REPORT

Changes in the Chemistry of Small Irish lakes

Andrew W. Burton, Julian Aherne

Abstract A re-survey of acid-sensitive lakes in Ireland (initial survey 1997) was carried out during spring 2007 ($n = 60$). Since 1997, atmospheric emissions of sulfur dioxide and deposition of non-marine sulfate (SO_4^{2-}) in Ireland have decreased by ~ 63 and 36%, respectively. Comparison of water chemistry between surveys showed significant decreases in the concentration of SO_4^{2-}, non-marine SO_4^{2-}, and non-marine base cations. In concert, alkalinity increased significantly; however, no change was observed in surface water pH and total aluminum. High inter-annual variability in sea salt inputs and increasing (albeit non-significant) dissolved organic carbon may have influenced the response of pH and total aluminum (as $\sim 70\%$ is organic aluminum). Despite their location on the western periphery of Europe, and dominant influence from Atlantic air masses, the repeat survey suggests that the chemistry of small Irish lakes has shown a significant response to reductions in air pollution driven primarily by the implementation of the Gothenburg Protocol under the UNECE Convention on Long-Range Transboundary Air Pollution.

Keywords Lake chemistry · Sulfate · Emissions · Sea salts · Dissolved organic carbon

INTRODUCTION

The impact of acid rain on surface waters has been extensively studied in Europe and North America (Almer et al. 1978; Kähkonen 1996; Skjelkvåle et al. 2005). Since the 1980s, international policies have been implemented to reduce atmospheric emissions of anthropogenic sulfur (S) and nitrogen (N) compounds with the objective to promote chemical and biological recovery of impacted aquatic ecosystems (Bull et al. 2008). 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 ammonia in Europe (63, 41, and 17%, respectively) by 2010 (UNECE 1999). These emission reductions have stimulated widespread significant changes in the chemistry of acid-sensitive lakes (Stoddard et al. 1999; Skjelkvåle et al. 2005; Kopáček et al. 2004).

Repeat lake surveys in Europe and North America have generally observed a decrease in lake sulfate (SO_4^{2-}) concentrations consistent with decreases in precipitation concentrations (Skjelkvåle et al. 1998; Pilgrim et al. 2003; Stuchlik et al. 2006). Re-surveys in acid-sensitive regions such as the Adirondack and Catskill Mountains of New York, Tatra Mountains of Slovakia and Poland, and across the Nordic countries, have generally observed chemical recovery from acidification with decreases in SO_4^{2-}, nitrate (NO_3^-) and base cations, in conjunction with increases in pH and alkalinity (Skjelkvåle et al. 1998; Kopáček et al. 2006).

Ireland is located on the western periphery of Europe, and predominantly receives clean air masses from the Atlantic. As such, non-marine (nm) SO_4^{2-} deposition is low (<25 $mmol_c$ m^{-2} $year^{-1}$ [one mole of charge (mol_c) is numerically equal to one equivalent (eq)]) compared to other industrial regions of Europe (Aherne and Farrell 2002). Nonetheless, Ireland receives acidifying compounds associated with easterly air masses from Western Europe (Bowman and McGettigan 1994) and, to a lesser extent, pollutants carried in western air masses from North America (Huntrieser et al. 2005). The impact 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]). During 1997, a survey of predominantly small headwater lakes ($n = 200$) in remote, acid-sensitive, coastal regions found that $nmSO_4^{2-}$ (and NO_3^-) was the dominant source of acidity in 25% of the lakes (Aherne et al. [2002]). During the last two decades, decreases in air concentrations of sulfur dioxide (SO_2) and $nmSO_4^{2-}$ in precipitation have been observed in Ireland (Valentia: Bashir et al. [2008]).

The objective of this study was to determine differences in the chemistry of small headwater lakes in Ireland between 1997 and 2007, a period which has experienced significant reductions in the deposition of S across Europe owing to the Gothenburg Protocol. To meet the objective, 60 lakes sampled during 1997 (Aherne et al. [2002]) were re-surveyed during 2007; chemical observations common to both surveys were compared using the Wilcoxon rank paired test. Trends in atmospheric deposition and meteorology during the study period (1995–2007) were evaluated using the Mann–Kendall test. Emissions of SO_2 have decreased by $\sim 55\%$ in European Union member states between 1995 and 2007 (European Environment Agency [2009]). As such, it was anticipated that increases in pH and alkalinity would be observed along with decreases in SO_4^{2-}, base cations and aluminum (Al) concentrations, similar to other regions in Europe and North America (Stoddard et al. [1999]; Skjelkvåle et al. [2001]).

MATERIALS AND METHODS

Study Sites

During spring 1997, ~ 200 small lakes (mean lake area 5.8 ha, 222 m a.s.l.) were sampled in Ireland to determine their hydrochemical characteristics and acid status (Aherne et al. [2002]). Lakes were pseudo-randomly selected based on bedrock geology and soil characteristics, with greater weighting towards more remote, higher elevation, acid-sensitive regions. During spring 2007, 60 lakes (mean lake area 4.4 ha, 292 m a.s.l) from the 1997 survey were re-sampled (Fig. [1]). The majority of the lakes were located along the coastal margins in relatively undisturbed upland areas; nonetheless, there was a wide range in site characteristics such as lake area, catchment area and elevation (Table [1]). The dominant soil type was podzol or peaty podzol, land cover was dominated by moorland and the dominant land use was rough grazing.

Sampling and Analysis

Similar field and laboratory procedures were used during both lake surveys where possible. Shore water samples were collected 10–20 cm below the surface in HDPE bottles and kept cool ($\sim 4°C$) until analysis. Lake samples were analyzed for pH, conductivity, Gran alkalinity, major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^- and SO_4^{2-}) and total aluminum (Al_T). Lake pH and conductivity were analyzed using a low conductivity electrode. Gran alkalinity was measured using a PC titration Plus System. Anions (Cl^-, NO_3^-, and SO_4^{2-}) and cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) were analyzed using a Dionex 600 Ion Chromatograph (IC). Dissolved (0.45 μm) organic carbon (DOC) was estimated from absorbance at 320 nm (DOC $= 49.5 \times ABS_{320} + 1.69$) using a UV–VIS Spectrometer following Gorham ([1985]), consistent with the 1997 survey (Aherne et al. [2002]). Aluminum concentrations were analyzed using an Element2 High Resolution ICP-MS.

Standard QA/QC procedures were followed during sample collection, laboratory analysis and data analysis to ensure accurate, consistent and reliable data. Duplicate water samples ($\sim 20\%$) were sent to an external laboratory (Environment Canada) for independent analysis. Charge balance and conductivity checks were carried out following EMEP ([1996]) data checking protocols; notably none of the lakes had an invalid ion balance.

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, or variation in deposition ratios with distance from the ocean (Möller [1990]), leading to incongruent relations between ions (Aherne and Curtis [2003]). Charge balance acid neutralizing capacity (ANC) was calculated as the difference between base cations and acid anions (Reuss and Johnson [1986]).

Statistical differences in lake chemistry between the 1997 and 2007 surveys were evaluated using the Wilcoxon rank paired test (compares the medians of non-normally distributed data pairs: O'Brien and Fleming [1978]). If $p < 0.05$, the change in lake chemistry between surveys was assumed to be statistically significant.

Climate and Atmospheric Data

Daily climate data (temperature and precipitation) during the period 1995–2007 was obtained from 13 synoptic meteorological stations (Met Eireann) across Ireland (Fig. [1]). Atmospheric deposition data for the period 1995–2007 were obtained from five monitoring stations (Brackloon, Cloosh, Roundwood, Valentia and Lough Navar) remote from local sources of pollution (Fig. [1]). All monitoring stations measured precipitation volume, pH,

Fig. 1 Location of study lakes ($n = 60$), deposition stations ($n = 5$), and meteorological stations ($n = 13$). Also shown is the sensitivity of surface waters to acidification [based on geology and soil, darker shading indicates increasing sensitivity (Aherne et al. 2002)]
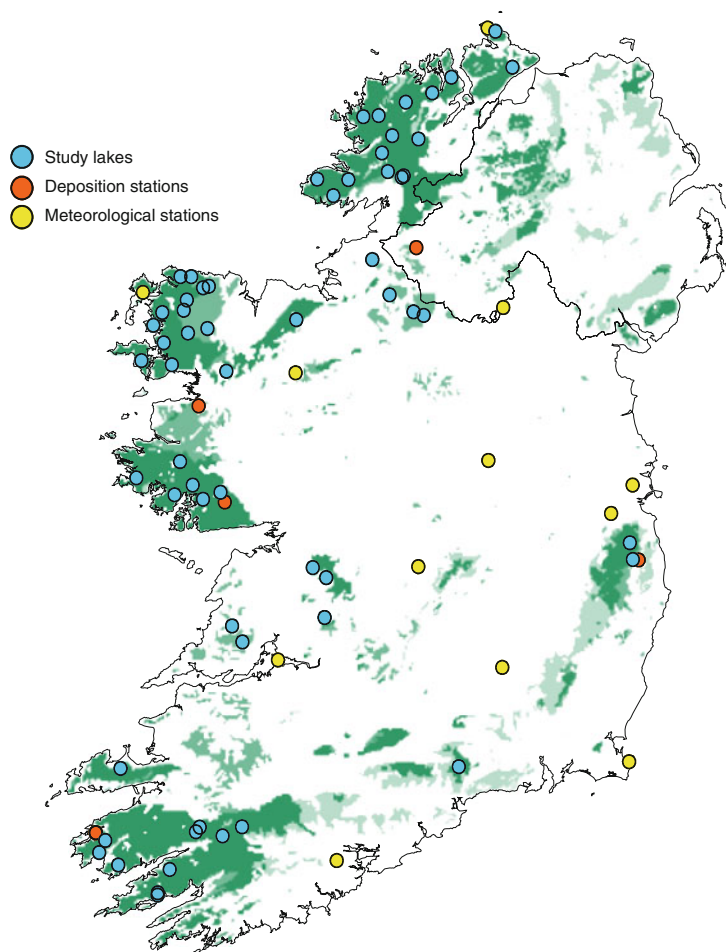
major cations, and anions on a bulk-weekly or wet-only daily (Valentia and Loch Navar) frequency. Monotonic trends in mean annual climate data and atmospheric deposition chemistry were statistically assessed using the non-parametric Mann–Kendall test (Salmi et al. 2002).

RESULTS

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 1), owing to the predominant westerly airflow from the North Atlantic. Chloride concentrations were high, ranging from 196.5 to 1322.0 μmol_c l^{-1} (median of 600.7 μmol_c l^{-1}), positively correlated to conductivity ($r^2 = 0.98$) and negatively correlated to elevation ($r^2 = 0.63$). Conductivity values ranged from 34 to 220 μS cm^{-1}; however, 85% of the lakes had values less than 150 μS cm^{-1}. There was a strong negative correlation between elevation and conductivity ($r = 0.79$ [Pearson product-moment]) owing to lower

catchment weathering or reduced marine inputs at higher elevations. 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. The most acidic lakes were in the northwest of the country (Fig. 2). Gran alkalinity was also low, ranging from −58.2 to 135.1 μmol_c L^{-1} (median: −3.6 μmol_c l^{-1}), and less than or equal to zero in 57% of the lakes. Dissolved organic carbon (DOC) concentration ranged from 1.8 to 12.7 mg l^{-1}, with a median of 4.9 mg l^{-1} (88% <10.0 mg l^{-1}). The highest DOC lakes were observed in the northwest consistent with low pH values (Fig. 2). In addition, DOC concentrations were generally higher in the lower elevation lakes (<300 m average: 6.6 mg l^{-1} [$n = 27$]) compared with higher (≥300 m average: 4.7 mg l^{-1} [$n = 33$]). Total Al was generally low, ranging from 0.4 to 9.5 μmol l^{-1} (median = 2.1 μmol l^{-1}), and dominated by organic Al (∼70%).

Sulfate concentrations in the study lakes ranged from 29.3 to 154.1 μmol_c l^{-1}, with a median of 69.3 μmol_c l^{-1}. The higher concentrations were observed nearest the west coast (Fig. 2) at the lower elevation lakes (<300 m average of 87.1 μmol_c l^{-1}) compared with higher elevation lakes (≥300 m average of 57.6 μmol_c l^{-1}). Non-marine sulfate

Table 1 Statistical summaries (mean, standard deviation [SD], 5th percentile, median, 95th percentile) of catchment characteristics and lake chemistry (2007) for the study catchments ($n = 60$; see Fig. 1)

Variable	Units	Mean	SD	5%-tile	Median	95%-tile
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	$\mu S\ cm^{-1}$ at 25°C	99.5	42.6	41.0	90.4	180.6
Alkalinity (Gran)	$\mu mol_c\ l^{-1}\ CaCO3$	−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	$mg\ l^{-1}$	5.7	2.8	2.2	4.9	11.1
Al_T	$\mu mol\ l^{-1}$	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

Nitrate (NO_3^-) was available for only ∼50% of the study lakes, *DOC* dissolved organic carbon estimated from absorbance at 320 nm (DOC = $49.5 \times ABS_{320} + 1.69$), Al_T total (labile and non-labile) aluminum, *ANC* charge balance acid neutralizing capacity, *nm* non-marine (negative concentrations of non-marine base cations and SO_4^{2-} may result from short-term variations in deposition). Units: 1 mol of charge (mol_c) is equal to 1 equivalent (eq)

($nmSO_4^{2-}$) ranged from −53.6 to 41.6 $\mu mol_c\ l^{-1}$, with a median of 9.7 $\mu mol_c\ l^{-1}$ (9 lakes <0 $\mu mol_c\ l^{-1}$). The highest concentrations of $nmSO_4^{2-}$ 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 concentration in Irish surface waters had a median of 55.1 $\mu mol_c\ l^{-1}$; 92% of the study lakes exhibited concentrations below 100 $\mu mol_c\ l^{-1}$, indicating limited catchment sources (e.g., low geochemical weathering). The distribution of low Ca^{2+} followed the pattern of low pH (and higher DOC), with the lowest concentrations in the northwest and southwest (Fig. 2). Non-marine base cations were dominated by Ca^{2+} and Mg^{2+} (Table 1); a small number of lakes ($Ca^{2+} = 1$, $Mg^{2+} = 4$) had negative concentrations suggesting retention in the catchments. The ANC was low with a median of 85.2 $\mu mol_c\ l^{-1}$ and ranged from −2.0 to 461.4 $\mu mol_c\ l^{-1}$ (Table 1). Acid neutralizing capacity is used as a water quality criterion for the survival of aquatic organisms (Henriksen et al. 1995); 10% of the study lakes had ANC values less than 20.0 $\mu mol_c\ l^{-1}$, which is a widely used limit for protection of fish species (Aherne and Curtis 2003).

Trends in Deposition Chemistry and Meteorology Between 1995 and 2007

All five monitoring stations (Cloosh, Brackloon, Roundwood, Valentia and Lough Navar) showed temporal changes in precipitation chemistry between 1995 and 2007, with statistically significant ($p < 0.05$) decreases in $nmSO_4^{2-}$ deposition, increases in pH, and no change in Cl^- deposition. Annual deposition of $nmSO_4^{2-}$ decreased at Cloosh, Brackloon, Roundwood, Valentia and Lough Navar by 21, 28, 48, 15, and 55%, respectively. A greater reduction in $nmSO_4^{2-}$ was observed at the more easterly sites (Roundwood and Lough Navar). The deposition of $nmSO_4^{2-}$ decreased on average from 27.6 $mmol_c\ m^{-2}$ in 1995 to 15.9 $mmol_c\ m^{-2}$ in 2007 (∼36%), and was strongly correlated to emission reductions ($r = 0.95$; Fig. 3). In concert, the atmospheric concentration of SO_2 at Valentia decreased by ∼34% during the same period. Nitrate deposition varied considerably with inter-annual variations showing no significant trend except at Roundwood (east coast: Fig. 1), which had a slight decreasing trend. Observed pH increased significantly ($p < 0.05$) at all monitoring stations except Lough Navar. There was no trend in Cl^- reflecting the strong inter-annual variations
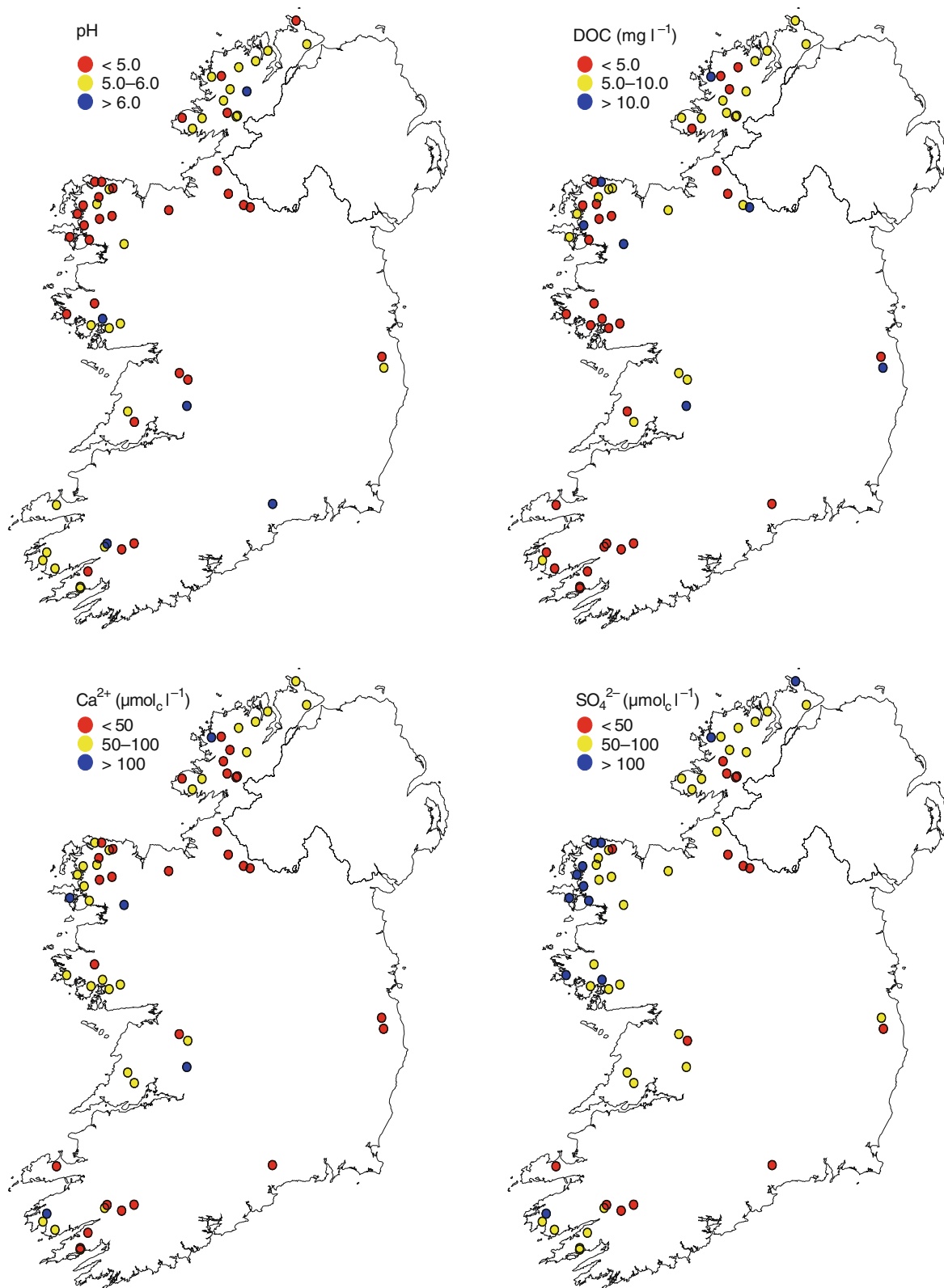
Fig. 2 Geographic distribution of pH, dissolved organic carbon (DOC), calcium (Ca^{2+}), and sulfate (SO_4^{2-}) for the study lakes in 2007 ($n = 60$)
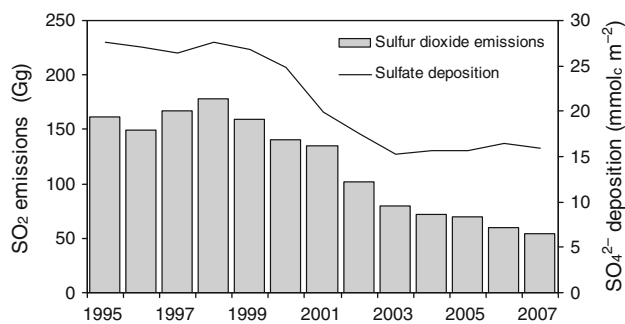
Fig. 3 Trends in sulfur dioxide (SO_2) emissions for Ireland (EPA 2009) and non-marine sulfate ($nmSO_4^{2-}$) deposition (3-year running mean of five deposition stations, see Fig. 1) in Ireland from 1995–2007. Annual emissions and deposition are strongly correlated ($r = 0.95$ [Pearson product-moment])

associated with weather patterns (e.g., frequency of dominant Atlantic air masses). Depositions of sea salts (Na^+ and Cl^-) were significantly higher at Cloosh, Brackloon and Lough Navar during 2007 compared with 1997; whereas, sea salt deposition was lower at Roundwood and Valentia.

Mean annual air temperature (at the 13 synoptic stations; Fig. 1) ranged from 8.5 to 11.7°C, with an overall average of 10.2°C across all stations. There was no trend in mean annual air temperature during the period 1995–2007. Mean annual rainfall varied greatly between years (ranging from 560 to 1923 mm year^{-1}, with an average of 1106 mm year^{-1}); however, no significant trend was observed.

Changes in Lake Chemistry Between 1997 and 2007

Statistically significant differences ($p < 0.05$) in surface water chemistry were observed between the 1997 and 2007 surveys, with declines in SO_4^{2-}, $nmSO_4^{2-}$, Ca^{2+} and non-marine base cations (Ca^{2+} and Mg^{2+}: Table 2). In contrast, statistically significant increases were observed for alkalinity and Cl^-. Despite chemical improvements in alkalinity, no change in pH or Al_T was observed.

Concentrations of SO_4^{2-} and $nmSO_4^{2-}$ decreased on average by 9 and 58%, respectively (Table 2 and Fig. 4). The mean decrease of $nmSO_4^{2-}$ in surface waters was consistent with the decrease in average deposition (36%; Fig. 3). In concert, concentrations of $nmCa^{2+}$ (Fig. 4) 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 increased inputs of marine ions (Table 2; Fig. 4). Furthermore, no statistically significant difference in DOC was observed between surveys; however, an increase was observed at higher elevation sites. There was no significant change in Al_T concentrations (Table 2 and Fig. 4) consistent with DOC. Alkalinity increased significantly by 47%,

(from 68 to 57% of lakes with alkalinity less than or equal to zero) while no significant difference in pH was observed, even for the more acidic lakes (i.e., pH < 5.5).

DISCUSSION

Emission and Deposition Reductions

Ireland is located on the western periphery of Europe and assumed to have generally 'clean' rain as it predominantly receives air masses from the Atlantic. Nonetheless, consistent with reductions in SO_2 emissions, widespread declines in SO_4^{2-} deposition have occurred over Ireland. Bashir et al. (2008) reported significant decreases in SO_2 air concentration and SO_4^{2-} in wet precipitation at Valentia monitoring station between 1980 and 2004. Similar declining temporal trends in precipitation chemistry have been reported for other regions in Europe (Fowler et al. 2007). In this study, annual deposition of $nmSO_4^{2-}$ decreased on average by approximately 36% (~ 12 mmol$_c$ m^{-2}) at five monitoring stations during the period 1995–2007. In addition, pH significantly increased at four of the five monitoring stations. While the deposition of long-range air pollution in Ireland is low, the implementation of the Gothenburg Protocol has led to significant changes in rainfall chemistry.

Changes in Lake Chemistry

The study lakes were predominantly headwater lakes located within rocky catchments characterized by shallow base poor mineral soils underlain by granite, quartzite, schist, and gneiss (Aherne et al. 2002). As such, the lake catchments were considered to be acid sensitive because of their slow geochemical weathering rates and low soil buffering capacity.

There were significant differences in water chemistry between the 1997 and 2007 lake surveys suggesting lakes have responded to reductions in emission of SO_2. 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) investigated trends in surface water quality in 23 countries (North America and Europe) and found widespread changes (decreased lake SO_4^{2-} concentrations) primarily related to reduced emission (and deposition) of S. In this study, the decrease in lake SO_4^{2-} (average of -0.8 μmol$_c$ l^{-1} year^{-1}) was less compared with regions in North America and Europe (-2.2 μmol$_c$ l^{-1} year^{-1} [Quebec] to -6.5 μmol$_c$ l^{-1} year^{-1} [southern Nordic countries] during the period 1990–2001: Skjelkvåle et al. 2005). However, observed differences may be related to the different study periods and different

Table 2 Changes (absolute [Δ] and percent [%]) in mean (and median) lake concentrations between the 1997 and 2007 lake surveys ($n = 60$). Statistical difference between surveys was assessed with the non-parametric Wilcoxon signed paired test

Variable	Units	Δ Change	% Change	Wilcoxon[§]
SO_4^{2-}	$\mu mol_c\ l^{-1}$	−7.6 (−12.0)	−9.3 (−14.8)	0.001
$nmSO_4^{2-}$	$\mu molc\ l^{-1}$	−10.5 (−8.1)	−57.6 (−46.2)	0.000
pH		−0.03 (0.08)	−0.60 (1.60)	0.352
Cl^-	$\mu molc\ l^{-1}$	28.6 (30.9)	4.6 (5.4)	0.025
Conductivity	$\mu S\ cm^{-1}$	−1.1 (−0.6)	−1.1 (−0.7)	0.763
Alkalinity	$\mu mol_c\ l^{-1}$	5.0 (6.1)	47.3 (62.5)	0.003
Ca^{2+}	$\mu mol_c\ l^{-1}$	−3.7 (0.1)	−5.9 (0.2)	0.007
Mg^{2+}	$\mu mol_c\ l^{-1}$	0.3 (−7.5)	0.2 (−5.6)	0.903
$nmCa^{2+}$	$\mu mol_c\ l^{-1}$	−4.8 (−0.4)	−11.8 (−1.4)	0.000
$nmMg^{2+}$	$\mu mol_c\ l^{-1}$	−5.3 (−7.8)	−22.9 (−35.9)	0.004
nmK^+	$\mu mol_c\ l^{-1}$	−0.3 (0.0)	−10.6 (2.2)	0.594
DOC	$mg\ l^{-1}$	0.7 (1.6)	13.7 (47.9)	0.054
Al_T	$\mu mol\ l^{-1}$	−0.03 (−0.002)	−1.2 (−0.1)	0.683

[§] Changes in lake chemistry between surveys were assumed to be statistically significant at $p < 0.05$. Units: 1 mol of charge (mol_c) is equal to 1 equivalent (eq)

levels of pollution. The ability of catchment soils to retain sulfate (i.e., adsorption or reduction), while Cl^- enters surface waters relatively unaltered, may lead to errors in the estimation of non-marine constituents. Negative $nmSO_4^{2-}$ concentrations were observed in 7 lakes in 1997 compared with 9 in 2007; the slight increase may be due to variation in sea salt inputs between surveys or reduced deposition of $nmSO_4^{2-}$ rather than changes in catchment retention. Decreased lake SO_4^2 concentration was observed in 73% of the study lakes between the 1997 and 2007 surveys.

Non-marine base cation (Ca^{2+} and Mg^{2+}) concentration decreased on average by 16% between surveys owing to decreased soil ion exchange under reduced acidic deposition (Reuss and Johnson 1986). The average base cation (Ca^{2+} and Mg^{2+}) decrease in the study lakes ($-3.4\ \mu mol_c\ l^{-1}\ year^{-1}$) was in agreement with other regions ($-2.\ \mu mol_c\ l^{-1}\ year^{-1}$) [east central Europe] to $-5.4\ \mu mol_c\ l^{-1}\ year^{-1}$ [west central Europe] during the period 1990–2001: Skjelkvåle et al. 2005), despite the higher sea salt inputs. Moreover, non-marine base cations decreased in 73% of the study lakes.

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 addition to strong acidic deposition, lake pH is largely controlled by organic anions (Sullivan et al. 2005) and sea salt inputs; both DOC (albeit non-significant) and sea salts were higher during the 2007 survey. In concert, the absence of a statistically significant change (decrease) in conductivity was largely related to the constant high input of sea salts. Aluminum concentrations were highly variable (Fig. 4) owing to the dominant influence of DOC and pH. In study lakes with pH >5.5 and DOC

<5.0, the average Al_T concentration was 1.1 $\mu mol\ l^{-1}$; however, lakes with pH < 5.5 and DOC >5.0 $mg\ l^{-1}$, the average Al_T concentration was 3.1 $\mu mol\ L^{-1}$. Moreover, the study lakes were dominated by organic Al (~70%), which supports the absence of a significant difference between surveys.

Lake surveys represent a water chemistry 'snapshot' at a specific time (or interval), providing spatially extensive assessments of current water quality status. However, surveys may be influenced by short-term or seasonal variations, and are typically carried out with decadal frequency; as such, repeat surveys with long intervals are insufficient to establish long-term trends in water chemistry. Nonetheless, despite the limitations, the extensive differences in water chemistry between surveys in this study are consistent with well-documented changes in surface water chemistry in the United Kingdom; long-term hydrochemical trends in 22 upland acid-sensitive surface waters have shown significant deceases in $nmSO_4^{2-}$ and base cation concentrations during the period 1988–2007 (United Kingdom Acid Waters Monitoring Network [UKAWMN]: Kernan et al. 2010). However, unlike the UKAWMN, increased pH, DOC and decreased Al_T between surveys were not observed in this study.

Despite the dominant westerly airflow and low level of transboundary air pollution, the results of the repeat survey suggest 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. However, similar to other lake surveys, the recovery of pH was not observed. Given the short time-scale (one decade), a significant change in pH may be difficult to detect.
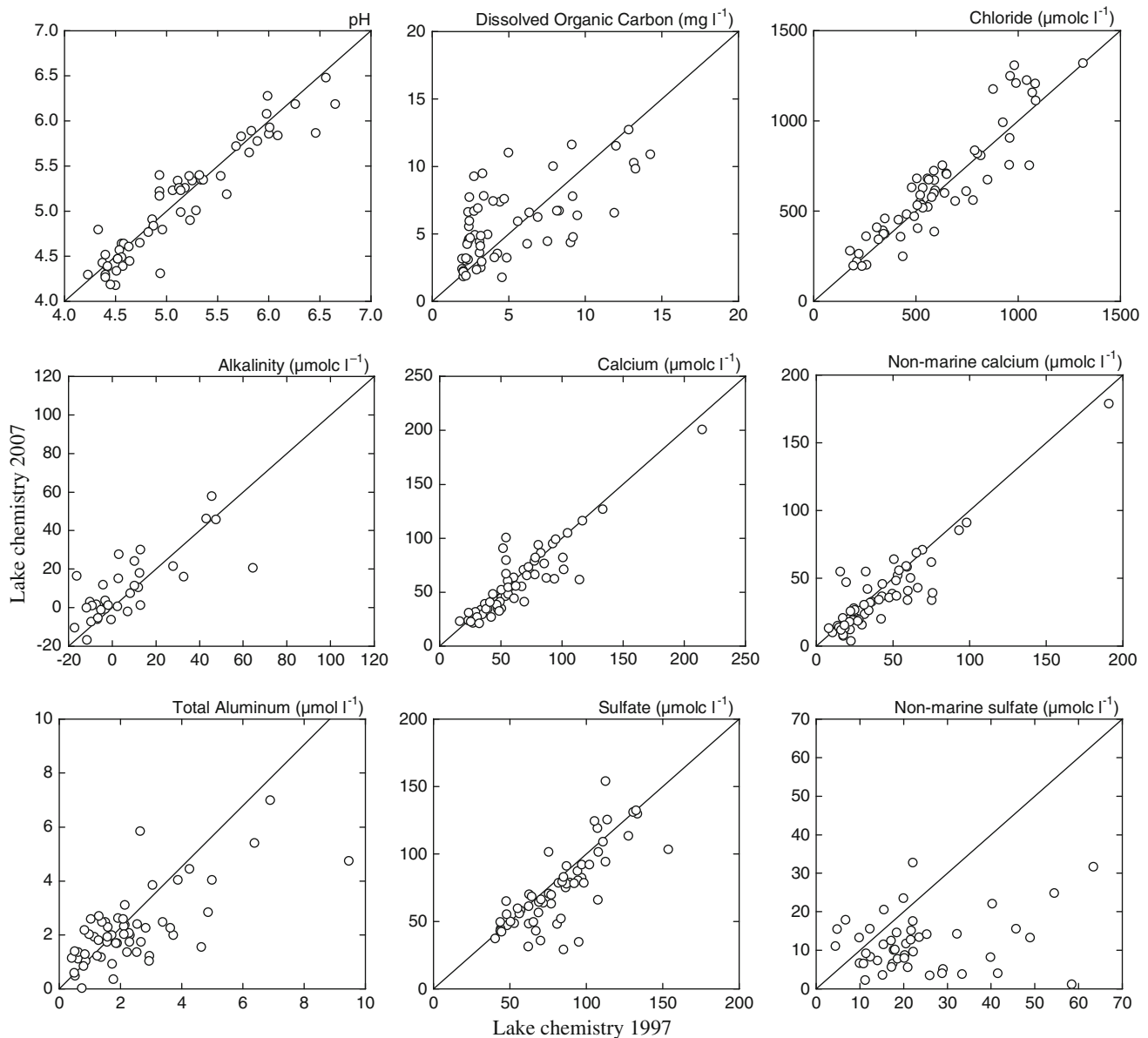
Fig. 4 Comparison of lake concentrations for pH, dissolved organic carbon, chloride, alkalinity, calcium, non-marine calcium, total dissolved aluminum, sulfate, and non-marine sulfate sampled during 1997 and 2007 ($n = 60$)

Moreover, short-term variations in DOC or sea salt episodes may be confounding factors (Skjelkvåle et al. 2003).

Factors Confounding Recovery of Surface Waters

Increases in surface water DOC has been well documented in a number of regions in Europe and North America (Evans et al. 2005; Skjelkvåle et al. 2001; Kopáček et al. 2006; Driscoll et al. 2003; Jeffries et al. 2003). Although the drivers associated with this increase are speculative, suggestions include decreased acidic deposition, increased temperatures owing to global warming, changes in hydrology and changes in land use (Evans et al. 2005). Increased organic acidity in

surface waters may offset decreases in mineral acid anions, suppressing the recovery of pH (Sullivan et al. 2005; Evans et al. 2008).

In this study, a statistically significant change in DOC concentration (estimated from absorbance at 320 nm) was not observed between the 1997 and 2007 surveys; however, there was a great deal of variability between surveys (Fig. 4) and a non-significant increase was observed (Table 2). Catchment soils were primarily composed of peaty podzols and blanket peats (high in organic matter), which have a significant influence on surface water DOC concentrations. Nonetheless, DOC was relatively low (53% below 5.0 mg l^{-1}) in the study lakes. Sea salt episodes,

typically linked to severe weather conditions, and potentially leading to the transfer of acidity from catchment soils to surface waters have been reported in coastal regions of Norway (Hindar et al. 1994), Scotland, western Ireland, eastern Canada and the United States (Harriman et al. 1995). Moreover, sea salt episodes have also been shown to depress the concentration of DOC in surface waters (Moldan et al. 2011). In this study, there was a significant increase in sea salts between the 1997 and 2007 surveys (Table 2).

Climate patterns in Ireland have experienced changes since the nineteenth century, with increasing temperatures (Butler et al. 2007) and more intense storm events (Sweeney et al. 2003). Climate change may have substantial consequences for the chemistry of Irish surface waters, leading to greater variability in DOC concentrations or sea salt episodes, and potentially confounding the response of lake chemistry to future emission reductions. As suggested by Harriman et al. (1995), caution should be taken when assessing the response of surface waters to declining SO_2 emissions in remote coastal regions exposed to sea salt episodes.

CONCLUSION

Irish lakes situated along the coastal mountain ranges, remote from local pollution sources, are ideal for investigating the impacts of long-range transboundary air pollution. 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 small Irish lakes have responded to reductions in long-range transboundary air pollution. In concert, significant increases in alkalinity were observed; however, there were no significant changes in surface water pH and Al_T. It is likely that inter-annual variations in sea salt inputs and DOC concentrations (organic acidity) may have contributed to the delay in recovery of pH. Nonetheless the study supports the far reaching benefits of emission reductions owing to the implementation of the Gothenburg Protocol under the UNECE Convention on Long-Range Transboundary Air Pollution.

Continued improvements in the chemistry of Irish lakes (e.g., decreasing SO_4^{2-} and increasing pH) are expected into the future under further emission reductions. However, continued monitoring is imperative to assess the combined impacts of changes in atmospheric deposition and climate on the chemical and subsequent biological status of Irish lakes.

REFERENCES

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

Aherne, J., and E.P. Farrell. 2002. Deposition of sulfur, nitrogen and acidity in precipitation over Ireland: Chemistry, spatial distribution and long-term trends. *Atmospheric Environment* 36: 1379–1389.

Aherne, J., M. Kelly-Quinn, and E.P. Farrell. 2002. A survey of lakes in the Republic of Ireland: Hydrochemical characteristics and acid sensitivity. *Ambio* 31(6): 452–459.

Almer, B., W. Dickson, C. Ekström, and E. Hornström. 1978. Sulphur pollution and the aquatic ecosystem. In *Sulfur in the environment*, ed. J.O. Nriagu, 271–311. New York: Wiley.

Bailey, M.D., J.J. Bowman, C. O'Connell, and P.J. Flanagan. 1986. *Air quality in Ireland*. Dublin: An Foras Forbartha.

Bashir, W., F. McGovern, M. Ryan, and L. Burke. 2008. Chemical trends in background air quality and the ionic composition of precipitation for the period 1980–2004 from samples collected at Valentia Observatory, CoKerry, Ireland. *Journal of Environmental Monitoring* 10: 730–738.

Bowman, J.J. 1991. *Acid sensitive waters in Ireland: The impact of a major new sulfur emission on sensitive surface waters in an unacidified region*. Dublin: Environmental Research Unit.

Bowman, J.J., and M. McGettigan. 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: 159–175.

Bull, K., M. Johansson, and M. Kryzanowski. 2008. Impacts of the convention on long-range transboundary air pollution on air quality in Europe. *Journal of Toxicology and Environmental Health: Part A* 71(1): 51–55.

Butler, C.J., A. García-Suárez, and E. Pallé. 2007. Trends in cycles in long Irish Meteorological Series. *Biology and Environment: Proceedings of the Royal Irish Academy* 107B(3): 157–165.

Driscoll, C.T., K.M. Driscoll, K.M. Roy, and M.J. Mitchels. 2003. Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. *Environmental Science and Technology* 37: 2036–2042.

EMEP. 1996. Manual for sampling and chemical analysis. http://www.tarantula.nilu.no/projects/ccc/qa.

European Environmental Agency. 2009. European community emission inventory report 1990–2007 under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP). EEA Technical Report No 8/2009, Copenhagen. doi:10.2800/12414.

Evans, C.D., D.T. Monteith, and D.M. Cooper. 2005. Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. *Environmental Pollution* 137: 55–71.

Evans, C.D., D.T. Monteith, B. Reynolds, and J.M. Clark. 2008. Buffering of recovery from acidification by organic acids. *Science of the Total Environment* 404: 316–325.

Flower, R.J., B. Rippey, N.L. Rose, P. Appleby, and R.W. Battarbee. 1994. Paleolimnological evidence for the acidification and contamination of lakes by atmospheric pollution in western Ireland. *Journal of Ecology* 82(3): 581–596.

Fowler, D., R. Smith, J. Muller, J.N. Cape, M. Sutton, J.W. Erisman, and H. Fagerli. 2007. Long term trends in sulfur and nitrogen deposition in Europe and the cause of non-linearities. *Water, Air, and Soil Pollution: Focus* 7: 41–47.

Gorham, E. 1985. The chemistry of bog waters. In *Chemical processes in lakes*, ed. W. Stumm, 330–363. New York: Wiley.

Harriman, R., H. Anderson, and J.D. Miller. 1995. The role of sea-salts in enhancing and mitigating surface water acidity. *Water, Air, and Soil pollution* 85: 553–558.

Henriksen, A., M. Posch, H. Hultberg, and L. Lien. 1995. Critical loads of acidity for surface waters—can the ANC$_{limit}$ be considered variable? *Water, Air, and Soil pollution* 85(4): 2419–2424.

Hindar, A., A. Henriksen, K. Torseth, and A. Semb. 1994. Acid water and fish death. *Nature* 372: 327–328.

Huntrieser, H., J. Heland, H. Schlager, C. Forster, A. Stohl, H. Aufmhoff, F. Arnold, H.E. Scheel, et al. 2005. Intercontinental air pollution transport from North America to Europe: Experimental evidence from airborne measurements and surface observations. *Journal of Geophysical Research Atmospheres* 110: 1–22.

Jeffries, D.S., T.A. Clair, S. Couture, P. Dillon, J. Dupont, B. Keller, D. McNicol, M. Turner, et al. 2003. Assessing the recovery of lakes in southeastern Canada from the effects of acidic deposition. *Ambio* 32(3): 176–182.

Kähkonen, A.M. 1996. Soil geochemistry in relation to water chemistry and sensitivity to acid deposition in Finnish Lapland. *Water, Air, and Soil pollution* 87: 311–327.

Kernan, M., R.W. Batterbee, C.J. Curtis, D.T. Monteith, and E.M. Shilland. 2010. *Recovery of lakes and streams in the UK from the effects of acid rain: UK acid waters monitoring network 20 year interpretive report*, 465. London: University College London.

Kopáček, J., D. Hardekopf, V. Majer, P. Psenakova, P. Stuchlik, and J. Vesely. 2004. Response of alpine lakes and soils to changes in acid deposition: the MAGIC model applied to the Tatra Mountain region, Slovakia-Poland. *Journal of Limnology* 63: 143–156.

Kopáček, J., E. Stuchlik, and D. Hardekopf. 2006. Chemical composition of the Tatra Mountain lakes: Recovery from acidification. *Biologia Bratislava* 61: 21–33.

Moldan, F., J. Hruška, C. Evans, and M. Hauhs. 2011. Experimental simulation of the effects of extreme climatic events on major ions, acidity and dissolved organic carbon leaching from a forested catchment, Gårdsjön, Sweden. Biogeochemistry. doi:10.1007/s10533-010-9567-6

Möller, D. 1990. The Na/Cl ratio in rainwater and the seasalt chloride cycle. *Tellus* 42B: 254–262.

O'Brien, P.C., and T.R. Fleming. 1987. A paired Prentice–Wilcoxon test for censored paired data. *Biometrics* 43: 169–180.

Pilgrim, W., T.A. Clair, J. Choate, and R. Hughes. 2003. Changes in acid precipitation related water chemistry of lakes from southwestern New Brunswick, Canada, 1986–2001. *Environmental Monitoring and Assessment* 88: 39–52.

Reuss, J.O., and D.W. Johnson. 1986. *Acid deposition and the acidification of soils and waters*. New York: Springer-Verlag.

Salmi, T., A. Määttä, P. Anttila, T. Ruoho-Airola, and T. Amnell. 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. Helsinki: Finnish Meteorological Institute.

Skjelkvåle, B.L., R. Wright, and A. Henriksen. 1998. Norwegian lakes show widespread recovery from acidification; Results from national surveys of lakewater chemistry 1986–1997. *Hydrology and Earth System Sciences* 2(4): 555–562.

Skjelkvåle, B.L., J. Mannio, A. Wilander, and T. Anderson. 2001. Recovery from acidification of lakes in Finland, Norway, and Sweden 1990–1999. *Hydrology and Earth System Science* 5(3): 327–337.

Skjelkvåle, B.L., C.D. Evans, T. Larsson, A. Hindar, and G.G. Raddum. 2003. Recovery from acidification in European surface waters: A view to the future. *Ambio* 32(3): 170–175.

Skjelkvåle, B.L., J. Stoddard, D.S. Jeffries, K. Torseth, T. Hogasen, J.J. Bowman, J. Mannio, D.T. Monteith, et al. 2005. Regional scale evidence for improvements in surface water chemistry 1991–2001. *Environmental Pollution* 137: 165–176.

Stoddard, J., D.S. Jeffries, A. Lükewille, T.A. Clair, P.J. Dillon, C.T. Driscoll, M. Forsius, M. Johannesson, et al. 1999. Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* 401: 575–578.

Stuchlik, E., J. Kopáček, J. Fott, and Z. Horicka. 2006. Chemical composition of the Tatra Mountain lakes: Response to acidification. *Biologia Bratislava* 61: 11–20.

Sullivan, T.J., M.C. Saunders, K.A. Tonnesson, B.L. Nash, and B.J. Miller. 2005. Application of a regionalized knowledge-based model for classifying the impacts of nitrogen, sulfur, and organic acids on lakewater chemistry. *Knowledge-Based Systems* 18: 65–68.

Sweeney, J., T. Brereton, C. Byrne, R. Charlton, C. Emblow, C. Fealy, N. Holden, M. Jones, et al. 2003. *Climate change: Scenarios and impacts*. Final report. Environmental RTDI Programme 2000–2006. Environmental Protection Agency, Ireland.

UNECE. 1999. *The 1999 protocol to abate acidification, eutrophication and ground-level ozone. Document ECE/EB.AIR/67*. New York, Geneva: United Nations Economic Commission for Europe.

AUTHOR BIOGRAPHIES

Andrew W. Burton (✉) is a research scientist at Trent University. His current research focuses on the influence of air pollution on lake chemistry, atmospheric ammonia, and biogeochemical cycling in upland soils.
Address: Environmental and Resource Studies, Trent University, 1600 West Bank Drive, Peterborough, ON, Canada K9J 7B8.
e-mail: andrewburton@trentu.ca

Julian Aherne is an Associate Professor in the Department of Environmental and Resource Studies, Trent University. His research concentrates on the impacts of anthropogenic disturbance (air pollution, land use management and climate change) on terrestrial and aquatic ecosystems.
Address: Environmental and Resource Studies, Trent University, 1600 West Bank Drive, Peterborough, ON, Canada K9J 7B8.
e-mail: jaherne@trentu.ca