epa
Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

Climate Change Research Programme (CCRP) 2007-2013
Report Series No. 31

Influence of Transboundary Air Pollution on Acid-sensitive Ecosystems

SSTI
Strategy for Science, Technology and Innovation

Comhshaol, Pobal agus Rialtas Áitiúil
Environment, Community and Local Government

Environmental Protection Agency

The Environmental Protection Agency (EPA) is a statutory body responsible for protecting the environment in Ireland. We regulate and police activities that might otherwise cause pollution. We ensure there is solid information on environmental trends so that necessary actions are taken. Our priorities are protecting the Irish environment and ensuring that development is sustainable.

The EPA is an independent public body established in July 1993 under the Environmental Protection Agency Act, 1992. Its sponsor in Government is the Department of the Environment, Community and Local Government.

OUR RESPONSIBILITIES

LICENSING

We license the following to ensure that their emissions do not endanger human health or harm the environment:

- waste facilities (e.g., landfills, incinerators, waste transfer stations);
- large scale industrial activities (e.g., pharmaceutical manufacturing, cement manufacturing, power plants);
- intensive agriculture;
- the contained use and controlled release of Genetically Modified Organisms (GMOs);
- large petrol storage facilities;
- waste water discharges;
- dumping at sea.

NATIONAL ENVIRONMENTAL ENFORCEMENT

- Conducting over 1200 audits and inspections of EPA licensed facilities every year.
- Overseeing local authorities' environmental protection responsibilities in the areas of - air, noise, waste, waste-water and water quality.
- Working with local authorities and the Gardaí to stamp out illegal waste activity by co-ordinating a national enforcement network, targeting offenders, conducting investigations and overseeing remediation.
- Prosecuting those who flout environmental law and damage the environment as a result of their actions.

MONITORING, ANALYSING AND REPORTING ON THE ENVIRONMENT

- Monitoring air quality and the quality of rivers, lakes, tidal waters and ground waters; measuring water levels and river flows.
- Independent reporting to inform decision making by national and local government.

REGULATING IRELAND'S GREENHOUSE GAS EMISSIONS

- Quantifying Ireland's emissions of greenhouse gases in the context of our Kyoto commitments
- Implementing the Emissions Trading Directive, involving over 100 companies who are major generators of carbon dioxide in Ireland.

ENVIRONMENTAL RESEARCH AND DEVELOPMENT

- Co-ordinating research on environmental issues (including air and water quality, climate change, biodiversity, environmental technologies).

STRATEGIC ENVIRONMENTAL ASSESSMENT

- Assessing the impact of plans and programmes on the Irish environment (such as waste management and development plans).

ENVIRONMENTAL PLANNING, EDUCATION AND GUIDANCE

- Providing guidance to the public and to industry on various environmental topics (including licence applications, waste prevention and environmental regulations).
- Generating greater environmental awareness (through environmental television programmes and primary and secondary schools' resource packs).

PROACTIVE WASTE MANAGEMENT

- Promoting waste prevention and minimisation projects through the co-ordination of the National Waste Prevention Programme, including input into the implementation of Producer Responsibility Initiatives.
- Enforcing Regulations such as Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS) and substances that deplete the ozone layer.
- Developing a National Hazardous Waste Management Plan to prevent and manage hazardous waste.

MANAGEMENT AND STRUCTURE OF THE EPA

The organisation is managed by a full time Board, consisting of a Director General and four Directors.

The work of the EPA is carried out across four offices:

- Office of Climate, Licensing and Resource Use
- Office of Environmental Enforcement
- Office of Environmental Assessment
- Office of Communications and Corporate Services

The EPA is assisted by an Advisory Committee of twelve members who meet several times a year to discuss issues of concern and offer advice to the Board.

EPA Climate Change Research Programme 2007–2013

Influence of Transboundary Air Pollution on Acid-sensitive Ecosystems

Assessing the Influence of Transboundary Air Pollution on Acid-sensitive Lakes and Soils: Survey of Upland Acidic Systems (SUAS)

(2007-CCRP-4.4.4b)

CCRP Report

Prepared for the Environmental Protection Agency

by

Trent University

Authors:
Julian Aherne, Andrew Burton, Heidi Scott, Colin Whitfield & Marta Wolniewicz

ENVIRONMENTAL PROTECTION AGENCY

An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353 53 916 0600 Fax: +353 53 916 0699
Email: info@epa.ie Website: www.epa.ie

ACKNOWLEDGEMENTS

This report is published as part of the Climate Change Research Programme 2007–2013. The programme is financed by the Interdepartmental Committee for Strategy for Science, Technology and Innovation and the Department of Environment, Heritage and Local Government. It is administered on behalf of the Department of the Environment, Heritage and Local Government by the Environmental Protection Agency which has the statutory function of co-ordinating and promoting environmental research.

The authors gratefully acknowledge the EPA for financial support, and in particular Dave Dodd for his dedication and patience as EPA project technical officer. The authors further acknowledge the time commitment and data contributions from many dedicated individuals (and agencies), such as Jim Bowman, Deirdre Tierney, Caroline Wynne, John Lucey, Phillip O'Brien (EPA), and Margaret Ryan (Met Éireann) to name a few. The project also benefited from the goodwill and support of many researchers; we are very grateful to Dr William (Bill) Patterson, University of Saskatchewan, for providing oxygen isotopes analysis, Dr Thomas Clair, Environment Canada, for providing quality control analysis on major ion chemistry, and Dr Tom Harner, Environment Canada, and Todd Gouin, Unilever, for support with persistent organic pollutants. In addition, we are very thankful to the many individuals at Trent University and University College Dublin who contributed to the research through data analysis, laboratory support and many hours in the field.

DISCLAIMER

The EPA CCRP Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

EPA CCRP PROGRAMME 2007–2013

Published by the Environmental Protection Agency, Ireland

ISBN: 978-1-84095-525-5

Price: Free **Online version**

Details of Project Partners

Julian Aherne
Environmental and Resource Studies
Trent University
1600 West Drive
Peterborough
Ontario K9J 7B8
Canada
Tel.: +1 705 748 1011
Email: jaherne@trentu.ca

Thomas Cummins
UCD School of Agriculture and Food Science
Agriculture and Food Science Centre
University College Dublin
Belfield
Dublin 4
Ireland
Tel.: +353 1 716 7744
Email: thomas.cummins@ucd.ie

Table of Contents

Report Contributors

Many individuals contributed to this research report and the project outputs (Appendix 1), including co-authors, and data and laboratory analysts. The contributors and their role are listed below (with relevant report sections).

Kevin Adkinson: water and soil laboratory analysis (Sections 3–5)
Julian Aherne: editor and lead author (Sections 1–5)
Carlo Arcieri: soil laboratory analysis (Section 4)
Andrew Burton: recovery and metals author, and soil analysis (Sections 3 and 4)
Thomas Cummins: field and UCD laboratory logistics (Sections 3 and 4)
Jason Henry: nitrogen deposition and soil laboratory analysis (Sections 2 and 4)
Carolyn Reid: soil laboratory analysis (Section 4)
Heidi Scott: mercury and persistent organic pollutants author (Section 5)
Colin Whitfield: trace gases author (Section 3)
Marta Wolniewicz: influence of sea-salts co-author (Section 3)
Cian Woods: back-trajectory data analysis (Section 5)

Field Personnel

The results of the research are primarily based on data collected during several extensive surveys of upland lakes and soils (see Appendix 2). The research would not have been possible without the dedicated commitment of many field personnel. Their input to the research is gratefully acknowledged.

Kevin Adkinson, Trent University: 2010–2011
Julian Aherne, Trent University: 2007, 2008, 2010, 2011
Carlo Arcieri, Trent University: 2009
Andrew Burton, Trent University: 2007–2011
Jason Henry, Trent University: 2009–2011
Christian Huber, Technical University of Munich, Freising: 2008
James Johnson, University College Dublin and Trent University: 2008–2010
Andrew McDonough, Trent University: 2009
Darragh O’Brien, University College Dublin: 2010–2011
James Ouellette, Trent University: 2009
Brent Parsons, Trent University: 2007–2008
Clare Ryan, University College Dublin: 2011
Heidi Scott, Trent University: 2010–2011
Timothy Seabert, Trent University: 2007–2008
Koji Tominaga, Trent University: 2008
Colin Whitfield, Trent University: 2008
Antoni Zbieranowski, Trent University: 2008–2009

Executive Summary

This report provides an overview on the current status of transboundary air pollution in Ireland, primarily with respect to the influence of emissions of sulphur dioxide (SO_2) and nitrogen oxides (NO_x) on previously surveyed acid-sensitive lakes, and the levels of trace metals, including mercury (Hg), and persistent organic pollutants (POPs) in relatively unimpacted[1] upland catchments. The report presents results from the EPA-funded research project 2007-CCRP-4.4.4b, 'Assessing the Influence of Transboundary Air Pollution on Acid-sensitive Lakes and Soils'. The research outputs directly support international policies under the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Air Pollution (LRTAP), EU Thematic Strategies on Air Pollution and the EU National Emission Ceilings Directive (NECD). Further, the results are highly relevant to the EU Water Framework and Habitats Directives.

Upland catchments provide a range of ecosystem services that are vital to human health – such as water supply and purification, climate regulation, and biological and genetic diversity. In addition, they have commercial importance for their recreational services, especially tourism. This is embodied in their designation as 'Annex 1'[2] habitats (under the Habitats Directive), their association with National Parks and a recognition that they represent areas of outstanding natural beauty.

Transboundary air pollution and its potential impacts on human health and the environment have been a major concern since the late 1960s. National and international policies have been implemented to reduce atmospheric emissions of anthropogenic compounds with the objectives of improving air quality, reducing acidic deposition and ultimately protecting the health of ecosystems. The principal objective of this research project was to assess the influence of major transboundary air pollutants on acid-sensitive lakes and soils in Ireland. Extensive physicochemical surveys of acid-sensitive lakes (previously surveyed during 1997) and soils in primarily upland regions were carried out during 2007–2008, with repeat sampling at a small network of upland lake catchments. The surveys provided an assessment of the chemical status of acid-sensitive ecosystems in relation to transboundary air pollution. Moreover, the research focused on filling knowledge gaps specifically in relation to the physicochemical characteristics of acid-sensitive soils, and the levels of greenhouse gases, trace metals, Hg and POPs in upland acid-sensitive lake catchments.

In recent decades, emissions of primary pollutants contributing to transboundary air pollution have changed substantially in response to international policies such as the UNECE Convention on LRTAP, and the EU NECD, which set limits for the emissions of key atmospheric pollutants including SO_2, NO_x and ammonia (NH_3) that Ireland had to achieve by 2010. The trends in the emission, concentration and deposition, and the response of soils and surface waters, may be summarised as follows:

- There have been statistically significant decreases in emissions of SO_2, NO_x, NH_3 and trace metals in Ireland consistent with reductions across Europe (in response to international control measures). Emissions of SO_2 have decreased by 82%, NO_x by 31% and NH_3 by 3% between 1991 and 2009. In 2010, national emissions for SO_2 and NH_3 were 38.3% and 8.4% below ceilings specified under the NECD; however, NO_x was 11.7% (7.6 Gg) above the ceiling limit.
- During the period 1991–2009, non-marine sulphate ($nmSO_4^{2-}$) deposition significantly decreased by ~60%; the observed decrease was proportional to increased rainfall pH. The reductions in annual average N (nitrate [NO_3^-] and ammonium [NH_4^+]) were lower (NO_3^- [36%] and NH_4^+ [22%]); nevertheless, the long-term patterns in rainfall chemistry were strongly correlated with national emissions reductions for SO_2 ($r = 0.88$), NO_x ($r = 0.44$) and NH_3 ($r = 0.53$).

---

[1] There are no longer any truly pristine ecosystems owing to long-range air pollution.

[2] Habitats which are considered to be of European interest, following criteria given in the EU Habitats Directives.

- There is evidence of widespread chemical recovery from acidification in upland acid-sensitive lakes with significant reductions in nmSO_4^{2-} (–58%) and increases in alkalinity (47%) owing to emissions reductions during the period 1997–2007. Further, the current levels of trace metals in upland lakes are representative of ‘background’ regions dominated by geochemical sources suggesting co-benefits from reduced emissions and catchment acidification recovery. It should be noted that acidification recovery is a slow process, which can be significantly influenced by sea-salt inputs and changes in organic carbon in surface waters. Nonetheless, continued improvements in the chemistry of acid-sensitive lakes are expected under future emissions reductions. In contrast, chronic elevated nitrogen deposition may alter plant species diversity in sensitive terrestrial habitats, and influence greenhouse gas efflux from upland lakes.
- Catchment soils are the primary determinant of the long-term chemical response of acid-sensitive surface waters to transboundary air pollution. The study results indicate quantitative links between the chemical status of upland acid-sensitive soils and atmospheric deposition, and the chemistry of surface waters. This suggests that the observed lake recovery is indicative of soil-acidification recovery. However, the response of surface waters is strongly related to soil type, with distinct divergences between catchments dominated by mineral and organic soils.
- The levels of Hg and POPs in upland headwater catchments in Ireland were low and commensurate with background levels in mid-latitude regions influenced primarily by long-range transboundary air pollution. Their ultimate environmental fate is strongly determined by the level of organic matter in catchment soils, suggesting potential re-emission owing to peat-harvesting for energy production. While recent levels have benefited from national and European emissions reductions, it is ultimately necessary to develop policies and emission-control measures at the hemispheric scale to reduce future concentrations.

Ireland is located on the western periphery of Europe and predominantly receives ‘clean’ air masses from the Atlantic. Nonetheless, long-range transboundary air pollution, and in particular acidic deposition borne on easterly air masses, has had an impact on the hydrogeochemistry of upland acid-sensitive lakes and soils. The reduction in emissions of primary pollutants has led to improvements in the acid status of impacted ecosystems. However, there are still knowledge gaps and significant challenges in meeting environmental-quality objectives. Further research is required on the impacts of chronic nitrogen deposition on biodiversity in terrestrial ecosystems, and greenhouse gases in aquatic systems, the control of intercontinental transport of pollutants such as POPs and Hg, the release of pollutants stored in organic soils under changing land use and climate, and the influence of sea-salt inputs associated with increased frequency and intensity of storms on acid-sensitive ecosystems. In addition, the response of surface waters to atmospherically deposited pollutants is strongly related to catchment and soil characteristics, with distinct differences between mineral and organic soils.

Long-term monitoring is required to evaluate atmospheric response to emission-control measures. Further, integrated monitoring at regional and national levels is essential to improve understanding of the impacts of atmospheric pollutants on upland ecosystems. The development of future policies to reduce transboundary air pollution needs to engage the scientific community in monitoring, process research and the assessment of effects to ensure long-term protection of ecosystem services.

1 Transboundary Air Pollution

1.1 Emissions Reductions and Study Objectives

Transboundary air pollution[3] and its potential impacts on human health and the environment have been a major concern since the late 1960s. Notably, a broad and increasing range of pollutants can undergo transboundary atmospheric transport owing to their low deposition velocities, atmospheric reactions forming secondary pollutants, chemical inertness or multi-hop pathways associated with pollutant volatility and environmental persistent. Major transboundary air pollutants include fine particulate matter, acidic deposition associated with sulphur (S) and nitrogen (N) emissions, mercury (Hg), and persistent organic pollutants (POPs). This report provides an overview on the current status of transboundary air pollution in Ireland, focusing on long-term trends in anthropogenic emissions, concentrations, and the deposition of atmospheric S and N during the period 1991–2009, and the response of acid-sensitive soils and surface waters, specifically the response of lakes previously surveyed during 1997.

Since 1979, the Convention on Long-range Transboundary Air Pollution (LRTAP) has addressed this issue in the United Nations Economic Commission for Europe (UNECE) region through scientific collaboration and policy negotiation. The Convention initially focused on acidic deposition, originating largely from anthropogenic emissions of gaseous S and N (sulphur dioxide [SO_2], nitrogen oxides [NO_x] and ammonia [NH_3]); however, it has expanded to include volatile organic compounds, heavy metals and POPs. One of the main subsidiary bodies of the Convention is the Working Group on Effects which provides information on the degree and geographic extent of impacts on human health and the environment. Its six International Cooperative Programmes (e.g., ICP Waters: ICP on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes) identify the most endangered areas, ecosystems and other receptors by considering damage to terrestrial and aquatic ecosystems and materials. An important part of this work is long-term monitoring,[4] which provides empirical support to the development of emission-control policies.

A second subsidiary body, the Cooperative Programme for Monitoring and Evaluation of Long-range Transmission for Air Pollutants in Europe (EMEP[5]), provides scientific support to the Convention on atmospheric monitoring and modelling, emission inventories and emission projections, and integrated assessment modelling. The programme is supported by a network of precipitation and air-monitoring stations across Europe that routinely submit data to EMEP's Chemical Co-ordinating Centre (CCC[6]). In Ireland, the EPA operates a network of EMEP stations with support from the Irish meteorological service (Met Éireann), Teagasc and the National Parks and Wildlife Service (Leinert et al., 2008).

The Convention has been extended by eight protocols that identify specific reductions in emissions of air pollutants, for example, the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone, the 'Gothenburg Protocol' (UNECE, 1999). In concert, the European Union (EU) introduced the National Emission Ceilings Directive (NECD 2001/81/EC) requiring member states including Ireland (EPA, 2011; 2012) to limit emissions of acidifying and eutrophying pollutants and ozone precursors.[7] The

---

[3] Long-range transboundary air pollution is defined as the anthropogenic emissions, directly or indirectly, of substances into the atmosphere which have deleterious effects on human health, the environment or material property in another country.

[4] URL: www.unece.org/env/lrtap

[5] EMEP: The European Monitoring and Evaluation Programme. URL: www.emep.int

[6] URL: www.nilu.no/projects/ccc

[7] Further, political and social changes in eastern Europe during the 1990s led to the closure of inefficient hydrocarbon powered industrial infrastructure (for economic reasons), which were major emission sources of acidifying substances.

goal of negotiated or legislated emission reductions is to improve air quality, reduce acidic deposition and ultimately improve the protection of human and ecosystem health.

During the period 1991–2009, there have been statistically significant decreases in emissions of SO_2, NO_x and NH_3 in Ireland,[8] consistent with European reductions (Tarrason et al., 2006). The greatest reductions were observed for SO_2, which decreased by 81.9%. Nitrogen oxide emissions decreased by 30.5%, and NH_3 emissions decreased by 3.2%.[9] However, the decrease in both oxidised and reduced N emissions was strongly influenced by the global recession that began during 2008, for example national NO_x emissions decreased by 20% between 2008 and 2009 (EPA, 2011; 2012). In 2010, national annual emissions for SO_2 and NH_3 were 38.3% and 8.4% below the limits specified under the NECD; however NO_x was 11.7% (7.6 Gg) above the ceiling limit. There have also been significant decreases in emissions of trace metals during the same period (1991–2009).[10]

The principal objective of this research project[11] was to assess the influence of major transboundary air pollutants on acid-sensitive lakes and soils, specifically focusing on the acid status of lakes previously surveyed during 1997 (Aherne et al., 2000). In addition, the project assessed long-term trends in the concentration and deposition of atmospheric S and N during the period 1991–2009, and addressed data and knowledge gaps in relation to the characteristics of acid-sensitive soils, and the levels of heavy metals and POPs in upland headwater lake catchments[12] owing to transboundary air pollution. The objectives were addressed through extensive surveys of acid-sensitive lakes and soils carried out during 2007–2008 in primarily upland regions, with repeat sampling at a small network of upland lake catchments. The principal research objective was addressed through several supporting tasks (identified below by report section). The results of the supporting tasks have been published in peer-review journals and presented at international conferences (see Appendix 1), and the associated data-sets have been submitted to the Secure Archive For Environmental Research (SAFER) managed by the EPA (see Appendix 2).

- Section 2: Spatial variation and long-term trends in precipitation chemistry in response to emissions reductions at monitoring stations contributing to EMEP;
- Section 3.2: Response of small upland acid-sensitive lakes to changes in atmospheric deposition;
- Section 3.3: Levels and controls on trace metals in acid-sensitive lakes;
- Section 3.4: Influence of sea-salt events on the chemistry of acid-sensitive lakes;
- Section 3.5: Controls on greenhouse gases in acid-sensitive lakes;
- Section 4.: Physicochemical characteristics of acid-sensitive soils;
- Section 5.2: Concentrations of Hg in upland headwater lake catchments;
- Section 5.3: Fate of POPs in soils and water of upland headwater lake catchments.

The project outputs directly support national obligations under the LRTAP Convention, Thematic

---

[8] Trend analysis based on Mann-Kendall (Z) statistic (Salmi et al., 2002) and national emission data (EPA, 2011; 2012); SO_2: $Z = –5.04$ $p \leq 0.001$, NO_x: $Z = –2.03$ $p \leq 0.05$, and NH_3: $Z = –2.24$ $p \leq 0.05$.

[9] Emissions reductions: SO_2 from 180.9 Gg to 32.7 Gg; NO_x from 127.8 Gg to 88.8 Gg, and NH_3 from 114.1 Gg to 107.8 Gg. Note: there are slight differences between emission data published by the EPA (URL: www.epa.ie/pubs/reports/air/airemissions) and the officially reported emission data available through the Centre on Emission Inventories and Projections (URL: www.ceip.at). The CEIP data indicate non-significant decreasing trends for NO_x and NH_3, and a slight increase in NH_3 between the years 1991 and 2009 (0.3%).

[10] Emissions reductions Pb: 86.8%, Zn: 60.9%, Cd: 50.9%, Cr: 49.9% and As: 31.1%. Data source URL: www.ceip.at

[11] Project 2007-CCRP-4.4.4b: ‘Assessing the Influence of Transboundary Air Pollution on Acid-sensitive Lakes and Soils: Survey of Upland Acidic Systems (SUAS)’.

[12] Headwater lake catchment refers to a lake and its surrounding contributing land area, which is the source of a river or stream system, i.e., the furthest place from its estuary or confluence with another river.

Strategies on Air Pollution and NECD. Further, the results are highly relevant to the EU Water Framework and Habitats Directives as upland catchments provide a range of ecosystem services that are vital to human health, such as water supply and purification, climate regulation, and biological and genetic diversity. In addition, they have commercial importance for their recreational services, especially tourism. The project outputs support the assessment of ecosystem status, their chemical response to existing emissions controls, and provide observations that support the development of future air-pollutions policies.

2 Precipitation Chemistry: Spatial Patterns and Long-term Trends

2.1 Precipitation Chemistry Monitoring Network

Routine observations of precipitation chemistry have been carried out in Ireland for more than half a century. The earliest recorded measurements were made at Valentia Observatory, Co. Kerry, during the late 1800s by Robert Angus Smith (Smith, 1872), who demonstrated that the chemistry of precipitation was linked to meteorology, proximity to the ocean and anthropogenic emissions (e.g., combustion, agriculture). Smith (1872) established the fundamental principles of air pollution, and was the first to note that 'acid rain' caused by SO_2 released from coal combustion had the potential to damage plants and materials. Further short-term precipitation chemistry studies carried out during 1955 (Gorham, 1957), and 1961–1962 (Sparling, 1967), assessed the link between the chemical composition of rainfall and its influence on ecosystem biogeochemistry.

In 1958, the Irish meteorological service (Met Éireann) began a programme of monthly sampling and analysis of precipitation chemistry at several stations throughout Ireland (Mathews et al., 1981). Data from this network have been widely used for assessment and mapping (e.g., Stevenson, 1968; Fisher, 1982; Jordan 1997). However, the network was not designed specifically to provide information for the assessment of acidic deposition (Mathews et al., 1981). The locations of the sites were not well suited for this purpose (three sites were at airports and most of the others were on the coast) and the analysis of precipitation chemistry was undertaken largely on the basis of monthly samples. Nevertheless, during 1980, Valentia Observatory began the daily collection and analysis of precipitation and air samples to assess transboundary air pollution (see Bashir et al., 2008) under EMEP. Since this period several 'background' stations have been established to support national reporting obligations under the Convention on LRTAP and to evaluate the effectiveness of international agreements to reduce transboundary air pollutants (Aherne and Farrell, 2002; Leinert et al., 2008).

During the period 1991–2009, there were eight monitoring stations in Ireland (Fig. 2.1 and Table 2.1) contributing precipitation chemistry data to the CCC under EMEP. However, only two stations (Valentia Observatory, Co. Kerry and Lough Navar, Co. Fermanagh [AEA Technology plc]) were in operation during the entire period. Three stations (Turlough Hill, The Burren and Ridge of Capard) were closed by

Table 2.1. Precipitation chemistry monitoring stations contributing to the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP) during the period 1991–2009; altitude (Alt.), co-ordinates, observation period and operating agencies.

Monitoring station	Alt.	Latitude	Longitude	Data period	Operator§§§
	(m)	(decimal degrees)		(open–closed)	
Valentia Observatory	9	51.934	–10.234	1980–	Met Éireann
Turlough Hill	420	53.034	–6.400	1991–2002	EPA
The Burren§	90	53.000	–9.100	1986–2002	ESB
Ridge of Capard§	340	53.117	–7.450	1986–2001	ESB
Oak Park	59	52.867	–6.917	2005–	EPA
Glenveagh	44	55.050	–7.934	2006–	EPA
Johnstown Castle	62	52.285	–6.501	2006–	EPA
Lough Navar§§	126	54.434	–7.867	1984–	AEA

§Wet-only collectors in operation since 1992; however, data only submitted to EMEP (Chemical Co-ordinating Centre) since 1997. §§Daily observations until 1999, fortnightly since 2001. §§§Environmental Protection Agency (EPA), Electricity Supply Board (ESB), and AEA Technology plc (AEA).

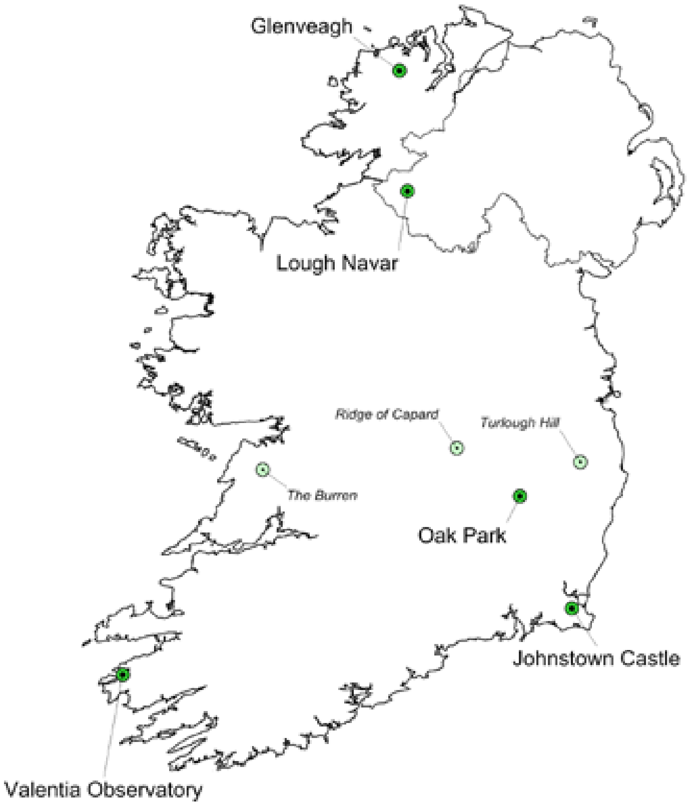


Figure 2.1. Location of precipitation chemistry monitoring stations contributing to the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP [Chemical Co-ordinating Centre]) during the period 1991–2009. Monitoring stations indicated by light-green filled circles are no longer in operation (see Table 2.1).

2003, replaced by three stations in 2005 (Oak Park, Glenveagh and Johnstown Castle) under the Irish EPA's new Transboundary Air Pollution Monitoring Network (Leinert et al., 2008). All stations were remote from local pollution sources (Fig. 2.1) and operated wet-only collectors, with daily sampling and analysis (Lough Navar had daily observations until 1999, and fortnightly since 2001). Since 2005, Met Éireann has carried out all precipitation chemistry analysis for the network at their laboratory in Glasnevin, Dublin.

The network of monitoring stations provides data to support the national mapping of atmospheric deposition, the assessment of long-term trends in anthropogenic S and N associated with long-range transboundary air pollution (i.e., non-marine sulphate [$nmSO_4^{2-}$], nitrate [NO_3^-] and ammonium [NH_4^+]) and their response to emission reductions. Non-marine ion concentrations were estimated using theoretical sea-salt ratios assuming that all the sodium in precipitation originated from sea-salt (e.g., [mol_c][13] ratio for SO_4^{2-}:Na^+ is 0.121:1; UBA, 2004).

2.2 Spatial Variation in Sulphur and Nitrogen Concentrations and Depositions

Annual average $nmSO_4^{2-}$ concentration in precipitation ranged from 5.49 μmol_c L^{-1} at Lough Navar to 10.96 μmol_c L^{-1} at Johnstown Castle during the period 2005–2009, which was assumed to represent 'current' precipitation chemistry (Table 2.2). The coefficient of variation[14] (CV) in annual average concentrations between stations was similar for anthropogenic pollutants ($nmSO_4^{2-}$ [31%], NO_3^- [31%] and NH_4^+ [35%]) and rainfall volume (32%) compared with marine ions

---

[13] Units: 1 mole of charge (mol_c) is equal to 1 equivalent (eq).

[14] The CV is a normalised measure of dispersion estimated as standard deviation divided by the mean and multiplied by 100.

Table 2.2. Volume-weighted annual average acidity (pH), non-marine sulphate ($nmSO_4^{2-}$),[§] nitrate (NO_3^-), ammonium (NH_4^+) and sodium (Na^+) in precipitation during the period 2005–2009.[§§]

Monitoring station	Rainfall	pH	$nmSO_4^{2-}$	NO_3^-	NH_4^+	Na^+
	Mm		$\mu mol_c\ L^{-1}$			
Valentia Observatory	1696.0	5.25	6.29	5.95	10.74	551.9
Oak Park	806.6	5.48	8.92	7.67	15.60	54.6
Glenveagh	1024.3	5.28	5.96	5.71	6.13	238.3
Johnstown Castle	881.9	5.19	10.96	11.45	17.09	131.9
Lough Navar	1294.5	5.36	5.49	6.86	11.65	152.7
Average (2005–2009)	1140.7	5.29	7.14	7.21	11.79	269.7
Average (1991–1995)[§§§]	1206.8	5.02	17.12	11.33	15.04	231.3

[§] $nmSO_4^{2-} = [SO_4^{2-}] - 0.121 \times [Na^+]$. [§§] Monitoring stations in Ireland contributing to the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP [Chemical Co-ordinating Centre]). [§§§] The long-term average (1991–1995) includes data from Valentia Observatory, Turlough Hill, The Burren, Ridge of Capard and Lough Navar (see Table 2.1 and Fig. 2.1).

(e.g., Na^+ [86%]), reflecting the very strong west–east gradient in marine inputs. Annual average concentrations of $nmSO_4^{2-}$ and NO_3^- were higher at the south-east monitoring stations (Oak Park and Johnstown Castle); this east–west gradient in transboundary air pollution is well established and associated with emissions in Europe (Bowman and McGettigan, 1994; Aherne and Farrell, 2002; Bashir et al., 2008). The lowest pH value was also observed at Johnstown Castle, followed by the more remote west-coast stations (Valentia Observatory and Glenveagh), with greater marine influence (see Na^+, Table 2.2). Ammonium concentrations were also higher in the south-east, reflecting the influence of national agricultural emissions on precipitation chemistry.

Spatially explicit estimates of total atmospheric deposition are central to the assessment of air pollution effects and the efficacy of emissions-control policies. Annual average total inorganic deposition was mapped by combining wet and dry deposition (Fig. 2.2). Wet deposition was estimated by combining interpolated precipitation chemistry (geostatistical kriging of observed data; Table 2.2) with mapped rainfall volume following Aherne and Farrell (2002). Dry deposition for NH_3 was derived from observed air concentrations (de Kluizenaar and Farrell, 2000[15]) in combination with literature-based habitat-specific dry-deposition velocities. In contrast, dry deposition of oxidised S and N was obtained from the EMEP chemical transport model.[16] The total deposition of S and N species showed distinctly different spatial patterns (Fig. 2.2); $nmSO_4^{2-}$ showed a north–south gradient, strongly influenced by greater rainfall volume at higher elevations. The average total $nmSO_4^{2-}$ deposition was 14.8 $mmol_c\ m^{-2}$ (1.7 × wet deposition). Average total NO_3^- deposition was 17.7 $mmol_c\ m^{-2}$ (1.5 × wet deposition) and showed a stronger east–west gradient, potentially reflecting national traffic-related emissions. Notably, anthropogenic deposition was dominated by average total NH_4^+ deposition, which was 69.6 $mmol_c\ m^{-2}$ (3.2 × wet deposition) and highest in the east and south-east. In contrast to $nmSO_4^{2-}$ and NO_3^- deposition, average total NH_4^+ deposition was dominated by dry deposition associated with NH_3 emissions from agriculture, predominantly dairy and other cattle (~75%; EPA, 2012). As such, average total N deposition in Ireland was dominated by reduced deposition (78%), reflecting the importance of national agricultural emissions rather than long-range transboundary sources.

---

[15] The location of NH_3 monitoring sites (n = 40) is shown in Fig. 2.2.

[16] For further details see URL: webdab.emep.int/Unified_Model_Results

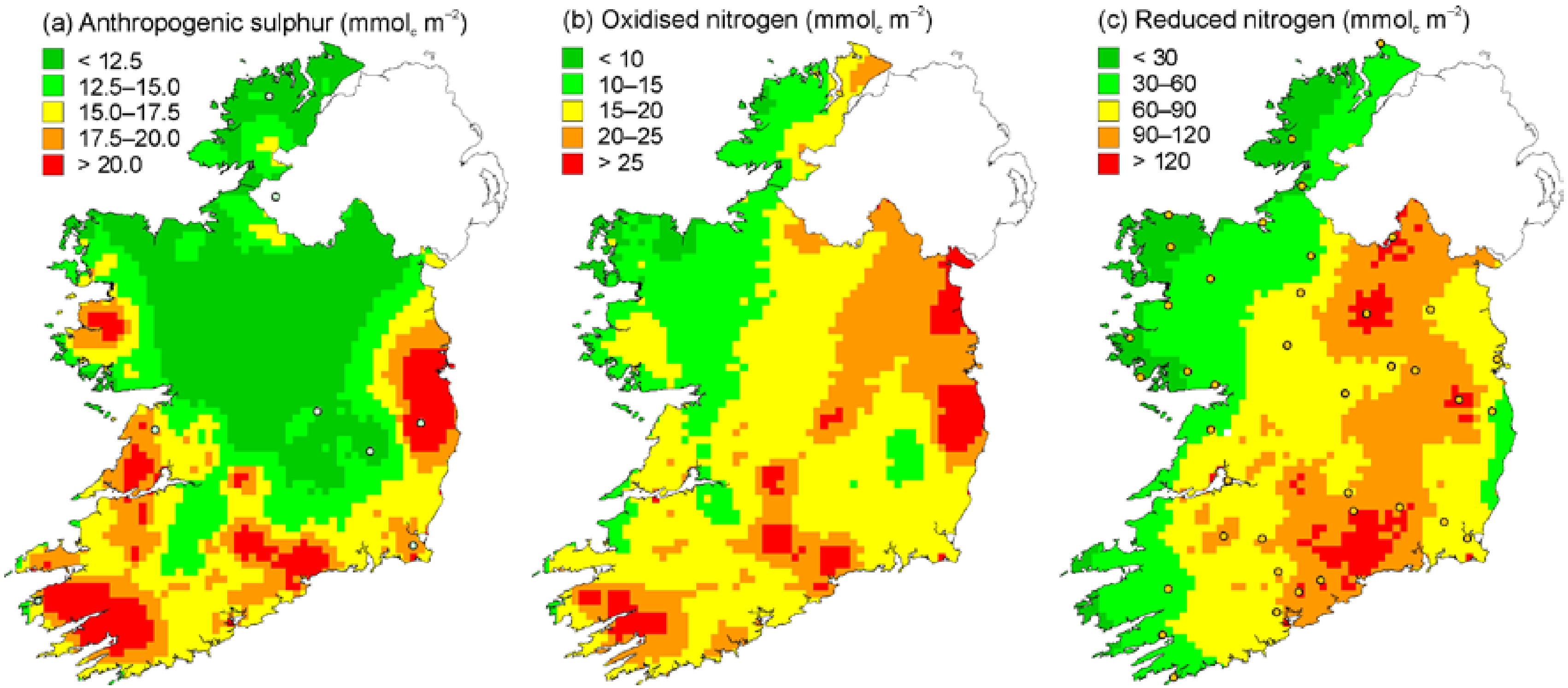


Figure 2.2. (a) Long-term annual total (wet and dry) anthropogenic sulphur deposition during the period 2005–2009. The location of precipitation chemistry-monitoring stations is also shown (see Fig. 2.1 and Table 2.1); (b) Total (wet and dry) oxidised nitrogen deposition during the period 1991–2009, and (c) total (wet and dry) reduced nitrogen deposition during the period 1991–2009. The location of ammonia passive sampler sites (n = 40) operated during 1999–2000 (de Kluizenaar and Farrell, 2000) is also shown. Data are presented on a 5 km × 5 km grid (based on the Irish grid).

2.3 Long-term Sulphur and Nitrogen Precipitation Concentrations

Annual average (five-year volume-weighted) precipitation concentrations of $nmSO_4^{2-}$, NO_3^- and NH_4^+ decreased between the periods 1991–1995 and 2005–2009 across all stations (Table 2.2). The largest decrease was observed in $nmSO_4^{2-}$ (–59%), which was proportionally similar to the decrease in hydrogen ion (H^+) concentration (–46%) suggesting that increased precipitation pH (5.02–5.29) was predominately driven by reductions in $nmSO_4^{2-}$. Further, there was a highly significant long-term decreasing trend[17] in median annual average $nmSO_4^{2-}$ across all stations during the period 1991–2009 (Fig. 2.3). In contrast, reductions in annual average N precipitation concentrations between the periods 1991–1995 and 2005–2009 were lower (NO_3^-: –36% and NH_4^+: –22%); and although a significant long-term decreasing trend was observed for NO_3^-, the trend was driven by the high scatter in annual data at three stations during the 1990s (Turlough Hill, The Burren and Ridge of Capard; Fig. 2.3). Further, the long-term trend in median annual average NH_4^+ concentration during the period 1991–2009 was not statistically significant (Fig. 2.3). The estimated change in precipitation chemistry between the periods 1991–1995 and 2005–2009 was influenced by the change in monitoring stations (Table 2.2). However, the long-term observations at Valentia Observatory showed changes similar to the station averages for $nmSO_4^{2-}$ (–55%), H^+ (–44%) and NO_3^- (–27%).

The long-term patterns in precipitation chemistry were strongly correlated with emissions during the period 1991–2009. For example, the observed decrease in median annual $nmSO_4^{2-}$ precipitation concentration (Fig. 2.3) was correlated with national SO_2 emission reductions during the same period (Pearson product-moment r = 0.88). Oxidised and reduced N precipitation concentrations were also correlated with national anthropogenic emission reductions, albeit statistically weaker (NO_x [r = 0.44] and NH_3 [r = 0.53]). Nonetheless, there was a statistically significant decrease in anthropogenic S and N concentrations in precipitation and a corresponding increase in pH owing to emissions reductions legislated nationally and internationally under EU directives and UNECE protocols. The correlation with European emission reductions was equally strong for SO_2 (r = 0.86) and NO_x (r = 0.49), but the correlation with European NH_3 emissions was weak (r = 0.02) highlighting further the importance of national emission sources for reduced N in precipitation.[18]

The largest changes in atmospheric deposition were observed for $nmSO_4^{2-}$. For example, average mapped wet deposition decreased from 22 $mmol_c\ m^{-2}$ during 1994–1998 (Aherne and Farrell, 2002) to 8.7 $mmol_c\ m^{-2}$ during the period 2005–2009. Within little more than a decade, there was a ~60% reduction in wet $nmSO_4^{2-}$ deposition. In concert, during the same period, a 68% reduction in national SO_2 emissions was observed, consistent with a 57% reduction in EU emissions. Across Europe and North America, several studies have shown widespread significant changes in the chemistry of acid-sensitive lakes and soils stimulated by emissions reductions (Stoddard et al., 1999; Skjelkvåle et al., 2005).

---

[17] Trend analysis based on Mann-Kendall (Z) statistic (Salmi et al., 2002) using median annual data; $nmSO_4^{2-}$: $Z = -4.13\ p \leq 0.001$, NO_3^-: $Z = -2.66\ p \leq 0.01$.

[18] The correlation with emissions from the United Kingdom was SO_2 r = 0.84, NO_x r = 0.46, and NH_3 r = 0.24.

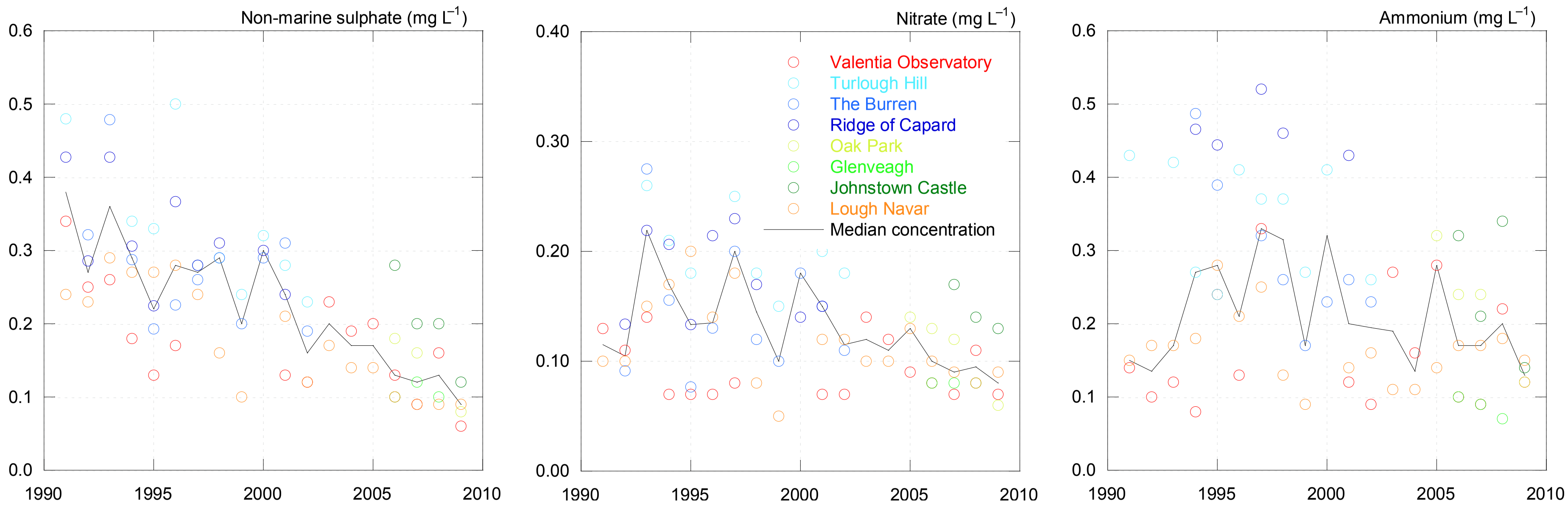


Figure 2.3. Long-term annual trend (1991–2009) in non-marine sulphate, nitrate and ammonium concentration in precipitation (mg L^{-1} [open circles]) at monitoring stations contributing to the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP). Volume-weighted annual average data were derived from daily observations at all monitoring stations except Lough Navar which changed from daily to fortnightly during 1999–2000. The median concentration across all stations is also shown (black line). Data source: Chemical Co-ordinating Centre of EMEP (URL: www.nilu.no/projects/ccc).

3 Influence of Transboundary Air Pollution on Acid-sensitive Lakes

3.1 Survey of Acid-sensitive Lakes

Freshwater ecosystems provide a range of services, including water supply, nutrient cycling, biological diversity, climate regulation and recreation. Further, it is well established that lakes are sentinels of environmental change as they integrate terrestrial and atmospheric processes (Williamson et al., 2009). In the current study, upland lakes situated along the coastal mountain ranges, remote from local pollution sources, were selected to investigate the impacts of long-range transboundary air pollution on relatively unimpacted (pristine) ecosystems; specifically, the study evaluated the response of surface water chemistry to changes in acidic deposition (Section 3.2), the importance of acidic deposition as a driver of trace metal concentrations (Section 3.3), the influence of sea-salts on surface water acidity (Section 3.4) and the role of these systems in greenhouse gas cycling (Section 3.5). During 2007 and 2008, extensive water-chemistry surveys were carried out in predominantly upland acid-sensitive regions (Fig. 3.1). In total, 142 lakes were surveyed, 20 during 2007 (May), 70 during spring 2008 (May), and a sub-set of 52 sampled during both years. The study lakes were pseudo-randomly selected based on bedrock geology and soil characteristics, with greater weighting towards higher elevation lakes in acid-sensitive regions; all lakes had been surveyed previously during February–May 1997 (see Aherne and Farrell, 2000; Aherne et al., 2002).

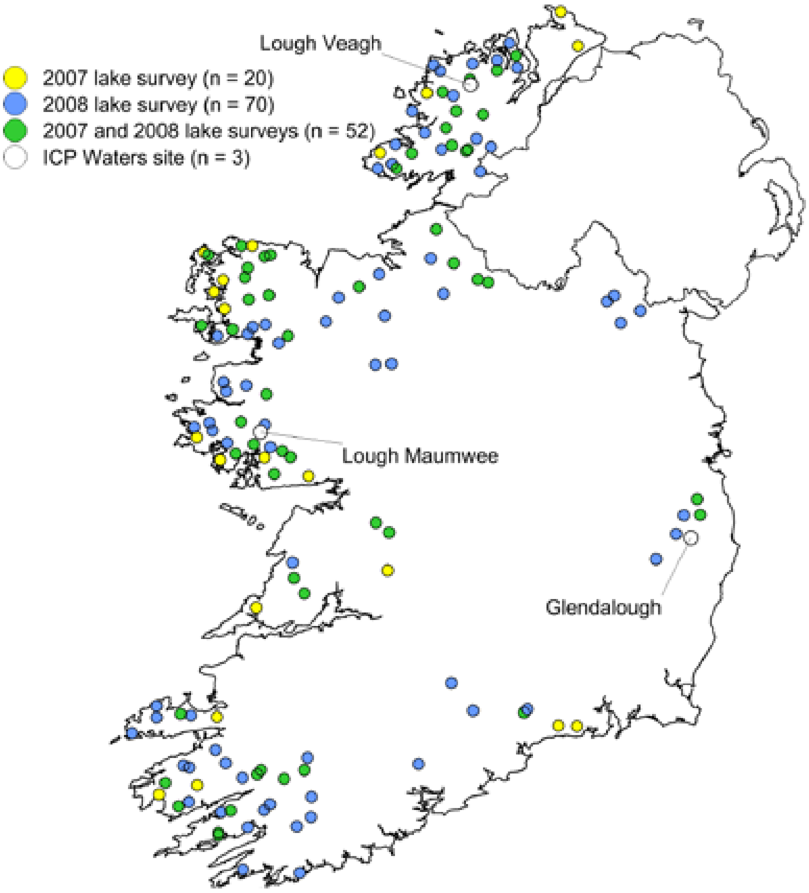


Figure 3.1. Location of study lakes (n = 142) surveyed for hydrochemistry during spring 2007 and 2008. Also shown is the location of three acid-sensitive lakes monitored by the EPA that have contributed data to ICP Waters (URL: www.icp-waters.no) since the 1980s.

Field and laboratory procedures were standardised across all lake surveys where possible (1997, 2007 and 2008); shore water samples were collected 10–20 cm below the surface in high-density polyethylene bottles and kept cool (~4°C) until analysis. Lake samples were analysed for pH, conductivity, Gran alkalinity, major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^- and SO_4^{2-}), nutrients (NO_3^-, NH_4^+, PO_4^{3-}), dissolved organic carbon (DOC), trace metals, trace gases, and oxygen isotopes (see Appendix 2). Further details on field and laboratory procedures are given by Whitfield et al. (2011), Burton and Aherne (2012), and Burton and Aherne (2013). There was a significant decrease in observed $nmSO_4^{2-}$ deposition during the survey periods in 1997 and 2007–2008; however, there was no significant long-term trend in sea-salt deposition or climate (air temperature and rainfall volume; Burton and Aherne, 2012).

3.2 Response of Acid-sensitive Lakes to Changes in Atmospheric Deposition

The impact of acidic deposition on surface waters has been studied extensively in Europe and North America (e.g., see Skjelkvåle et al., 2005). As noted in Section 1, international policies have been implemented to reduce atmospheric emissions of anthropogenic S and N compounds with the objective of promoting chemical and biological recovery of impacted ecosystems. In 1999, the effects-based Gothenburg Protocol on long-range transboundary air pollution was signed with the intent to reduce emissions of S and N oxides and NH_3 in Europe (63%, 41% and 17% respectively) by 2010 (UNECE, 1999). These emissions reductions have stimulated widespread significant changes in the chemistry of acid-sensitive lakes (Wright et al., 2007). Repeat lake surveys in Europe and North America have generally observed a decrease in lake SO_4^{2-} concentrations consistent with decreases in precipitation concentrations (Skjelkvåle et al., 2005).

The objective of this study was to determine differences in the chemistry of small headwater lakes between 1997 and 2007, a period which has experienced significant reductions in the deposition of S (see Section 2.3 and Fig. 2.3). To meet this objective, 60 lakes[19] sampled during 1997 (Aherne et al., 2002) were re-surveyed during 2007 (Fig. 3.1; Burton and Aherne, 2012), and chemical observations common to both surveys were compared using the Wilcoxon rank paired test. It was anticipated that increases in pH and alkalinity would be observed along with decreases in SO_4^{2-}, base cations and aluminium (Al) concentrations, similar to studies in Europe and North America (Skjelkvåle et al., 2005; Stoddard et al., 1999).

3.2.1 *Lake chemistry: 2007 survey*

Lake chemistry was dominated by marine ions ($Cl^- > Na^+ > Mg^{2+}$), which constituted more than 82% of the total ionic concentration (Table 3.1) owing to atmospheric deposition associated with the predominant south-westerly airflow from the North Atlantic (see Aherne and Farrell, 2002; Aherne et al., 2002). In general, surface water pH was low, ranging from 4.18 to 6.48 (median: 5.08), and less than or equal to pH 5.5 in 77% of the lakes. Gran alkalinity was also low, ranging from –58.2 to 135.1 $\mu mol_c\ L^{-1}$ (median: –3.6 $\mu mol_c\ L^{-1}$), and less than or equal to zero in 57% of the lakes. Dissolved organic carbon[20] ranged from 1.8 to 12.7 mg L^{-1}, with a median of 4.9 mg L^{-1} (88% less than 10.0 mg L^{-1}). Total Al (Al_T) was generally low, ranging from 0.4 to 9.5 $\mu mol\ L^{-1}$ (median = 2.1 $\mu mol\ L^{-1}$), and dominated by organic Al (~60%; see Section 3.3).

Non-marine SO_4^{2-} ranged from 0[21] to 41.6 $\mu mol_c\ L^{-1}$, with a median of 9.7 $\mu mol_c\ L^{-1}$ (9 lakes less than 0 $\mu mol_c\ L^{-1}$).[22] The highest concentrations occurred in the east and near the border with Northern Ireland. This is consistent with previous studies (Bowman and McGettigan, 1994) that found higher $nmSO_4^{2-}$ deposition in the east and north associated with easterly air masses. Calcium lake concentration had a median of 55.1 $\mu mol_c\ L^{-1}$; 92% of the study lakes exhibited concentrations less than

---

[19] The 2007 survey included 72 lakes (see Fig. 3.1) but 12 were excluded owing to site suitability.

[20] Estimated from absorbance at 320 nm [DOC = 49.5 x ABS_{320} + 1.69] consistent with the 1997 survey (Aherne et al., 2002).

[21] The lowest value was –53.6 $\mu mol_c\ L^{-1}$.

[22] Non-marine concentrations of SO_4^{2-} and base cations were estimated as the difference between total and marine concentrations based on the assumption that all Cl^- in lake water originated from sea-spray, i.e., (mol_c) ratio for SO_4^{2-}:Cl^- is 0.103:1. Negative concentrations of non-marine SO_4^{2-} and base cations may result from short-term variations in deposition, such as high inputs of sea-salts, variation in deposition ratios with distance from the ocean (Möller 1990), or catchment retention.

Table 3.1. Summary statistics (mean, standard deviation [SD], 5th, 50th and 95th percentile) of physical and chemical characteristics in the study lakes (n = 60; see Fig. 3.1) in 2007.

Variable	Unit	Mean	SD	Percentiles		
				5th	50th	95th
Lake size	ha	4.4	8.4	0.5	1.6	13.3
Catchment size	ha	63.7	262.5	2.1	11.0	153.5
Elevation	m	291.6	169.1	28.8	278.0	561.2
pH		5.1	0.6	4.3	5.1	6.2
Conductivity	µS cm^{-1} at 25°C	99.5	42.6	41.0	90.4	180.6
Alkalinity§	$\mu mol_c\ L^{-1}\ CaCO_3$	–5.6	32.3	–51.7	–3.6	45.9
Ca^{2+}	$\mu mol_c\ L^{-1}$	59.5	31.5	23.1	55.1	105.4
Mg^{2+}	$\mu mol_c\ L^{-1}$	145.5	70.4	57.0	127.3	289.1
K^+	$\mu mol_c\ L^{-1}$	14.2	8.1	5.2	12.2	31.6
Na^+	$\mu mol_c\ L^{-1}$	621.6	325.7	223.8	546.5	1323.5
SO_4^{2-}	$\mu mol_c\ L^{-1}$	74.1	29.0	35.9	69.3	129.9
Cl^-	$\mu mol_c\ L^{-1}$	644.5	303.0	220.3	600.7	1227.0
NO_3^{-}§	$\mu mol_c\ L^{-1}$	4.6	4.0	0.7	2.8	12.5
DOC_{abs}§	mg L^{-1}	5.7	2.8	2.2	4.9	11.1
Al_T §	µmol L^{-1}	2.5	1.9	0.5	2.1	6.9
ANC §	$\mu mol_c\ L^{-1}$	120.0	108.1	7.4	85.2	352.5
$nmCa^{2+}$§	$\mu mol_c\ L^{-1}$	35.7	27.7	8.2	32.0	72.7
$nmMg^{2+}$	$\mu mol_c\ L^{-1}$	17.9	17.4	–0.4	13.7	59.8
nmK^+	$\mu mol_c\ L^{-1}$	2.6	5.8	–6.3	2.4	10.7
$nmSO_4^{2-}$	$\mu mol_c\ L^{-1}$	7.8	14.7	–13.9	9.7	25.6

§Gran alkalinity; Nitrate (NO_3^-) was available for only ~50% of the study lakes; DOC = dissolved organic carbon estimated from absorbance at 320 nm ($DOC_{abs} = 49.5 \times ABS_{320} + 1.69$); Al_T = total (labile and non-labile) aluminium; ANC = charge balance acid neutralizing capacity ($[Ca^{2+} + Mg^{2+} + K^+ + Na^+ + NH_4^+] – [SO_4^{2-} + NO_3^- + Cl^-]$); and nm = non-marine.

100 $\mu mol_c\ L^{-1}$, indicating limited catchment sources (e.g., low geochemical weathering; see Section 4). Non-marine base cations were dominated by Ca^{2+} and Mg^{2+}; a small number of lakes had negative concentrations (one lake for Ca^{2+} and four for Mg^{2+}), suggesting retention in catchment soils. Charge balance acid neutralising capacity (ANC calculated as the difference between base cations and acid anions; Reuss and Johnson, 1986) was low with a median of 85.2 $\mu mol_c\ L^{-1}$ and ranged from –2.0 $\mu mol_c\ L^{-1}$ to 461.4 $\mu mol_c\ L^{-1}$ (Table 3.1). Acid-neutralising capacity is used as a water-quality criterion for the survival of aquatic organisms; 10% of the study lakes had ANC values less than 20.0 $\mu mol_c\ L^{-1}$, which is a widely used limit for the protection of fish species (Aherne and Curtis, 2003).

3.2.2 Changes in lake chemistry between 1997 and 2007

Statistically significant differences in lake chemistry were observed between the 1997 and 2007 surveys; concentrations of SO_4^{2-} and $nmSO_4^{2-}$ decreased on average by 9% and 58% respectively (Table 3.2). The mean decrease of $nmSO_4^{2-}$ in the study lakes was consistent with the decrease in precipitation chemistry (59%; see Section 2.3). In concert, concentrations of $nmCa^{2+}$ and $nmMg^{2+}$ decreased on average by 16%.

Despite the decrease in $nmSO_4^{2-}$ and base cation concentration, no significant difference in conductivity was observed owing to the variability in inputs of marine ions between surveys (Table 3.2). Furthermore, no statistically significant differences in DOC or Al_T were

Table 3.2. Changes (absolute [△] and percent [%]) in mean (and median) lake concentrations between 1997 and 2007 lake surveys (n = 60). Statistical difference between surveys was assessed using the non-parametric Wilcoxon signed paired test.

Variable	Unit	△ Change	% Change	Wilcoxon§
SO_4^{2-}	µmol$_c$ L^{-1}	–7.6 (–12.0)	–9.3 (–14.8)	0.001
$nmSO_4^{2-}$	µmol$_c$ L^{-1}	–10.5 (–8.1)	–57.6 (–46.2)	0.000
pH		–0.03 (0.08)	–0.60 (1.60)	0.352
Cl^-	µmol$_c$ L^{-1}	28.6 (30.9)	4.6 (5.4)	0.025
Conductivity	µS cm^{-1}	–1.1 (–0.6)	–1.1 (–0.7)	0.763
Alkalinity	µmol$_c$ L^{-1}	5.0 (6.1)	47.3 (62.5)	0.003
Ca^{2+}	µmol$_c$ L^{-1}	–3.7 (0.1)	–5.9 (0.2)	0.007
Mg^{2+}	µmol$_c$ L^{-1}	0.3 (–7.5)	0.2 (–5.6)	0.903
$nmCa^{2+}$	µmol$_c$ L^{-1}	–4.8 (–0.4)	–11.8 (–1.4)	0.000
$nmMg^{2+}$	µmol$_c$ L^{-1}	–5.3 (–7.8)	–22.9 (–35.9)	0.004
nmK^+	µmol$_c$ L^{-1}	–0.3 (0.0)	–10.6 (2.2)	0.594
DOC_{abs}	mg L^{-1}	0.7 (1.6)	13.7 (47.9)	0.054
Al_T	µmol L^{-1}	–0.03 (–0.002)	–1.2 (–0.1)	0.683

§Changes in lake chemistry were assumed to be statistically significant at $p < 0.05$.

observed between surveys (albeit almost significant for DOC). Alkalinity increased significantly by 47%, while no significant difference in pH was observed.

Previous studies during the late 1980s suggested that surface waters were generally free of ‘acid rain’ impacts owing to Ireland’s location on the western fringe of the European continent (Bowman, 1991[23]). In contrast, this study suggests that reductions in SO_2 emissions across Europe (and to a lesser extent across North America) have resulted in significant changes in surface water chemistry despite the dominant westerly airflow and the relatively low level of transboundary air pollution across Ireland. The most significant observation was the widespread decrease in lake SO_4^{2-} and $nmSO_4^{2-}$ concentrations between surveys, which is consistent with other studies in Europe and North America (Skjelkvåle et al., 2005; Stoddard et al., 1999). Non-marine base cation (Ca^{2+} and Mg^{2+}) concentration decreased between surveys owing to decreased soil ion exchange under reduced acidic deposition (Reuss and Johnson, 1986), suggesting potential recovery in catchment soils. Despite significant increases in alkalinity and decreases in lake SO_4^{2-}, no significant difference in pH and Al_T was observed between surveys. In contrast, a previous study[24] in Ireland noted a marked increase in surface water pH in concert with decreases in SO_4^{2-} during both summer and winter in acid-sensitive lakes surveyed in 1987–1989 and 1998–2000 (McGarrigle et al., 2002). Lake pH is largely controlled by the acidity of precipitation, the acidity and concentration of organic anions draining from the surrounding catchment soils and sea-salt inputs; both DOC (albeit non-significant) and sea-salts were higher during the 2007 survey. The absence of a statistically significant change (decrease) in conductivity was largely related to the constant high input of sea-salts. Aluminium concentrations were highly variable owing to the dominant influence of DOC and pH on Al_T draining catchment soils, as such, a decreasing trend in Al_T was unlikely given its positive relationship with DOC.

---

[23] The report indicated that acid-sensitive water bodies had relatively low proton and labile Al concentrations, which were not sufficient to adversely impact aquatic biota in the study sites. The waters were shown to contain healthy populations for a range of acid-sensitive organisms, indicating an unimpacted condition. However, the report did note chronic acidification in run-off waters from afforested catchments with negative impacts to biota.

[24] Sixty-nine lakes located on granite bedrock in the Connemara area of Co. Galway.

3.2.3 Chemical recovery of acid-sensitive lakes

Significant decreases in SO_4^{2-}, $nmSO_4^{2-}$ and non-marine base cations were observed between the 1997 and 2007 lake surveys, suggesting that acid-sensitive lakes and their catchment soils have responded to reductions in long-range transboundary air pollution. In concert, significant increases were observed in alkalinity; however, there were no significant changes in surface water pH. It is likely that inter-annual variations in sea-salt inputs and DOC concentrations (organic acidity) may have contributed to the lack of observed recovery of pH; previous studies have suggested that increasing trends in surface DOC may lead to increased buffering of changes in pH (Skjelkvåle et al., 2005). Nonetheless, the study supports the far-reaching benefits of emission reductions owing to the implementation of the Gothenburg Protocol under the UNECE Convention on LRTAP and EU NECD. Continued improvements in the chemistry of acid-sensitive lakes are expected under further emission reductions. However, continued monitoring of upland lakes is imperative in order to assess the combined impacts of changes in atmospheric deposition, climate and land use on the chemical and subsequent biological status of these systems.

3.3 Controls on Trace Metals in Acid-sensitive Lakes

The objective of this study was to determine the concentration and potential controls on trace metals in acid-sensitive lakes. The background concentration of trace metals in surface waters in relatively unimpacted remote areas is related to a number of factors, including lithology of the terrestrial catchment, climatic conditions and long-range atmospheric transport associated with the emission and deposition of acidifying compounds (Tarvainen et al., 1997; Steinnes, 2001). Moreover, in acid-sensitive regions, acidic deposition has led to the mobilisation of metals from catchment soils (Lydersen et al., 2002). The potential toxic effect of elevated 'free' trace metals caused by anthropogenic acidic deposition has prompted lake surveys in Europe and North America, notably in regions dominated by acid-sensitive soils and geology (Norway: Skjelkvåle et al., 2001; Italy: Tornimbeni and Rogora, 2012). While several studies have investigated the concentrations of trace metals in Irish soils (Fay et al., 2007), lake sediments and mosses (FLAME project: Bowman and Harlock, 1998; Rose et al., 1998), few studies exist for surface waters.

During spring 2008, 126 lakes[25] were sampled and analysed for total (unfiltered), dissolved (<0.45 µm filter) and organically bound (fractionated using solid phase extraction [SPE]; Tangen et al., 2002) metals. All sample fractions were analysed for trace elements (As, B, Se) and trace metals (Al, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, Ti, Tl, U, Zn, V and Hg[26]) using an Element2 High Resolution ICP-MS, except total Hg (n = 56) which was analysed using a TEKRAN 2600 series CVASF Mercury Analysis System (for further details, see Burton and Aherne, 2013). The relative importance of potential controls or drivers of concentrations in surface waters was investigated by redundancy analysis (RDA),[27] primarily focusing on four explanatory variables: (i) organic matter (expressed as DOC), (ii) geochemical weathering (expressed as lake Ca^{2+}), (iii) marine sources (expressed as lake Cl^-) and (iv) atmospheric transport (expressed as $nmSO_4^{2-}$ deposition, see Fig. 2.2) following Skjelkvåle et al. (2001). All statistical analysis incorporated trace metal observations reported as below detection (BDL) by following standard data-imputation techniques. Therefore, observations BDL were simulated by randomly sampling between zero and the reported detection limit.

---

[25] The 2008 survey included 122 lakes (see Fig. 3.1) originally surveyed during 1997 (Aherne and Farrell, 2000; Aherne et al., 2002) and 4 new lakes analysed for trace metal analysis.

[26] Concentrations of Se and Hg were analysed for only a sub-set of samples.

[27] Redundancy analysis is a multivariate statistical test used to express how a set of dependent variables (the Y-matrix) relate to a set of independent variables (the Z-matrix); it is the intermediate between principle component analysis and separate multiple regressions of each of the dependent variables. The output of RDA is presented as an ordination diagram where the independent variables are indicated by arrows and the dependent variables are indicated by points. Variables located along roughly the same arrow have a positive correlation, variables crossing at right angles have no correlation, and variables in opposite directions have a strong negative correlation. The importance of variables in the analysis is described by the length of the arrow (or distance from the origin) and is proportional to the rate of change.

Table 3.3. Summary statistics (mean, standard deviation [SD], and 5th, 50th, 95th percentile) of physical and chemical characteristics and total trace metal concentrations in the study lakes (n = 126) in 2008.

Variable	Units	Mean	SD	Percentiles			BDL[$]
				5th	50th	95th	%
Lake size	ha	5.3	8.2	0.5	2.5	24.8	
Altitude	m	278.8	163.5	67.8	254.5	593.3	
Air temperature	°C	9.7	0.5	8.9	9.5	10.4	
Precipitation	mm yr^{-1}	1568.2	355.9	1094.5	1506.5	2227.0	
pH		4.9	1.1	4.2	5.9	7.7	
Conductivity	µS cm^{-1} at 25°C	127.7	67.1	43.7	109.9	253.5	
DOC	mg L^{-1}	5.0	2.9	1.5	4.3	11.0	
Ca^{2+}	µmol$_c$ L^{-1}	227.0	412.4	40.6	91.9	971.3	
Cl$^-$	µmol$_c$ L^{-1}	789.0	442.6	265.9	698.4	1518.2	
Al	µg L^{-1}	50.57	40.27	14.92	38.60	127.29	0
As	µg L^{-1}	0.88	1.21	0.01	0.31	3.49	2
B	µg L^{-1}	9.21	3.75	4.48	8.22	16.77	0
Ba	µg L^{-1}	8.30	15.03	0.50	3.36	29.27	0
Bi	µg L^{-1}	0.78	0.33	0.39	0.68	1.28	4
Co	µg L^{-1}	0.05	0.06	0.00	0.04	0.20	91
Cr	µg L^{-1}	0.36	0.19	0.16	0.31	0.72	4
Cu	µg L^{-1}	0.27	0.66	0.01	0.05	1.04	63
Fe	µg L^{-1}	122.97	165.67	7.75	64.87	442.35	0
Hg	ng L^{-1}	3.13	1.22	1.79	2.78	5.37	0
Mn	µg L^{-1}	47.53	72.94	2.29	22.58	166.36	0
Mo	µg L^{-1}	1.35	1.06	0.65	1.05	2.79	2
Ni	µg L^{-1}	0.38	0.56	0.02	0.18	1.51	25
Pb	µg L^{-1}	0.14	0.23	0.00	0.06	0.54	20
Se	µg L^{-1}	0.99	0.57	0.14	1.03	1.74	20
Sr	µg L^{-1}	22.05	25.42	5.65	13.49	78.26	0
Ti	µg L^{-1}	2.25	3.40	0.44	1.09	10.87	1
Tl	µg L^{-1}	0.08	0.03	0.02	0.09	0.13	24
U	µg L^{-1}	0.06	0.04	0.03	0.05	0.12	23
V	µg L^{-1}	0.11	0.16	0.01	0.05	0.50	65
Zn	ng L^{-1}	2.45	3.59	0.17	0.80	8.52	62

[$] Observations below detection were simulated by randomly sampling between zero and the reported analytical limit; the proportion of lake samples below the detection limit (%BDL: proportion of imputed data) is indicated for each metal analysis.

3.3.1 Total trace metal concentrations in acid-sensitive lakes

In general, trace metal concentrations in the study lakes were low (Table 3.3), within the range of background (relatively unpolluted) surface water concentrations (Galvin, 1996). The order (highest to lowest) of total trace metal concentrations (µg L^{-1}) was: Fe > Al > Mn > Sr > B > Ba > Ti > Mo > Zn > Bi > As > Cr > Ni > Tl > Pb > Cu > U > V > Co (> Se > Cd > Be > Hg).[28] The study lakes were strongly dominated by Fe, Al and Mn and to a lesser extent by Sr and B total concentrations (Table 3.3). Given the low concentrations, measurements BDL were common for certain elements such as Co, V, Cu and Zn.

---

[28] Concentrations of Cd and Be were below detection, and Se and Hg were only analysed on a sub-set of lake samples.

The majority of the trace metals were within or towards the lower end of the expected range for unimpacted surface waters, for example, Pb concentrations in freshwaters typically range between 0.1 and 1.5 μg L^{-1} (Allen and Hansen, 1996); in the study lakes, median Pb was 0.06 μg L^{-1}. Total Hg ranged between 0.2 and 7.5 ng L^{-1} (median 2.8 ng L^{-1}); typical concentrations for surface waters range from 1 to 10 ng L^{-1} (Ravichandran, 2004). In contrast, B ranged from 3.7 to 25.1 μg L^{-1} (median of 8.2 μg L^{-1}) compared with typical concentrations in surface waters of 5 to 10 μg L^{-1} (Zhu and Wang, 2007), owing to a contribution from marine sources in the study lakes. Several trace metals (such as As, Cr, Al, Hg, Zn and Pb) showed a decreasing concentration westward, away from point sources of pollution in western Europe. Bowman and Harlock (1998) reported that metal concentrations in surface sediments in acid-sensitive Irish lakes were consistent with background levels found in the more remote parts of Europe. Further, higher concentrations were generally associated with local geochemical sources. Nonetheless, they also noted that selected lakes along the east coast had a transboundary air pollution influence.

Many trace metals in the study lakes (i.e., Al, Mn, Fe, As, B, Ba, Cu, Ni, Pb, Sr and V) were predominantly in dissolved form, although elevated particulate fractions were observed for Mn (20%), Al (24%) and Fe (33%). The labile phase (estimated as the difference between dissolved and non-labile) was the dominant dissolved form for Ba (99%), Mn (98%), Sr (98%) and Mo (79%). In contrast, the dissolved non-labile phase was dominant for Cu (97%), As (75%), Pb (62%), Fe (58%), Ni (48%) and Al (47%). Metals such as B, As, Mo, Se and Cr typically exist in surface waters at natural pH ranges in the negatively charged ionic form of borate, arsenate, molybdate, selenate and chromate; therefore, concentrations passed through the SPE column.

3.3.2 Relationship between trace metals and explanatory variables

Redundancy analysis indicated that the four explanatory variables (DOC, Ca^{2+}, Cl^- and $nmSO_4^{2-}$) explained much of the variation in the total metal dataset (Fig. 3.2). The first three axes (RDA 1 = 61.5%, RDA 2 = 19.5% and RDA 3 = 15.7% [RDA 3 not shown]) explained 97% of the variance; the first axis was dominated by Ca^{2+} (r = 0.99), suggesting that geochemical weathering was the most important control on trace metals in the study lakes. The second axis was dominated by DOC (r = 72), indicating metal complexation (with humic substances, e.g., Al and Fe) or release from sounding peat soils because of acidic or redox processes. The third axis was dominated by Cl^- (r = 0.87), and primarily reflected correlation with B (r = 0.87). An exceptionally deep Atlantic depression between 09 and 11 March 2008 led to very high wind gusts (westerlies) and the wettest March in more than a decade at a number of monitoring stations across Ireland (Met Éireann, 2008), potentially influencing the dominance of marine ions in the study lakes (see Section 3.4).

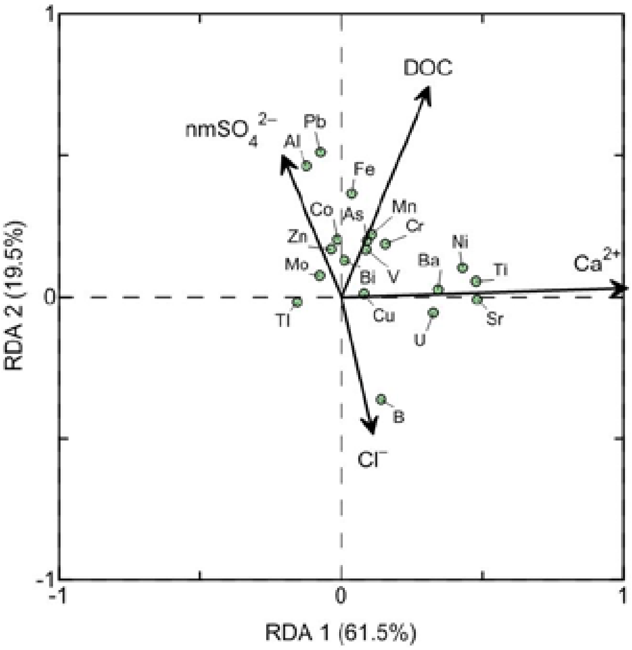


Figure 3.2. Redundancy analysis (RDA) ordination plots for total trace metals in the study lakes during 2008. Arrow lines (independent variables, vectors) indicate the biplot of each of the explanatory variables (organic matter [DOC], geochemical weathering [Ca^{2+}], marine sources [Cl^-] and atmospheric transport [$nmSO_4^{2-}$ deposition]); filled circles indicate trace metals (dependent variables).

Redundancy analysis has been used widely to evaluate controls on trace metal concentrations (e.g., see Skjelkvåle et al., 2001). In the current study, Ca^{2+} described most of the variation in total trace metal concentrations, suggesting geochemical controls. Redundancy analysis also highlighted DOC as a dominant driver, indicating a strong positive relationship with many metals. Similarly, variability in trace metals (Cd, Pb, As, Zn, Cu, Ni, Co, Fe, Mn, Cr and V) in the 1995

'Nordic Lake Survey' (n = 3000: Skjelkvåle et al., 2001) was predominantly associated with organic carbon (particularly for Fe and Mn and to a certain degree for As, Cr and V). Nonetheless, in the current study many trace metals were also directly related to long-range air pollution or indirectly through acidification. The variation in total Mo, Pb, Co, Zn and Al was influenced by the deposition of $nmSO_4^{2-}$; in addition, correlation analysis indicated a positive relationship between Hg and $nmSO_4^{2-}$.

3.3.3 *Exceedance of critical thresholds*

The concentration of total dissolved Cd, Zn, and inorganic dissolved Mn and Al are of particular interest because their observed levels may be harmful to freshwater organisms.[29] Cadmium at a concentration greater than 0.1 µg L^{-1} has been reported to affect the reproductive function of certain aquatic organisms (Tarvainen et al., 1997). In the current study, 4% of the lakes were above this limit despite the high proportion below detection (96%). Zinc concentrations greater than 5 µg L^{-1} have been reported to be harmful to brook trout in acidic waters (Sayer et al., 1989); 55% of the study lakes exhibited concentrations greater than 5 µg L^{-1} and 16% exhibited concentrations greater than 10 µg L^{-1}. Elevated Cd and Zn concentrations observed during the FLAME project (Bowman and Harlock, 1998) were reported to be associated with local geochemical deposits rather than long-range air pollution; nonetheless, their mobilisation may be influenced by acidic deposition. Labile Mn concentrations greater than 50 µg L^{-1} have been reported as toxic to brown trout (Lydersen et al., 2002); 22% of observed values were above this limit. Similarly, concentrations of inorganic monomeric Al greater than 20 µg L^{-1} may be toxic to aquatic organisms in acidic environments (Lydersen et al., 2002); 21% of the study lakes were above this limit.

3.3.4 *Long-term controls on trace metals*

Redundancy analysis suggested that geochemical weathering was the predominant control on trace metal concentrations in the study lakes. In addition, many metals had a strong positive relationship (or affinity) with DOC. Nonetheless, the variation in total Mo, Pb, Co, Zn and Al was also influenced by the acidic deposition. Since the 1980s, emission and deposition of long-range air pollution have declined in Europe and North America. This decrease has led to significant changes in the chemical composition of surface waters. As further declines in acidic input (primarily $nmSO_4^{2-}$) occur across Ireland, reduced soil acidity is expected to reduce the solubility and mobility of many trace metals (i.e., Al, Zn, Cd, Mn, Pb and Hg) to surface waters. In contrast, potential increases in DOC may enhance metal concentrations in surface waters through increasing complexation and export from the terrestrial catchment. However, organic bound metal complexes are typically less toxic than inorganic fractions (Tipping et al., 1998).

3.4 Influence of Sea-Salt Events on the Chemistry of Acid-sensitive Lakes

Climate variability and atmospheric deposition of marine ions have been shown to influence surface water chemistry on an inter-annual and potentially longer-term cyclical basis (Evans et al., 2001; Hindar et al., 2004). These factors not only influence the concentrations of marine ions in surface waters, i.e., Na^+, Cl^-, Mg^{2+}, SO_4^{2-}, but also the chemical indicators of acidification recovery: pH, alkalinity and Al concentrations. The objective of this study was to evaluate the influence of sea-salt events on acid-sensitive lakes and to assess the extent to which climate, sea-salts and anthropogenic acidic deposition influence long-term acid-base chemistry.

In general, acid-sensitive surface waters do not respond linearly to changes in acidic deposition owing to confounding factors that overshadow the anthropogenic signal. For example, extreme inputs of marine ions have been shown to cause episodic acidification, which is known as the sea-salt effect, where Na^+ and Mg^{2+} inputs displace H^+ or Al on the soil-exchange complex in shallow base-poor mineral or organic soils. Sea-salt episodes are associated with heavy storms that originate over oceans typically during the winter months. As such, the influence of the sea-salt effect is considered to be transient.

The influence of a major storm during spring 2008 was evaluated using data from the 2007 and 2008 lake surveys (Fig. 3.1). In addition, larger-scale climate

---

[29] Water Framework Directive standards for Ireland (Bowman, 2009) set annual average limits for Cd at 0.08 µg L^{-1} and Zn (in acidic water, i.e., < 10 mg $CaCO_3$) at 8 µg L^{-1}.

(North Atlantic Oscillation Index: NAOI)[30] and local climate or weather parameters (i.e., temperature, atmospheric pressure, wind speed and rainfall), acidic ($nmSO_4^{2-}$) deposition and sea-salt (Mg^{2+}) deposition[31] were used to predict lake water pH, alkalinity, Al and colour (surrogate for organic acidity) in three acid-sensitive lakes: Lough Maumwee, Co. Galway, Lough Veagh, Co. Donegal, and Glendalough, Co. Wicklow (see Fig. 3.1).

3.4.1 *Influence of a major sea-salt event*

On 10 March, 2008, a major storm moved across the south-west of Ireland as evidenced by the lowest mean sea-level pressure on record for March (950 hPa) measured at Shannon Airport. Further, all areas received heavy rains during 9–11 March, resulting in saturated soils (Met Éireann, 2008). In concert, extreme sea-salt inputs (Na^+ and Cl^-) were observed at precipitation monitoring stations located along the west coast, for example Valentia Observatory and Glenveagh. The highest daily precipitation Cl^- concentrations during 2008 were observed on 10 March; approximately 1.4 (Glenveagh 119.8 mg L^{-1}) to 5.4 (Valentia Observatory 1967 mg L^{-1}) times larger than the next highest daily observation (Fig. 3.3).

Extreme inputs of sea-salts can lead to Na^+ retention on the soil-exchange complex resulting in a reduced Na:Cl ratio in soil leachate (0.858 in sea water, typically higher in lake water owing to contribution from soil exchange; Farrell, 1995). During the May 2007 lake survey, the average Na:Cl ratio was 0.96 (n = 77;[32] Fig. 3.3). The second survey was carried out during May 2008, approximately two months after the 10 March sea-salt event. The average Na:Cl ratio during this survey was 0.82 (n = 126) suggesting Na^+ retention on the exchange complex compared with 2007. Moreover, a significantly reduced Na:Cl ratio was observed across much of the western half of the country during 2008 compared with 2007 (Fig. 3.3), suggesting a significant areal impact of sea-salts on small headwater lake catchments.

A sub-set of the 2007 survey lakes was also re-sampled during the 2008 survey (n = 52; Fig. 3.1). Sea-salt episodes have been shown to decrease pH (Allott and Brennan, 2000) and increase metal concentrations in surface waters (i.e., Al and Mn; Hindar et al., 2004). In the current study, there was a statistically significant decrease in pH, DOC and alkalinity ($p < 0.001$[33]); the median pH was 5.30 during 2007 compared with pH 4.77 during 2008 (Fig. 3.4). In concert, there was a statistically significant increase in lake Cl^- and Ca^{2+} ($p < 0.001$), as noted in previous studies (Farrell, 1995; Allott and Brennan, 2000; Evans et al., 2001). An increase in total Al was not observed, possibly because of decreased export from the terrestrial catchment associated with decreased DOC export (Al_T was primarily composed of organic bound fractions ~60%; see Section 3.3). However, there was a significant increase in Mn (see Fig. 3.4), which was not as strongly bound to organics (~20% of total Mn was bound to organic ions). The influence of the 10 March storm on lake chemistry was evident during May 2008, suggesting longer-term impacts of sea-salt events on small upland lake catchments dominated by organic soil. The re-establishment of equilibrium on the soil-exchange complex is a slow process; longer-term impacts on peats soils have been previously noted at a forested peatland plot on the west coast of Ireland (Farrell, 1995).

3.4.2 *Long-term drivers of acid-base lake chemistry*

Lough Maumwee, Lough Veagh and Glendalough have the longest continuous observed water chemistry record (since 1984) for acid-sensitive surface waters in Ireland (Bowman, 1986). They were originally selected in 1983 as part of a national acid-sensitive lake water survey, as they are remote from local industrial and agricultural influences (Bowman, 1986, 1991); they are also part of ICP Waters. The lakes were sampled in general

---

[30] The North Atlantic Oscillation Index (NAOI), defined as the difference in atmospheric pressure between Iceland and the Azores, is an index of inter-annual variability in precipitation over Europe, particularly during winter and spring. High positive values of NAOI during winter months have been associated with strong westerly winds, frontal precipitation and relatively high temperatures in the United Kingdom and Scandinavia (Hindar et al., 2004).

[31] Magnesium deposition was used as the indicator of sea-salt deposition, as sea spray is the primary source of Mg^{2+} in coastal regions.

[32] The 2007 survey included 72 lakes (see Fig. 3.1) originally surveyed during 1997 (Aherne and Farrell, 2000; Aherne et al., 2002) and five new lakes.

[33] Statistical comparison was carried out using a paired t-test or Wilcoxon test based on the data distribution.

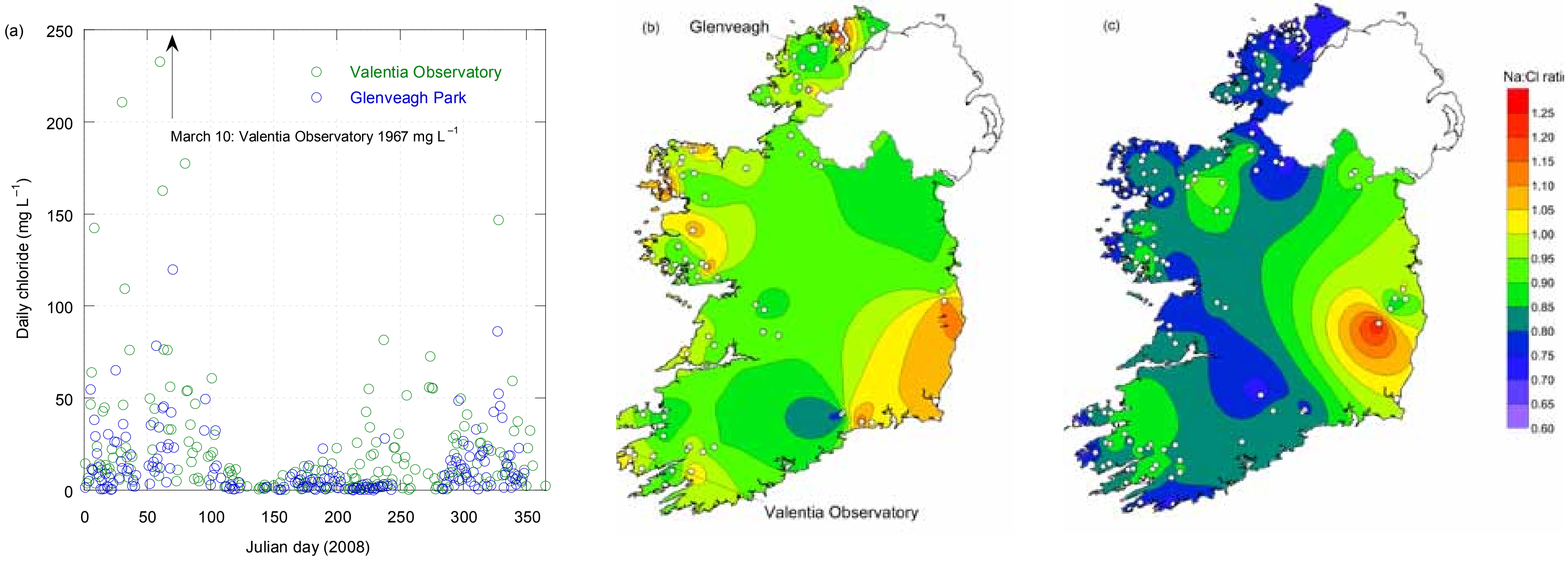


Figure 3.3. (a) Daily chloride concentrations (mg L^{-1}) at Valentia Observatory, Kerry, and Glenveagh, Donegal, during 2008 indicating elevated observations on 10 March 2008 at both monitoring stations (data source: Chemical Co-ordinating Centre of EMEP), (b) interpolated sodium:chloride ratios in lakes (n = 77) during the May 2007 survey (average ratio = 0.94), and (c) interpolated sodium:chloride ratios in lakes (n = 126) during the May 2008 survey (average ratio = 0.82), two months after the 10 March 2008 sea-salt event.

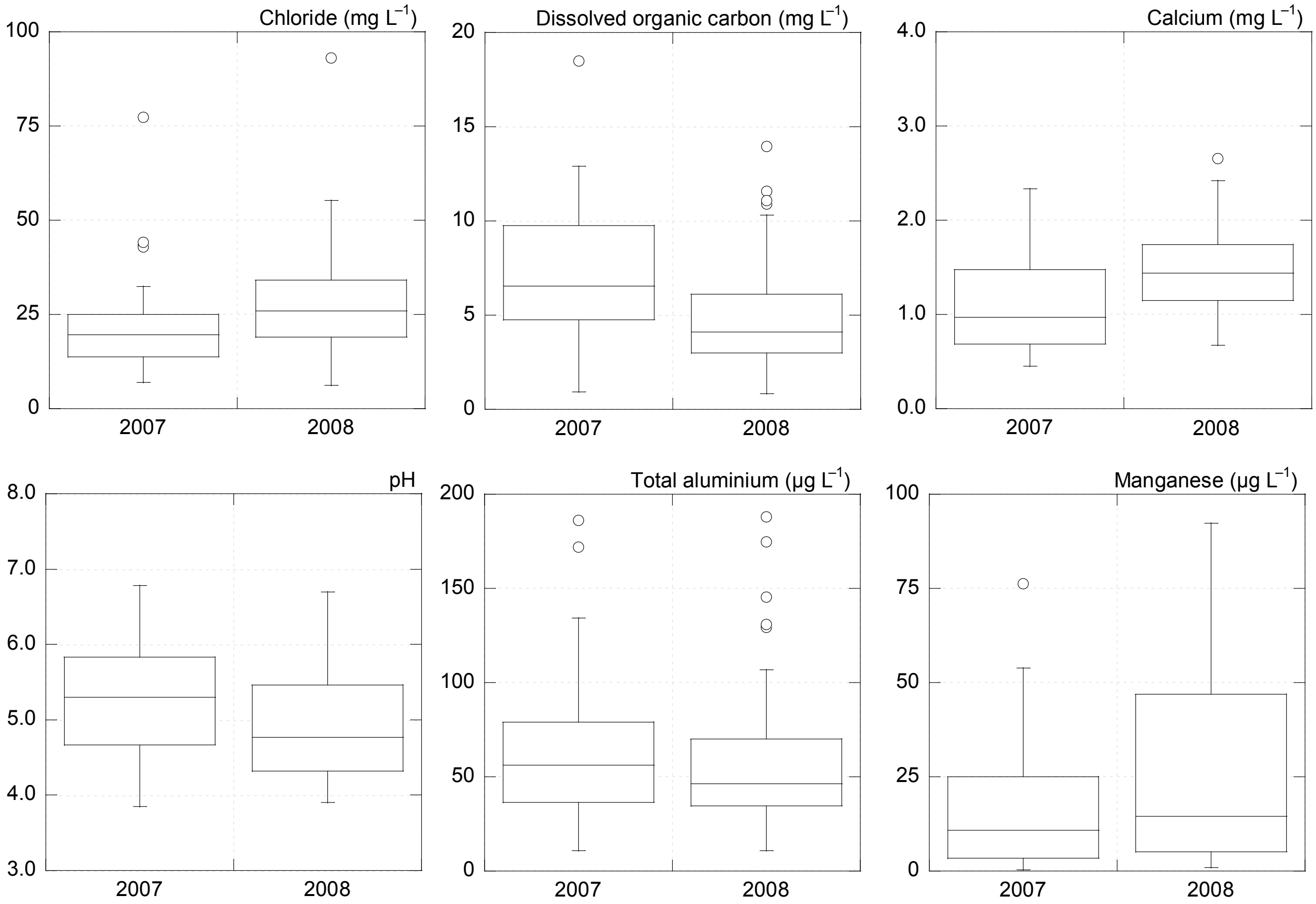


Figure 3.4. Box-plot comparison of paired lake chemistry observations from the 2007 and 2008 surveys (n = 52), before and after the 10 March 2008 sea-salt event. The box encloses 50% of the data, with the median displayed as a line. The whiskers represent 1.5 times the interquartile distance, and open circles represent observations outside this range.

on a bi-annual basis (winter [typically November or December] and late spring [May or June]) during 1984–2009 (1988 for Lough Veagh), with greater frequency[34] during 1984–1985, 1987–1989 and 2007–2009. To maintain consistency between data (lake chemistry, precipitation chemistry and meteorology), only data from 1991 onwards were included in this study, and lake samples during 2007–2009 were selected to coincide with sample months during the earlier period. To accommodate seasonal variation in water chemistry, separate assessments were performed for winter–spring and summer–autumn. The long-term pattern in wet deposition chemistry at each study lake was taken from the nearest monitoring stations. Similarly, precipitation volume, average temperature, wind speed and atmospheric pressure data were taken from the synoptic meteorological station[35] closest to the lakes. Mean monthly NAOI values were obtained from the National Weather Service, Climate Prediction Centre.[36]

---

[34] Lough Maumwee and Glendalough were sampled at a frequency of 20 times per year during 1984–1985, 10 times per year during 1987–1989 and bi-annually thereafter until 2007 when approximately monthly sampling began. Lough Veagh was examined 10 times per year during 1988–1989 and bi-annually thereafter until 2007 when approximately monthly sampling began.

[35] Met Éireann URL: www.met.ie

[36] URL: www.cpc.ncep.noaa.gov

The influence of marine ions, acidic deposition and climate on surface water parameters, that is, pH, alkalinity, and colour, was assessed using stepwise multiple linear regression for the temporal window 1991–2008. To reduce the potential of collinearity among predictor variables, the variance inflation factor (VIF, which quantifies the severity of multicollinearity in ordinary least squares regression analysis) was used to ensure that highly correlated variables were not included in the same predictive model. In addition, a predictor variable was added only if it explained more than 1% of the variation in a water chemistry parameter (significant relationships were identified at $p < 0.05$).

3.4.3 *Influence of climate and deposition drivers on acid-base chemistry of lakes*

Atmospheric deposition and climate drivers explained between 30 and 90% of the variation in lake acid-base chemistry (Table 3.4). Local climate variables indicative of storminess or heavy precipitation, that is high wind

Table 3.4. Multiple linear regression models for the study lakes: Glendalough, Lough Maumwee and Lough Veagh for winter–spring (WS) and summer–autumn (SA) seasons.[\$]

Season	Dependent	R^2	n	p	Variable	Coefficient	p
	Glendalough						
SA	pH	0.86	7	0.001	Constant	134.55	0.031
					Air pressure	–0.13	0.035
					Mg^{2+}	0.15	0.008
	Colour	0.72	7	0.034	Constant	–267.12	0.040
					Wind speed	37.07	0.018
					Mg^{2+}	–7.40	0.046
	Aluminium	0.90	5	0.013	Constant	2.37	0.485
					$nmSO_4^{2-}$	0.76	0.013
WS	Aluminium	0.62	9	0.012	Constant	9.60	0.001
					$nmSO_4^{2-}$	0.26	0.012
Lough Maumwee							
SA	Alkalinity	0.32	13	0.045	Constant	702.18	0.021
					Wind speed	–50.06	0.045
	pH	0.55	12	0.006	Constant	6.70	<0.0001
					Mg^{2+}	–0.02	0.006
WS	pH	0.32	14	0.035	Constant	6.23	<0.0001
					NAOI	–0.48	0.035
	Colour	0.35	12	0.043	Constant	63.75	0.006
					Wind speed	–2.99	0.043
	Aluminium	0.57	10	0.012	Constant	3.96	<0.0001
					NAOI	3.65	0.012
Lough Veagh							
SA	Alkalinity	0.59	12	0.003	Constant	–17114.31	0.004
					Air pressure	17.00	0.003
	pH	0.60	12	0.006	Constant	12.20	<0.0001
					Wind speed	–0.45	0.002
					Mg^{2+}	0.04	0.041
	Colour	0.53	11	0.011	Constant	76.06	<0.0001
					$nmSO_4^{2-}$	–9.94	0.011
WS	Colour	0.30	13	0.050	Constant	59.12	<0.0001
					Mg^{2+}	–0.47	0.050

[\$] Model predictive ability was based on adjusted R^2, only significant models ($p < 0.05$) are shown. Note difference in the number of observations (n) for each regression model.

speed and low air pressure, predicted 32 and 59% of the variation in alkalinity during summer–autumn at Lough Maumwee and Lough Veagh, respectively. The variability in pH and colour was related to sea-salt inputs; Mg^{2+} deposition in combination with wind speed or air pressure were the best predictors of summer–autumn lake pH at Glendalough and Lough Veagh, while Mg^{2+} deposition was the best predictor of pH in Lough Maumwee. Colour in lakes during the summer–autumn season was related to wind speed and Mg^{2+} deposition at Glendalough, or negatively to $nmSO_4^{2-}$ at Lough Veagh. These results are consistent with previous studies suggesting that elevated DOC is related to declines in marine and anthropogenic SO_4^{2-} deposition (Monteith et al., 2007). In contrast, higher $nmSO_4^{2-}$ deposition was associated with higher Al concentrations in Glendalough during both summer–autumn and winter–spring seasons. This is expected as inputs of acidity associated with anthropogenic deposition, particularly in acid-sensitive terrain, can replace Al on the soil exchange complex.

Drivers and their predictive potential varied among study lakes, seasons and lake parameters. Nonetheless, local climatic variables contributed to more predictive models than NAOI. The models for the study lakes indicate that in addition to anthropogenic influences local climate and marine deposition exert control on water chemistry in acid-sensitive lakes (along coastal margins). As such, future extreme weather events potentially associated with increased climate variability will play a significant role in the long-term chemistry of acid-sensitive lakes.

3.5 Controls on Greenhouse Gas Concentrations in Acid-sensitive Lakes

There are more than 9000 small lakes (<50 ha) across Ireland (many located in acid-sensitive regions) that provide a range of ecosystem services. Freshwater ecosystems worldwide are well-known sources of greenhouse gases to the atmosphere (Cole et al., 2007; Tranvik et al., 2009). Moreover, small lakes have been identified as having disproportionately high fluxes of gases relative to their area. However, there are few observations of greenhouse gases in acid-sensitive lakes in Ireland and limited understanding on their controls. The objective of this study was to investigate open-water concentrations of carbon dioxide, methane and nitrous oxide greenhouse gases (CH_4, CO_2 and N_2O) in acid-sensitive lakes (n = 121) and to explore their relationships[37] to lake and catchment characteristics (water chemistry, hydrology and physical landscape features).

Lake samples for greenhouse gas analysis were collected using a headspace analysis technique. A 1.1 L heavy-walled glass bottle was overfilled and capped, and a 60 mL headspace (ambient air) was immediately introduced to the sealed bottle by simultaneously extracting an equivalent volume of water using a double-syringe system. The sample bottle was shaken vigorously for 2 minutes to equilibrate the dissolved gases with the headspace. Two 12 mL headspace samples were removed from the bottle by sequentially re-injecting aliquots of displaced lake water. Each headspace sample was injected into a pre-evacuated Exetainer® vial for storage until analysis. At approximately half of the lakes, a 12 mL ambient air sample was also collected from a height of 2 m and injected into a pre-evacuated vial. Trace gas concentrations in the headspace and ambient air samples were analysed by gas chromatography (see Whitfield et al., 2011 for further details).

3.5.1 Greenhouse gas concentrations and relationships with environmental variables

The study lakes were predominantly supersaturated with biogenic greenhouse gases. Median concentrations of CO_2, CH_4 and N_2O were 21 μmol L^{-1}, 56 nmol L^{-1}, and 11 nmol L^{-1}, respectively (Fig. 3.5 and Table 3.5). Nitrous oxide showed the least variability of the three gases with dissolved concentrations being close to saturation (average 1.1 times saturation); 19 of the study lakes were undersaturated. Average saturation was somewhat higher for CO_2 (1.8 times saturation), with a comparable number of undersaturated lakes (n = 20). In contrast, CH_4 concentration, while more variable than the other gases, was above saturation in all of the lakes.

---

[37] Gas concentrations expressed as the difference between measured and saturation (equilibrium) concentrations (delta [Δ]).

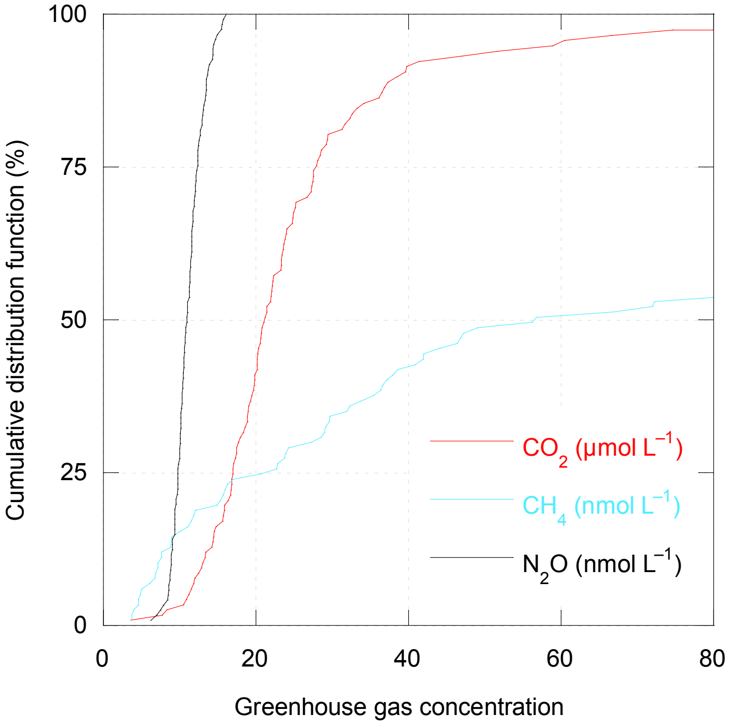


Figure 3.5. Cumulative distribution function of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) gas concentrations in the study lakes during the 2008 survey.

There were a number of significant relationships between dissolved gases and environmental variables, with catchment structure and hydrology variables among the strongest (Table 3.5). Individually, however, none of the relationships explain more than a moderate amount of the variability in the gas concentrations. Delta CO_2 was significantly related to only two variables, DOC (positive) and lake area (negative). Further, DOC was the only variable significantly related to both ΔCH_4 and ΔCO_2, and while the carbon gases were significantly related to one another the relationship was not particularly strong.

Delta CH_4 was significantly related to many of the environmental parameters; DOC and inorganic carbon were among the strongest of the relationships. Delta CH_4 was lower in higher elevation catchments and those with greater areas of rock, and was positively related to forest and grassland coverage, suggesting that as catchment land cover transitions from rock to vegetation cover the amount of allochthonous carbon contributed to the lakes increases. A significant negative relationship between d-excess[38] and ΔCH_4 was observed, indicating that CH_4 concentrations were higher in catchments where water movement was more sluggish and the lakes were more evaporatively enriched. The significant correlations observed for ΔN_2O were generally opposite to those for CH_4. Significant positive relationships with catchment elevation and d-excess, and negative with grassland cover, suggested that N_2O tended to be more supersaturated in rocky throughflow catchments at higher elevation. Nitrous oxide was supersaturated even in these oligotrophic lakes, suggesting that, under natural conditions, small headwater acid-sensitive lakes typically act as N_2O sources to the atmosphere.

---

[38] Deuterium (^2H) excess (d-excess) is an indicator of the offset below the global meteoric water line of Craig (1961), arising due to enrichment of heavy isotopes in residual waters produced during open water evaporation. In surface waters, d-excess can be used as an indicator of the hydrologic character of a catchment, where sluggish flow and high evaporation losses yield lower d-excess values, and more throughflow type systems are associated with d-excess values closer to the signature of precipitation in the region.

Table 3.5. Median lake chemistry and catchment characteristics for the study lakes (n = 121), and Spearman's rank correlation coefficients between lake and catchment characteristics and excess concentrations§ of dissolved carbon dioxide (ΔCO_2), methane (ΔCH_4), and nitrous oxide (ΔN_2O). Significant correlations are denoted by an asterisk ($p \leq 0.01$) or double asterisk ($p \leq 0.001$).

Variable			Correlation coefficients		
	Units	Median	ΔCO_2	ΔCH_4	ΔN_2O
Conductivity	µS cm^{-1}	110	–0.01	0.43**	–0.36**
pH		5.8	–0.06	0.17	–0.20
Gran alkalinity	mg L^{-1}	0.7	0.03	0.26*	–0.21
DOC	mg L^{-1}	4.2	0.31**	0.55**	–0.32**
Inorganic carbon	mg L^{-1}	0.7	0.16	0.42**	–0.25*
Chloride	mg L^{-1}	24.8	–0.02	0.20	–0.19
Calcium	mg L^{-1}	1.8	0.14	0.47**	–0.26*
SiO_2	mg L^{-1}	0.08	–0.02	–0.04	0.17
NH_4-N	µg L^{-1}	10	0.20	0.20	–0.18
NO_3-N	µg L^{-1}	10	–0.17	–0.25	0.07
Precipitation	M	1.6	–0.04	–0.27	0.18
Forest cover	%	0	0.20	0.35**	–0.15
Heath cover	%	41	0.14	0.01	0.13
Grassland cover	%	0	0.10	0.44**	–0.33**
Rock cover	%	12	–0.20	–0.38**	0.13
Catchment elevation	M	258	–0.06	–0.51**	0.32**
Lake area	Ha	2	–0.28*	–0.14	–0.13
Catchment area	Ha	17	–0.16	–0.08	–0.04
Relative area		0.12	–0.10	–0.05	–0.07
d-excess	‰	8	–0.09	–0.30*	0.30**
CO_2	µmol L^{-1}	21			
CH_4	nmol L^{-1}	56			
N_2O	nmol L^{-1}	11			

§Excess concentrations are expressed as the difference between measured and saturation (equilibrium) concentrations (delta [Δ]).

Table 3.6. Average and standard deviation of estimated atmosphere–lake flux rates of carbon dioxide, methane and nitrous oxide between lake and atmosphere. Negative flux rates indicate movement of the gas from the atmosphere to the lake.

Gas	CO_2 (± SD)	CH_4 (± SD)	N_2O (± SD)
	mmol m^{-2} d^{-1}	mmol m^{-2} d^{-1}	µmol m^{-2} d^{-1}
Undersaturated	–3.3 ± 3.3	–	–0.66 ± 1.0
Supersaturated	17 ± 29	0.36 ± 0.7	1.7 ± 1.4
All lakes	14 ± 28	0.36 ± 0.7	1.3 ± 1.6

The average CO_2 emissions for all study lakes was 14 mmol CO_2 m^{-2} d^{-1}, including lakes that were sources and sinks (Whitfield et al., 2011). This corresponded to an average partial pressure of 615 µatm which is comparable with the average for temperate systems (Sobek et al., 2005). Although a small number of lakes were undersaturated with CO_2, these lakes were generally close to atmospheric equilibrium and therefore had low rates of CO_2 uptake (Table 3.6). All lakes were supersaturated with CH_4 and the average efflux to the atmosphere was 0.36 mmol m^{-2} d^{-1}. The average flux rate for N_2O across all lakes (sinks and sources) were low (1.3 µmol m^{-2} d^{-1}) and exhibited low variability. In general, the flux rates in the current study were comparable to emissions estimates for lakes of a similar size in Finland (Huttunen et al., 2002).

The current study suggests that small headwater acid-sensitive lakes are predominantly supersaturated with CO_2, CH_4 and N_2O gases. These lakes have the potential to efflux biogenic gases on a continual basis, as they are generally ice-free and exposed to strong winds that keep them well mixed. Further, catchment structure and hydrologic character had an influence on gas dynamics, suggesting that climate-induced changes in hydrology, changes in land management or atmospheric deposition (specifically N deposition) may affect the future greenhouse gas dynamics of these lakes.

4 Physicochemical Characteristics of Upland Acid-sensitive Soils

4.1 Survey of Upland Acid-sensitive Soils

In general, lake catchments are spatially dominated by soils, which mediate their response to acidic deposition because a greater proportion of deposition falls onto the terrestrial catchment and percolates through soil before reaching the lake. Further, soils may act as long-term sinks for many atmospheric pollutants, reducing their input to lakes. The response of acid-sensitive aquatic ecosystems to changes in inputs of atmospheric pollutants is strongly dependent on the physicochemical characteristics of the catchment soils, as groundwater inputs are typically negligible in upland ecosystems. However, there are fewer observations of soils in upland catchments; soil surveys and associated chemical analysis of modal profiles are predominantly limited to agricultural soils (e.g., see General Soil Map of Ireland, Gardiner and Radford, 1980), owing to their accessibility and economic importance.

The National Soils Database[39] and Irish Soil Information System (ISIS) have greatly increased observational data on the national soil resource; nonetheless, both have limited physicochemical and geochemical data for upland acid-sensitive regions. The objectives of this study were to describe the physicochemical characteristics of acid-sensitive soils (Section 4.2), evaluate the relationship between soil and lake chemistry (Section 4.3), and evaluate long-term soil weathering rates (Section 4.4). Soil sampling was carried out in conjunction with lake surveys, that is, soils were sampled within lake catchments during 2008 and at representative acid-sensitive mineral soil sites during 2009 based on the General Soil Map of Ireland (Mountain and Hill, and Hill physiographic divisions; Gardiner and Radford, 1980). The study provided a comprehensive assessment of the environmental status of upland acid-sensitive soils, filling key knowledge gaps in relation to their physicochemical and geochemical characteristics.

During 2008 and 2009, soil samples were collected at 60 sites in upland acid-sensitive regions (Fig. 4.1). Soils were sampled by fixed depth; at each site soil was collected by auger from the corner points and the centre point of a 20 m × 20 m sampling grid at three depths (0–10 cm, 15–25 cm and 40–50 cm). Soils were composited by depth to give a maximum of three samples per site depending on soil depth (n = 155 from a maximum of 180). In addition, bulk density samples were collected from three depths (0–10 cm, 15–25 cm and 40–50 cm) at the centre sampling point. Bulk density was sampled using standard sharpened steel cylinders of fixed volume. A comprehensive suite of physical, chemical and geochemical analysis was carried out on all sites (see Table 4.1 and Appendix 2).

4.2 Physicochemical Characteristics of Acid-sensitive Soils

The median site-average soil pH (H_2O) was 4.03 (range 3.28–6.78), with the soil cation exchange complex dominated by exchangeable H^+, Al^{3+} and Ca^{2+}. Soil physicochemical properties were strongly influenced by the level of organic matter as determined by loss-on-ignition (LOI; average 36% and range 4–97%), with significant differences between organic and mineral soils. Average soil physicochemical properties[40] categorised by LOI, that is soils with <20% classified as mineral (Table 4.1), were statistically different[41] between organic and mineral soils, except for exchangeable Ca^{2+}, Al^{3+}, and Mn^{2+}, and inorganic phosphorous. Similarly, the spatial pattern in average soil pH (weighted by bulk density) was strongly influenced by organic matter, with organic soils (LOI > 20%) showing lower pH values owing to greater levels of organic acids (Fig. 4.1).

---

[39] URL: erc.epa.ie/nsdb

[40] Weighted-average based on bulk density.

[41] Mann-Whitney U-test $p< 0.05$.

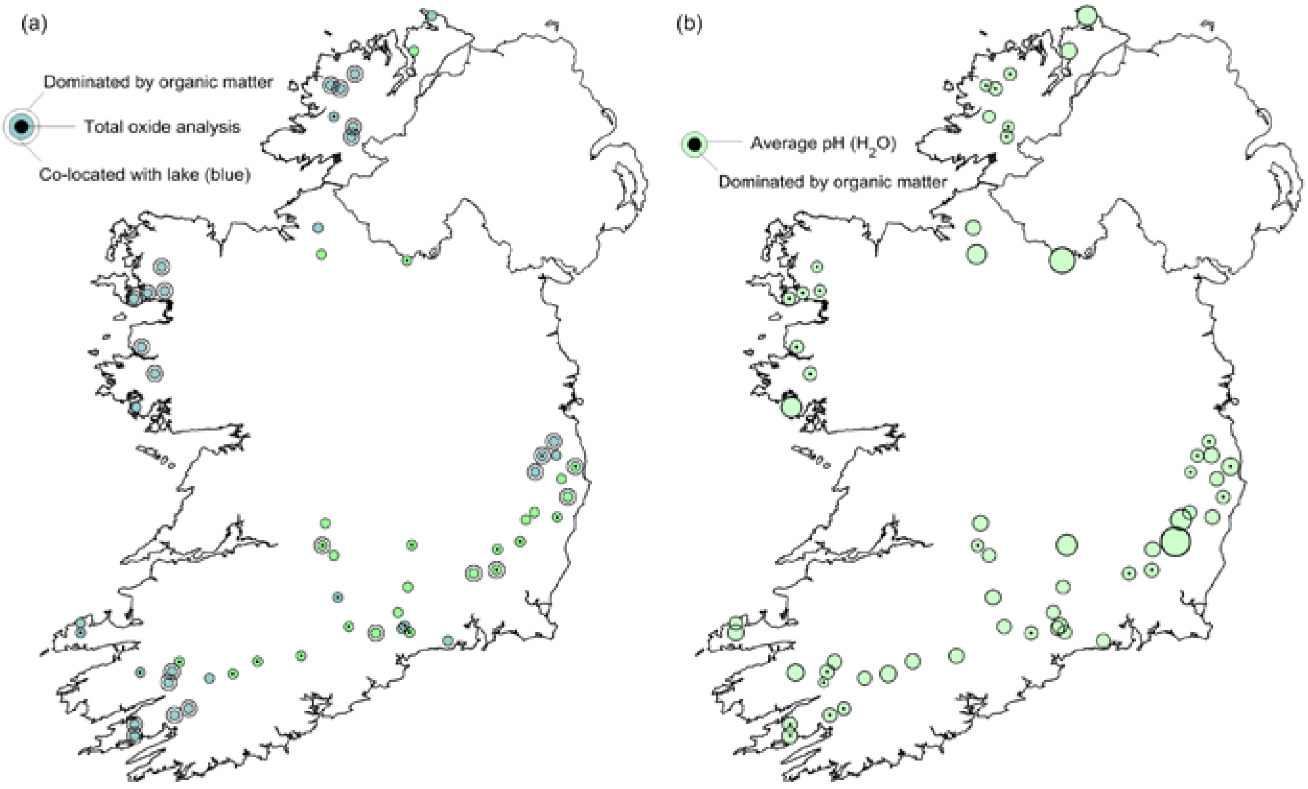


Figure 4.1. (a) Location of soil survey sites (n = 60) sampled during 2008 and 2009. Soil survey pits co-located with survey lakes (n = 31; see Fig. 3.1) are indicated by blue-filled circles. Soils dominated by organic matter (i.e., profile weighted-average loss-on-ignition [LOI] > 20%) are indicated by an outer circle. The sub-set of soil survey sites (n = 20) with total oxide analysis are indicated by an inner filled black circle. (b) Soil profile weighted-average (by bulk density) pH (H_2O) for the study sites (n = 60). Circle size indicates range in pH (3.28–6.78); soils dominated by organic matter (i.e., profile weighted-average LOI > 20%) are indicated by an inner filled black circle.

Loss-on-ignition was also a strong predictor of soil physicochemical properties, for example, bulk density, carbon, cation exchange capacity (CEC) and exchangeable acidity (Fig. 4.2). The predictive capacity of LOI for bulk density ($R^2 = 0.75$) and carbon ($R^2 = 0.92$) is consistent with previous studies (Hyland et al., 2013; de Vos et al., 2005a, 2005b). Similarly, higher CEC and exchangeable acidity is typically associated with higher organic matter content, as it is the dominant source of soil surface charge in course-grained soils (Johnson, 2002); the study soils were dominated by sand compared with clay (site average: ~50% compared with <2%; Table 4.1). Exchangeable iron and aluminium were highly correlated to exchangeable acidity,[42] as it is a measure of the amount of acid cations (e.g., iron, aluminium and hydrogen) on the CEC. There are many sources of acidity in soil, for instance the formation of carbonic acid from atmospheric CO_2, the decomposition of organic matter and the input of acidic deposition. In the study soils, in addition to LOI, anthropogenic SO_4^{2-} deposition (see Fig. 2.2) was also a predictor of exchangeable Fe and Al (Fig. 4.2). This suggests a relationship between air pollution, rainfall and soil hydrogen concentration.

---

[42] Pearson product-moment r = 0.57 and r = 0.63 respectively.

Table 4.1. Summary soil physicochemical characteristics[§] averaged (weighted on bulk density) by soil organic matter (organic [LOI > 20%] and mineral [LOI <20%]) and soil types from the general soil map of Ireland[§§] (Gardiner and Radford 1980).

Soil type (n)	ρ	pH	LOI	Sand	Clay	ExAc	Ca^{2+}	Mg^{2+}	K^+	Na^+	Al^{3+}	Mn^{2+}	Fe^{3+}	CEC	P_{inorg}	P_{org}
	$g\ cm^{-3}$	H_2O	%	%	%	$mmol_c\ kg^{-1}$									$mg\ g^{-1}$	
Organic (27)	0.253	3.87	47.4	47.1	1.6	47.20	27.72	16.78	9.83	7.12	32.44	4.60	2.59	212.83	0.09	0.43
Mineral (33)	0.737	4.17	8.9	50.8	1.9	24.65	24.64	8.14	2.81	1.62	23.47	1.62	1.46	93.50	0.08	0.25
Blanket peat (5)	0.393	4.21	22.8	47.8	2.4	28.48	60.36	7.95	4.07	3.61	20.76	0.99	1.35	147.26	0.06	0.38
Lithosols (23)	0.462	3.96	22.6	51.0	1.3	32.99	16.12	6.86	6.43	3.63	27.87	1.89	2.09	130.51	0.09	0.32
Peaty podzols (20)	0.540	4.14	15.0	53.1	1.7	29.28	18.60	13.99	3.17	2.34	26.01	2.23	1.48	88.88	0.06	0.24
Brown podzolics (8)	0.638	4.17	14.1	47.7	2.3	31.15	37.51	7.30	3.36	1.79	26.66	4.59	2.20	135.13	0.12	0.35
Acid brown earth (3)	0.801	4.24	7.9	38.5	4.1	28.67	18.67	8.56	3.69	1.90	23.95	0.75	1.27	110.89	0.03	0.18

[§] Bulk density (ρ), pH (H_2O), loss-on-ignition (LOI), sand, clay (silt = 100 – sand – silt), exchangeable acidity (ExAc), exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, Mn^{2+} and Fe^{3+}), cation exchange capacity (CEC), inorganic phosphorous (P_{inorg}) and organic phosphorous (P_{org}; Total P = P_{inorg} + P_{org}); exchangeable base cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) determined by ammonium chloride extraction; exchangeable acidity and exchangeable cations (Al^{3+}, Mn^{2+} and Fe^{3+}) determined by potassium chloride extraction. [§§] National coverage of soil types (% of terrestrial Republic of Ireland): blanket peat (10.8%), brown podzolics (12.0%), ǀLithosols and outcroping rock (3.1%), peaty podzols (7.3%), and acid brown earth (9.4%).

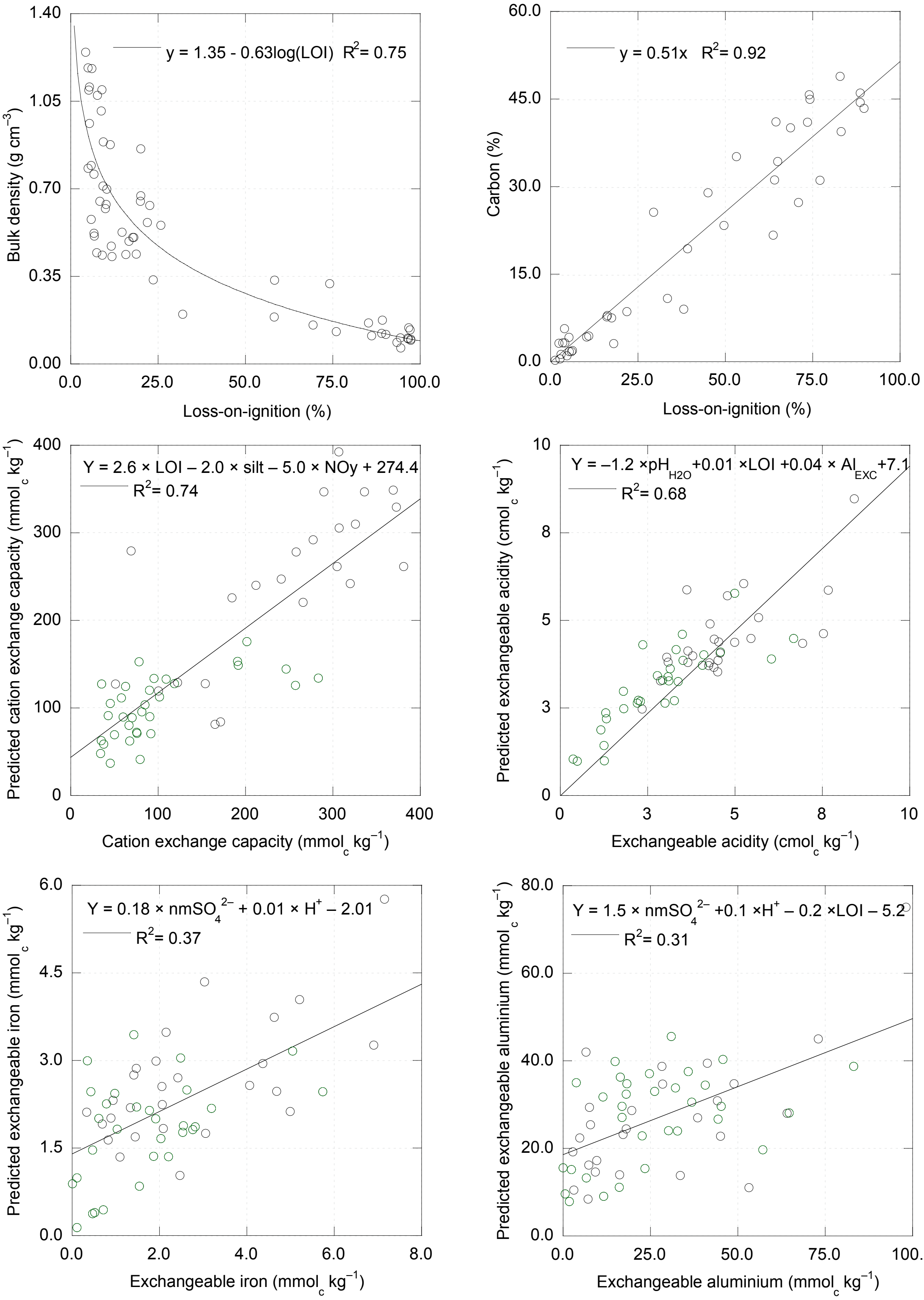


Figure 4.2. Relationships between site-average soil physicochemical properties (n = 60); soil loss-on-ignition (LOI) against bulk density and organic carbon, and predicted cation exchange capacity (CEC) (where NOy = oxidised nitrogen deposition), predicted exchangeable acidity (where Al_{EXC} = exchangeable aluminium), predicted exchangeable iron (where $nmSO_4^{2-}$ = anthropogenic sulphate deposition and H^+ = soil hydrogen [H_2O]) and predicted exchangeable aluminium against observed. Predictive models were derived using multiple linear regression. Sites with profile-average (weighted by bulk density) LOI <20% (mineral soils) are indicated by a green circle.

4.3 Relationship between Lake and Soil Chemistry

A sub-set of the soil study sites were located within the lake survey catchments (see Fig. 4.1) providing co-located chemistry data for soils and surface waters. Several statistically significant relationships were observed between lake and soil chemistry variables, suggesting connectivity (see Fig. 4.3); however, the relationships differed for organic and mineral soils. Lake Na^+ concentration was related to soil exchangeable Na^+; the relationship was stronger for organic soils (R^2= 0.47), suggesting a greater connectivity between organic soils and adjacent surface waters. The large difference in slope between organic and mineral soils was reduced when considering pool size as bulk density was considerably lower for organic soils (see Table 4.1).

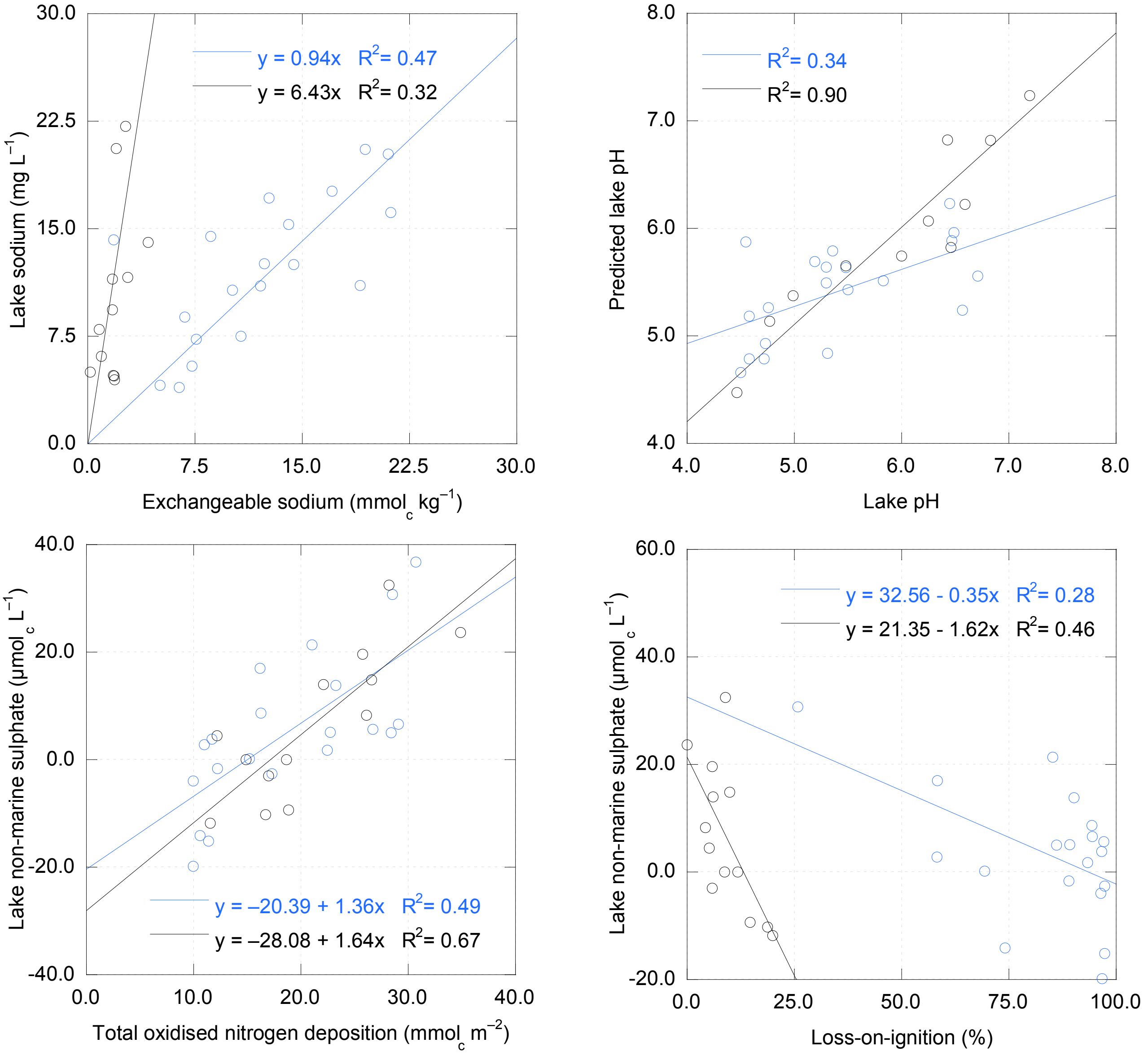


Figure 4.3. Relationships between site-average soil physicochemical properties and co-located lake chemistry (n = 33) for mineral (n = 13) and organic soils (n = 20); soil exchangeable sodium against lake sodium concentration, observed and predicted pH (mineral: 0.67 × clay + 0.12 × anthropogenic sulphate deposition – 0.11 × oxidised nitrogen deposition + 4.71 and organic: 0.86e–3 × rainfall – 0.88e–3 × hydrogen [$CaCl_2$]+ 4.02), oxidised nitrogen deposition against lake non-marine sulphate, and loss-on-ignition against lake non-marine sulphate. Predictive models were derived using (multiple) linear regression. Sites with profile-average (weighted by bulk density) loss-on-ignition > 20% (organic soils) are indicated by a blue circle.

Lake pH was also significantly related to soil properties; predicted lake pH in acid-sensitive catchments dominated by mineral soils was strongly related to the proportion of soil clay content, with higher clay, indicative of greater soil mineral weathering, and higher lake pH ($R^2 = 0.90$). In addition to clay content, anthropogenic deposition was a significant predictor variable, suggesting lake pH was influenced by acidic deposition (see Fig. 4.3). In contrast, predicted lake pH for acid-sensitive catchments dominated by organic soil was related to soil hydrogen ($CaCl_2$) and rainfall volume.

Non-marine SO_4^{2-} in lakes was strongly related to anthropogenic deposition.[43] The relationship was slightly stronger for mineral soils ($R^2 = 0.67$); however, the slopes were similar for both soil types, suggesting comparable increases in surface waters SO_4^{2-} concentrations with increasing anthropogenic deposition. However, SO_4^{2-} lake concentration was also related to organic matter in the catchment soils, suggesting that higher LOI was associated with greater retention of SO_4^{2-} in catchment soils (or reduction in organic soils). As such, the long-term chemical response of surface waters to transboundary air pollution is dependent upon the physicochemical properties of the surrounding catchment soils, with significant differences between organic and mineral soils. The observed relationships in the study catchments suggest that soils mediate the influence of acidic deposition on surface waters; SO_4^{2-} is considered to be a 'mobile' anion with limited adsorption in mineral soils as seen in study catchments. The associated acidity may be buffered by catchment soils or transported to surface waters.

4.4 Soil Geochemistry and Weathering

The sensitivity of soils and adjacent surface waters to acidic deposition is strongly related to geochemical weathering, which represents the only long-term supply of base cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) other than atmospheric deposition to buffer incoming acidic deposition. Soils with low weathering rates are inherently sensitive to acidic deposition as they have lower buffering potential. Chemical weathering ultimately depends on the mineralogy of the soil parent material, acidity of soil solution, temperature and subsequent surface reaction rates of the soil minerals (Jönsson et al., 1995).

Ternary plots[44] based on major element or total oxide chemistry can be used to quantitatively understand the bulk chemical changes associated with weathering and soil formation. For instance, A–CN–K (Al_2O_3–$CaO+Na_2O$–K_2O) ternary diagrams (Nesbitt and Young, 1989) have been used widely to evaluate major element data from soils in terms of mineralogical composition and degree of weathering; chemical weathering leads to a loss of Na^+ and Ca^{2+}, changing mineralogical compositions towards the apex of the A–CN–K ternary diagram. Total oxide analysis was carried out at a subset of the soil study sites (n = 20; see Fig. 4.1). On the A–CN–K ternary diagram, the majority of the study sites plotted close to the idealised mineral compositions for muscovite and illite (taken from McLennan, 1995), which are structurally similar phyllosilicate minerals composed of aluminium and potassium (Fig. 4.4). These minerals are common in argillaceous sedimentary rocks; based on the Bedrock Geological Map of Ireland (1:500,000; McConnell and Gatley, 2006), the majority of the study sites were classified as sedimentary rocks, for example, sandstone, greywacke and shale. As such, the majority of the study sites with total oxide analysis had a similarly high degree of weathering and soil formation. In contrast, the sites classified as granite were positioned between plagioclase and K-feldspar in the A-CN-K ternary plot. The majority of the acid-sensitive mineral soils in the south (Fig. 4.1) were predominantly associated with sandstone parent material, whereas granite parent material was confined to Wicklow, Galway and Donegal, and predominantly associated with organic soils.

Similar to A–CN–K diagrams, chemical weathering indices are commonly used to characterise weathering profiles. The indices incorporate bulk major element oxide chemistry into a single value for different parent materials. The Chemical Index of Weathering (CIW; $100 \times [Al_2O_3 / (Al_2O_3 + CaO + Na_2O)]$) is essentially a measure of the extent of conversion of feldspars to clays

---

[43] Notably oxidised N deposition rather than $nmSO_4^{2-}$, suggesting that mapped oxidised N deposition may provide a better spatial representation of anthropogenic deposition (see Fig. 2.2).

[44] A ternary or triangle plot is a barycentric plot on three variables which sum to a constant, i.e., it graphically depicts the ratios of three variables as positions on an equilateral triangle.

(Harnois, 1988). It represents a ratio of predominantly immobile Al_2O_3 to the mobile cations Ca^{2+} and Na^+ given as oxides in molecular proportions. The index ranges between 50 and 100; a higher index represents more weathered soils that are poor in basic minerals. There was a significant negative relationship between CIW and soil exchangeable Ca^{2+} ($R^2 = 0.66$) at the sub-set of sites with total oxide analysis (see Fig. 4.4). This suggests that the more weathered (base poor) soils had lower exchangeable Ca^{2+} and lower long-term acid buffering. Exchangeable Ca^{2+} was also strongly correlated to average soil pH ($r = 0.86$) at sites with total oxide analysis. In general, the CIW and A-CN-K plot suggest that the majority of the soil study sites had highly weathered acid-sensitive parent material, dominated by phyllosilicate minerals such as muscovite, with low chemical weathering of base cations. These acid-sensitive soils historically had limited buffering capacity to chronic elevated acidic deposition, leading to greater mobilisation of metals such as Al^{3+}, and potentially greater impacts on aquatic biota (Bowman and Bracken, 1993). Under reduced acidic deposition, recovery will initially replenish base cations lost from the soil cation exchange complex, delaying chemical recovery in surface water.

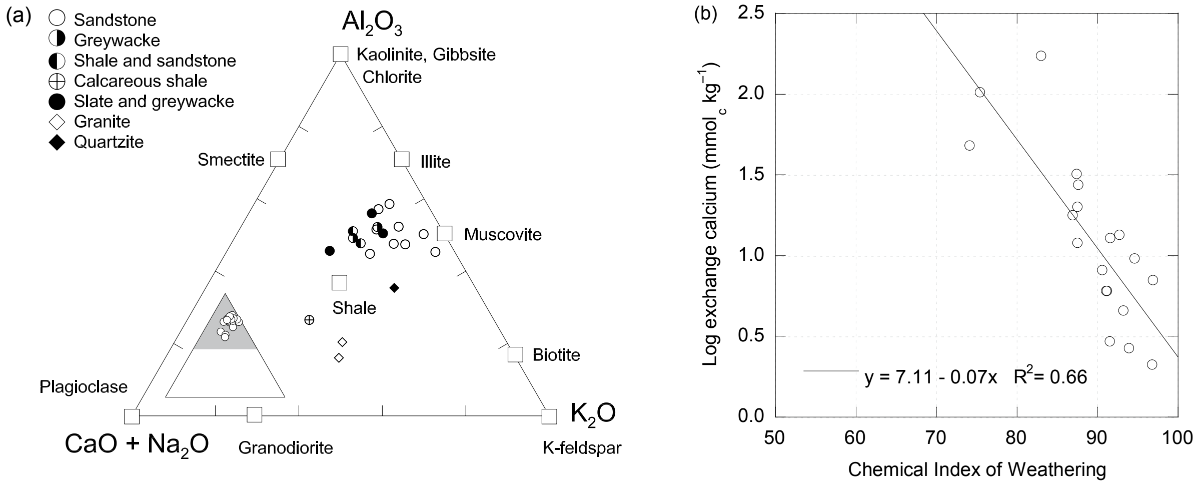


Figure 4.4. (a) Ternary plot of A–CN–K (A = Al_2O_3, CN = $CaO + Na_2O$ and K = K_2O in molecular proportions) after Nesbitt and Young (1989) showing sites with total oxide analysis (n = 20) classified by bedrock geology, idealised mineral compositions (McLennan, 1995) are also shown (open squares); the inset ternary plot depicts the region (grey shading) shown in the larger (outer) plot. (b) Relationships between site-average Chemical Index of Weathering (molecular proportions of oxides) and log exchangeable calcium (ammonium chloride extractions [see Table 4.1]; n = 20).

5 Upland Lake Catchments: Persistent Organic Pollutants and Mercury

5.1 Monitoring of Upland Catchments

A network of upland headwater lakes (n = 5) was selected from the survey lakes (Section 3) to provide a catchment-based assessment of the influence of major transboundary air pollutants on acid-sensitive lakes and soils. The five study sites (Lough Cummeenoughter [L0808], Lough Adanacleveen [L0931], Mullincrick Lough [L1841], Sgilloge Lough [L2211], and Cleevaun Lough [L3020]) were located in headwater catchments in upland regions to minimise the influences of local emissions (Figures 5.1 and 5.2; Appendix 3: Table A3.1). In addition, the catchments were selected to represent a transboundary network analogous to the atmospheric monitoring network operated by the Irish EPA (see Fig. 2.1; Leinert et al., 2008). During the period July 2009 to October 2011, a catchment-based assessment of the fate and movement of Hg (Section 5.2) and POPs (Section 5.3) was carried out at the network sites.

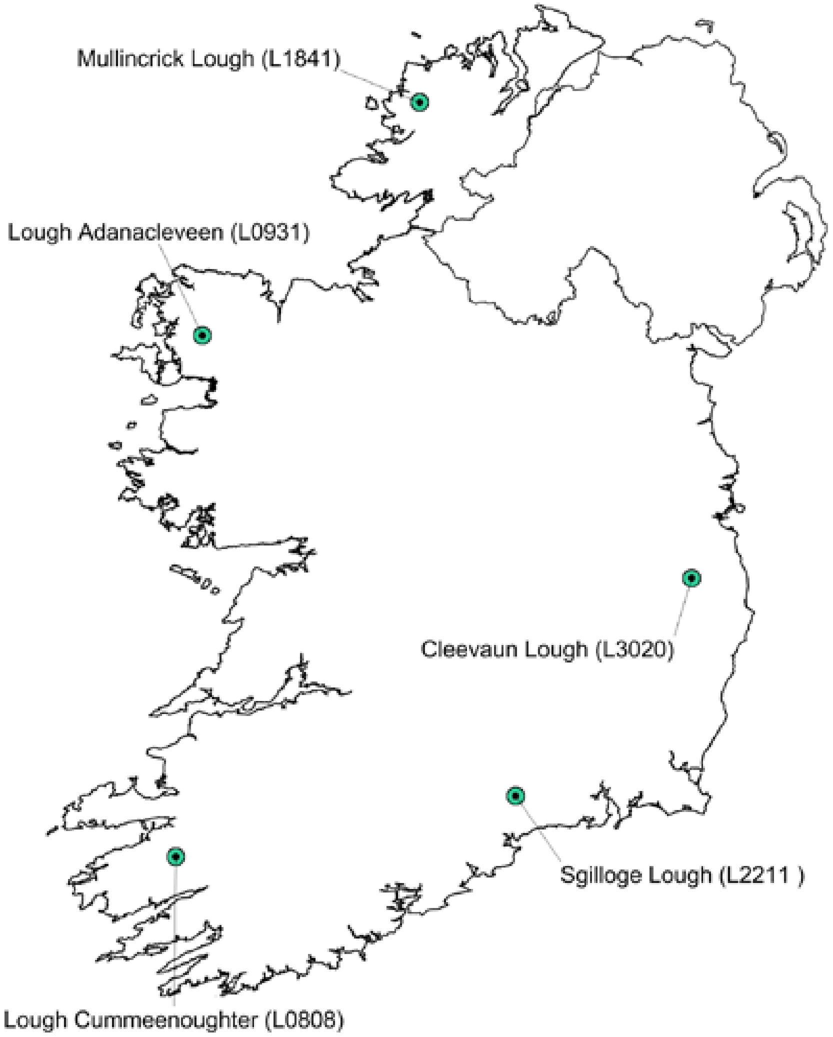
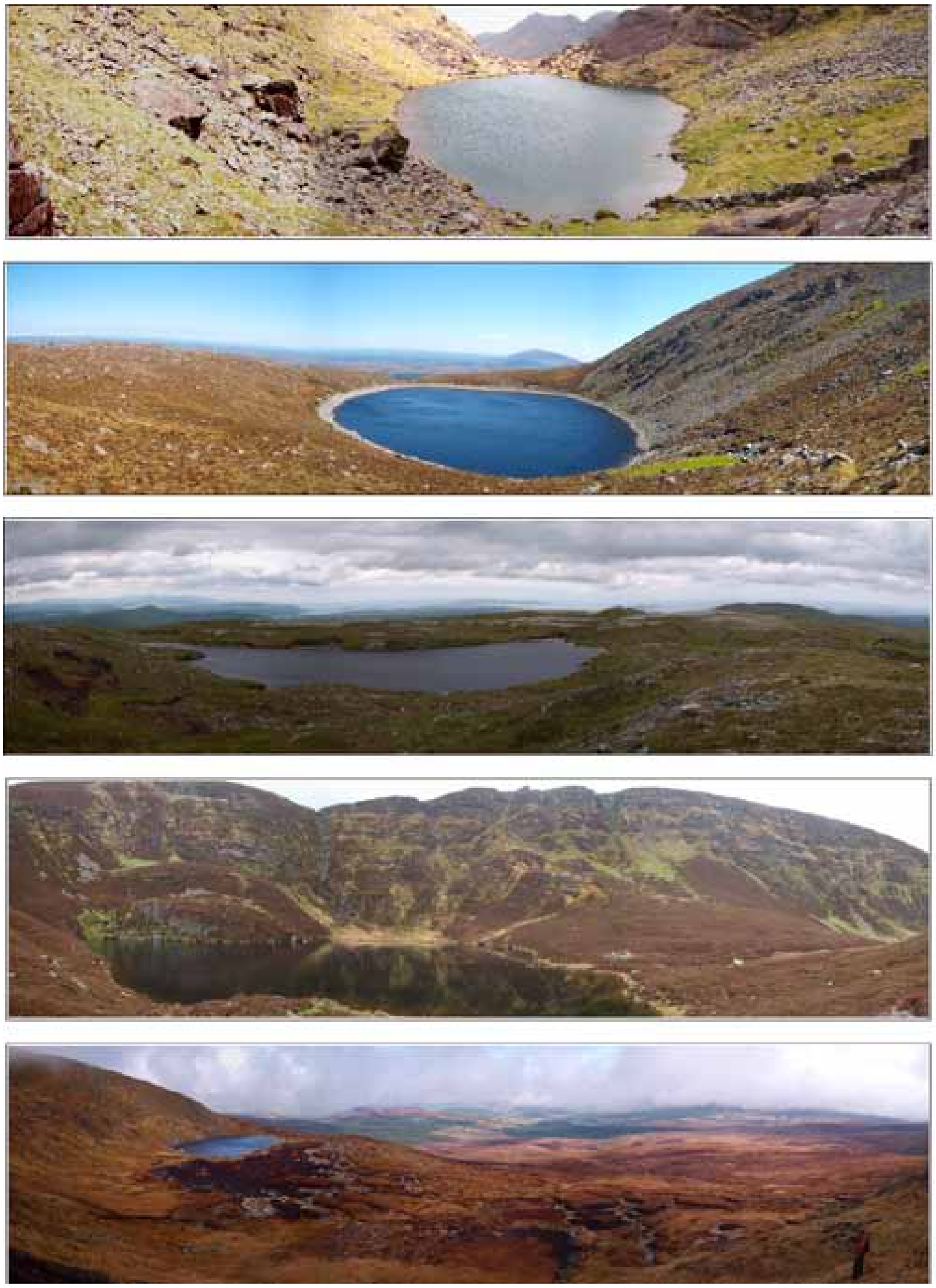


Figure 5.1. Location of the lake catchments (n = 5) selected for mercury and persistent organic pollutant analysis in soil and water. Location (geographic co-ordinates) and lake elevation are given in Appendix 3 (Table A3.1).



Photographs: Andrew Burton, 201

Figure 5.2. Study catchments (from top to bottom): Lough Cummeenoughter, Kerry (L0808); Lough Adanacleveen, Mayo (L0931); Mullincrick Lough, Donegal (L1841); Sgilloge Lough, Waterford (L2211); and Cleevaun Lough, Wicklow (L3020).

The study catchments were seasonally sampled for lake chemistry from 2009–2011 (n = 9; Appendix 3: Table A3.2), and data loggers were installed for continuous (hourly) measurement of lake and soil temperature (Appendix 3: Fig. A3.1). Soil samples were also collected approximately seasonally during 2010–2011 to estimate mineralisation (buried-bag) and nutrient supply rates based on Plant Root Simulator[45] probes (Appendix 3: Table A3.3). The source regions of atmospheric input at the study sites were evaluated using back-trajectory analysis (Appendix 3: Fig. A3.2).

---

[45] Plant Root Simulator (PRS™) URL: www.westernag.ca/innovations

The analysis focused on estimating the proportion of air that crossed source region land masses, for example Europe, Great Britain, Northern Ireland, Ireland, North America, etc., before arriving at the study sites. Further, trajectory source regions were classified into directional sectors, i.e., north, north-east, east, and so on and visualised as wind rose plots.

The study catchments ranged in elevation from 495 m (L1841) to 715 m (L0808) (mean ~600 m), representing some of the highest elevation lakes nationally. In concert, annual average rainfall at the lakes was high, ranging from more than 1700 m (L0931) to 3060 mm (L0808). The lakes ranged in size from 0.35 ha (L0808) to 2.36 ha (L2211) (mean 1.4 ha), and catchments from 1.9 ha (L0808) to 63.4 ha (L2211). Daily average lake temperature ranged from approximately 0–18°C during June 2010–June 2011, with average temperature below 5°C from November 2010–March 2011; December 2010 was the coldest on record (Met Éireann, 2010). The dominant wind direction was from the west and south-west for all catchments, indicative of an Atlantic marine source region; nonetheless, there were site-specific differences in the proportion of air from terrestrial source regions, that is Republic of Ireland, Northern Ireland and Great Britain, arriving at the catchments (Appendix 3: Fig. A3.2). Lake chemistry reflected an east–west gradient; there were higher anthropogenic inputs of SO_4^{2-} and NO_3^- in the east (L3020 and L2211) compared with sea-salts on the west (L0931 and L1841). Lake pH was influenced by organic acids associated with the dominance of organic soil in the catchments in addition to soil weathering inputs (see Ca^{2+} Appendix 3: Tables A3.2 and Fig. A3.3).

5.2 Mercury in Upland Acid-sensitive Catchments

Mercury (Hg) is naturally present in the Earth's crust. However, anthropogenic activities such as coal-burning have increased emissions and atmospheric concentrations globally. Mercury is a semi-volatile substance that readily undergoes long-range atmospheric transport owing to its long atmospheric residence time. Atmospheric Hg deposition to terrestrial and aquatic systems can undergo methylation in the presence of sulphate-reducing bacteria producing monomethylmercury (MMHg) which is toxic to humans and wildlife. Ireland is used as an unpolluted Northern Hemisphere reference for transboundary atmospheric research; as such, atmospheric Hg has been monitored at the Mace Head Atmospheric Research Station since 1995 (Ebinghaus et al., 2002; 2011). Although ongoing atmospheric Hg research is essential for assessing response to emissions reductions, there is limited knowledge of the environmental fate of Hg deposited on soils and surface waters of natural ecosystems in Ireland.

The objective of this study was to investigate the levels and controls of Hg at the upland catchment study sites (n = 5). In October 2010, three surface soil samples (0–5 cm) were collected from each catchment using fixed volume cores. Dried soil samples were analysed in triplicate for total Hg (THg) on a Mercury Analyser (Leco AMA 254). In addition, two unfiltered water samples were collected seasonally from the lake shore in 40 mL glass I-Chem vials between April 2010 and July 2011, and analysed for THg on an ICP-MS. Two additional unfiltered samples were collected seasonally in 125 mL amber glass Boston bottles between October 2010 and July 2011, and analysed for MMHg on a TEKRAN 2600 series CVASF Mercury Analyser. Once collected, water samples were acidified with 2% reagent grade HCl, and kept cool and out of direct sunlight prior to laboratory analysis. Further details on field and laboratory procedures are given by Scott and Aherne (2013).

5.2.1 Mercury in lakes and soils

Total Hg and MMHg were detected in all samples. Mean THg in lakes ranged from 1.6 ng L^{-1} (L0808) to 3.4 ng L^{-1} (L1841), the observed concentration at L0808 was significantly different from L0931 and L1841 (Fig. 5.3). The highest mean concentrations of THg were measured in January 2011 (2.90 ng L^{-1}) and July 2011 (2.93 ng L^{-1}), with the highest value (4.4 ng L^{-1}) observed at L1841 during January 2011,[46] while the lowest concentrations were measured in April 2010 (1.92 ng L^{-1}) and April 2011 (1.95 ng L^{-1}) across all study lakes. Concentrations of THg in lake water were correlated with several physical and chemical site parameters. Total Hg was significantly correlated with pH (r = –0.59), alkalinity (r = –0.61), DOC (r = 0.45),

---

[46] Water Framework Directive standards for Ireland set annual average limits for THg at 50.0 ng L^{-1} (Bowman, 2009).

and conductivity (r = 0.48); further, average THg was strongly correlated with soil moisture content (r = 0.93), albeit only based on October 2010 observations.

On average, MMHg contributed ~3.3% of THg in lakes (range 1.1–10.7%), and the two forms were not significantly correlated. Average concentrations of MMHg in lakes ranged from 0.04 ng L^{-1} (L0808) to 0.11 ng L^{-1} (L1841) and did not vary significantly between lakes. The highest seasonal average MMHg was observed during April 2011 (0.10 ng L^{-1}), which was opposite to the seasonal pattern for THg. Similar to THg, MMHg showed a negative correlation with pH (r = –0.56), and significant positive correlations with conductivity (r = 0.54) and soil moisture content (r = 0.77). In addition, MMHg concentrations showed a positive correlation with SO_4^{2-} (r = 0.55).

The concentrations of THg in soils (ng g^{-1}) clustered into two significantly different groups: L0931, L1841, L3020 > L0808, L2211; however, THg soil pools (mg m^{-2}) did not vary significantly (Fig. 5.3). The highest

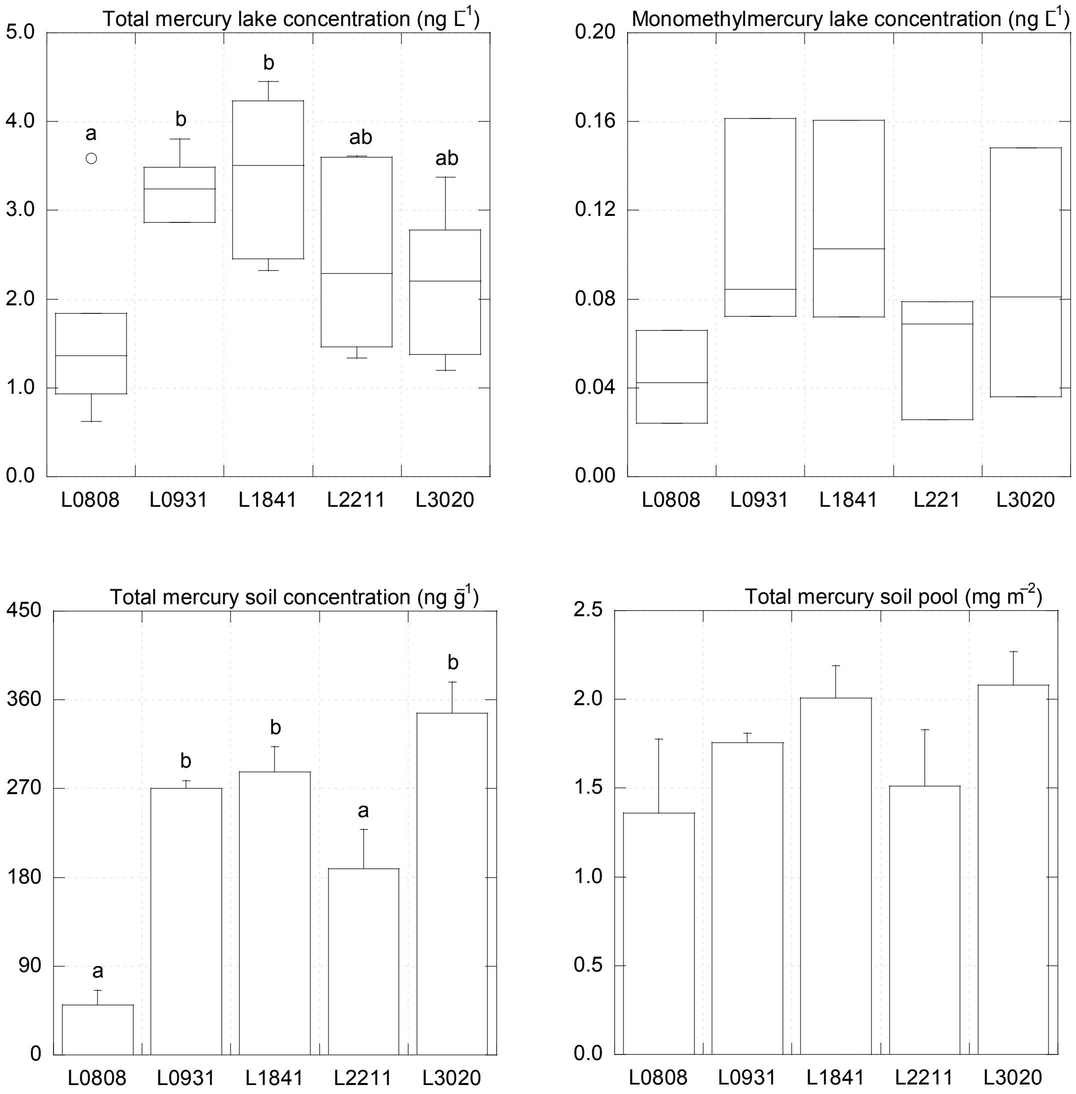


Figure 5.3. Box-plot[47] comparison of total mercury (n = 6) and monomethylmercury (n = 4) concentrations in the study lakes between 2010 and 2011. Concentrations (ng g^{-1}) and pools (mg m^{-2}) of total mercury in top soil (0–5 cm) collected October 2010 at each study catchment. Different letters indicate significant differences based on a one-way ANOVA followed by Tukey pairwise comparison ($p<0.05$). Error bars represent standard deviation among all soil samples (n = 3) per site.

---

[47] The box encloses 50% of the data, with the median displayed as a line. The whiskers represent 1.5 times the interquartile distance, and open circles represent observations outside this range.

average concentrations of THg were found at L3020 (346.7 ng g^{-1}) and lowest at L0808 (50.4 ng g^{-1}). The concentration of THg in soil was not significantly correlated with THg or MMHg in the lakes; however, they had the same general pattern between the study sites, that is L0808 consistently had the lowest levels of Hg in water and soil owing to the lower organic matter content in the catchment soils. Concentrations and pools of THg (ng g^{-1} and mg m^{-2}) in soils were negatively correlated to several lake chemistry parameters, including pH ($r = -0.95$ and $r = -0.91$, respectively) and alkalinity ($r = -0.89$ and $r = -0.88$, respectively). In addition, THg in soil was significantly correlated with DOC in lakes ($r = 0.98$ and $r = 0.92$, respectively); however, no correlation was observed between THg in soil and soil organic matter.

5.2.2 *Fate of mercury in upland catchments*

In general, upland headwater catchments in Ireland are representative of mid-latitude background regions owing to their low levels of Hg, solely from atmospheric deposition. Observed concentrations were within, or below, the range of ‘background’ values observed in European and North American studies (e.g., Wiener et al., 2006; Marusczak et al., 2011; Tipping et al., 2011). The highest concentrations of THg and MMHg in the study lakes were observed in the north-western region, which is counterintuitive given their location on the western periphery of Europe receiving ‘clean’ Atlantic air. Atmospheric deposition and soil organic matter are key determinants of aquatic Hg and its response to future emissions reductions; nonetheless, catchment physicochemical characteristics exerted important controls on the biogeochemical cycling of Hg in the study lakes, for example pH, TOC and conductivity, influenced surface water mobilisation, transport or reflected potential marine sources in the current study. Further, inter-annual variation of Hg concentrations was associated with changes in meteorology, hydrology, and soil moisture content of peat soils.

The relationship between Hg and organic matter is fundamental to understanding the former’s environmental behaviour. Catchment substrate (i.e., mineral versus organic) has been widely shown to be a good predictor of Hg in lakes as it greatly influences transport to lakes and overall retention associated with soil organic matter, as evidenced by the significant correlation between DOC and THg in lakes in the current study consistent with previous studies (e.g., Wiener et al., 2006; Kolka et al., 2011). The variability in concentrations of THg and MMHg between the study lakes was principally related to Hg retained in catchment soils, with the highest pools in the north-west associated with peat soils. Mercury concentration in dated peat cores has shown significant declines in Hg during the last few decades in response to regulation of Hg emissions (Scott and Aherne, 2013), providing insight into the potential response under future reductions. Nonetheless, the organic-rich soils that dominate Ireland are a natural sink for THg, which is sequestered in the substrate with little opportunity for revolatilisation (<1%; Tipping et al., 2011). This is a concern as peat-harvesting for energy production may potentially release Hg stores from deeper layers.

5.3 Persistent Organic Pollutants in Upland Acid-sensitive Catchments

'Persistent toxic substances' is an overarching term used to describe several classes of organic chemicals, including polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), and polybrominated diphenylethers (PBDEs). Organic pollutants are released into the environment through anthropogenic activities, including historical and present-day production and use of industrial chemicals such as dielectric and coolant fluids, flame retardants, pesticides, and as by-products of incomplete combustion (van Drooge, 2004). Their mobility, persistence, toxicity and potential to bioaccumulate in the natural environment has prompted global concern: for example, the Stockholm Convention (2008) annexes compounds for elimination or restricted production including various OCPs, PCBs, and PBDEs. The Global Atmospheric Passive Sampling (GAPS) network[48] has monitored the concentrations of POPs (i.e., OCPs, PCBs, and PBDEs) at locations around the globe to establish worldwide baseline levels and to evaluate response to emissions controls (Lee et al., 2007); nonetheless, there is limited knowledge of their fate in natural ecosystems.

---

[48] The GAPS network includes one monitoring station in Ireland located at Malin Head, considered to be a background region.

The objective of this study was to investigate the concentrations of POPs (i.e., OCPs, PCBs, PBDEs) and PAHs in soil and water at the upland catchment study sites (n = 5). Dissolved concentrations of POPs in lakes were measured using semi-permeable membrane devices (SPMDs;[49] Huckins et al., 1993; 2002), submerged at a depth of ~1 m in each lake during July 2009 and retrieved in January 2010. In the laboratory, POPs were extracted from the SPMDs using hexane. During 2010, surface soils (0–5 cm) were sampled in each catchment with a stainless steel corer; soil samples were placed into a 125 mL solvent-washed amber glass jar, refrigerated and freeze dried for subsequent analysis. In the laboratory, POPs were extracted from the soils using accelerated solvent extraction. The SPMD and soil extracts were analysed for 24 OCPs and 36 PCB congeners by gas chromatography with an electron capture detector (GC-ECD). In addition, 7 PBDEs and 15 'priority' PAHs (defined by the US EPA) were analysed using gas chromatography with low-resolution mass spectrometry (GC-LRMS). Further details on field and laboratory procedures are given by Scott et al. (2012) and Scott and Aherne (2014).

5.3.1 Persistent organic pollutants in lakes and soils

Polychlorinated biphenyls: total estimated PCBs in lake water were relatively low compared to other POPs, for example, endosulfan, and PAHs. Total dissolved PCBs were highest at L0931 and L2211 on the east coast, and significantly greater than L3020 (Fig. 5.4). In concert, total PCBs in water were negatively correlated with easting, suggesting a decrease in concentration away from European emission sources (r = –0.98). Concentrations and pools of total PCBs in soils at L2211 were almost six-fold higher than any other site (14.5 ng g^{-1} [115.8 μg m^{-2}]; Fig. 5.4), e.g., levels at L0808 and L1841 were almost negligible (<1 ng g^{-1}).

Organochlorine pesticides (HCH): concentrations of HCH in SPMDs were elevated relative to other OCPs making up more than 30% of the total OCPs in lakes (Fig. 5.4). Total HCH isomer concentrations in lakes were significantly higher at L1841 compared with L3020, L0808, and L0931. Lindane (γHCH) dominated (47% of total) HCHs in all lakes, except L1841, which was dominated (63%) by βHCH. Lindane was negatively correlated with dissolved oxygen (r = –0.89). Concentrations and pools of total HCHs in soils were highest at L0931 (1.7 ng g^{-1} [11.3 μg m^{-2}]), which displayed the lowest levels of HCH isomers in lakes. Total HCH isomers made up 15% of total OCPs detected in the soil. The proportions of HCH isomers in soils were also different from water as 71% of HCHs in soils were comprised of δHCH, which made up only 4% of total HCHs in lakes.

Organochlorine pesticides (Endosulfan): total endosulfan in the study lakes was among the highest of any OCP measured (~50%; Fig. 5.4). No significant differences in concentrations of total endosulfan were observed between sites, and all lakes were dominated by endosulfan II (~87%). Total endosulfan concentrations in water were highly correlated with easting (r = 0.98), and $nmSO_4^{2-}$ (r = 0.88), suggesting proximity to emissions sources in the east. In contrast, total endosulfan concentrations in soil were low at <1 ng g^{-1} at all sites and comprised only 1% of OCPs analysed in soils, suggesting that endosulfan does not bind to soil organic matter making it available for bioaccumulation in lake water.

Organochlorine pesticides (Cyclodienes-a): the concentration of cyclodienes-a in lakes were lowest at L0808 and significantly different compared with other sites (Fig. 5.4). Total dissolved cyclodienes-a was largely dominated by dieldrin (58%), followed by heptachlor epoxide A and B (34%). Total cyclodienes-a was significantly correlated with DOC (r = 0.96) and soil LOI (r = 0.87). The cyclodienes-a group made up 8% of total OCPs observed in the lakes compared with 25% of total OCPs detected in soils, suggesting dissolved lake concentrations are strongly related to organic bound fractions. The highest concentrations and pools in soils were found at L2211 (5.4 ng g^{-1} [42.8 μg m^{-2}]).

---

[49] Semi-permeable membrane devices are oil-filled sacks designed to mimic the parts of animals that cause bioconcentration. Hydrophobic contaminants pass through the outer membrane and dissolve in the oil just as they do in the fats of a fish. The levels of dissolved hydrophobic contaminants observed in SPMD can be used to back-calculate waterborne concentrations.

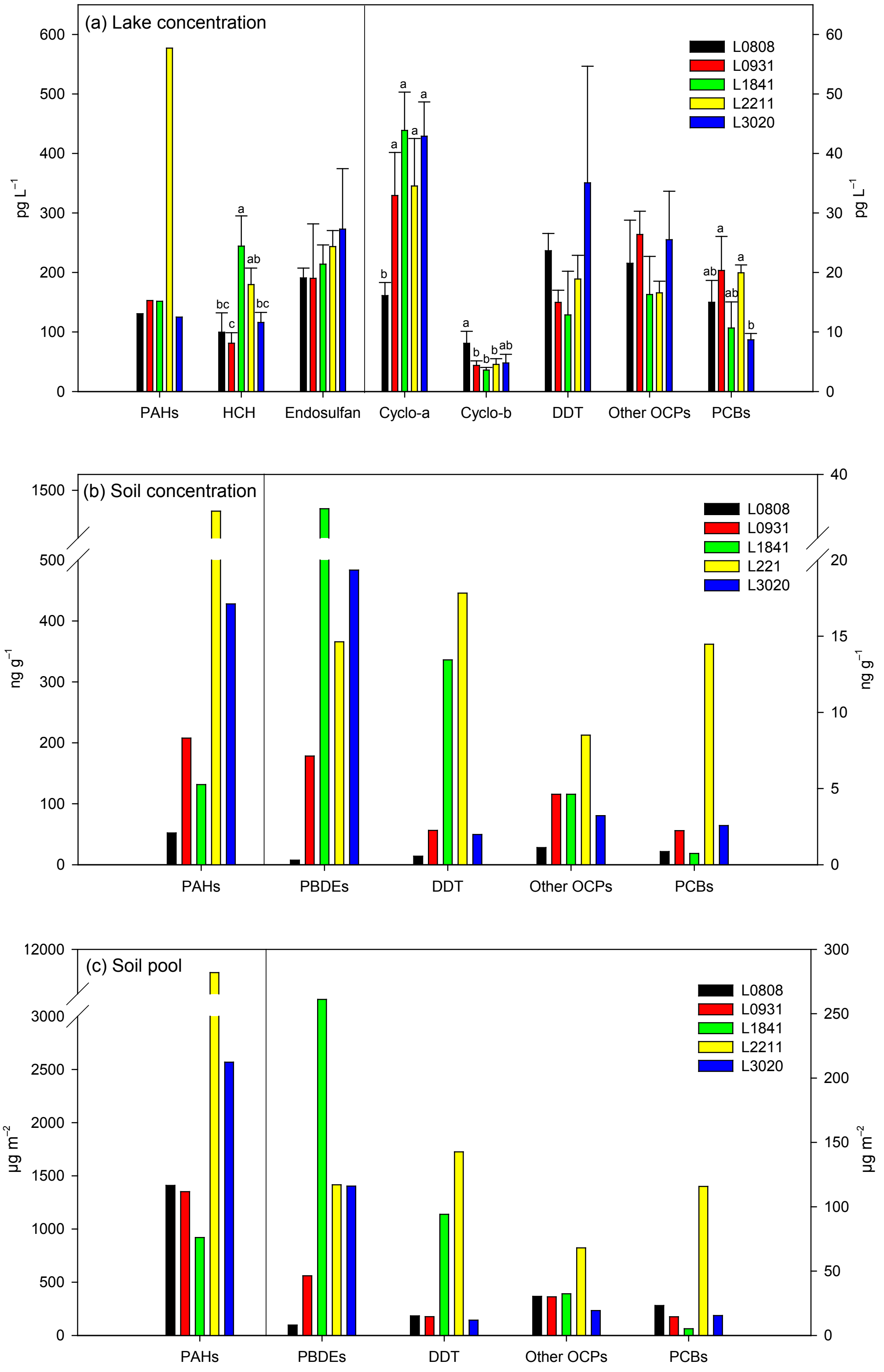


Figure 5.4. (a) Average (n = 3) concentrations of total dissolved POPs in lakes estimated from SPMDs at the five study catchments. Different letters indicate significant differences between sites based on one-way ANOVA and Tukey pairwise comparison ($p<0.001$). Other OCPs include OCS, HCB, methoxyxhlor and pentachloranisole. Error bars represent standard deviation; (b) concentrations (ng g^{-1}) and (c) pools (µg m^{-2}) of POPs measured in soils at the five study catchments sampled during October 2010. Other OCPs include HCHs, cyclodienes-a and b, endosulfan, OCS, HCB, methoxyxhlor and µentachloranisole.

Organochlorine pesticides (Cyclodienes-b): the observed pattern for cyclodienes-b in lakes was opposite to cyclodienes-a. The highest concentrations were observed at L0808, at levels significantly different from L1841, L0931, and L3311 (Fig. 5.4). Cis-chlordane (36%) was the principle constituent of total cyclodienes-b across all the sites. Cyclodienes-b made up the smallest proportion of chemical groups analysed in SPMDs and contributed only ~3% to all OCPs in the study lakes. In contrast to cyclodienes-a, concentrations of cyclodienes-b in lakes were negatively correlated with soil LOI (r = –0.98). Overall, total cyclodienes-b was detected at very low concentrations in soils at all five sites (<1 ng g^{-1}), with the exception of L2211 (1.2 ng g^{-1}).

Organochlorine pesticides (DDT): estimated dissolved concentrations of DDT isomers showed no significant differences between lakes (Fig. 5.4); DDT congeners comprised the greatest proportion of total DDT at L3020 (59%) and L2211 (60%) on the east coast, while L0931, L1841, and L0808 had the highest proportions of DDE (57–69%), the metabolised analyte of DDT. However, DDT comprised a very small percentage of total OCP concentrations in the lakes (5%; Fig. 5.4). Total DDT was significantly correlated with $nmSO_4^{2-}$ (r = 0.93); while DDE was positively correlated with elevation (r = 0.98). Levels of DDT congeners in soils were lowest at L0808 (<1 ng g^{-1}). However, the soil pool was comparable with L0931 and L3020 (Fig. 5.4). In contrast, the concentrations at L2211 were 32 fold higher (17.8 ng g^{-1}). Overall, total DDT made up the largest proportion of OCPs measured in soils at all study sites (49%), primarily comprised of the DDE isomer (54%), with the exception of L1841, which comprised 89% of the DDT congener.

Polycyclic aromatic hydrocarbons: concentrations of total PAHs were elevated in soils and water relative to organochlorine compounds. The highest concentrations of PAHs were observed at L2211 for both soil and water. Estimated concentrations in water were three times higher at L2211 than any other site (Fig. 5.4), with the remaining sites displaying a similar range of concentration (125–153 pg L^{-1}). Total PAHs in lakes were comprised largely of phenanthene (57%) and fluoranthene (22%), which was negatively correlated with lake:catchment ratio (r = –0.86). Similarly, the levels of PAHs in soils were at least three-fold higher at L221 (1369 ng g^{-1} [11.0 mg m^{-2}]). In contrast, L0808 exhibited the lowest levels of total PAHs; however, the soil pool at L0808 was larger than L0931 and L1841 (Fig. 5.4). Proportions of total PAHs in soils were dominated by fluoranthene (31%) and pyrene (20%) across all five sites in contrast to PAH concentration in water. The fluoranthene:fluoranthene plus pyrene ratios in soil across the study sites were consistent with sources originating from combustion of grass, coal, or wood rather than fossil fuels (Yunker et al., 2002). The highest ratio was observed at L2211, which is the only site located in an agricultural region where *Calluna vulgaris* burning is common.

Polybrominated diphenylethers: levels of total dissolved PBDEs in the SPMDs were below detection; however, PBDEs were detected in soils at all study sites. Total PBDEs were generally higher in soils compared to OCPs (Fig. 5.4), and were dominated almost exclusively by PBDE 47, which comprised 97–99% at most sites, with the exception of L0808 (70%). Since the 1990s, there has been a ban on the use of PBDEs as flame retardants in Europe: in contrast, North America production has increased. Industrial processing of penta-BDEs in North America accounts for the majority of global demand (97%); penta-BDEs are believed to subsequently degrade to tri-BDEs (i.e., BDE 47: Alcock et al., 2003), the dominant PBDE in soils at the study sites. The distribution and transport of PBDEs in soils is strongly influenced by organic matter, which prohibits uptake by SPMDs in lake water.

5.3.2 Fate of persistent organic pollutants in upland catchments

Upland acid-sensitive headwater catchments were representative of mid-latitude background regions owing to their low levels of POPs, solely from atmospheric deposition. Observed concentrations were within, or below, the range of 'background' values observed in European studies (e.g., Meijer et al., 2003; Fernandez and Grimalt, 2003; Creaser et al., 2007); however, the mean concentration of PBDEs in soils was high compared with previous studies (Hassanin et al., 2004). In general, the highest concentrations of POPs and PAHs in soil were observed at L2211, owing to its geographical location on the east coast, proximity to an intensive agricultural region and burning of *Calluna vulgaris* locally. The fate and transport of POPs in upland headwater lakes is primarily related to the long-range transport of contaminants and catchment soil organic matter content, which has been previously identified as a significant determinant (Meijer et al., 2003). In addition, individual site characteristics exhibited correlations with POPs in SPMDs and soil samples, such as lake:catchment ratio, rainfall, and lake water DOC. The role of media partitioning dominated the concentration of many compounds; even in highly organic soils, HCHs, HCB, endosulfan, and less-chlorinated PCBs have a tendency to re-volatilise or washout more readily and are more likely to be captured in SPMDs (Fernandez and Grimalt 2003). However, 'heavier' compounds such as PAHs, PBDEs and the more-chlorinated PCBs bind to soil and sediments.

6 Conclusions and Recommendations

Ireland is located on the western periphery of Europe and predominantly receives 'clean' air masses from the Atlantic. Nevertheless, long-range transboundary air pollution, and in particular acidic deposition, has had a marked influence on the hydrogeochemistry of upland acid-sensitive lakes and soils. Since the 1990s there have been significant decreases in emissions of SO_2, NO_x and NH_3 largely owing to the implementation of the Gothenburg Protocol under the UNECE Convention on LRTAP, and EU NECD. As a result, there has been a significant long-term decreasing trend in non-marine sulphate ($nmSO_4^{2-}$) deposition; trends were less clear for nitrogen (N) deposition. The reductions in emissions and atmospheric deposition (primarily S) has led to widespread improvements in the acid status of upland lakes and their catchment soils. In addition, there have been co-benefits with respect to the mobilisation of trace metals, and deposition of mercury (Hg) and other contaminants. The results of this study are in general agreement with the recent review of transboundary air pollution in the United Kingdom (RoTAP, 2012), notwithstanding the dominant influence of sea-salts on Irish ecosystems, and the greater coverage of organic soils in upland regions. Recovery is a slow process: as such, continued improvements in the chemistry of acid-sensitive lakes and soils are expected under future emissions reductions.

Nonetheless, knowledge gaps and significant challenges in meeting environmental quality objectives persist. Further research is necessary on the impacts of chronic nitrogen deposition on biodiversity in terrestrial ecosystems and greenhouse gases in lakes, the control of intercontinental transport of pollutants such as POPs and Hg, the release of pollutants stored in organic soils under changing land use and climate, and the influence of sea-salt inputs associated with increased frequency and intensity of storms on acid-sensitive ecosystems. In addition, the response of surface waters to atmospherically deposited pollutants is strongly related to catchment and soil characteristics, with distinct differences between mineral and organic soils.

There are several recommendations stemming from this research:

- The EMEP (European Monitoring and Evaluation Programme) transboundary atmospheric monitoring network operated by the EPA and Met Éireann provides important information on long-term trends in the chemical climate, and the responses to emissions control measures. It is recommended that the network is maintained through the coming decades.
- Nitrogen deposition is dominated by reduced N; however, there are few national observations of atmospheric ammonia (NH_3). It is recommended that existing stations be augmented to monitor NH_3, for example, using passive samplers, with a view to establishing a long-term reduced N network.
- Quantification of improvements in natural ecosystems requires systematic monitoring of water, soil and vegetation. Existing long-term networks, such as ICP Waters and ICP Forests sites, should be built upon to meet this need. The analysis of long-term datasets further requires the establishment of a national archive for historic data. It is recommended that an integrated monitoring programme is established at a national level to ensure that the effects and recovery from air pollution can be reported with accuracy in Ireland.
- Continued monitoring at the upland catchments network established under this project is strongly recommended. The network can provide important information on changes in water quality under major pressures facing upland waters, including acidic and nutrient deposition, climate change, sea-salt episodes, land-use and land-management change and their associated influence on carbon dynamics, toxic substance remobilisation and greenhouse gas dynamics.

- The emissions and deposition of oxidised and reduced nitrogen have changed little since the 1990s; there is widespread growing concern that N deposition will reduce the diversity of plant species per unit area in sensitive habitats of high conservation value. Further research is recommended to determine the ecological impacts of N deposition on sensitive ecosystems.
- There is limited monitoring of persistent organic pollutants (POPs) in the Irish environment (air, soil and water). It is recommended that further research and monitoring be carried out in sensitive ecosystems or protected habitats, such as Natura 2000 sites, to meet national reporting requirements.

References

Aherne J, Farrell EP (eds), 2000. Determination and Mapping of Critical Loads for Sulphur and Nitrogen and Critical Levels for Ozone in Ireland. Final Report. R&D Report Series No. 7. Environmental Protection Agency, Ireland, 225 pp [URL: erc.epa.ie/safer/resource?id=b931d553-2076-102f-a0a4-f81fb11d7d1c].

Aherne J, Farrell EP, 2002. Deposition of sulphur, nitrogen and acidity in precipitation over Ireland: chemistry, spatial distribution and long-term trends. Atmospheric Environment 36, 1379–89.

Aherne J, Kelly-Quinn M, Farrell EP, 2002. A survey of lakes in the Republic of Ireland: Hydrochemical characteristics and acid sensitivity. Ambio 31:6, 452–9.

Aherne J, Curtis CJ, 2003. Critical loads of acidity for Irish lakes. Aquatic Sciences 65: 21–35.

Alcock R, Sweetman A, Prevedouros K, Jones K, 2003. Understanding levels and trends of BDE-47 in the UK and North America: an assessment of principal reservoirs and source inputs. Environment International 29, 691–8.

Allen HE, Hansen DJ, 1996. The importance of trace metal speciation to water quality criteria. Water Environment Research 68:1, 42–54.

Allott N, Brennan M, 2000. Nature and origin of acid episodes in western Ireland. Internationale Vereinigung für Theoreische und Angewandte Limnologie 27:4, 2471–4.

Bashir W, McGovern F, Ryan M, Burke L, 2008. Chemical trends in background air quality and the ionic composition of precipitation for the period 1980–2004 from samples collected at Valentia Observatory, Co. Kerry, Ireland. Journal of Environmental Monitoring 10, 730–8.

Bowman J, 1986. Precipitation Characteristics and the Chemistry and Biology of Poorly Buffered Irish Lakes: A western European Baseline for 'Acid Rain' Impact Assessment. An Foras Forbartha, Dublin. WR/G14.

Bowman J. 1991. Acid-sensitive Surface Waters in Ireland. Environment Research Unit, Dublin, Ireland, 321 pp.

Bowman J. 2009. New Water Framework Directive environmental quality standards and biological and hydromorphological classification systems for surface waters in Ireland. Biology and Environment: Proceedings of the Royal Irish Academy 109B, 247–60.

Bowman JJ, Bracken JJ, 1993. Effect of run-off from afforested and non-afforested catchments on the survival of brown trout *Salmo trutta L.* in two acid-sensitive rivers in Wicklow, Ireland. Biology and Environment: Proceedings of the Royal Irish Academy 93B:3, 143–50.

Bowman J, Harlock S, 1998. The spatial distribution of characterized fly ash particles and trace metals in lake sediments and catchment mosses: Ireland. Water, Air and Soil Pollution 106, 263–86.

Bowman JJ, McGettigan M, 1994. Atmospheric deposition in acid-sensitive areas of Ireland – the influence of wind direction and a new coal burning electricity-generation station on precipitation quality. Water Air and Soil Pollution 75:1–2, 159–75.

Burton A, Aherne J, 2012. Changes in the chemistry of small Irish lakes. Ambio 41:2, 170–9.

Burton A, Aherne J, Hassan N, 2013. Trace metals in upland headwater lakes in Ireland. Ambio 42:6, 702–14 [DOI: 10.1007/s13280-013-0381-y].

Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ, Striegl RG, Duarte M, Kortelainen P, Downing JA, Middelburg JJ, Melack J, 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems 10, 171–84.

Craig H, 1961. Isotopic variations in meteoric waters. Science 133, 1702–3.

Creaser CS, Wood MD, Alcock R, Copplestone D, Crook PJ, 2007. UK soil and herbage pollutant survey: Environmental concentrations of polychlorinated biphenyls (PCBs) in UK soil and herbage. Environment Agency, UKSHS Report No. 8.

Dee DP, Uppala SM, Simmons AJ, Berrisford P, Poli P, Kobayashi S, Andrae U, Balmaseda MA, Balsamo G, Bauer P, Bechtold P, Beljaars ACM, van de Berg L, Bidlot J, Bormann N, Delsol C, Dragani R, Fuentes M, Geer AJ, Haimberger L, Healy SB, Hersbach H, Hólm EV, Isaksen L, Kållberg P, Köhler M, Matricardi M, McNally AP, Monge-Sanz BM, Morcrette JJ, Park B-K, Peubey C, de Rosnay P, Tavolato C, Thépaut JN, Vitart F, 2011. The ERA-Interim reanalysis: configuration and performance of the data assimilation system. Quarterly Journal Royal Meteorological Society 137, 553–97.

de Kluizenaar Y, Farrell EP, 2000. Ammonia Monitoring in Ireland: A Full Year of Ammonia Monitoring, Set-up & Results. Final Report. Environmental Research, R&D Report Series No. 8. Environmental Protection Agency, Ireland [URL: erc.epa.ie/safer/resource?id=408a1a9a-2072-102f-a0a4-f81fb11d7d1c].

de Vos B, Deckers J, Muys B, 2005b. Capability of loss-on-ignition as a predictor of total organic carbon in non-calcareous forest soils. Communications in Soil Science and Plant Analysis 36, 2899–921.

de Vos B, Van Meirvenne M, Quataert P, Deckers J, Muys B, 2005a. Predictive quality of pedotransfer functions for estimating bulk density of forest soils. Soil Science Society of America Journal 69, 500–10.

Ebinghaus R, Kock H, Coggins A, Spain T, Jennings S, Temme C, 2002. Long-term measurements of atmospheric mercury at Mace Head, Irish west coast, between 1995 and 2001. Atmospheric Environment 36, 5267–76.

Ebinghaus R, Jennings SG, Kock HH, Derwent RG, Manning AJ, Spain TG, 2011. Decreasing trends in total gaseous mercury observations in baseline air at Mace Head, Ireland from 1996 to 2009. Atmospheric Environment 45, 3475–80.

EPA (Environmental Protection Agency), 2011. Ireland's Transboundary Gas Emissions in 2009. Environmental Protection Agency, Wexford, Ireland. [URL: epa.ie/downloads/pubs/air/airemissions].

EPA, 2012. Ireland's Transboundary Gas Emissions in 2010. Environmental Protection Agency, Wexford, Ireland. [URL: epa.ie/downloads/pubs/air/airemissions].

Evans CD, Monteith DT, Harriman R, 2001. Long-term variability in the deposition of marine ions at west coast sites in the UK Acid Waters Monitoring Network: impacts on surface water chemistry and significance for trend determination. Science of the Total Environment 265, 115–29.

Farrell EP, 1995. Atmospheric deposition in maritime environments and its impact on terrestrial ecosystems. Water, Air and Soil Pollution 85, 123–30.

Fay D, McGrath D, Zhang C, Carrigg C, O'Flaherty V, Carton OT, and Grennan E, 2007. Towards a National Soil Database. Synthesis Report: 2001-CD/S2 M2. Environmental Protection Agency, Dublin, Ireland 22 pp.

Fisher BEA, 1982. Deposition of sulphur and the acidity of precipitation over Ireland. Atmospheric Environment 1611, 2725–34.

Fernandez P, Grimalt J, 2003. On the global distribution of persistent organic pollutants. Chimia 57, 514–21.

Galvin RM, 1996. Occurrence of metals in waters: An overview. Water South Africa 22:1, 7–18.

Gardiner MJ, Radford T, 1980. Soil associations of Ireland and their land use potential. An Foras Talúntais, Dublin.

Gorham E, 1957. The chemical composition of rain from Rosscahill in County Galway. The Irish Naturalists' Journal 12:5, 122–6.

Hassanin A, Breivik K, Meijer S, Steinnes E, Thomas G, Jones K, 2004. PBDEs in European background soils: Levels and factors controlling their distribution. Environmental Science and Technology 38, 738–45.

Harnois L, 1988. The CIW index: a new Chemical Index of Weathering. Sedimentary Geology 55, 319–22.

Hindar A, Tørseth K, Henriksen A., Orsolini Y, 2004. The significance of the North Atlantic Oscillation (NAO) for sea-salt episodes and acidification-related effects in Norwegian rivers. Environmental Science and Technology 38, 26–33.

Huckins J, Manuweera G, Petty J, Mackay D, Lebo J. 1993. Lipid-containing semipermeable-membrane devices for monitoring organic contaminants in water. Environmental Science and Technology 27, 2489–96.

Huckins J, Petty J, Lebo J, Almeida F, Booij K, Alvarez D, Clark R, Mogensen B, 2002. Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices. Environmental Science and Technology 36, 85–91.

Huttunen JT, Väisänen TS, Heikkinen M, Hellsten S, Nykänen H, Nenonen O, Martikainen PJ, 2002. Exchange of CO_2, CH_4 and N_2O between the atmosphere and two northern boreal ponds with catchments dominated by peatlands or forests. Plant and Soil 242, 137–46.

Hyland A, Aherne J, Johnson JJ, Cummins T, Farrell EP, Neville P, O'Dea P, 2013. Investigating the predictive capacity of pedotransfer functions for estimating the bulk density and soil organic carbon of Irish forest and moorland soils. The Scientific World Journal [submitted].

Johnson CE, 2002. Cation exchange properties of acid forest soils of the northeastern USA. European Journal of Soil Science 53, 271–82.

Jönsson C, Warfvinge P, Sverdrup H, 1995. Uncertainties in predicting weathering rate and environmental stress factors with the PROFILE model. Water, Air and Soil Pollution 81, 1–23.

Jordan C, 1997. Mapping of rainfall chemistry in Ireland 1972–94. Biology and Environment 97B:1, 53–73.

Kolka RK, Mitchell CPJ, Jeremiason JD, Hines NA, Grigal DF, Engstrom DR, Coleman-Wasik JK, Nater EA, Swain EB, Monson BA, Fleck JA, Johnson B, Almendinger JE, Branfireun BA, Brezonik PL, Cotner JB, 2011. Mercury cycling in peatland watersheds. Chapter 11.In: Kolka RK, Sebestyen SD, Verry ES, Brooks KN (eds), Peatland Biogeochemistry and Watershed Hydrology at the Marcell Experimental Forest. Boca Raton, Florida, CRC Press, 349–70.

Lee SC, Harner T, Pozo K, Shoeib M, Wania F, Muir DCG, Barrie LA, Jones KC, 2007. Polychlorinated naphthalenes in the Global Atmospheric Passive Sampling (GAPS) study. Environmental Science and Technology 41, 2680–7.

Leinert S, McGovern F, Jennings SG, 2008. New Transboundary Air Pollution Monitoring Capacity for Ireland: Environmental Research Centre Report Series No.10. Environmental Protection Agency, Ireland.

Lydersen E, Lofgren S, Arnesen RT, 2002. Metals in Scandinavian surface waters: effects of acidification, liming, and potential reacidification. Critical Reviews in Environmental Science and Technology 32:2, 73–295.

Marusczak N, Larose C, Dommergue A, Paquet S, Beaulne J, Maury-Brachet R, Lucotte M, Nedjai R, Ferrari CP. 2011. Mercury and methylmercury concentrations in high altitude lakes and fish (Arctic charr) from the French Alps related to watershed characteristics. Science of the Total Environment 409, 1909–15.

Mathews RO, McCaffery F, Hart E, 1981. Acid rain in Ireland. Irish Journal of Environmental Science 1:2, 7–50.

McConnell B, Gatley S, 2006. Bedrock Geology of Ireland, 1:500,000 scale map. Geological Survey of Ireland [URL: www.gsi.ie/gsishop/Product.aspx?Productid=292].

McGarrigle M, Bowman J, Clabby K, Lucey J, Cunningham P, MacCárthaigh M, Keegan M, Cantrell B, Lehane M, Clenaghan C, Toner PF, 2002. Water Quality in Ireland 1998–2000. Environmental Protection Agency, Ireland, 124 pp (+ Appendices).

McLennan SM, 1995. Sediments and soils: chemistry and abundances. In: Rock Physics and Phase Relations, a hand book of physical constants. AGU Reference Shelf 3, American Geophysical Union, 8–19.

Meijer S, Ockenden W, Sweetman A, Breivik K, Grimalt J, Jones K, 2003. Global distribution and budget of PCBs and HCB in background surface soils: Implications or sources and environmental processes. Environmental Science and Technology 37, 667–72.

Met Éireann, 2008. Met Éireann Monthly Weather Bulletin, March 2008 [URL: www.met.ie/climate/monthly-weather-bulletin-2008.asp].

Met Éireann, 2010. Met Éireann Monthly Weather Bulletin, December 2010 [URL: www.met.ie/climate/monthly-weather-bulletin-2010.asp].

Möller, D. 1990. The Na/Cl ratio in rainwater and the seasalt chloride cycle. Tellus 42B, 254–62.

Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Høgåsen T Wilander A, Skjelkvåle L, Jeffries DS, Vuorenmaa J, Keller B, Kopácek J, Vesely J. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450:22, 537–41.

Nesbitt HW, Young GM, 1989. Formation and diagenesis of weathering profiles. Journal of Geology 97, 129–47.

Ravichandran M, 2004. Interactions between mercury and dissolved organic matter – a review. Chemosphere 55, 319–31.

Reuss JO, Johnson DW, 1986. Acid Deposition and the Acidification of Soils and Waters. New York: Springer-Verlag, 119 pp.

Rose NL, Alliksaar T, Bowman JJ, Boyle J, Coles B, Fott J, Harlock S, Juggins S, Punning JM, Clair-Gribble K, Vukic J, Watt J, 1998. The FLAME research project: Introduction and methods. Water, Air and Soil Pollution 106:(3–4), 205–18.

RoTAP, 2012. Review of Transboundary Air Pollution: Acidification, Eutrophication, Ground Level Ozone and Heavy Metals in the UK. Report to the Department for Environment, Food and Rural Affairs. Centre for Ecology and Hydrology, United Kingdom.

Salmi T, Määttä A, Anttila P, Ruoho-Airola T, Amnell T, 2002. Detecting trends of annual values of atmospheric pollutants by the Mann-Kendall test and Sen's slope estimates — the Excel template application MAKESENS. Publications on Air Quality No. 31. Finnish Meteorological Institute, Helsinki, 35 pp.

Sayer MDJ, Reader JP, Morris R, 1989. The effect of calcium concentration on the toxicity of copper, lead and zinc to yolk-sac fry of brown trout, *Salmo trutta L.* in soft acid water. Journal of Fish Biology 35, 323–32.

Scott HEM, Aherne J, Metcalfe CD, 2012. Fate and transport of polycyclic aromatic hydrocarbons in upland Irish headwater lake catchments. The Scientific World Journal Volume 2012, Article ID 828343 [DOI: 10.1100/2012/828343].

Scott HEM, Aherne J, 2013. Mercury concentrations in Irish headwater lake catchments. Biogeochemistry 116:1, 161–73 [DOI: 10.1007/s10533-013-9885-6].

Scott HEM, Aherne J, 2014. Persistent organic pollutants in Irish headwater lake catchments. Science of the Total Environment [submitted].

Skjelkvåle BL, Andersen T, Fjeld E, Mannio J, Wilander A, Johansson K, Jensen JP, Moiseenko T, 2001. Heavy metal surveys in Nordic lakes; concentrations, geographic patterns and relation to critical limits. Ambio 30:1, 2–10.

Skjelkvåle BL, Stoddard JL, Jeffries DS, Tørseth K, Høgåsen T, Bowman J, Mannio J, Monteith DT, Mosello R, Rogora M, Rzychon D, Vesely J, Wieting J, Wilander A, Worsztynowicz A, 2005. Regional scale evidence for improvements in surface water chemistry 1991–2001. Environmental Pollution 137, 165–76.

Smith RA, 1872. Air and rain: The beginnings of a chemical climatology. Longmans, Green and Co., London, 600pp.

Sobek S, Tranvik LJ, Cole JJ, 2005. Temperature independence of carbon dioxide supersaturation in global lakes. Global Biogeochemical Cycles 19, Gb2003, doi: 10.1029/2004gb002264

Sparling JH, 1967. The occurrence of Schoenus Nigricans L. in blanket bogs: I. environmental conditions affecting the growth of S. Nigricans in blanket bog. Journal of Ecology 55:1, 1–13.

Steinnes E, 2001. Metal contamination of the natural environment in Norway from long–range atmospheric transport. Water, Air and Soil Pollution: Focus 1, 449–60.

Stevenson CM, 1968. An analysis of the chemical composition of rain-water and air over the British Isles and Eire for the years 1959–1964. Quaternary Journal of the Royal Meteorological Society 96, 56–70.

Stockholm Convention, 2008. Protecting human health and the environment from persistent organic pollutants [URL: chm.pops.int/Convention/tabid/54/language/en-GB/Default.aspx].

Stoddard JL, Jeffries DS, Lükewille A, Clair TA, Dillon PJ, Driscoll CT, Forsius M, Johannessen M, Kahl JS, Kellogg JH, Kemp A, Mannio J, Monteith D, Murdoch PS, Patrick S, Rebsdorf A, Skjelkvåle BL, Stainton MP, Traaen TS, van Dam H, Webster KE, Wieting J, Wilander A, 1999. Regional trends in aquatic recovery from acidification in North America and Europe. Nature 401, 575–8.

Tangen G, Wickstøm T, Lierhagen S, Vogt R, Lund W, 2002. Fractionation and determination of aluminum and iron in soil water samples using SPE cartridges and ICP-AES. Environmental Science and Technology 36, 5421–5.

Tarvainen T, Lahermo P, Mannio J, 1997. Sources of trace metals in streams and headwater lakes in Finland. Water, Air and Soil Pollution 94, 1–32.

Tipping E, Loft S, Lawlor AJ, 1998. Modelling the chemical speciation of trace metals in surface waters of the Humber system. Science of the Total Environment 210–211, 63–77.

Tipping E, Poskitt JM, Lawlor AJ, Wadsworth RA, Norris DA, Hall JR, 2011. Mercury in United Kingdom topsoils; concentrations, pools, and critical limit exceedances. Environmental Pollution 159, 3721–9.

Tarrason L, Fagerli H, Klein H, Simpson D, Benedictow AC, Vestregn V, Rigler E, Emberson L, Posch M, Spranger T., 2006. Transboundary Acidification, Eutrophication and Ground Level Ozone in Europe from 1990 to 2004 in support for the review of the Gothenburg Protocol, EMEP Status Report 1/2006, Meteorological Institute, Oslo.

Tornimbeni O, Rogora M, 2012. An evaluation of trace metals in high-altitude lakes of the central Alps present levels, origins and possible speciation in relation to pH values. Water, Air and Soil Pollution 223:4, 1895–909.

Tranvik LJ, Downing JA, Cotner JB, Loiselle SA, Striegl, RG, Ballatore TJ, Dillon P, Finlay K, Fortino K, Knoll LB, Kortelainen PL, Kutser T, Larsen S, Laurion I, Leech DM, McCallister S, McKnight DM, Melack JM, Overholt E, Porter JA, Prairie Y, Renwick WH, Roland F, Sherman BS, Schindler DW, Sobek S, Tremblay A, Vanni MJ, Verschoor AM, von Wachenfeldt E, Weyhenmeyer GA, 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnology and Oceanography 54, 2298–314.

UBA (Umweltbundesamt) 2004. Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends; Federal Environment Agency, Texte 52/04, Berlin, Germany [URL: www.icpmapping.org].

UNECE (United Nations Economic Commission for Europe) 1999. The 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone. Document ECE/ EB.AIR/67, United Nations Economic Commission for Europe, New York and Geneva.

Van Drooge B, Grimalt J, Camarero L, Catalan J, Stuchlik E, Garcia C, 2004. Atmospheric semivolatile organochlorine compounds in European high-mountain areas (Central Pyrenees and High Tatras). Environmental Science and Technology 38, 3525–32.

Whitfield CJ, Aherne J, Baulch HM, 2011. Controls on greenhouse gas concentrations in polymictic headwater lakes in Ireland. Science of the Total Environment 410:411, 217–25.

Wiener JG, Knights BC, Sandheinrich MB, Jeremiason JD, Brigham ME, Engstrom DR, Woodruff LG, Cannon WF, Balogh SJ, 2006. Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): Importance of atmospheric deposition and ecosystem factors. Environmental Science and Technology 40:20, 6261–8.

Williamson CE, Saros JE, Schindler DW, 2009. Sentinels of change. Science 323:5916, 887–8.

Wright RF, Posch M, Cosby BJ, Forsius M, Skjelkvåle BL, 2007. Review of the Gothenburg Protocol: Chemical and biological responses in surface waters and soils. International Cooperative Programme on Assessement and Monitoring of Acidification of Rivers and Lakes. OR-5475 Norwegian Institute for Water Research, Oslo.

Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S, 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 33:4, 489–515.

Zhu E, Wang E, 2007. Boron environmental geochemistry and its environmental response. In, Xu F (editor), p 383–91, Advances in Plant and Animal Boron Nutrition, Springer 380 pp.

Acronyms and Abbreviations

Al	Aluminium
ANC	Acid neutralising capacity
BDL	Below detection limit
C	Carbon
CCC	Chemical Co-ordinating Centre
CEC	Cation exchange capacity
CH_4	Methane
CIW	Chemical Index of Weathering
Cl^-	Chloride
CO_2	Carbon dioxide
DOC	Dissolved organic carbon
EMEP	Cooperative Programme for Monitoring and Evaluation of Long-range Transmission for Air Pollutants in Europe
EU	European Union
GHG	Greenhouse gases
GWP	Global warming potential
HCH	Hexachlorocyclohexane
Hg	Mercury
ICP	International Cooperative Programmes
ISIS	Irish Soil Information System
LOI	Loss-on-ignition
LRTAP	Long-range Transboundary Air Pollution
MMHg	Monomethylmercury
N	Nitrogen
N_2O	Nitrous oxide
Na^+	Sodium
NAOI	North Atlantic Oscillation Index
NEC	National Emission Ceilings
NH_3	Ammonia
NH_4^+	Ammonium
Nm	Non-marine
NO_x	Nitrogen oxides
NO_3^-	Nitrate
OCP	Organochlorine pesticides
OCS	Octachlorostyrene

PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenylethers
PCB	Polychlorinated biphenyls
POP	Persistent organic pollutants
RDA	Redundancy analysis
S	Sulphur
SAFER	Secure Archive For Environmental Research
SD	Standard deviation
SO_2	Sulphur dioxide
SO_4^{2-}	Sulphate
SPE	Solid phase extraction
SPMD	Semi-permeable membrane devices
UNECE	United Nations Economic Commission for Europe
URL	Uniform resource locator
VIF	Variance inflation factor

Appendix 1. Project Outputs

A1.1 Peer-Review Publications

Burton A and Aherne J, 2012. Changes in the chemistry of small Irish lakes. Ambio 41:2, 170–79 [DOI: 10.1007/s13280-011-0177-x].

Burton A, Aherne J and Hassan N, 2013. Trace metals in upland headwater lakes in Ireland. Ambio 42:6, 702–14 [DOI: 10.1007/s13280-013-0381-y].

Scott HEM, Aherne J and Metcalfe CD, 2012. Fate and transport of polycyclic aromatic hydrocarbons in upland Irish headwater lake catchments. The Scientific World Journal Volume 2012, Article ID 828343 [DOI: 10.1100/2012/828343].

Scott HEM and Aherne J, 2013. Mercury concentrations in Irish headwater lake catchments. Biogeochemistry 116:1, 161–73 [DOI: 10.1007/s10533-013-9885-6].

Whitfield CJ, Aherne J and Baulch HM, 2011. Controls on greenhouse gas concentrations in polymictic headwater lakes in Ireland. Science of the Total Environment 410:411, 217–25 [DOI: 10.1016/j.scitotenv.2011.09.045].

Hyland A, Aherne J, Johnson JJ, Cummins T, Farrell EP, Neville P and O'Dea P, 2013. Investigating the predictive capacity of pedotransfer functions for estimating the bulk density and soil organic carbon of Irish forest and moorland soils. The Scientific World Journal [submitted].

Scott HEM and Aherne J, 2014. Persistent organic pollutants in Irish headwater lake catchments. Science of the Total Environment [submitted].

Wolniewicz MB, Aherne J and Bowman JJ, 2014. Influence of climate, sea-salts and acidic deposition on the long-term variability in the surface water chemistry of three acid sensitive Irish lakes. Science of the Total Environment [submitted].

A1.2 Conferences: Oral and Poster Presentations

Aherne J. The impacts of transboundary air pollution on acid-sensitive lakes in Ireland. Ireland's Environment 2012: EPA-STRIVE Research Conference, Trinity College Dublin, 28 June, 2012 [oral presentation].

Burton A and Aherne J. A decade of change: acid status of Irish lakes since the 1997 survey. 22nd Annual Gananoque Conference on Environmental Science and Engineering, Gananoque, Ontario, 1–3 February, 2008 [oral presentation].

Burton A and Aherne J. Changes in the chemistry of small Irish lakes between 1997 and 2008. ENVIRON 2009, 19th Irish Environmental Researchers' Colloquium, Waterford Institute of Technology, Waterford, 18–20 February, 2009 [oral presentation].

Burton A, Aherne J and Hassan N Trace metals in small Irish lakes, Biogeomon 2009 Symposium, Helsinki, Finland, 29 June–3 July 2009 [oral presentation].

Burton A, Aherne J, Cummins T and Whitfield CJ. Physicochemical properties of upland soils. Soil Science Society of Ireland Spring Meeting, University College Dublin, Dublin, 11 March, 2011 [poster presentation].

Cummins T and Aherne J. Critical loads for Ireland [2007-CCRP-4.4.4b and 2008-CCRP-4.1a]. EPA Transboundary Air Pollution Research Workshop, Radisson Blu Hotel, Galway, 8–9 September, 2010 [oral and poster presentation].

Cummins T and Aherne J. New insights into acidic deposition and nutrient loading. AgMet, Custom House, Dublin, 29 February, 2012 [oral presentation].

Hyland A, Aherne J, Burton A, Cummins T, Farrell EP, Harrington F, Johnson J, Neville P and O'Dea P. The predictive capacity of pedotransfer functions for estimating soil bulk density. Soil Science Society of Ireland Spring Meeting, University College Dublin, Dublin, 11 March, 2011 [poster presentation].

Scott HEM. Use of Semi-permeable Membrane Devices to Measure Persistent Organic Pollutants in Irish Upland Lakes. Symons Seminar Series, Trent University, Ontario, 8 February, 2012 [oral presentation].

Scott HEM, Aherne J and Hintelmann H. Head for the hills: mercury in upland catchments in Ireland. 7th international symposium on ecosystem behaviour BIOGEOMON 2012, Maine, 15–19 July, 2012 [poster presentation].

Scott HEM, Aherne J, Metcalfe CD and Metcalfe TL. Ain't no mountain high enough: persistent organic pollutants in remote Irish lake catchments. SETAC North America's 32nd Annual Meeting, Boston, 13–17 November, 2011 [poster presentation].

Scott HEM, Aherne J, Metcalfe CD and Metcalfe TL. The hills are alive: persistent organic pollutants in headwater catchments of Ireland. 7th international symposium on ecosystem behaviour BIOGEOMON 2012, Maine, 15–19 July, 2012 [oral presentation].

Scott HEM, Aherne J, Metcalfe CD and Metcalfe TL. Reach for the Peak: POPs in Irish Headwater Lake Catchments. Society of Environmental Toxicology and Chemistry (SETAC), 33rd Annual Meeting, Long Beach, California, 11–15 November 2012 [poster presentation].

Whitfield CJ, Aherne J and Baulch HM. Greenhouse gas efflux from Irish headwater lakes' at the 3rd Joint CMOS-CGU Congress, Ottawa, 31 May–4 June, 2010 [oral presentation].

Whitfield CJ, Aherne J and Baulch HM. Greenhouse gas efflux from Irish headwater lakes. 31st Congress of the International Limnological Society (SIL 2010), Cape Town, 15–20 August, 2010 [oral presentation].

A1.3 Research Dissertations

Hyland A, 2008. Investigating the predictive capacity of pedotransfer functions for estimating the bulk density and soil organic carbon of Irish forest and moorland soils. MSc Thesis, Environmental and Resource Management, University College Dublin.

Burton A, 2009. Influence of air pollution on the hydrochemistry of small Irish lakes. MSc Thesis, Environmental & Life Science Graduate Program, Trent University.

Scott HEM, 2012. Persistent organic pollutants and mercury in headwater catchments in Ireland. MSc Thesis, Environmental & Life Science Graduate Program, Trent University.

Appendix 2. Data Submitted to the Secure Archive for Environmental Research

Table A2.1. Lake chemical analysis (by sampling event) submitted to the Secure Archive For Environmental Research (SAFER); [F] is a field observation.

Analyte: Equipment [Method]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
pH, Conductivity & Temperature: [F] Hanna meter HI 98129	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
Dissolved Oxygen & Water Pressure : [F] YSI DO meter									×		×	×	×	×	×	
Carbon Dioxide & Barometric Pressure: [F] PP Systems EGM-4 Monitor	×		×													
Temperature: [F] HOBO Pendant Data Logger				×	×	×	×	×	×	×	×	×	×	×		
Conductivity: [F] HOBO U24 Logger									×	×	×	×	×	×	×	×
Water Level: [F] HOBO U20 Logger									×	×	×	×	×	×	×	×
Nitrate: Hach DR 890 Colourimeter [Cadmium Reduction]	×		×	×	×	×	×	×	×	×	×	×	×	×		
Ammonia: Hach DR 890 Colourimeter [Salicylate]	×	×	×	×	×	×	×	×	×		×	×	×	×		
Orthosphosphate: Hach DR 890 Colourimeter [Ascorbic Acid]	×	×	×	×	×	×	×	×	×		×	×	×	×		
Silicate: Hach DR 890 Colourimeter [Heteropoly Blue]			×	×	×	×	×	×	×		×	×	×	×		
Fluoride: Hach DR 890 Colourimeter [SPADNS]			×	×	×	×	×	×	×		×	×	×	×		
Turbidiy: Hach DR 890 Colourimeter [Absorpometric]			×	×	×	×	×	×	×		×	×	×	×		
pH & Conductivity: Low Conductivity Electrode	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
Gran Alkalinity: PC titration Plus System	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
Total Organic Carbon: TOCV-cph Shimazdu Analyser	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
Methane, Nitrous Oxide and Carbon Dioxide: Gas Chromatography [UWO]			×					×	×		×	×	×	×		
Anions [Sulphate, Chloride and Nitrate]: Dionex IC	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
Base Cations [Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}]: Dionex IC	×	×	×	×	×	×	×									
Base Cations [Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}]: Varian FAAS								×	×	×	×	×				
Base Cations [Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}]: PerkinElmer ICP-OES			×	×	×	×	×	×	×	×	×	×	×	×	×	×
Absorbance: UV-VIS Spectrometer	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
Oxygen18 & Deteurium: Thermo Finnigan TC/EA Delta Plus XL [USASK]	×	×	×	×	×	×	×	×	×	×	×	×	×	×		
Trace Metals: Element2 High Resolution ICP-MS	×	×	×						×							
Trace Metals [Cu, Fe, Mn, Al]: PerkinElmer ICP-OES			×	×	×	×	×	×	×	×	×	×	×	×	×	×
Persistent Organic Pollutants [SPMD]: Gel Chromatography & GC-ECD					×	×	×									
Methylmercury: ICP-MS											×	×	×	×		
Total Mercury: TEKRAN 2600 series CVASF Mercury Analysis System			×	×				×	×		×	×	×	×		

Table A2.2. Soil chemical analysis (by sampling event) submitted to the Secure Archive For Environmental Research (SAFER); [F] is a field observation.

Analyte: Equipment [Method]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Temperature: [F] HOBO Pendant Data Logger								×	×		×		×	×		
Nutrient Supply Rates : [F] PRS Probes [Western Ag Innovations]				×	×			×	×		×	×	×			
Nitrogen Mineralization: Buried Bag Technique [KCl extraction]								×	×		×	×	×	×		
Bulk Density Soil: Fixed Volume Core [AMS]			×		×				×		×	×	×			
Loss-on-Ignition: Muffle Furnace	×	×	×		×				×		×	×	×			
Particle Size: Horiba Partica LA 950	×	×	×		×				×							
pH [H2O & CaCl2]: OakTon pH/mV meter	×	×	×		×				×		×	×	×			
Exchangeable Cations: Varian FAAS [NH_4Cl / NaCl Extraction]	×	×	×		×											
Cation Exchange Capacity: Varian FAAS [NH_4Cl / NaCl Extraction]	×	×	×		×											
Exchangeable Acidity: Titration [1.0 M KCl Extraction]	×	×	×		×				×		×					
Exchangeable Cations: PerkinElmer ICP-OES [1.0 M KCl Extraction]	×	×	×		×				×							
Carbon, Nitrogen, Sulphur: Elementar Macro Vario Analyser	×	×														
Phosphorus: UV-VIS Spectrometer	×	×	×		×											
Mineralogy: X-Ray Diffraction [UBC]	×	×														
Total Oxide Analysis: X-Ray Fluorescence [UWO]			×		×											
Persistent Organic Pollutants: Gel Permeation Chromatography & GC-ECD											×					
Total Mercury: Leco AMA 254 Mercury Analyser											×					

Column label (sampling event [month-year and number of samples]): 1 (May 07 [n = 77 (soil n = 7)]), 2 (Oct 07 [n = 11 (soil n = 3)]), 3 (May 08 [n = 126 (soil n = 25)]), 4 (Jan 09, [n = 7]), 5 (Jul 09 [n = 7 (soil n = 29)]), 6 (Nov 09 [n = 4]), 7 (Jan 10 [n = 7]), 8 (Apr 10 [n = 7]), 9 (Jul 10 [n = 6]), 10 (Aug 10 [n = 2]), 11 (Oct 10 [n = 6]), 12 (Jan 11 [n = 7]), 13 (Apr 11 [n = 6]), 14 (Jul 11 [n = 6]), 15 (Aug 11 [n = 1]) and 16 (Oct 11 [n = 1]).

Appendix 3. Upland Study Catchments: Site Characteristics

Table A3.1. Description (site ID, lake name, co-ordinates [WGS84], etc.) of the five study catchments (see Fig. 5.1).

ID	Lake name	Mountain range	County	Latitude	Longitude	Altitude	Area (ha)		Rainfall	OSI
				(decimal degrees)		(m)	Lake	Catchment	(mm)	
L0808	Lough Cummeenoughter	MacGillycuddy's Reeks	Kerry	52.00292	–9.74550	715	0.35	1.9	3060	78
L0931	Lough Adanacleveen	Slieve Carr	Mayo	54.06572	–9.65259	555	1.52	15.5	1701	23
L1841	Mullincrick Lough	Crocknafarragh	Donegal	54.99745	–8.19536	495	0.85	4.5	2003	01
L2211	Sgilloge Lough	Comeragh	Waterford	52.25440	–7.56608	505	2.36	63.4	1895	74
L3020	Cleevaun Lough	Mullaghcleevaun	Wicklow	53.10605	–6.40174	685	1.78	10.1	1847	56

Table A3.2. Average lake water chemistry [§] for the upland study catchments (n = 5) sampled (n = 9) during the period 2009–2011.

ID	EC	pH	ALK	DOC	Cl^-	SO_4^{2-}	PO_4^{3-}	NO_3^-	NH_4^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	Al	Fe	Mn	Cu	SiO_2
	µS cm^{-1}	mg L^{-1}												µg L^{-1}				mg L^{-1}
L0808	24.8	5.77	0.43	1.07	5.96	1.38	0.11	0.30	0.04	0.46	0.43	0.21	3.11	25.6	15.0	5.3	13.8	0.58
L0931	51.2	4.58	–0.70	4.10	12.12	2.00	0.05	0.37	0.04	0.40	0.70	0.43	6.39	80.0	44.9	8.8	26.5	0.54
L1841	49.7	4.67	–0.57	4.45	13.06	2.24	0.09	0.16	0.05	0.35	0.83	0.38	7.05	90.8	79.4	18.8	10.7	0.41
L2211	25.1	5.36	0.25	3.81	4.86	1.44	0.05	0.44	0.07	0.36	0.57	0.22	2.84	70.1	94.2	12.1	18.9	0.50
L3020	25.2	4.60	–0.58	5.84	4.45	1.57	0.07	0.41	0.05	0.27	0.34	0.32	2.71	74.7	32.9	9.0	11.8	1.09

[§] Chemical observations: conductivity (EC at 25°C), gran alkalinity (ALK), dissolved organic carbon (DOC), chloride, sulphate, phosphate, nitrate, ammonium, calcium, magnesium, sodium, total aluminium, total iron, total manganese, total copper, and silica oxide.

Table A3.3. Soil physicochemical characteristics (bulk density [ρ], pH, loss-on-ignition [LOI], nitrogen [N], carbon [C] and sulphur [S]) and average bioavailable nutrient supply rates based on Plant Root Simulator (PRS™) probes installed during the period 2009–2011 at the upland lake catchments.

ID	ρ	pH	LOI	N	C	S	NO_3^--N	NH_4^+-N	Ca^{2+}	Mg^{2+}	K^+	Al^{3+}	Fe^{3+}	Mn^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}
	g cm^{-3}		%	%	%	%	(µg per 10 cm^{-2} per burial length §)											
L0808	0.536	4.33	7.0	0.31	3.46	0.05	15.2	4.0	737.1	957.6	22.7	72.4	6.3	19.5	0.1	4.2	0.9	0.1
L0931	0.125	4.00	96.2	1.69	47.46	0.34	3.5	3.8	642.3	1119.6	10.6	16.0	75.9	6.5	0.2	9.5	15.8	0.1
L1841	0.142	3.95	96.0	1.66	47.49	0.30	2.2	4.6	631.4	1059.1	22.3	34.3	46.3	8.5	0.7	7.6	8.6	0.1
L2211	0.163	3.81	92.9	2.07	47.72	0.35	2.6	3.7	789.7	1060.9	12.2	27.9	17.3	4.1	0.1	15.1	3.7	0.2
L3020	0.116	3.82	85.1	2.00	44.37	0.37	7.5	4.9	701.3	731.2	37.2	97.6	92.4	3.8	0.1	22.0	6.0	0.3

§Exposure weighted average of five sampling periods, approximately 85 days per exposure.

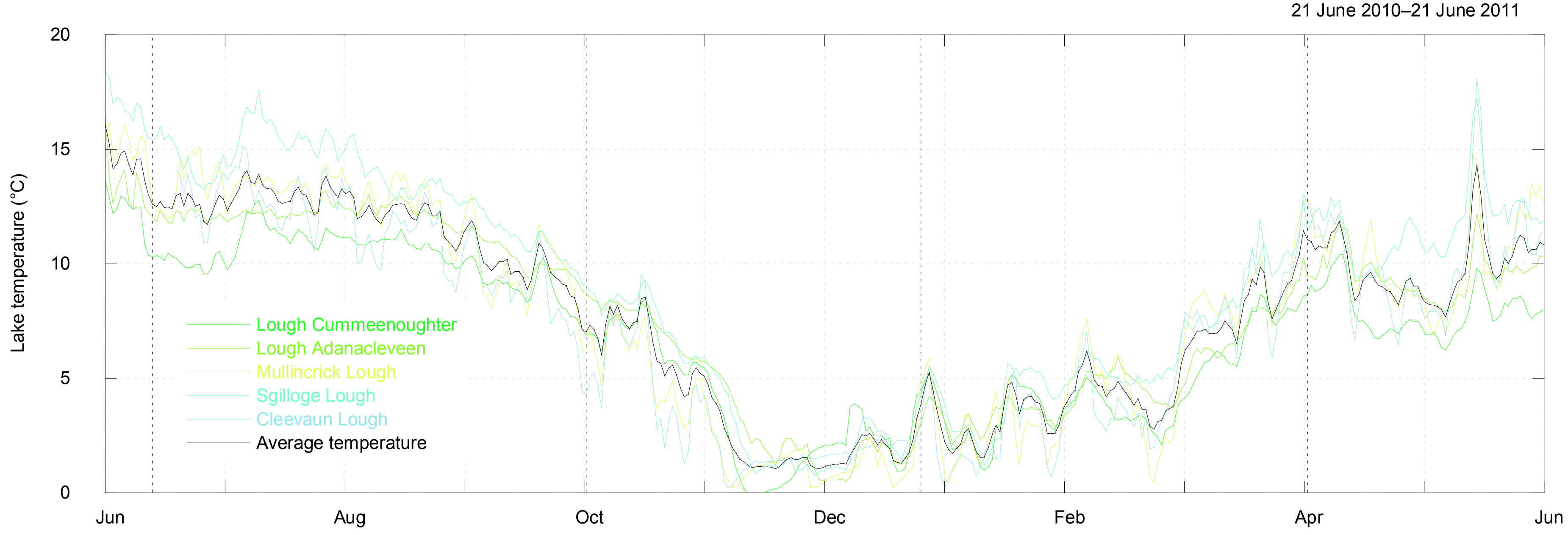


Figure A3.1. Water temperature (°C) for the upland study lakes during the period June 2010–June 2011. Average water temperature of the five lakes is also shown (black line). Dates of hydrochemical sampling during the period are indicated by dashed-black horizontal lines (n = 4).

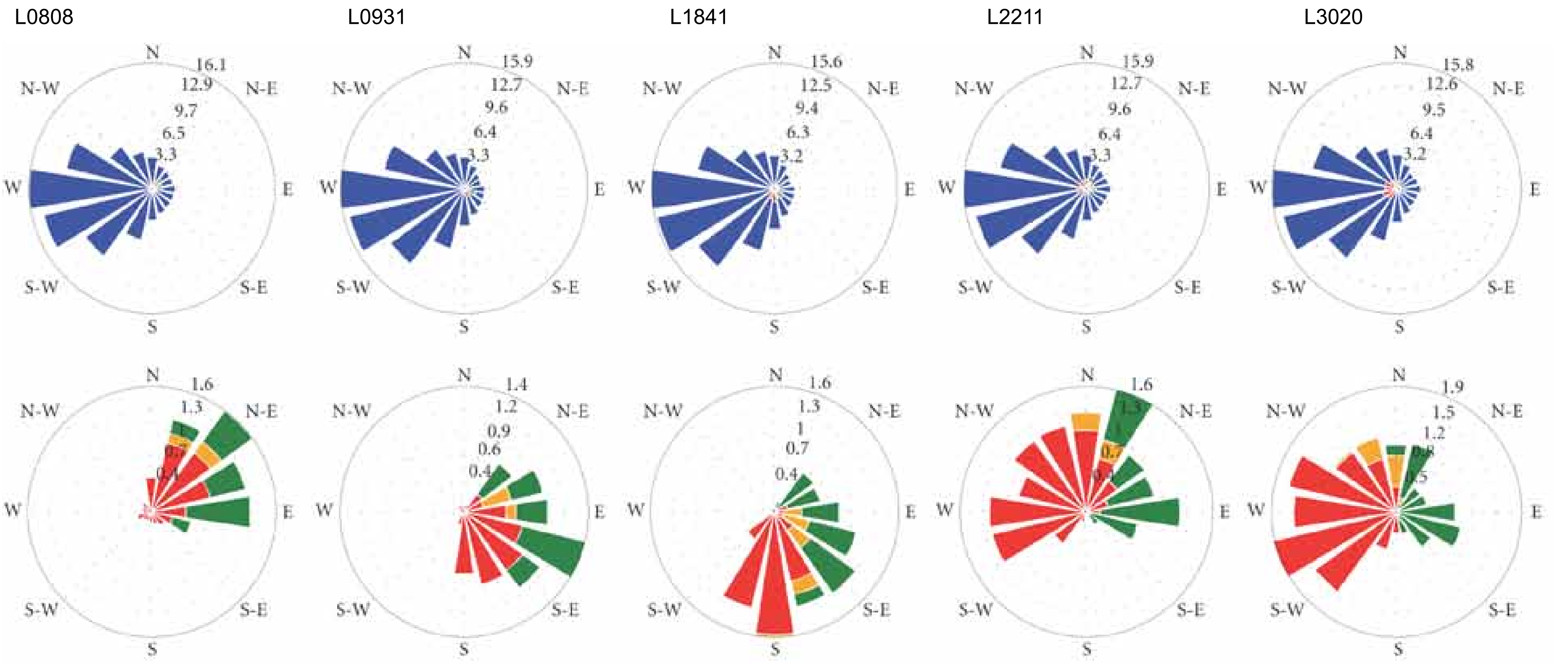


Figure A3.2. Upper: Wind rose source-receptor plots showing the proportion (%) of air by direction and source (Republic of Ireland [red], northern Ireland [orange], Great Britain [green] and Marine and other regions [blue]) arriving at the upland study catchments (receptors; arrival height of 850 hPa) based on two-day back-trajectories estimated every six hours during the period 1989–2009 using historical wind fields (observed data and model output) smoothed onto a 3-dimensional grid with 16 pressure levels and a horizontal resolution of 1 × 1 degree obtained from the ECMWF ERA Interim data set (Dee et al., 2010). Lower: Close-up showing the proportion (%) of air by direction from three terrestrial source regions: Republic of Ireland (red), northern Ireland (orange) and Great Britain (green) only.

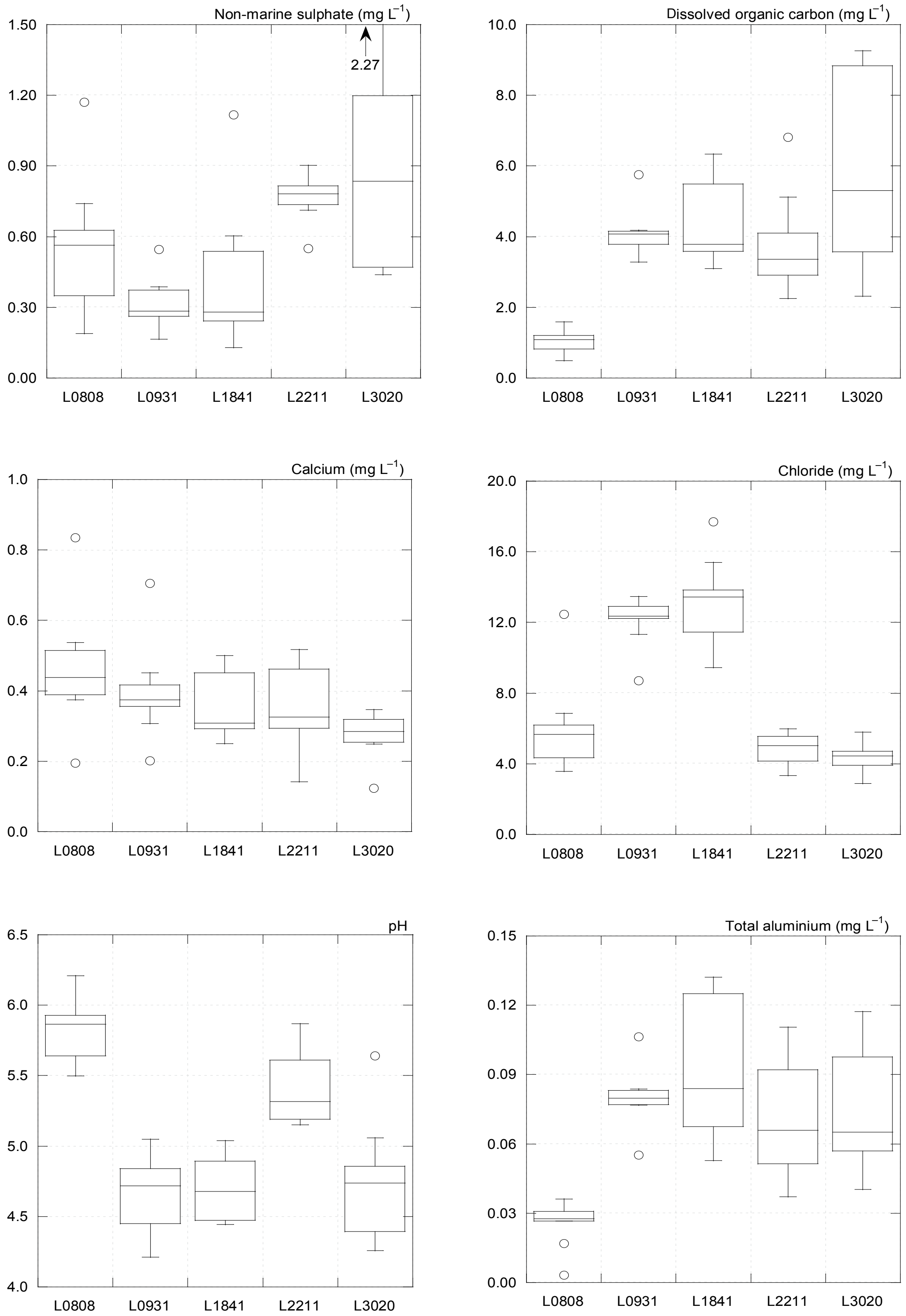


Figure A3.3. Box-plot comparison of lake water chemistry (non-marine sulphate, dissolved organic carbon, calcium, chloride, pH and total aluminium) at the upland study catchments (n = 5) sampled (n = 9) during the period 2009–2011. See Table A3.1 for site description and Table A3.2 for average lake chemistry. Non-marine sulphate estimated as $[SO_4^{2-}] - 0.121 \times [Na^+]$.

An Ghníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomhnithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Ghníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil, Pobal agus Rialtais Áitiúil.

ÁR bhFREAGRACHTAÍ

CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreail;
- scardadh dramhuisce;
- dumpáil mara.

FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisce agus caighdeán uisce
- Obair le húdaráis áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí comhordú a dhéanamh ar líonra forfheidhmithe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a ngníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOL

- Monatóireacht ar chaighdeán aeir agus caighdeáin aibhneacha, locha, uiscí taoide agus uiscí talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntí a dhéanamh.

RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

TAIGHDE AGUS FORBAIRT COMHSHAOIL

- Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdéan aeir agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

MEASÚNÚ STRAITÉISEACH COMHSHAOIL

- Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le pleananna bainistíochta dramhaíola agus forbartha).

PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

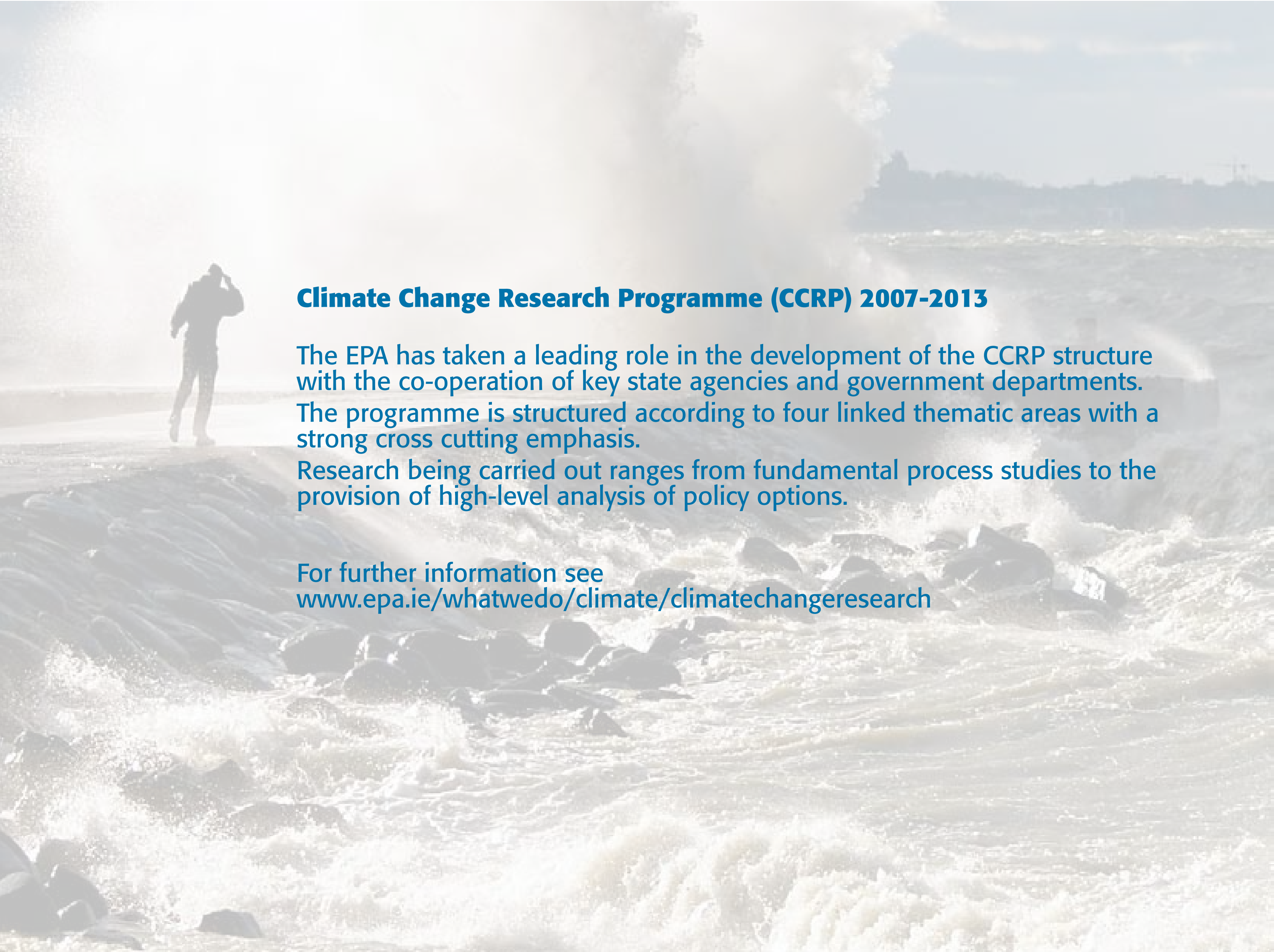
STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Ghníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstiúrthóir agus ceithre Stiúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmiúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.



Climate Change Research Programme (CCRP) 2007-2013

The EPA has taken a leading role in the development of the CCRP structure with the co-operation of key state agencies and government departments. The programme is structured according to four linked thematic areas with a strong cross cutting emphasis. Research being carried out ranges from fundamental process studies to the provision of high-level analysis of policy options.

For further information see
www.epa.ie/whatwedo/climate/climatechangeresearch

Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

ENVIRONMENTAL PROTECTION AGENCY
PO Box 3000, Johnstown Castle Estate, Co. Wexford, Ireland
t 053 916 0600 f 053 916 0699
LoCall 1890 33 55 99
e info@epa.ie w http://www.epa.ie

SSTI
Strategy for Science, Technology and Innovation

Comhshaol, Pobal agus Rialtas Áitiúil
Environment, Community and Local Government