank correlations between lake chemistry, physical and climate characteristics, and easting and northing in upland lakes in the Republic of Ireland (n=68) sampled April–July 2017 & 2018. alk=gran alkalinity, cond=conductivity, DOC=dissolved organic carbon, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio, temp=temperature (°C), rad=solar radiation, pr=precipitation, θ=soil moisture, %peat=peatland coverage, elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, SUVA=specific ultraviolet absorbance, E2:E3=absorbance ratio 254 nm/365 nm, 285:254=absorbance ratio 285 nm/254 nm, THg=total mercury, THg/OC=total mercury normalized by organic carbon, E=easting, N=northing; element concentrations use standard symbols.

Table A3-5: Redundancy Analysis (RDA) loadings for analysis of total mercury (THg) and total mercury normalized by organic carbon (THg/OC) in upland lake water (n=68) in the Republic of Ireland, sampled April–July 2017 & 2018. elev=elevation, LA=lake area, CA=catchment area, L:C=lake to catchment ratio, rad=solar radiation, temp=temperature (°C), pr=precipitation, θ=soil moisture, %peat=peatland coverage, alk=gran alkalinity, cond=conductivity, DOC=dissolved organic carbon, nmSO4=non-marine sulphate, Na:Cl=sodium to chloride ratio, SUVA=specific ultraviolet absorbance, E2:E3=absorbance ratio 254 nm/365 nm, 285:254=absorbance ratio 285 nm/254 nm; element concentrations use standard symbols.

	Axis 1	Axis 2
XY corr. (R)	0.8327	0.7308
%	66.98	1.815
Eigenvalue	11.807	0.32001
Response		
THg	0.999796	-0.0202014
THg/OC	0.0202014	0.999796
Explanatory		
cond	0.0784558	-0.336717
alk	-0.431714	-0.354072
Ca	-0.295165	-0.436509
Mg	-0.143548	-0.317949
K	0.258346	-0.0174366
Na	0.198059	-0.147825
Cl	0.287858	-0.144056
SO4	0.2875	-0.130628
DOC	0.760106	-0.569971
Na:Cl	-0.244461	0.137813
nmSO4	0.0603464	-0.0235781
pH	-0.649272	-0.156225
temp	0.201718	0.00626656
pr	-0.302431	0.470442
%peat	0.188538	0.0953604
θ	0.381278	-0.261922
rad	-0.409592	0.0287599
elev	-0.302551	0.327804
LA	-0.345469	-0.181499
CA	-0.321795	0.0868434
L:C	0.419237	-0.146511
SUVA	0.742563	-0.124379
E2:E3	0.0702337	-0.129298

285:254	0.397912	-0.0232083

Table A3-6: Wilcoxon signed rank test for changes in lake chemistry for upland Irish lakes (n=24) sampled in May 2008 and re-sampled in April to July 2017–2018.

Variable	**Significant change?**	**Direction of Change**
THg	Yes	Increase
THg/OC	Yes	Increase
Conductivity	Yes	Decrease
pH	Yes	Increase
Gran alkalinity	Yes	Increase
DOC	Yes	Increase
Calcium	No	Slight decrease
Magnesium	Yes	Decrease
Potassium	Yes	Decrease
Sodium	Yes	Decrease
Chloride	Yes	Decrease
Sulphate	Yes	Decrease
Na:Cl	Yes	Increase
Non-marine sulphate	No	Slight Increase

Table A3-7: Significant changes ($p<0.05$; Mann-Kendall trend tests) in total mercury (THg), dissolved organic carbon (DOC), conductivity, and pH in upland lakes in Ireland (n=7) from October 2007 (May 2008 for THg) to December 2018

Lake ID	# obs	THg	# obs	DOC	Conductivity	pH
L0808	11		25	Decrease		
L0931	7		14		Decrease	
L1841	12		29			Increase
L2211	13		29			
L2211x	12	Increase	27			Increase
L2445	4		11			Increase
L3020	11		22			

Table A3-8: Median concentrations of total mercury (THg), total mercury normalized by organic carbon (THg/OC), and dissolved organic carbon (DOC) for the 2008–2011 sampling events and 2017–2018 sampling events for seven upland lakes in the Republic of Ireland. Significant differences between the periods (Wilcoxon signed rank test; $p<0.05$) indicated by an asterisk.

	THg*		THg/OC*		DOC	
Lake ID	2008–2011	2017–2018	2008–2011	2017–2018	2008–2011	2017–2018
L0808	1.6	4.4	1.5	7.2	1.1	0.7
L0931	3.2	8.2	0.8	2.0	3.9	4.2
L1841	3.9	6.2	0.7	2.4	3.8	2.7
L2211	2.3	7.1	0.9	2.2	3.3	3.0
L2211x	1.8	4.5	0.9	2.0	2.5	2.0

L2445	3.3	13.8	0.3	1.4	12.7	9.7
L3020	2.6	4.9	0.4	0.4	4.7	5.0

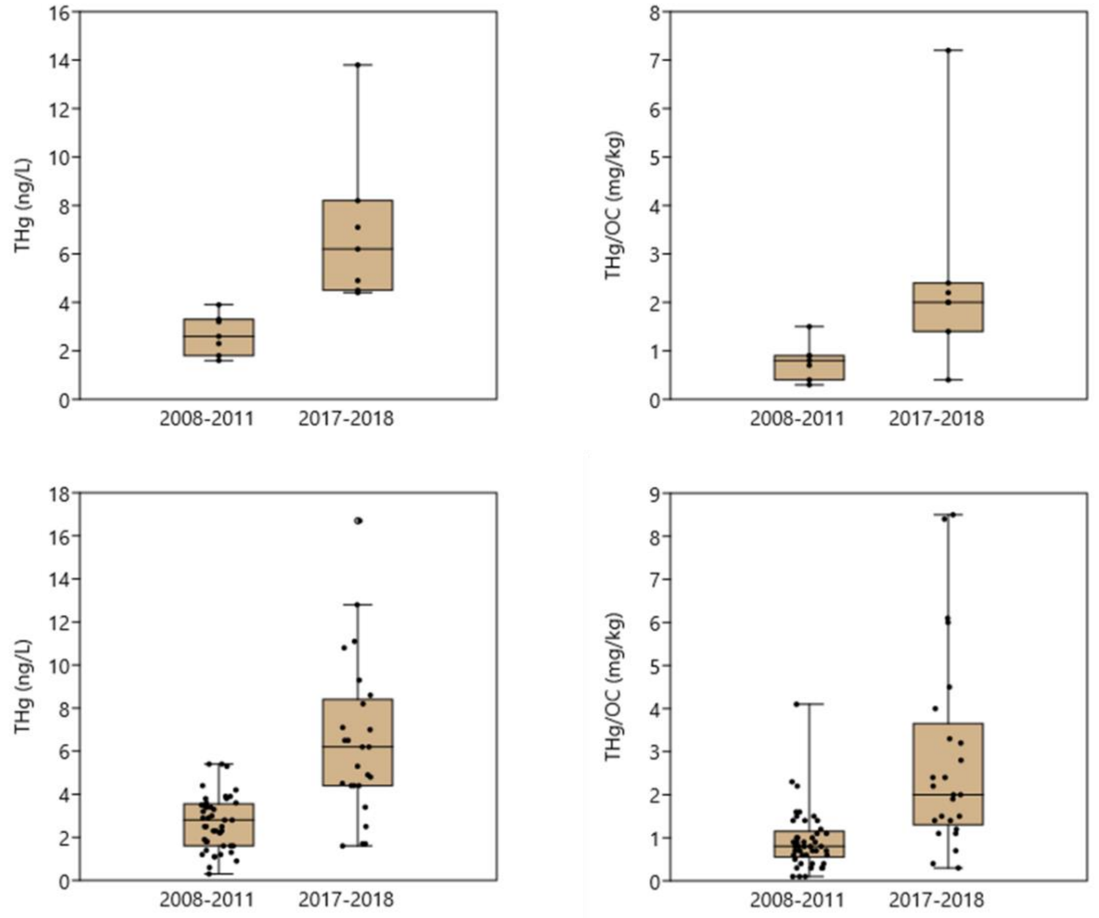

Figure A3-3: Median total mercury (THg) concentrations (left) and THg normalized by organic carbon (THg/OC) concentrations (right) in seven upland lakes in the Republic of Ireland, for the periods of 2008–2011 and 2017–2018. Forty-five observations 2008–2011 and 25 observations 2017–2018.

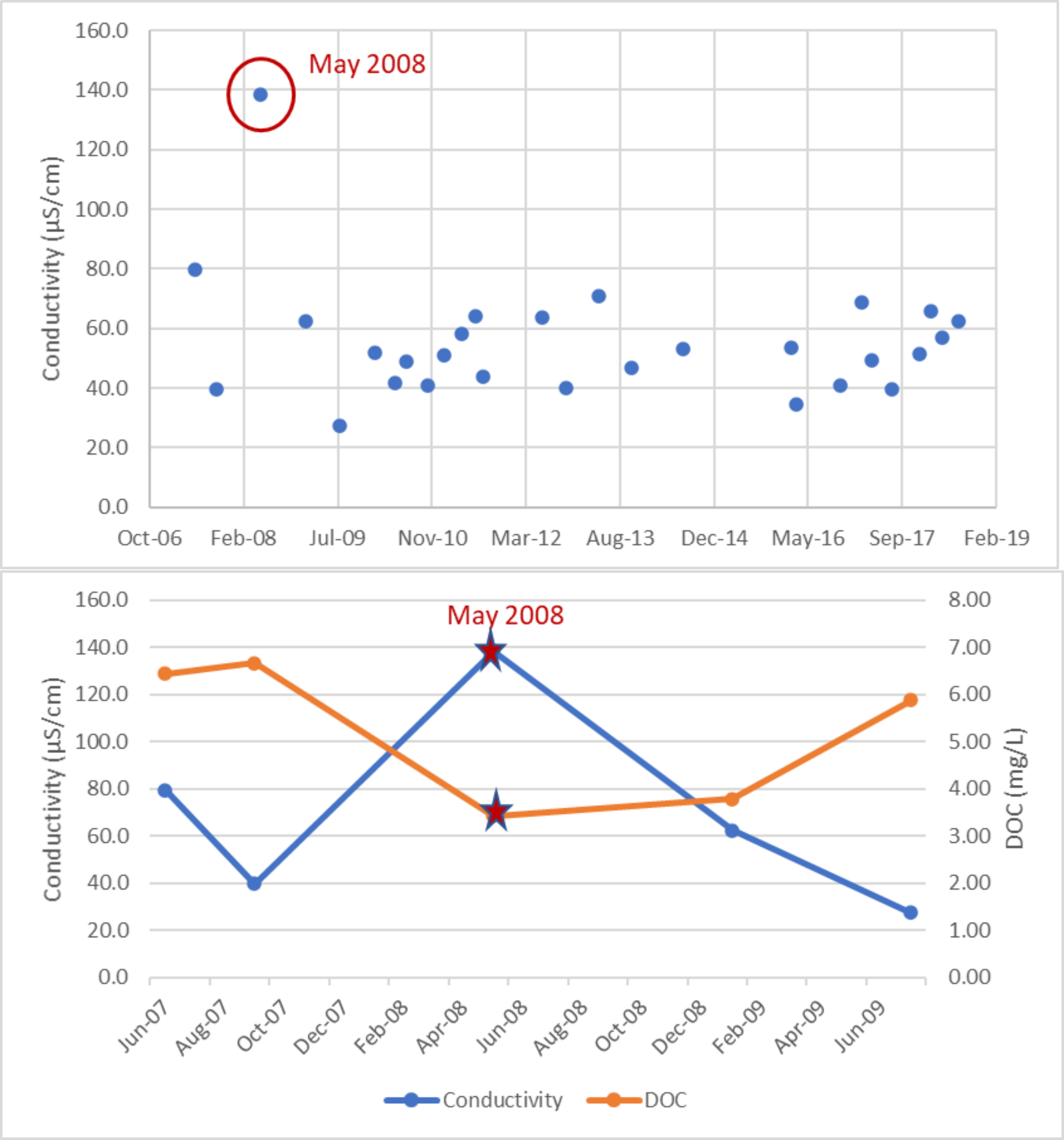

Figure A3-4: Evidence of DOC suppression from sea salt could be seen in the plotted trend data, as the spike in conductivity can be seen to correspond to decreased DOC in the May 2008 sampling. Example graphs below show lake L1841.

Table A3-9: Total mercury normalized by organic carbon (THg/OC) using original dissolved organic carbon (DOC) concentrations compared to THg/OC using DOC concentrations with a 20% increase to represent particulate organic matter. Sixty-eight upland lakes sampled May to July, 2017–2018 in the Republic of Ireland.

	THg/OC	THg/OC with 20% increase in DOC
Median (mg/kg)	1.4	1.1
Mean (mg/kg)	1.5	1.3
NMAD*	26%	28%
Lakes with THg/OC > 1 mg/kg	78%	69%

* Normalized median absolute deviation

Chapter Four Appendices

Appendix 4.1:

Total Hg (THg) in catchment soil was quantified as soil THg pool, using soil THg concentrations and the bulk density measurements:

$$\frac{ng\ THg}{g\ soil} \times \frac{g\ soil}{cm^3} \times \frac{10\ cm\ depth}{1} \times \frac{1\ \mu g}{1000\ ng} \times \frac{10\ 000\ cm^2}{1\ m^2} = \frac{\mu g\ THg}{m^2}$$

Example calculation:

$$\frac{307\ ng\ THg}{g\ soil} \times \frac{0.132\ g\ soil}{cm^3} \times \frac{10\ cm\ depth}{1} \times \frac{1\ \mu g}{1000\ ng} \times \frac{10\ 000\ cm^2}{1\ m^2} = \frac{4052\ \mu g\ THg}{m^2}$$

Total Hg normalized by organic carbon (THg/OC) in water was calculated using lake water THg and DOC concentrations:

$$\frac{mg\ THg}{L\ water} \div \frac{mg\ DOC}{L\ water} = \frac{mg\ THg}{mg\ DOC}$$

Example calculation:

$$\frac{4.56\ ng\ THg}{L\ water} \times \frac{1\ mg}{1\ 000\ 000\ ng} = \frac{4.56\ \times 10^{-6}\ mg\ THg}{L\ water}$$

$$\frac{4.56 \times 10^{-6}\ mg\ THg}{L\ water} \div \frac{3.81\ mg\ DOC}{L\ water} = \frac{1.2 \times 10^{-6}\ mg\ THg}{mg\ DOC}$$

$$\frac{1.2 \times 10^{-6}\ mg\ THg}{mg\ DOC} \times \frac{1\ 000\ 000\ mg}{1\ kg} = \frac{1.2\ mg\ THg}{kg\ DOC}$$

Total Hg normalized by organic carbon (THg/OC) in sediment and soil was calculated using THg concentrations and percent organic matter data. The widely used 'van Bemmelen factor' (1.72) was first used to convert percent organic matter to organic carbon (Wolff, 1864; van Bemmelen, 1890), then THg was divided by organic carbon and presented as mg of THg per kg of organic carbon:

$$(\%OM \div 1.72) \times 10 = \frac{mg\ OC}{g\ soil}$$

$$\frac{ng\ THg}{g\ soil} \div \frac{mg\ C}{g\ soil} = \frac{ng\ THg}{mg\ OC} = \frac{mg\ THg}{kg\ OC}$$

Example Calculation:

$$(79.6\%\ OM \div 1.72) \times 10 = \frac{463\ mg\ OC}{g\ soil}$$

$$\frac{194\ ng\ THg}{g\ soil} \div \frac{463\ mg\ C}{g\ soil} = \frac{0.419\ ng\ THg}{mg\ OC}$$

$$\frac{0.419\ ng\ THg}{mg\ OC} \times \frac{1\ 000\ 000\ mg}{1\ kg} \times \frac{1\ mg}{1\ 000\ 000\ ng} = \frac{0.419\ mg\ THg}{kg\ OC}$$

The Normalized Median Absolute Deviation (NMAD) was calculated as:

$$Median\ [ABS(x_1 - y), ABS(x_2 - y) \ldots ABS(x_{31} - y)]\ \div y\ \times 100\%$$

where ABS is absolute value, x is the individual value of the variable of interest, and y is the median of the variable of interest. Note: Variability in pH was calculated using the concentration of H^+ ion because NMAD underestimated the variability of pH when using pH units, due to the logged scale and finite range of values.

References:

Van Bemmelen, J.M. (1890). Über die Bestimmung des Wassers, des Humus, des Schwefels, der in den colloïdalen Silikaten gebundenen Kieselsäure, des Mangans usw im Ackerboden. Die Landwirthschaftlichen Versuchs-Stationen, 37(279).

Wolff, E. (1864). Entwurf zur bodenanalyse. Zeitschrift für analytische Chemie, 3(1), 85–115.

Appendix 4.2:

Table A4-1: Physical and climate characteristics of upland lake catchments (n=31) sampled during April–July 2017 and 2018 in the Republic of Ireland. Note: NMAD=Normalized Median Absolute Deviation.

	Units	**Min–Max**	**Median**	**NMAD (%)**
Site Characteristics				
Elevation	masl	247–712	476	25
Lake Surface Area	ha	0.12–13	1.6	51
Catchment Area	ha	0.56–65	11	87
Lake:Catchment		0.03–0.5	0.17	52
Solar Radiation	kJ/m^2/d	8444–9507	9021	3
Air Temperature	°C	5.5–9.1	7.4	11
Precipitation	m/yr	1.3–3.4	2.1	15
Soil Moisture	m^3/m^3	0.4–0.9	0.5	19
Peatland Coverage	%	0–100	100	0[1]

[1] Due to limited data variation, and half the upland lakes having a peatland coverage of 100%, NMAD (%) was 0.

Fig. A4-1 Photograph of two of the 31 upland lakes sampled during April–July 2017 and 2018 in the Republic of Ireland. The lake catchments varied between peat bog (upper) and rocky terrain (lower), with the southern sites tending to have more exposed rock.

Table A4-2: Quality control information for total mercury and dissolved organic carbon analysis in upland lake water, sampled in the Republic of Ireland, 2017 & 2018.

	Detection Limit*	Lab Blanks	Field Blanks	Variance between replicates (%CV)
Total Mercury (ng/L)				
n	8	47	9	99
Mean	1.9	0.7	1.8	17%
Median	1.1	0.4	1.3	10%
NMAD (%)	48	51	18	
Dissolved Organic Carbon (mg/L)				
n	6	20		9
Mean	0.177	0.490		7%
Median	0.171	0.352		5%
NMAD (%)	29	44		

* Detection limit = average of blanks + (3 x standard deviation)

Table A4-3: Quality control information for total mercury analysis in upland lake sediment and catchment soil, sampled in the Republic of Ireland, 2017 & 2018.

	THg (ng)
Detection Limit*	0.00001
Lab Blanks	n=6
	Mean: 0.00154
	Median: 0.00001
Variance between replicates (%CV)	n=8
	Mean: 28%
	Median: 22%

* Machine detection limit

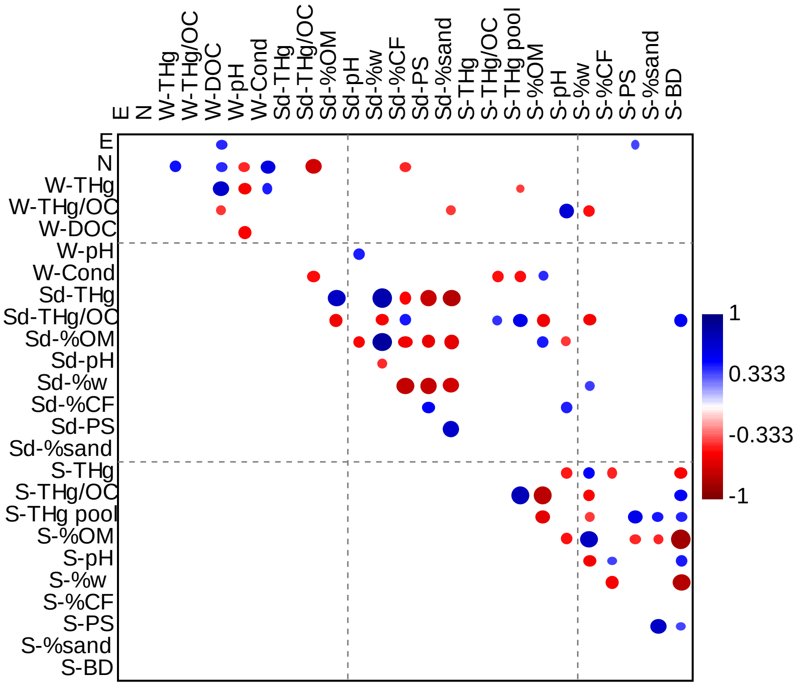

Fig. A4-2 Spearman rank correlations in upland lake water, sediment, and catchment soil (n=31) in the Republic of Ireland, sampled during April–July 2017 and 2018. Note: W indicates water chemistry parameter, Se indicates lake sediment, S indicates catchment soil, E=easting, N=northing, THg=total mercury, THg/OC=total mercury normalized by organic carbon, DOC=dissolved organic carbon, %w=sample moisture, CF=coarse fragments, %OM=organic matter, PS= particle size geometric mean, BD=bulk density.

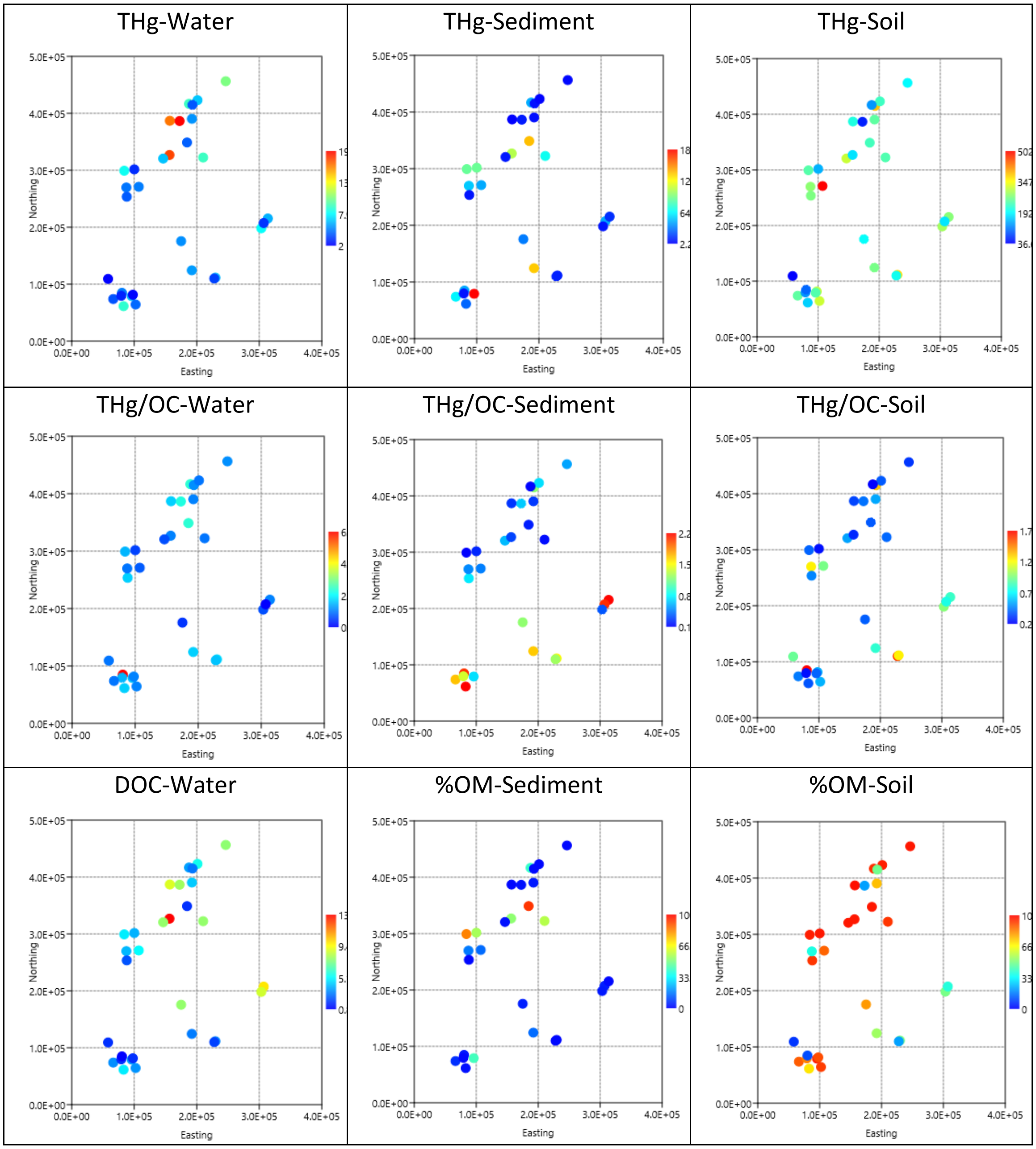

Fig. A4-3 Bubble plots showing the regional patterns of total mercury (THg; ng/L), total mercury normalized by organic carbon (THg/OC; mg/kg), and organic carbon (or matter) content in water, sediment, and soil (n=31) in upland lakes in the Republic of Ireland, sampled during April–July 2017 and 2018. Organic content quantified as dissolved organic carbon (DOC; mg/L) in water, and percent organic matter by weight (%OM) for soil and sediment.