Trace Metals in Upland Headwater Lakes in Ireland

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Abstract Trace elements ($n = 23$) in Irish headwater lakes ($n = 126$) were investigated to determine their ambient concentrations, fractionation (total, dissolved, and non-labile), and geochemical controls. Lakes were generally located in remote upland, acid-sensitive regions along the coastal margins of the country. Total trace metal concentrations were low, within the range of natural pristine surface waters; however, some lakes ($\sim 20\%$) had inorganic labile aluminum and manganese at levels potentially harmful to aquatic organisms. Redundancy analysis indicated that geochemical weathering was the dominant controlling factor for total metals, compared with acidity for dissolved metals. In addition, many metals were positively correlated with dissolved organic carbon indicating their affinity (or complexation) with humic substances (e.g., aluminum, iron, mercury, lead). However, a number of trace metals (e.g., aluminum, mercury, zinc) were correlated with anthropogenic acidic deposition (i.e., non-marine sulfate), suggesting atmospheric sources or elevated leaching owing to acidic deposition. As transboundary air pollution continues to decline, significant changes in the cycling of trace metals is anticipated.

Keywords Water chemistry · Long-range atmospheric transport · Fractionation · Dissolved organic carbon · Geochemical weathering · Marine inputs

INTRODUCTION

The concentration of trace metals in pristine surface waters is related to a number of factors including lithology of the terrestrial catchment, atmospheric inputs, and climatic conditions (Tarvainen et al. 1997). Although metals are a

natural component of the environment, human activities have greatly contributed to their elevated concentration in surface waters (Skjelkvåle et al. 2001a), e.g., long-range atmospheric transport associated with the emission and deposition of acidifying compounds (Dickson 1980; Borg 1986; Steinnes 2001). Moreover, in acid-sensitive regions, acidic deposition has led to the mobilization of metals from catchment soils and increased concentrations in surface waters (Morel and Hering 1993; Lydersen et al. 2002).

The physico-chemical form (speciation) and concentration of metals in surface waters is determined by interactions between pH, redox potential, the presence of complexing anions, and the availability of organic ligands (Gundersen and Steinnes 2003). Trace metals in natural waters exist as free ‘labile’ ions, inorganic and organic complexes, colloids, or suspended (particulate) solids; free metal ion concentrations are associated with toxicity to aquatic organisms (Gundersen and Steinnes 2003).

The potential toxic effect of elevated ‘free’ trace metals owing to acidic deposition has prompted lake surveys in Europe and North America, notably in regions dominated by acid-sensitive soils and geology [Finland (Verta et al. 1990; Mannio et al. 1995; Tarvainen et al. 1997; Mannio 2001), Norway (Henriksen and Wright 1978; Skjelkvåle et al. 2001b), Sweden (Borg 1983, 1986; Borg and Johansson 1989), Italy (Tornimbeni and Rogora 2012), United States of America (Schindler 1988; Baker et al. 1991), and Canada (Dillon et al. 1988; Shotyk and Krachler 2009)].

Ireland is located on the western periphery of Europe and predominantly receives clean air masses from the Atlantic. Nonetheless, the impacts of acidic deposition has been a potential concern since the 1980s (Bailey et al. 1986) owing to the preponderance of surface waters in acid-sensitive regions (Bowman 1991; Flower et al. 1994)

and long-range transport of acidifying compounds associated with easterly air masses from western Europe (Bowman and McGettigan 1994). While several studies have investigated the concentrations of trace metals in Irish soils (Fay et al. 2007), lake sediments and mosses (Bowman and Harlock 1998; Rose et al. 1998), few studies, if any, exist for surface waters.

The objective of this study was to determine the concentration, fractionation (labile vs non-labile), and potential sources of trace metals in upland headwater lakes in Ireland. In total, 126 lakes were sampled during spring 2008 and analyzed for total (unfiltered), dissolved ($<0.45\ \mu\text{m}$ filter) and organically bound [fractionated using solid phase extraction (SPE)] metals, and major elements including dissolved organic carbon (DOC) and pH. The relative importance of potential sources or drivers was investigated by redundancy analysis (RDA), primarily focusing on four explanatory variables: organic matter (expressed as DOC), geochemical weathering [expressed as lake calcium (Ca^{2+})], marine sources [expressed as lake chloride (Cl^-)] and atmospheric transport [expressed as non-marine sulfate (nmSO_4^{2-}) deposition] following Skjelkvåle et al. (2001b).

MATERIALS AND METHODS

Study Sites

During May 2008, 126 small headwater lakes [average area = 5.3 ha (Table 1)] in the Republic of Ireland were sampled to determine baseline ambient concentrations of trace metals. The study sites were selected to be free from local sources of pollution and were generally located in remote, predominantly upland acid-sensitive regions along the coastal margins of the country (Fig. 1). The study lakes were a sub-set of an acid-status lake survey conducted in 1997 (Aherne et al. 2002) and re-surveyed during 2007–2008 (Whitfield et al. 2011; Burton and Aherne 2012). Lakes were pseudo-randomly selected based on bedrock geology and soil characteristics, with greater weighting towards higher elevation, acid-sensitive regions (for further details see Aherne et al. 2002).

The study lakes ranged in elevation from 36 to 704 masl (average = 279 masl), land cover was dominated by moorland, vegetation included coarse grasses (*Juncus squarrosus*, *Carex*, and *Nardus* spp.), peat moss (*Sphagnum* spp.), and heather (*Calluna vulgaris*), and occasional rough grazing was the principal land use. The dominant soil types were classified as lithosols with outcropping rock, blanket peat, or peaty podzol (Fig. 1). The climate of Ireland is moderated by the Atlantic Ocean, exhibiting a humid maritime climate with mild winters and short warm summers; long-term (1961–1990) annual precipitation volume

at the study lakes ranged from 967 to 3044 mm year⁻¹ and annual average air temperature from 8.8 to 10.5 °C.

Sampling and Analysis

Lake samples were collected in 250 mL plastic HDPE bottles; acid washed (10 % HCl) and rinsed three times with de-ionized water. Samples for total mercury (Hg^{2+}) were collected in 40 mL glass i-Chem vials and acidified with 2 % reagent grade concentrated hydrochloric (HCl) acid. All water samples were collected 10–20 cm below the lake surface in near shore areas free from vegetation and away from lake inlets and outlets. Comparison between shore and center lake samples (and surface and depth samples) for a sub-set of lakes indicated no statistical difference in chemistry, as lakes were generally shallow ($<10\ \text{m}$) and well-mixed owing to the mild and windy climate (annual average wind speeds range from 11 km h⁻¹ in the south to 29 km h⁻¹ in the north). Prior to sample collection, all bottles were rinsed five times with lake water. To minimize headspace, all samples were capped underwater. Upon collection, sample bottles were kept cool, out of sunlight, and sent for analysis as soon as possible.

In the laboratory, lake water was transferred into triplicate 15 mL falcon tubes for analysis of total, dissolved, and fractionated (non-labile) trace metals. Dissolved samples were passed through a 0.45 μm filter, and non-labile samples were subsequently passed through a Varian ELUT jr SPE fractionation cartridge. It is generally accepted that ‘dissolved’ refers to the fraction of water that has passed through a 0.45 μm filter. This classification is operationally defined, as the filtrate may contain metals bound to colloids with clay, humic acids (size range 10–450 nm), metal organic and inorganic complexes, or free inorganic ions. Nonetheless, dissolved concentrations better approximate the bio-available fraction of water-borne metals. In the SPE column, neutral or negatively charged metal species (e.g., organic bound) passed through, while free labile metals were trapped; see Tangen et al. (2002) for further details. All samples [total, dissolved, and fractionated (non-labile)] were acidified and preserved with 2 % ultrapure grade nitric (HNO_3) acid.

All sample fractions were analyzed 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 (Se and Hg only analyzed on a sub-set of samples)] using an Element2 High Resolution ICP-MS. Total mercury ($n = 56$) was analyzed using a TEKRA 2600 series CVASF Mercury Analysis System. In addition, all lake samples were analyzed for pH, conductivity, alkalinity, major ions, and DOC; pH and conductivity were analyzed using a low conductivity electrode. Gran alkalinity was measured using a PC titration Plus System. Anions (Cl^- ,

Table 1 Summary statistics [5th, 25th, 50th, 75th, 95th percentile, mean, and standard deviation (SD)] for chemical characteristics and trace metal concentrations in small Irish lakes ($n = 126$) surveyed during 2008. 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

Variable	Units	5th	25th	50th	75th	95th	Mean	SD	%BDL ^a
Lake size	ha	0.5	1.0	2.5	4.8	24.8	5.3	8.2	
Altitude	m	67.8	148.5	254.5	381.8	593.3	278.8	163.5	
Air temperature	°C	8.9	9.0	9.5	9.9	10.4	9.7	0.5	
Precipitation	mm year ⁻¹	1094.5	1320.3	1506.5	1775.5	2227.0	1568.2	355.9	
SO ₄ ²⁻ deposition	meq m ⁻²	12.7	16.8	21.0	25.8	38.1	22.4	7.9	
pH		4.2	4.8	5.9	6.5	7.7	4.9	1.1	
Conductivity	μS cm ⁻¹	43.7	87.6	109.9	147.5	253.5	127.7	67.1	
DOC	mg L ⁻¹	1.5	3.0	4.3	6.6	11.0	5.0	2.9	
Ca ²⁺	μeq L ⁻¹	40.6	68.0	91.9	146.7	971.3	227.0	412.4	
Cl ⁻	μeq L ⁻¹	265.9	513.9	698.4	980.0	1518.2	789.0	442.6	
Al	μg L ⁻¹	14.92	26.31	38.60	62.74	127.29	50.57	40.27	0
As	μg L ⁻¹	0.01	0.07	0.31	0.69	3.49	0.88	1.21	2
B	μg L ⁻¹	4.48	6.90	8.22	10.50	16.77	9.21	3.75	0
Ba	μg L ⁻¹	0.50	1.37	3.36	9.07	29.27	8.30	15.03	0
Bi	μg L ⁻¹	0.39	0.67	0.68	0.81	1.28	0.78	0.33	4
Co	μg L ⁻¹	0.00	0.02	0.04	0.05	0.20	0.05	0.06	91
Cr	μg L ⁻¹	0.16	0.24	0.31	0.44	0.72	0.36	0.19	4
Cu	μg L ⁻¹	0.01	0.03	0.05	0.20	1.04	0.27	0.66	63
Fe	μg L ⁻¹	7.75	26.44	64.87	163.09	442.35	122.97	165.67	0
Hg ^a	ng L ⁻¹	1.79	2.27	2.78	3.82	5.37	3.13	1.22	0
Mn	μg L ⁻¹	2.29	6.81	22.58	62.46	166.36	47.53	72.94	0
Mo	μg L ⁻¹	0.65	0.95	1.05	1.32	2.79	1.35	1.06	2
Ni	μg L ⁻¹	0.02	0.07	0.18	0.41	1.51	0.38	0.56	25
Pb	μg L ⁻¹	0.00	0.00	0.06	0.14	0.54	0.14	0.23	20
Se ^a	μg L ⁻¹	0.14	0.70	1.03	1.31	1.74	0.99	0.57	20
Sr	μg L ⁻¹	5.65	9.07	13.49	21.97	78.26	22.05	25.42	0
Ti	μg L ⁻¹	0.44	0.75	1.09	1.87	10.87	2.25	3.40	1
Tl	μg L ⁻¹	0.02	0.08	0.09	0.10	0.13	0.08	0.03	24
U	μg L ⁻¹	0.03	0.05	0.05	0.06	0.12	0.06	0.04	23
V	μg L ⁻¹	0.01	0.02	0.05	0.13	0.50	0.11	0.16	65
Zn	μg L ⁻¹	0.17	0.49	0.80	3.21	8.52	2.45	3.59	62

^a Chemical analysis only available for a sub-set of lakes (Hg = 54, Se = 10); observations for total Be and Cd concentrations were below detection in all lakes (100 % BDL)

SO₄²⁻) and cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) were analyzed using a Dionex 600 Ion Chromatograph, and DOC was determined on a TOCV-cph Shimadzu analyzer.

Quality Control

All precautions were taken to avoid contamination of lake samples. High-purity de-ionized distilled water (18 MΩ cm⁻¹) was used for all standard and sample solutions. All plastic ware was rinsed three times with Milli-Q water, soaked with 10 % HCl (ultrapure grade) for 3 days, and rinsed again three times with Milli-Q water. Gloves were

used at all times during trace metal sampling and analyses. All glass i-Chem vials were soaked (at room temperature) in bromine chloride (BrCl) solution (16 L H₂O, 160 mL HCl, and 80 mL BrCl) for 3 days, washed with Milli-Q water, and oven dried at 60–80 °C. Further, i-Chem vials were rinsed with 10 mL of lake water prior to sample collection, and transported using double Ziploc bags.

Water samples were analyzed for trace metal concentrations at the Trent University Water Quality Centre. All analysis was conducted in a filtered air clean room environment that exceeded Class-100 specifications. The standard working solutions and the verification standards of Be,

Fig. 1 Location of study lakes ($n = 126$); green shading indicates the distribution of organic (peaty podzols [light green] to peat [dark green]) soils (source: General soil map of Ireland; Gardiner and Radford 1980)

B, Al, V, Cr, Mn, Sr, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, Tl, Pb, Bi, and U were prepared from a 10 mg L^{-1} multi-element standard stock solution by diluting to different volumes with 2 % HNO_3 (v/v) solution to encompass the anticipated elemental concentrations of certified reference materials in the ICP-MS analysis solution. The sample solution and the multi-element internal standards solution consisting of $1.0 \text{ } \mu\text{g L}^{-1}$ of Sc, In, and Rh, were used to cover the entire mass region of interest. The ICP-MS was optimized daily by aspirating a $1.0 \text{ } \mu\text{g L}^{-1}$ solution of ^7Li ,

^{115}In , ^{238}U in 2 % (v/v) HNO_3 solution. The sample solution and the internal standard solution were delivered via a peristaltic pump and mixed before being introduced into the ICP-MS nebulizer. Standard and sample solutions were stored in Teflon bottles, soaked in 5 % (v/v) HNO_3 and rinsed with de-ionized water before use. The ICP-MS calibration/verification standards ($100 \text{ } \mu\text{g L}^{-1}$ multi-element) were prepared by diluting 1 mL of the premixed standards (PlasmaCal—ICP-MS, SCP Science, Baie D Urfé, QC, Canada). The tuning solution of $1 \text{ } \mu\text{g L}^{-1}$ of Li,

In, and U in 2 % HNO₃ and the internal standard solution of 1 µg L⁻¹ of Sc, Rh, and In in 2 % HNO₃ were prepared from CLMS2 multi-element standards.

Emission and Deposition of Metals

Metal emission data (Gg year⁻¹) for Ireland during the period 1990–2008 were obtained from the Centre on Emission Inventories and Projections under EMEP [the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (www.ceip.at)]. In addition, metal concentrations in bulk precipitation during the period 2004–2009 were acquired for Lough Navar, Northern Ireland via the Chemical Coordinating Centre under EMEP (www.nilu.no/projects/ccc). Monthly precipitation was analyzed for As, Cd, Cr, Cu, Pb, Ni, Zn (µg L⁻¹) and Hg (ng L⁻¹) using ICP-MS (pollutantdeposition.defra.gov.uk). The Mann–Kendall test (Salmi et al. 2002) was employed to determine the long-term (monotonic) trend in metal emission data.

Statistical Analysis

All statistical analysis incorporated trace metal observations reported as below detection by following standard data imputation techniques, i.e., observations below detection were simulated by randomly sampling between zero and the reported limit. Nonetheless, statistical relationships for metals with a large proportion of samples reported as ‘below detection’ (Table 1) should be viewed as tentative.

The potential sources or drivers of trace metals in the study lakes were investigated using RDA. Metals were excluded if analysis was not available for the full set of study lakes ($n = 126$), e.g., total trace metal concentrations of Hg and Se. 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 (Ter Braak and Prentice 1988). 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. The objective of the analysis was to determine the (minimum number of) variables that explained the observed metal concentrations; the selection of explanatory variables followed (and built upon) Skjelkvåle et al.

(2001b). All data were transformed (centered and standardized) prior to data analysis. Further, a wider range of explanatory variables including climate [precipitation and altitude (temperature surrogate)] and transboundary transport (expressed as longitude reflecting the strong east to west gradient associated with anthropogenic emissions from Europe) were evaluated using Pearson product–moment correlation coefficients as a measure of linear association with metal concentrations.

Finally, a simple input–output budget (total deposition minus lake export) was employed to investigate the importance of atmospheric sources for As, Cr, Cu, Ni, Pb, and Zn. The budget calculation (annual average metal concentration in precipitation at Lough Navar [2006–2008] × lake rainfall volume minus average lake concentration × catchment runoff volume) was used to estimate the proportion of metal input from atmospheric sources compared with output.

RESULTS

Emission and Deposition of Metals

Emissions of trace metals in Ireland were low given the low population (<1 % of the Europe Union 27 member states); however, the ratio of As and Ni emissions to Gross Domestic Product (GDP) is notably higher than in other industrialized western European countries (with similar GDP) such as the United Kingdom, Belgium, France, and Germany (see Table 2). Trace metal emissions in Ireland during 2007–2008 from highest to lowest (56.7–0.6 tons year⁻¹) followed the order; Ni > Cu > Zn > Pb > Cr > Se > As > Hg > Cd. Emissions in Ireland significantly ($p \leq 0.05$) decreased for As ($r^2 = 0.88$; 35 %), Cd ($r^2 = 0.48$; 37 %), Cr ($r^2 = 0.94$; 47 %), Pb ($r^2 = 0.85$; 87 %), and Zn ($r^2 = 0.68$; 56 %) between 1990 and 2009 owing to reduction in metal production, part replacement of coal and peat by natural gas, gas oil and kerosene energy production, and the use of unleaded fuel gasoline. In contrast, emissions significantly increased for Cu ($r^2 = 0.90$; 53 %), Ni ($r^2 = 0.15$; 12 %), and Se ($r^2 = 0.18$; 10 %) owing to increases in manufacturing, and construction industries, and vehicular transport. Further, the lack of a significant trend for Hg has been attributed largely to combustion sources in manufacturing and construction industries.

Metal concentration in precipitation at Lough Navar followed emissions decreasing for Cd ($r^2 = 0.58$; 67 %), Cr ($r^2 = 0.36$; 34 %), and Pb ($r^2 = 0.52$; 44 %) between 2004 and 2009. In contrast, no clear change in As, Ni, or Zn precipitation concentration was observed owing to minimal changes in emissions since 2004. Further, Cu declined in deposition, but increased in emissions. The disconnect

between deposition and emission for Cu, As, Ni, and Zn may be related to the limited precipitation chemistry data, high rainfall amounts (washout effect), or metal influx from transboundary sources (e.g., Great Britain). The transboundary transport of metals (e.g., Cd, Pb, Hg) was estimated to be responsible for approximately half of the anthropogenic deposition in Ireland during 2009 (Ilyin et al. 2011).

Hydrochemical Characteristics of Small Irish Lakes

The study lakes were dilute (median conductivity 109.9 $\mu\text{S cm}^{-1}$), softwater lakes with low pH (median 5.9) and moderately high DOC concentration (median 4.3 mg L^{-1}); the pH ranged from 3.88 to 8.02, and a wide range in DOC concentrations was observed (from 0.6 to 14.0 mg L^{-1}) owing to the variability of peat soil coverage within the lake catchments (Table 1). Lake chemistry was dominated by the influence of air masses from the Atlantic Ocean, carrying high concentrations of sea-salts (primarily Cl^- , Na^+ , Mg^{2+} , and SO_4^{2-}). Accordingly, the highest conductivity was observed in lakes nearest to the coast at lower elevation, with values ranging from 35.2 to 405.0 $\mu\text{S cm}^{-1}$. Moreover, Cl^- (40 % of total ion equivalent concentration) and Na^+ (33 % of total ion equivalent concentration) were the dominant ions in the study lakes. Chloride concentrations ranged from 175.6 to 2807.3 $\mu\text{eq L}^{-1}$ with a median of 697.2 $\mu\text{eq L}^{-1}$, and were strongly correlated to Na^+ ($r^2 = 0.99$), Mg^{2+} ($r^2 = 0.61$), and SO_4^{2-} ($r^2 = 0.30$) indicating their dominant marine source. In contrast, Ca^{2+} was poorly correlated with Cl^- indicating geochemical sources in the study catchments. Calcium concentration in the study lakes was generally low, with a median of 91.4 $\mu\text{eq L}^{-1}$ (range from 37.7 to 2977 $\mu\text{eq L}^{-1}$).

Trace Metal Concentrations and Geographic Distribution

In general, trace metal concentrations in the study lakes were low (Table 1), within the range of pristine (unpolluted) surface water concentrations (Galvin 1996). The order (highest to lowest) of total trace metal concentrations ($\mu\text{g L}^{-1}$) was: $\text{Fe} > \text{Al} > \text{Mn} > \text{Sr} > \text{B} > \text{Ba} > \text{Ti} > \text{Mo} > \text{Zn} > \text{Bi} > \text{As} > \text{Cr} > \text{Ni} > \text{Tl} > \text{Pb} > \text{Cu} > \text{U} > \text{V} > \text{Co}$ [$> \text{Se} > \text{Cd} > \text{Be} > \text{Hg}$ (Cd and Be were below detection, and Se and Hg were only analyzed on a sub-set of lake samples)]. The study lakes were strongly dominated by Fe, Al, and Mn and to a lesser extent by Sr and B concentrations (Table 1). Given the low concentrations, measurements BDL were common for certain elements such as Co (91 %), V (65 %), Cu (63 %), and Zn (62 %).

The majority of the trace metals were within or towards the lower end of the expected range for pristine surface

waters, e.g., Pb concentrations in pristine freshwaters typically range between 0.1 and 1.5 $\mu\text{g L}^{-1}$ (Allen and Hansen 1996); in the study lakes, median Pb was 0.06 $\mu\text{g L}^{-1}$ (Table 1). Total Hg ranged between 0.2 and 7.5 ng L^{-1} (median 2.8 ng L^{-1}); typical concentrations for pristine surface waters range from 1 to 10 ng L^{-1} (Ravichandran 2004). The observed concentrations for Co, Cu, Ti, and U were below the expected level for unpolluted surface waters, e.g., Cu [median of 0.05 $\mu\text{g L}^{-1}$ (reported as below detection)] was below the typical concentration range of 0.5–1.0 $\mu\text{g L}^{-1}$ (Lydersen et al. 2002); similarly Ti (median of 1.1 $\mu\text{g L}^{-1}$) was below the natural surface water range of 2–100 $\mu\text{g L}^{-1}$. In contrast, B ranged from 3.7 to 25.1 $\mu\text{g L}^{-1}$ (median of 8.2 $\mu\text{g L}^{-1}$) compared with typical concentrations in surface waters of 5–10 $\mu\text{g L}^{-1}$ (Zhu and Wang 2007), owing to contribution from marine sources in the study lakes. Several trace metals [such as As, Cr, Al, Bi, Hg, Zn, and Pb (Fig. 2; Table 2)] showed a decreasing concentration westward, away from point sources of pollution in Western Europe.

Partitioning of Trace Metals

Trace metals (i.e., Al, Mn, Fe, As, B, Ba, Cu, Ni, Pb, Sr, and V) in the study lakes were predominantly in dissolved form; although elevated particulate fractions (estimated as the difference between total and dissolved concentrations) were observed for Mn (20 %), Al (24 %), and Fe (33 %); dissolved fractions were significantly lower ($p < 0.001$) compared with total (Fig. 3). The dissolved labile phase (estimated as the difference between dissolved and non-labile) was the dominant 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.

The results were consistent with other speciation studies, i.e., trace metals such as Zn, Ni, Mn, and As have been found to be mainly in dissolved form and Al, Fe (Fig. 3), and Cu in dissolved or colloidal organic complexes (Morel and Hering 1993). Nonetheless, the relationship between trace metals and water chemistry, primarily pH and DOC, tend to alter the speciation (physico-chemical form) of trace metals.

Relationship Between Water Chemistry and Other Explanatory Variables

The RDA indicated that the four variables (DOC , Ca^{2+} , Cl^- , and nmSO_4^{2-}) explained much of the variation in total metal concentrations (Fig. 4). The first three axes

Fig. 2 Geographic distribution of total concentrations for lead (Pb), arsenic (As), nickel (Ni), and manganese (Mn) for the study lakes ($n = 126$) in 2008 delineating median and 75th percentile ranges as given in Table 1 (<median [*blue*], median to 75th percentile [*yellow*], and >75th percentile [*red*])

Table 2 Ratio of average annual national metal emission (g year^{-1}) for 2006–2008 to Gross Domestic Product (GDP; millions US dollars)

Country	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn
Ireland	14.0	2.8	21.9	124.5	3.7	264.4	79.3	17.3	93.2
United Kingdom	6.2	1.3	13.5	26.4	3.0	49.5	35.4	16.2	169.2
France	3.8	1.5	12.6	61.7	1.8	41.1	39.3	5.0	79.0
Netherlands	1.1	2.2	2.7	100.2	1.0	11.6	47.4	1.7	103.9
Sweden	1.8	1.0	22.8	102.3	1.2	32.3	23.0	1.4	310.8
Belgium	9.6	5.9	39.4	116.2	6.5	55.1	163.1	24.5	275.3
Germany	2.0	1.6	29.0	597.7	2.0	38.6	83.9	1.1	527.0

Source: Centre on Emission Inventories and Projections under the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (www.ceip.at)

Fig. 3 Box plots showing total, dissolved, and non-labile aluminum, manganese, and iron in the study lakes ($n = 126$). 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

Fig. 4 Redundancy analysis (RDA) ordination plots for total (*left*) and dissolved (*right*) trace metals in the study lakes (see Fig. 1) during 2008. Arrow lines (independent variables, vectors) indicate the biplot of each of the explanatory variables; filled circles indicate trace metals (dependent variables)

(RDA 1 = 61.5 %, RDA 2 = 19.5 %, and RDA 3 = 15.7 %) explained 97 % of the variance (Fig. 4). The first axis was dominated by Ca^{2+} ($r = 0.99$), suggesting that geochemical weathering was the most important determinant of trace metals in the study lakes; Ca^{2+} was positively correlated with Ti ($r = 0.88$), Sr ($r = 0.86$), Ni ($r = 0.80$), Ba ($r = 0.64$), and U ($r = 0.62$). Similarly, these metals

were positively correlated with pH (Table 3). The second axis was dominated by DOC ($r = 0.72$) indicating complexation with humic substances (e.g., Al and Fe, see Fig. 3) or release from sounding peat soils owing to acidic or redox processes. Dissolved organic carbon was positively correlated with many metals (Table 3), e.g., Hg ($r = 0.60$), Fe ($r = 0.48$), and Pb ($r = 0.45$). Surface water

Table 3 Pearson product-moment correlation coefficients (r values) for total trace metals and environmental variables [altitude (ALT), precipitation (PPT), lake pH, dissolved organic carbon (DOC), calcium (Ca^{2+}), chloride (Cl^-), non-marine sulfate deposition (nmSO_4^{2-}), and longitude (xLON)] in the study lakes ($n = 126$) indicating significant ($p \leq 0.05$) positive (+) and negative (−) correlations. Higher correlation coefficients ($r \geq 0.5$) are gray-shaded

Metals	ALT	PPT	pH	DOC	Ca^{2+}	Cl^-	nmSO_4^{2-}	xLON
Al			−	+	−	−	+	+
As		−		+				+
B	−	−		+		+	−	−
Ba	−	−	+		+			
Bi							+	+
Co				+				+
Cr		−	+	+	+			+
Cu			+					
Fe	−	−		+				
Hg			−	+		−	+	+
Mn	−	−		+	+			
Mo			−					
Ni	−	−	+	+	+			
Pb			−	+				+
Sr	−	−	+	+	+	+	−	+
Ti	−	−	+	+	+			+
Tl	+	+	−		−			−
U		−	+		+			
V				+				+
Zn			−				+	+

Longitude (xLON) was assumed to be a surrogate of transboundary air pollution, given the east to west gradient in anthropogenic (higher in the east) and marine (higher in the west) emission sources. However, there is an east to west distribution in the coverage of organic soils and survey lake density; as such longitude incorporates several spatial gradients

acidity (dominated by organic acidity) was negatively correlated with Pb ($r = -0.43$), Hg ($r = -0.42$), Al ($r = -0.39$), and Zn ($r = -0.20$); notably Hg and Pb were more strongly correlated to DOC. The third axis was dominated by Cl^- ($r = 0.87$), and primarily reflected correlation with B ($r = 0.87$).

A second RDA was performed on dissolved trace metals (Fig. 4), the first three axes explained 96 % of the variance (RDA 1 = 44.1 %, RDA 2 = 40.5 % and RDA 3 = 11.3), and suggested a shift in the dominance of geochemical weathering for dissolved metals. The first axis was dominated by Cl^- ($r = 0.90$) associated with B, Se, and V. The second axis was dominated by Ca^{2+} ($r = -0.85$) and negatively related to many metals (Pb, Al, Ti, Zn, Fe, see Fig. 4) suggesting an association with acidity not driven by acidic deposition. An exceptionally deep Atlantic depression between March 09–11, 2008 led to the highest ever wind gusts (westerlies) and the wettest March in over a decade at a number of monitoring stations across Ireland (Met Éireann 2008) potentially influencing the dominance of marine ions leading to displacement of acidity from the soil exchange complex.

DISCUSSION

Comparison to the 1995 Nordic Lake Survey

There have been several extensive (national or regional scale) trace metal surveys across Europe, primarily in acid-sensitive regions in Finland (464 lakes), Norway (925 lakes), Sweden (820 lakes), Russian Kola (460 lakes) (Skjelkvåle et al. 2001b), and Italy (32 lakes; Tornimbeni and Rogora 2012). In general, total metal concentrations in the study lakes were similar to other northern latitude countries. Trace metal concentrations were comparable or lower for Ni, Cu, Pb, Zn, and Fe (with the exception of Fe for Italy), e.g., Ni concentration in the study lakes (median = $0.18 \mu\text{g L}^{-1}$) were similar to concentrations in Finland ($0.37 \mu\text{g L}^{-1}$), Norway ($0.24 \mu\text{g L}^{-1}$), Sweden ($0.35 \mu\text{g L}^{-1}$), Russian Kola ($0.33 \mu\text{g L}^{-1}$), and Italy ($0.35 \mu\text{g L}^{-1}$). The median Zn concentration in the study lakes was $<1.0 \mu\text{g L}^{-1}$, compared with $2.2 \mu\text{g L}^{-1}$ (Finland), $1.1 \mu\text{g L}^{-1}$ (Norway), $1.5 \mu\text{g L}^{-1}$ (Sweden), $1.4 \mu\text{g L}^{-1}$ (Russian Kola), and $3.1 \mu\text{g L}^{-1}$ (Italy). In concert, metal concentrations in the study lakes were lower compared with the 1995 European surveys (Skjelkvåle et al. 2001b) owing to decreased acidic and metal deposition across Europe during the last decade (Harmens et al. 2010). In contrast, metal concentrations were higher for Mn, Cr, and As in the study lakes; median Mn concentration was $22.5 \mu\text{g L}^{-1}$, compared with Finland ($21.0 \mu\text{g L}^{-1}$), Norway ($2.3 \mu\text{g L}^{-1}$), Russian Kola ($5.0 \mu\text{g L}^{-1}$), Sweden ($14.5 \mu\text{g L}^{-1}$), and Italy ($1.1 \mu\text{g L}^{-1}$). Higher lake As concentrations are consistent with higher national emissions compared with other European countries (Table 2); however, the simple input–output budget indicated that catchment sources were an important component of lake As concentrations.

Controls of Trace Metals

Redundancy analysis has been widely used to evaluate trace metal concentrations including studies of aquatic organisms, lake waters, lake sediments or catchment soils and vegetation (Johnson et al. 1997; Stemberger and Chen 1998; Rognerud et al. 2000; Skjelkvåle et al. 2001a). In the current study, the variable describing most of the variation in total trace metal concentrations was Ca^{2+} 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. 2001b)] was predominantly associated with organic carbon (particularly for Fe and Mn and to a certain degree for As, Cr and V). In the current study, correlation analysis incorporating a wider range of

explanatory variables found the strongest coefficients associated with Ca^{2+} (geochemical) and DOC (organic matter); however, a greater number of significant positive relationships were observed with DOC (13 of 20 metals). Nonetheless, many trace metals were also directly related to long-range air pollution or indirectly through acidification. The variation in total and dissolved Mo, Pb, Co, Cd, 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-} (and DOC and acidity). The importance of deposition sources was further evaluated by input–output budget for As, Cr, Cu, Pb, Ni, and Zn.

The budget suggested catchment retention for Zn, Cu, and Pb as average input (via atmospheric deposition) was >1.5 times average output from the lakes; in contrast, atmospheric deposition only represented 30–60 % of lake output for Cr (32 %), As (34 %), and Ni (62 %) suggesting important catchment sources. The input–output budget provides at best a semi-quantitative estimate of the importance of deposition; nonetheless total Zn was positively correlated to nmSO_4^{2-} deposition, and Ni and Cr positively correlated to geochemical sources. However, As, Cr, and Pb were strongly related to DOC and longitude reflecting complex interrelationships between sources and geospatial factors. The strong west–east gradient in As and Cr may reflect proximity to source emissions in the east or greater retention in organic soils which are dominant in the west (Fig. 1).

During the last three decades, emission and deposition of long-range air pollution has declined in Europe and North America. This decrease has led to significant changes in the chemical composition of surface waters. In Ireland, a repeat lake survey ($n = 60$) assessing the changes in chemistry of small headwater lakes between 1997 and 2007 indicated significant decreases in lake SO_4^{2-} , nmSO_4^{2-} , and Ca^{2+} along with increases in alkalinity owing to decreases in acidic deposition (Burton and Aherne 2012). However, no change in total Al concentrations was observed owing to increased DOC (suggesting increases in the non-labile fraction; 47 % of total Al in the current study).

As further declines in acidic input (primarily nmSO_4^{2-}) occur over 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. However, organic bound metal complexes are typically less toxic than inorganic fractions (Tipping et al. 1998).

Partitioning of Trace Metals

In the current study, the dissolved organic (non-labile) fraction was the dominant form for As [75 % (25 %

dissolved labile)], Fe [58 % (9 %)], Pb [62 % (19 %)], Ni [48 % (39 %)], and Al [47 % (29 %)], and all were significantly correlated to DOC in lake water (Table 3) consistent with previous studies (Gjessing 1964; Tipping 1981). Further, a large proportion of Fe, Al, and Mn were in particulate form potentially bound to larger organic molecules or sediment; their dissolved fractions spanned a wide ratio of non-labile to labile speciation, indicating varying affinity for organic matter. Dissolved Fe was dominated by non-labile, Al more equally balanced and Mn dominated by labile fractions (Fig. 3). The dissolved inorganic (labile) fraction was the dominant form for several other metals, e.g., Ba, B (100 %), and Sr, consistent with other surveys suggesting either free ions or inorganic complexes with bicarbonate, sulfate, or hydroxide (Kirchner and Grabowski 1972; Borg 1986).

Many metals were not influenced by a single factor, e.g., dissolved Cu was dominated by the organic fraction, however, a weak non-significant correlation was observed between Cu and DOC, despite studies discussing the strong binding affinity of Cu to organic matter (Allen and Hansen 1996; Kramer et al. 2004). Other studies have reported similarly weak relationships between Cu and DOC or pH (Huser et al. 2011). The speciation and mobility of V is largely influenced by redox conditions owing to multiple oxidation states. Typically, V exists in the dissolved fraction in surface waters and forms complexes with organics or oxyhydroxides. In the current study, V was predominantly observed in dissolved form, dominated by the organic fraction. Similar results have been observed with other oxyanion forming elements such as As and Cr (Skjelkvåle et al. 2001b).

Several studies suggest that Ni complexes with organic ligands (Sedlak et al. 1997; Xue et al. 2001) and inorganic compounds such as hydrous oxides of Fe and Mn, and clay minerals (Boyle and Robinson 1988). In the current study, a large proportion of Ni was in the dissolved organic fraction (48 % non-labile) similar to Skjelkvåle et al. (2001). However, Ni concentration increased with increasing pH and was more strongly correlated with Ca^{2+} suggesting the concentration was influenced by geochemical weathering (see Fig. 4). Nickel theoretically does not increase with decreasing pH, and therefore Ni speciation is not determined by acidity (Mukherjee 1998).

Aluminum is known to complex with both organic and inorganic ligands, typically in dissolved form; however, polymeric Al cations and particulate species may occur (Driscoll 1985). In the study lakes, Al was dominated by the dissolved organic fraction and correlated with DOC; however, a significant portion was found in the inorganic and particulate fraction. The inorganic (labile) fraction increased with decreasing pH (maximum concentration at pH 5.0), consistent with numerous studies (Driscoll 1985;

Lydersen et al. 1992; Vesely and Majer 1996). Increased labile concentrations also occurred at lower pH for several metals, e.g., Pb and Zn, consistent with other studies (Borg 1983; Campbell et al. 1985; Gundersen and Steinnes 2003).

Exceedance of Surface Water Guidelines

The concentration of total dissolved Cd, Zn, and inorganic dissolved Mn, and Al are of particular interest because their levels may be harmful to freshwater organisms. Cadmium $>0.1 \mu\text{g L}^{-1}$ has been reported to affect the reproductive function of certain aquatic organisms (Tartvainen et al. 1997). In the current study, 4 % of the lakes exhibited concentrations above this limit despite the high proportion below detection [96 % (note the detection limit was $0.1 \mu\text{g L}^{-1}$)]. Zinc $>5 \mu\text{g L}^{-1}$ has been reported to be harmful to brook trout in acidic waters (Sayer et al. 1989). In total, 55 % of the study lakes exhibited concentrations greater than $5.0 \mu\text{g L}^{-1}$ and 16 % exhibited concentrations greater than $10 \mu\text{g L}^{-1}$. Labile Mn concentrations $>50 \mu\text{g L}^{-1}$ 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 $20 \mu\text{g L}^{-1}$ may be toxic to aquatic organisms in acidic environments (Schofield and Trojnar 1980; Baker and Schofield 1982; Lydersen et al. 2002); 21 % of the study lakes were above this limit. It is important to note that the metal tolerance and uptake by organisms differ between species.

CONCLUSION

In general, trace metal concentrations in small headwater Irish lakes were low, within, or below observations for unpolluted (background) surface waters. The study lakes were dominated by Fe, Al, Mn, and to a lesser extent by Sr and B. However, dissolved Zn and Cd, and inorganic dissolved Mn and Al were at levels of potential concern in some lakes. Redundancy analysis suggested an association between deposition of nmSO_4^{2-} and several metals (e.g., Pb, Zn, Co, Al); in concert, input–output budgets tentatively suggested atmospheric deposition was a dominant source for several metals. However, DOC was also significantly correlated to many trace metals (Al, Mn, Fe, Ni, Pb, Hg, and Sr), and recent observations of (ubiquitous) increasing DOC in surface waters may lead to increases in trace metal concentrations; notably organic bound fractions are less toxic to aquatic organisms. Finally, Ca^{2+} was positively correlated with many metals (Ni, Sr, Ba, Cu, Ti, Cr, and U) suggesting geochemical weathering as their predominant source.

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