

Water quality of a small headwater lake reflects long-term variations in deposition, climate and in-lake processes

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Small headwater lakes reflect the changes in atmospheric pollution, and are also indicators of climate change. This study examined water chemistry changes in a pristine small lake in southern Finland during the period 1990–2009. Recovery from acidification was indicated, while no major changes in trace metal concentrations were found. In the course of the study, total phosphorus concentration was fluctuating in deteriorated oxygen conditions in the hypolimnion. However, total and organic nitrogen remained stable, but inorganic nitrogen concentration increased during the period, and was more dependent on the hydrology and in-lake processes than nitrogen deposition. Dissolved organic and inorganic carbon concentrations also increased, presumably due to decreasing acidity and changes in runoff, and increased alkalinity and decreased phytoplankton production, respectively. The results emphasise the importance of integrated intensive long-term monitoring of physical, chemical and biological variables for detecting impacts of changing environmental conditions.

Introduction

Increased emissions of air pollutants and greenhouse gases into the atmosphere since the 1950s have escalated environmental problems from the local to the global scales. The long-range transport of sulphur and nitrogen oxides has caused widespread acidification of acid-sensitive aquatic ecosystems in Europe and North

America (e.g. Rodhe *et al.* 1995). Airborne trace metals, such as mercury, and persistent organic pollutants have also reached the most remote regions of the world (e.g. AMAP 1998). At the same time, emissions of greenhouse gases into the atmosphere are causing global warming, and consequent climate change is considered to be among the most severe threats to the ecosystems (e.g. Rosenzweig *et al.* 2007). There is growing

evidence that climate-change-driven warming of lakes has taken place throughout the world, particularly in northern Europe and North America (Schneider and Hook 2010, Hook *et al.* 2012), and its impacts on the chemistry and ecology of lake ecosystems have also been documented (e.g. Adrian *et al.* 2009, Shimoda *et al.* 2011, Jeppesen *et al.* 2012).

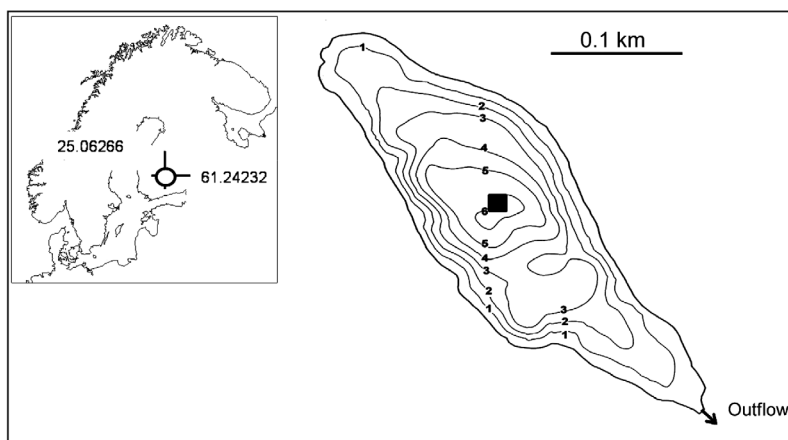
Detrimental effects of transboundary air pollution led to international agreements to reduce emissions of SO₂ and NO_x in Europe and North America. International negotiations on emission reductions have been conducted under the Convention on Long-Range Transboundary Air Pollution (CLRTAP), signed in 1979 under the UN Economic Commission of Europe (UNECE 1996). Since the 1980s, environmental regulations have led to declining emissions of air pollutants in Europe and North America. In Europe, overall emissions of SO₂ declined between 1990 and 2009 by 73%, and NO_x and NH₃ by 36% and 31%, respectively (Fagerli *et al.* 2011). Similarly, anthropogenic emissions of trace metals have been significantly reduced in Europe: between 1990 and 2010, lead emissions were reduced by 90%, and those of cadmium and mercury by 60% (Travnikov *et al.* 2012).

Small headwater lakes are susceptible to inputs of pollutants and reflect the changes in the atmospheric load (e.g. Mannio 2001a). Lake ecosystems also provide indicators of climate change either directly or indirectly through the catchment (e.g. Adrian *et al.* 2009, Arvola *et al.* 2010a, Shimoda *et al.* 2011). During the past 20 years, lake ecosystems in Europe and North America experienced changes with respect to recovery from acidification (e.g. Evans *et al.* 2001, Skjelkvåle *et al.* 2005, Garmo *et al.* 2011), increasing dissolved organic carbon (DOC) concentrations (e.g. Monteith *et al.* 2007) and increasing lake temperatures (e.g. Schneider and Hook 2010, Hook *et al.* 2012). In the past, nitrogen played a minor role in acidification, but its relative importance is increasing because N emissions have decreased less than those of sulphur. Recently, the deposition of reactive nitrogen has been shown to pose a threat to remote terrestrial and aquatic ecosystems through nutrient enrichment (Stevens *et al.* 2011, Lepori and

Keck 2012). However, there are no uniform regional trends in nitrate concentrations in sensitive freshwaters in Europe (Garmo *et al.* 2011). Catchments continue to be enriched by nitrogen deposition, which may result in nitrogen saturation, and excess nitrate (NO₃) leach to surface waters (e.g. Dise and Wright 1995, Macdonald *et al.* 2002, Moldan *et al.* 2006, Oulehle *et al.* 2012). Climate change may also enhance nitrogen leaching (e.g. Wright and Jenkins 2001, Moore *et al.* 2010).

In order to assess the impacts of air pollution and climate change in the environment, a long-term integrated monitoring approach in remote undisturbed areas including physical, chemical and biological variables is needed. The multidisciplinary International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM) is one of the activities set up under the UNECE CLTRAP to develop the necessary international co-operation in the assessment of pollutant effects and ecosystem impacts of climate change. In this study, we summarise the long-term changes in water chemistry in an ICP IM monitoring lake (Lake Valkea-Kotinen in southern Finland) that took place during a 20-year period (1990–2009). As the strongest decrease of European sulphur and nitrogen emissions and a decline in sulphate deposition in Finland started in the late 1980s (e.g. Lövblad *et al.* 2004, Vuorenmaa 2004), our study covers the period of recovery from acidification in Finnish lakes (Vuorenmaa and Forsius 2008, Rask *et al.* 2014b) and elsewhere in Europe (e.g. Garmo *et al.* 2011). In the period 1990–2010, the Valkea-Kotinen region experienced a change in its climate. The recorded increases in annual and spring mean air temperatures of 0.4 °C, thinning of the annual mean snow cover by ~1 cm, shortening of the lake ice season by 15 days and an advance of its end by six days, all given per decade, are already currently statistically significant, and these trends are also likely to continue in the future (Holmberg *et al.* 2014, Jylhä *et al.* 2014). Moreover, in addition to the changes in the ice-cover period, significant increases in epilimnetic water temperatures and thermal stability have also been found in Lake Valkea-Kotinen in the same period.

Fig. 1. Bathymetric map and location of Lake Valkea-Kotinen. Black box in the middle of the lake indicates the sampling point.



Material and methods

Site description

The study site, Lake Valkea-Kotinen (0.042 km²), is a boreal, humic, headwater lake with a small pristine catchment area (0.22 km²) in southern Finland (Fig. 1 and Table 1). The area is supra-aquatic, i.e. it has mostly been above water since the last glaciation. Its bedrock is acid-sensitive, dominated by slow-weathering granitoids and gneisses. The soil type is mostly Dystric Cambisols, developed on glacial drift but around the lake there is also peatland (histosols). The forest mainly consists of the old-growth Norway spruce (*Picea abies*), with the Scots pine (*Pinus sylvestris*), the aspen (*Populus tremula*) and the birch (*Betula* spp.). The catchment is located inside a conservation area and has been intact for over 100 years. There is no local pollution, and therefore long-range transported air pollutants and climate change are the only external disturbances (Ruoho-Airola *et al.* 1998).

Water sampling and chemistry

Chemical monitoring of the lake was carried out by the Environmental Administration (Finnish Environment Institute and Centre for Economic Development, Transport and the Environment for Häme) and the Lammi Biological Station of the University of Helsinki. The monitoring for

the effect of air pollution impacts was carried out by the Environmental Administration. Water samples were taken monthly in March–August, and once in October and December from the depths of 1, 3 and 5 m. Weekly nutrients and carbon samples were taken from 0 to 6 m depth at 1-m intervals between May and October by the Lammi Biological Station. All samples were taken at the site of the maximum depth, in the middle of the lake (cf. Fig. 1).

In the laboratories of the Environmental Administration, chemical variables were determined using standardised methods. pH was measured at 25 °C with a pH meter along with the titration of alkalinity (Gran plot). Ca, Mg, Na and K were determined by flame-AAS, and SO₄ and Cl by ion chromatography. The sum of NO₃-N and NO₂-N, here referred to as NO₃-N, was measured following a reduction in a Cu-Cd

Table 1. Basic morphometric, hydrographic and meteorological characteristics of Lake Valkea-Kotinen and its catchment.

Elevation (m)	156
Lake area (km ²)	0.042
Maximum depth of the lake (m)	6.5
Lake volume (m ³)	103000
Retention time (yr)	1.0
Catchment area (km ²)	0.22
Peatland (%)	14
Mean air temperature (1990–2009, °C)	4.6
Mean precipitation (1990–2009, mm a ⁻¹)	628
Mean runoff (1990–2009, mm a ⁻¹)	198

column and colorimetric determination of azo-colour. Trace metals Al (referred hereafter to as Al_{tot}), As, Cd, Cr, Cu, Pb, Ni, Zn and V were determined by ICP-MS. Hg was determined using cold vapour atomic fluorescence detection. For measurements of labile aluminium (referred hereafter to as Al_{lab}) concentrations, aluminium fractions were included in the routine analysis only between the years 1992 and 2006. For labile aluminium concentrations, total reactive and non-labile fractions were determined using a spectrophotometric FIA analyser with pyrocatechoviolet reaction. Al_{lab} was calculated by subtracting non-labile aluminium from the total reactive aluminium. Trace metal records have been available since 1994, when regular monitoring and analysis of metals using ICP-MS technique was started. An alternative chemical criterion to describe the acid-base status and buffering capacity of water, charge-balance acid neutralising capacity (ANC_{CB}), was calculated (Reuss and Johnson 1986), and defined as the equivalent sum of base cations minus the equivalent sum of strong mineral acid anions: $(Ca + Mg + Na + K) - (SO_4 + NO_3 + Cl)$. Sulphate and the sum of base cations (Ca, Mg, Na and K) are expressed as non-marine fractions (xSO_4 and xBC , respectively), and were estimated as the differences between total concentrations and concentrations attributable to marine salts, the latter based on ratios to Cl in seawater.

Nitrate nitrogen (NO_3-N), ammonium nitrogen (NH_4-N), total nitrogen (N_{tot}), phosphate phosphorus (PO_4-P), total phosphorus (P_{tot}), dissolved organic (DOC), inorganic carbon (DIC) and water colour were determined weekly in the laboratory at the Lammi Biological Station. Dissolved oxygen (DO) concentrations in epilimnion (1 m) and hypolimnion (5 m) were measured weekly *in situ* using a YSI 55 temperature-oxygen meter (Yellow Springs Instruments Inc., Yellow Springs, OH, USA). Dissolved PO_4-P , NO_3-N and NH_4-N concentrations were determined with a Lachat FIA analyser after filtration of samples through 0.2 μm Millipore membrane filters. The detection limit for dissolved PO_4-P was 2 $\mu g\ l^{-1}$ and for the inorganic fractions of nitrogen 10 $\mu g\ l^{-1}$. P_{tot} and N_{tot} concentrations were determined similarly after persulphate wet oxidation (Koroleff 1983). Water colour

was determined after filtration through 0.2 μm membrane or GF/C glass fibre filters (no significant difference in the results between the filters was found) with a spectrophotometer at 420 nm against Pt-Co standards (APHA 2000). DOC was determined by combustion at 900–950 °C (Salonen 1979) or, since 2001, at 680 °C with a Shimadzu TOC 5000 analyser. The possible major difference between the results of these methods stems from particles which are included in the determination by the method of Salonen (1979) but which may partly be excluded in the procedure used in the Shimadzu method. Differences vary from sample to sample, but may reach up to 1 mg C l^{-1} so that it should not exceed 10% in the samples from Lake Valkea-Kotinen.

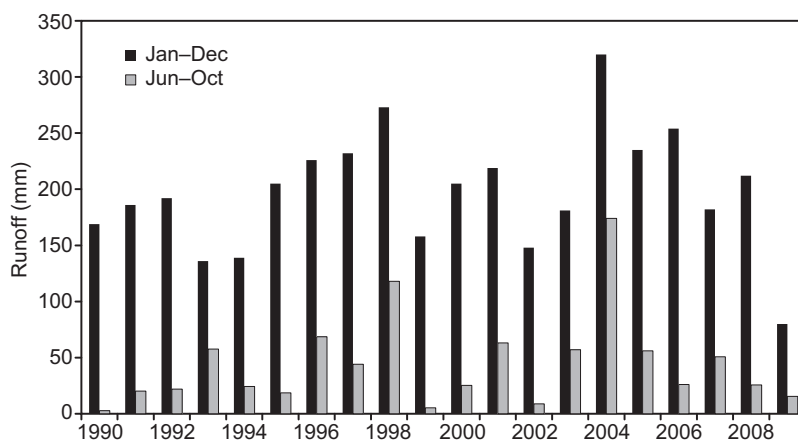
Runoff

Continuous runoff monitoring (based on water level recording calibrated against discharge) was performed at the overflow-measuring weir in the outflow stream, 140 m downstream from the lake. Monthly runoff ($mm\ month^{-1}$) was calculated as a sum of mean daily runoff values.

Trend analysis

The Seasonal Kendall test (SKT, Hirsch *et al.* 1982, Hirsch and Slack 1984) was used for detecting long-term monotonic trends in water chemistry. SKT is one of the most popular trend analyses for detecting monotonic trends in water chemistry records because it is not particularly sensitive to missing data or outliers, and is robust with respect to non-normality and serial character (e.g. seasonal changes), but it does not allow multiple monthly data. For trends in nutrients, carbon and water-colour weekly results were reduced to monthly medians, and the trends in monthly median values were evaluated. Trends in key acidification parameters and trace metals were evaluated using monthly values. A visual basic program for multivariate and conditional Mann-Kendall test of monotonic trends (available at www.slu.se/PageFiles/62531/Mann-Kendall_Sen.xls) was used for trend detection, and a multivariate technique, in which correction

Fig. 2. Annual and seasonal (June–October) runoff at the measurement station of the Valkea-Kotinen catchment in 1990–2009.



for covariates and trend detection are carried out simultaneously, was applied (Libiseller and Grimvall 2002). The long-term trends were calculated only for samples taken from the depth of 1 m or integrated 0–1 m samples for the period 1990–2009. On an annual scale, the samples represented almost the entire year (March–December) or only the ice-free period (May–October). The gradient of the trend (annual change), i.e. the slope of the linear trend, was calculated according to Sen's slope estimation method (Sen 1968). A statistical significance threshold of $p < 0.05$ was applied to the trend analysis. SKT computes the test statistics, S , which is derived from the difference between the later-measured value and all earlier-measured values, and assigns the integer value of 1, 0, or –1 to positive differences, no differences, and negative differences, respectively. The test statistic, S , is then computed as the sum of the integers. When S is a large positive number, later-measured values tend to be larger than the earlier ones which indicates an increasing trend. When S is a large negative number, later values tend to be smaller than the earlier ones which indicates a decrease-

ing trend. When the absolute value of S is small, no trend exists.

Results

Runoff

In 1990–2009, the mean annual runoff was about 200 mm yr⁻¹ without any significant seasonal or long-term trend (Table 2). The highest annual runoff occurred in 1998 (273 mm yr⁻¹) and in 2004 (320 mm yr⁻¹), when heavy precipitation in June–October (465 mm and 516 mm, respectively) resulted in high runoff during the same period (118 mm in 1998 and 174 mm in 2004; see Fig. 2).

Acidification parameters and trace metals

In the 1990s, low pH and Gran alkalinity values indicated highly acidic conditions in the lake (values commonly ≤ 5 and ≤ 0 $\mu\text{eq l}^{-1}$, respec-

Table 2. Monthly and annual trends in runoff (Seasonal Kendall test, Sen's slope) and mean monthly and annual runoff (mm month⁻¹ and mm yr⁻¹, respectively) in the Valkea-Kotinen catchment in 1990–2009.

Statistics	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan–Dec
Slope	0.41	–0.05	–0.42	–0.95	–0.96	0.06	0.12	0.19	0.08	0.23	0.74	0.77	0.08
p	0.36	0.95	0.23	0.15	0.19	0.72	0.54	0.11	0.58	0.54	0.30	0.17	0.54
Runoff	15	14	15	37	31	9.5	11	8.5	5.9	10	20	20	198

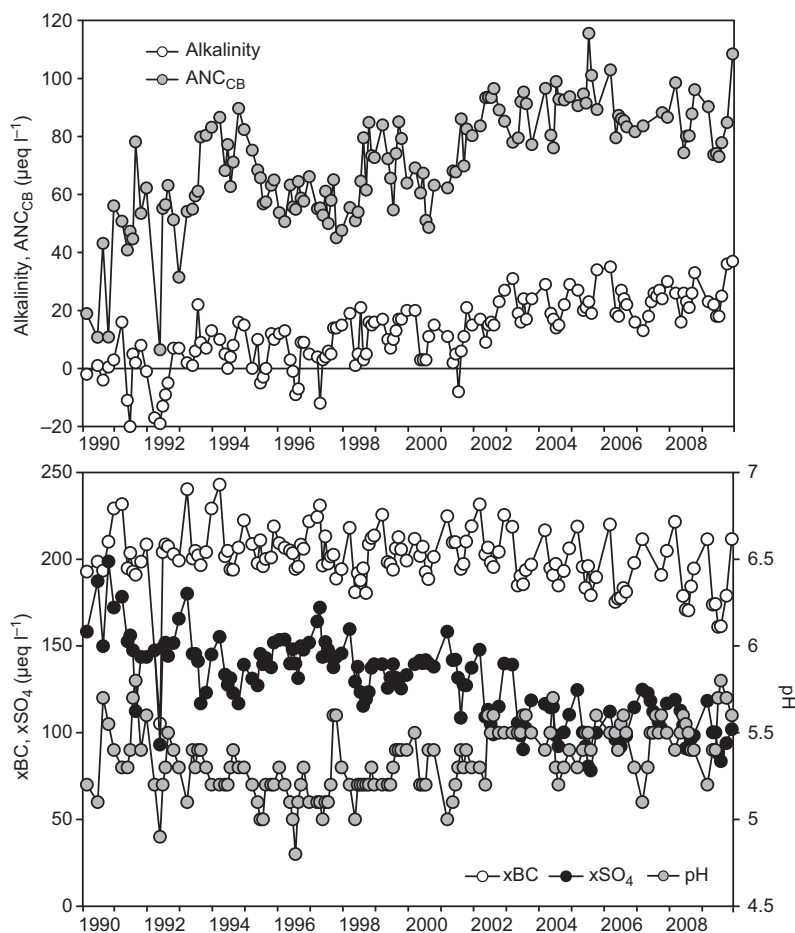


Fig. 3. Alkalinity (measured) and charge-balance acid neutralising capacity (ANC_{CB} , calculated) (upper), and non-marine base cations (xBC) and sulphate (xSO_4) concentrations and pH (lower) at the depth of 1 m in Lake Valkea-Kotinen in 1990–2009.

tively; Fig. 3). During the study period, however, xSO_4 concentration decreased (SKT: $-3.3 \mu\text{eq l}^{-1} \text{yr}^{-1}$, $S = -827$, $n = 137$, $p < 0.001$; see Table 3) by about 40% with consequent increase in pH (SKT: $0.014 \text{ pH unit yr}^{-1}$, $S = 412$, $n = 138$, $p < 0.01$) and buffering capacity, indicated by alkalinity (SKT: $1.6 \mu\text{eq l}^{-1} \text{yr}^{-1}$, $S = 811$, $n = 136$, $p < 0.001$) and ANC_{CB} (SKT: $2.1 \mu\text{eq l}^{-1} \text{yr}^{-1}$, $S = 550$, $n = 127$, $p < 0.001$). Concentration of base cations (xBC) declined (SKT: $-1.2 \mu\text{eq l}^{-1} \text{yr}^{-1}$, $S = -417$, $n = 127$, $p < 0.001$), but to a lesser extent than that of xSO_4 , resulting in an increase in ANC_{CB} (by about 70% since 1990). There was no significant trend in Al_{lab} concentration in 1992–2006. The annual average Al_{lab} concentrations for the 5-year periods 1992–1996, 1997–2001 and 2002–2006 were $17 \mu\text{g l}^{-1}$, $18 \mu\text{g l}^{-1}$ and $12 \mu\text{g l}^{-1}$, respectively. A decreased Al_{lab} concentration in the period 2002–

2006 probably reflects the decrease in acidity (i.e. increase in pH) in the lake during the 2000s (Fig. 3).

There were no significant long-term trends in trace metal concentrations from 1994 to 2009, except for Al_{tot} (SKT: $3.1 \mu\text{g l}^{-1} \text{yr}^{-1}$, $S = 313$, $n = 108$, $p < 0.01$) (Table 4). For Pb and Ni, however, the median concentrations decreased by 10%–20%, and maximum concentrations (as expressed by 90th percentile) by 20%–50% between the periods 1994–1999 and 2000–2009 (Table 4). Correspondingly, the maximum concentrations for Zn and Cu also decreased, by 30%–60%, between these two decades. Cd concentration was mostly below the detection limits ($\leq 0.03 \mu\text{g l}^{-1}$ in 1994–2004 and $\leq 0.01 \mu\text{g l}^{-1}$ in 2005–2009). Total Hg concentrations were not measured before December 2002, and therefore the data is insufficient for revealing long-term trend analysis.

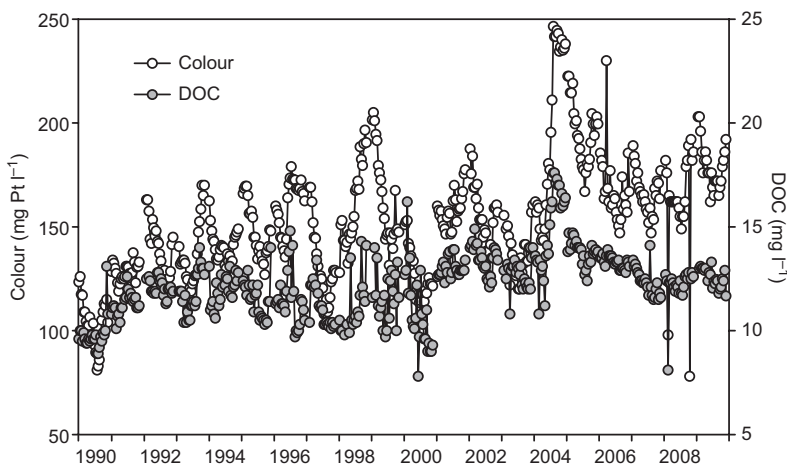


Fig. 4. Water colour and dissolved organic carbon (DOC) concentration at the depth of 0–1 m in Lake Valkea-Kotinen in 1990–2009.

Dissolved organic and inorganic carbon

In Lake Valkea-Kotinen, both DOC concentration (SKT: 0.12 mg l⁻¹ yr⁻¹, $S = 435$, $n = 120$, $p <$

0.01) and water colour (SKT: 2.7 mg Pt l⁻¹ yr⁻¹, $S = 574$, $n = 120$, $p < 0.001$) increased, particularly during the 2000s (Fig. 4). Since 1990, the DOC concentration has increased by approximately

Table 3. Long-term trends (1990–2009) in alkalinity (measured), charge-balance acid neutralizing capacity (ANC_{CB}, calculated), pH, H⁺, non-marine sulphate (xSO₄), sum of non-marine base cations (xBC) and labile aluminium (Al_{lab}) in Lake Valkea-Kotinen. For the annual change, a statistically significant trend (Seasonal Kendall-test, Sen's slope) is denoted with asterisks ($p < 0.001^{***}$, $p < 0.01^{**}$, $p < 0.05^{*}$).

Variable	Unit	Mar	May	Jun	Jul	Aug	Oct	Dec	Mar–Dec
Alkalinity	μeq l ⁻¹ yr ⁻¹	1.58**	1.50***	1.76***	1.48**	1.41***	1.63***	1.60***	1.57***
ANC _{CB}	μeq l ⁻¹ yr ⁻¹	2.39**	2.50**	2.09**	1.87*	1.76**	1.97**	2.42**	2.11***
pH	pH-unit yr ⁻¹	0.006	0.02**	0.02**	0.02*	0.007	0.01*	0.008	0.014**
H ⁺	μeq l ⁻¹ yr ⁻¹	-0.10	-0.26**	-0.24**	-0.17*	-0.06	-0.10*	-0.10	-0.15**
xSO ₄	μeq l ⁻¹ yr ⁻¹	-3.24***	-2.85**	-3.41***	-4.00***	-3.21***	-3.35***	-3.14***	-3.30***
xBC	μeq l ⁻¹ yr ⁻¹	-0.93	-0.49	-1.45*	-1.69**	-1.67**	-1.05**	-0.79	-1.21***
Al _{lab}	μg l ⁻¹ yr ⁻¹	-0.71	0	-0.46	-1.00	0	-0.74	0	-0.42

Table 4. Percentiles (10%, median and 90%) of the concentrations for the two periods (1994–1999 vs. 2000–2009) and long-term trends (1994–2009) for trace metals Al_{tot}, As, Cd, Cr, Cu, Pb, Ni, Zn, V and Hg in Lake Valkea-Kotinen. For the annual change, a statistically significant trend (Seasonal Kendall-test, Sen's slope) is denoted with asterisks ($p < 0.001^{***}$, $p < 0.01^{**}$, $p < 0.05^{*}$). n.d. = no data.

Variable	Percentiles 1994–1999 (μg l ⁻¹)			Percentiles 2000–2009 (μg l ⁻¹)			Trend 1994–2009 (μg l ⁻¹ yr ⁻¹)
	10%	Median	90%	10%	Median	90%	
Al _{tot}	112	130	151	130	150	200	3.07**
As	0.22	0.27	0.32	0.24	0.27	0.30	0
Cd	< 0.03	< 0.03	0.03	< 0.01	< 0.03	< 0.03	0
Cr	0.16	0.27	0.45	0.20	0.30	0.42	0.001
Cu	0.14	0.22	0.73	0.17	0.24	0.32	0.003
Pb	0.30	0.42	0.65	0.25	0.35	0.52	-0.006
Ni	0.39	0.48	1.11	0.36	0.43	0.51	-0.003
Zn	2.9	4.5	33	3.0	6.8	25	0.13
V	0.26	0.29	0.36	0.24	0.29	0.40	0.002
Hg	n.d.	n.d.	n.d.	0.003	0.004	0.006	n.d.

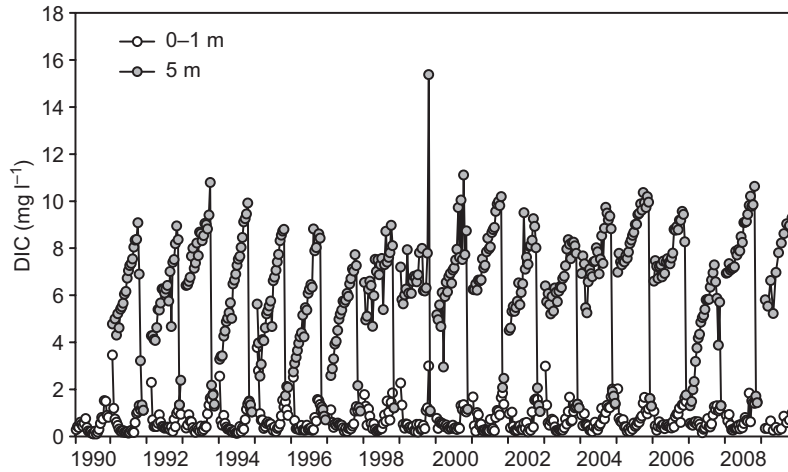


Fig. 5. Dissolved inorganic carbon (DIC) concentrations at the depths of 0–1 m and 5 m in Lake Valkea-Kotinen in 1990–2009.

2 mg l⁻¹ and water colour 50 mg Pt l⁻¹ (Table 5).

In the epilimnion (0–1 m), DIC concentration increased (SKT: 0.008 µeq l⁻¹ yr⁻¹, *S* = 241, *n* = 119 *p* < 0.05) (Table 5), and especially a distinct increase was found in August and October when concentrations increased by 0.3–0.4 mg C l⁻¹. Vertically, the stratification of DIC was steepest in August following by July, June and September, when the autumnal mixing already starts. In the hypolimnion (5 m), DIC concentrations increased, on average, by > 15% from the 1990s (mean 5.9 mg C l⁻¹ in 1991–1999) to the 2000s (mean 6.9 mg C l⁻¹ in 2000–2009) (Fig. 5).

Nitrogen and phosphorus

During the period 1990–2009, DIN concentra-

tions increased (SKT: 0.79 µg l⁻¹ yr⁻¹, *S* = 468, *n* = 120, *p* < 0.001) (Fig. 6), with an increase in NO₃-N (SKT: 0.42 µg l⁻¹ yr⁻¹, *S* = 364, *n* = 120, *p* < 0.01) and NH₄-N (SKT: 0.35 µg l⁻¹ yr⁻¹, *S* = 328, *n* = 120, *p* < 0.05) (Table 5). In the epilimnion (0–1 m), the mean NO₃-N concentration (13 µg l⁻¹) equalled the mean NH₄-N concentration (14 µg l⁻¹), and the highest DIN concentrations were typically found at the beginning and the end of the thermal stratification period. They have a temporary nature and hence they are sensitive to the timing of sampling, and may not provide useful information on long-term trends. Instead, during summer stratification in June–September both NO₃-N and NH₄-N concentration steadily increased. No significant trends were found in N_{tot} and organic nitrogen concentrations (TON, calculated by subtracting DIN from N_{tot}). As a con-

Table 5. Long-term trends (1990–2009) in dissolved organic carbon (DOC), water colour, dissolved inorganic carbon (DIC), nitrate (NO₃-N), ammonium (NH₄-N), dissolved inorganic nitrogen (DIN = NO₃-N + NH₄-N), total nitrogen (N_{tot}), organic nitrogen (TON), ratio of DIN/N_{tot} and total phosphorus (P_{tot}) in Lake Valkea-Kotinen. For the annual change, a statistically significant trend (Seasonal Kendall-test, Sen's slope) is denoted with asterisks (*p* < 0.001***, *p* < 0.01**, *p* < 0.05*).

Variable	Unit	May	Jun	Jul	Aug	Sep	Oct	May–Oct
DOC	mg l ⁻¹ yr ⁻¹	0.13***	0.15**	0.12*	0.10	0.11*	0.09	0.12**
Colour	mg Pt l ⁻¹ yr ⁻¹	2.73**	2.68**	2.28***	2.53**	3.00**	2.76**	2.68***
DIC	mg l ⁻¹ yr ⁻¹	-0.004	0.000	0.006	0.017**	0.012	0.019**	0.008*
NO ₃ -N	µg l ⁻¹ yr ⁻¹	-0.30	0.51**	0.39**	0.43*	0.56**	0.58*	0.42**
NH ₄ -N	µg l ⁻¹ yr ⁻¹	0.07	0.23	0.42**	0.36*	0.47*	0.76	0.35*
DIN	µg l ⁻¹ yr ⁻¹	-0.41	0.68***	0.96***	0.92**	0.95***	1.28	0.79***
N _{tot}	µg l ⁻¹ yr ⁻¹	-1.21	1.00	-0.18	-2.03	-0.63	-0.56	-0.60
TON	µg l ⁻¹ yr ⁻¹	0.44	0.06	-1.25	-3.26	-1.53	-2.00	-1.38
DIN/N _{tot}	% yr ⁻¹	-0.07	0.15***	0.21***	0.23**	0.22***	0.29*	0.19***
P _{tot}	µg l ⁻¹ yr ⁻¹	0.1	-0.06	-0.18	-0.32	-0.03	0.03	-0.02

Fig. 6. Total nitrogen (N_{tot}) and dissolved inorganic nitrogen ($\text{DIN} = \text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) concentrations at the depth of 0–1 m in Lake Valkea-Kotinen in 1990–2009.

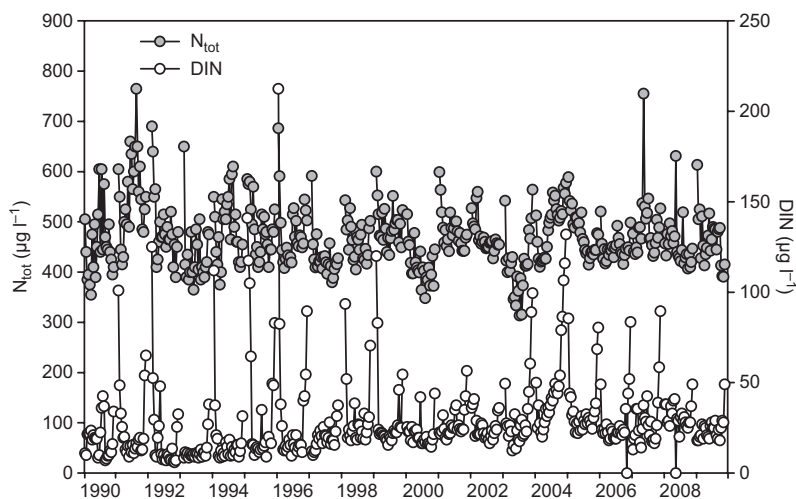
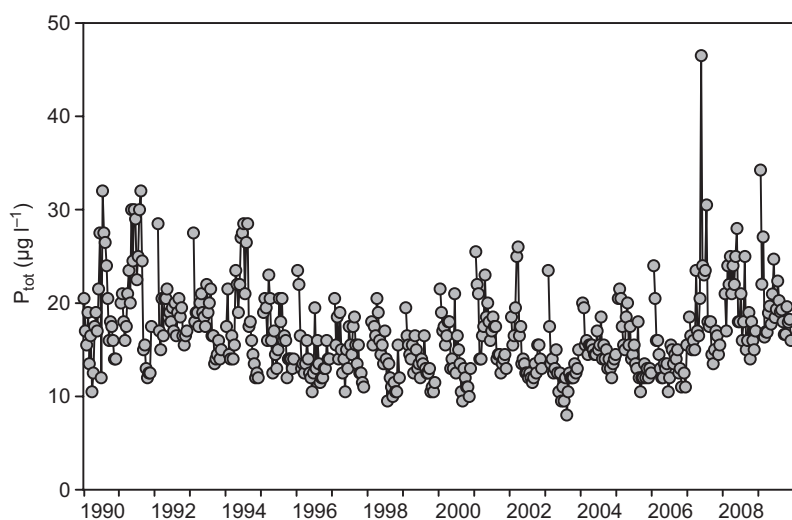


Fig. 7. Total phosphorus (P_{tot}) concentration at the depth of 0–1 m in Lake Valkea-Kotinen in 1990–2009.



sequence, the proportion of DIN in N_{tot} increased ($\text{SKT}: 0.19\% \text{ yr}^{-1}$, $S = 489$, $n = 120$, $p < 0.001$).

No consistent trend was found in P_{tot} concentration in the epilimnion in 1990–2009 (Table 5). However, in 1990–1999 the concentration decreased ($\text{SKT}: -0.62 \mu\text{g l}^{-1} \text{ yr}^{-1}$, $S = -134$, $n = 60$, $p < 0.01$) and in 2000–2009 it increased ($\text{SKT}: 0.5 \mu\text{g l}^{-1} \text{ yr}^{-1}$, $S = 106$, $n = 60$, $p < 0.05$) (Fig. 7). During the 2000s, the increase in P_{tot} concentration was pronounced in the hypolimnion (5 m) in May (Fig. 8).

Dissolved oxygen concentration

During the 2000s, dissolved oxygen concentra-

tion drastically decreased in the hypolimnion, especially in spring. In the course of the last 12 years of the study, the bottom layer (5 m) was nearly anoxic ($\text{DO} < 1 \text{ mg l}^{-1}$) in May with the exception of 2000, 2002 and 2007 (Fig. 8).

Discussion

Airborne pollutants

Sulphur deposition declined in south Finland by about 60%–70% since the late 1980s, while the decline in the nitrogen deposition was about 30%–40% (Vuorenmaa 2007, Ruoho-Airola *et al.* 2014). In line with a recovery of small

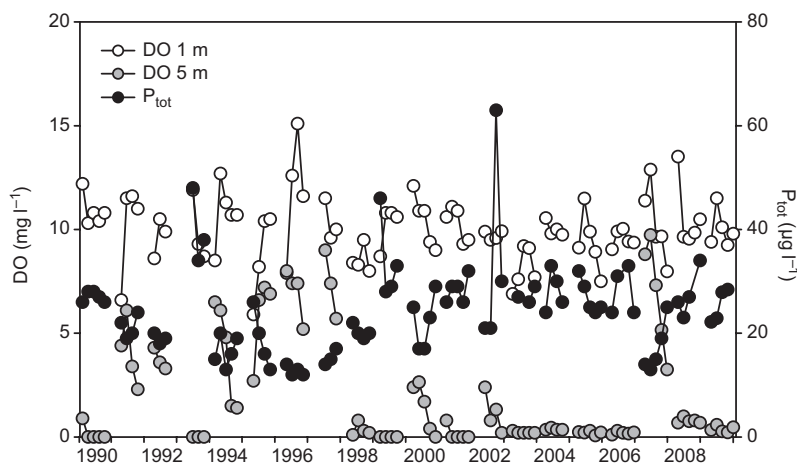


Fig. 8. Dissolved oxygen (DO) concentrations at the depths of 1 m and 5 m and total phosphorus (P_{tot}) concentration at the depth of 5 m in May in Lake Valkea-Kotinen in 1990–2009.

headwater lakes from acidification in Finland (Mannio 2001b, Vuorenmaa and Forsius 2008) and elsewhere in Europe and North America with decreasing concentrations of sulphate and a subsequent increase in alkalinity (e.g. Skjelkvåle *et al.* 2005, Garmo *et al.* 2011), the acidification reversal was also recorded in Lake Valkea-Kotinen. The decrease in $x\text{SO}_4$ concentrations exceeded that in $x\text{BC}$ concentrations, indicating the improved acid-base status of soils, and led to increased buffering capacity and pH in runoff and lake water.

Low pH is generally associated with elevated labile aluminium concentrations (e.g. Rask *et al.* 1995). However, in Lake Valkea-Kotinen Al_{lab} concentration was clearly lower (mean $16 \mu\text{g l}^{-1}$ in 1992–2006) as compared with that measured in acidic clear-water lakes ($> 100 \mu\text{g l}^{-1}$, Vuorenmaa and Forsius 2008, Rask *et al.* 2014b), presumably due to humic substances, which are known to complex and reduce the concentrations of toxic forms of inorganic aluminium (e.g. Henriksen *et al.* 1989).

In the 1990s, the recovery of buffering capacity in Lake Valkea-Kotinen was slower than in many clear water lakes in southern Finland. A more consistent recovery took place in the 2000s, while a clear increase in alkalinity in clear water lakes took place since the early 1990s (Vuorenmaa and Forsius 2008, Rask *et al.* 2014b). In Lake Valkea-Kotinen, the decrease in $x\text{SO}_4$ concentration was also slower in the 1990s, contrary to clear water lakes having the steepest decrease in $x\text{SO}_4$ in the 1990s (Vuorenmaa 2007). This

indicates a delayed response in sulphate output in the catchment to decreased deposition, and variation in $x\text{SO}_4$ with recovery from acidification and its reversal in Lake Valkea-Kotinen may be a result of the retention and release processes of sulphate. At the beginning of the 1990s, the Valkea-Kotinen catchment retained 30% of sulphate deposition due to strong retention of SO_4 in peatlands and in catchments with peaty soils (Forsius *et al.* 1995), but after the mid-1990s the catchment shifted from retention to net release (output > input) of sulphate (Forsius *et al.* 2005, Vuorenmaa *et al.* 2012). This shows that forest soils are now releasing stored airborne sulphur that had accumulated in the past, and the results are consistent with mass balance budget calculations for a number of European forested catchments (Prechtel *et al.* 2001, de Vries *et al.* 2003, Vuorenmaa *et al.* 2012). Variation in runoff and leaching of humic-derived organic acids may also have affected alkalinity, because in the pH range 4–7 a significant fraction of organic acids can be considered strong and may have a large influence on pH and alkalinity (e.g. Munson and Gherini 1993). Therefore, runoff-induced surges of organic acids can be an important factor suppressing recovery of pH and alkalinity in acid-sensitive Finnish lakes (Vuorenmaa and Forsius 2008, Arvola *et al.* 2010b, Nyberg *et al.* 2010).

Although the net release of sulphate from the catchment was indicated, $x\text{SO}_4$ concentration in the lake dropped clearly after 2001, and the trend levelled off between 2004 and 2009. However, the change in the sulphate concentration level

evidently increased the buffering capacity and pH in the lake. The mean annual SO_4 deposition between the periods 1993–2002 and 2003–2011 decreased by 35% (Ruoho-Airola *et al.* 2014), contributing to a decrease in xSO_4 in the lake. Due to the net release of sulphate, it is suggested that SO_4 remains the dominant source of actual soil acidification despite the generally lower input of S than N in European forested ecosystems (deVries *et al.* 2003). Continued work on processes regulating S retention and release in terrestrial ecosystems is therefore needed. This is important for assessing the effects of emission reductions on acidification recovery. Several processes, including desorption and excess mineralisation, and re-oxidation of reduced sulphur regulate the long-term response of soil S, and a differentiation is necessary for predictions of future responses (e.g. Prechtel *et al.* 2001). Many of these processes are also sensitive to changes in climatic variables, and would therefore be affected by climate change (e.g. Wright 1998).

Along with decreased acidifying emissions, emissions of trace metals, particularly of Hg, Cd and Pb, substantially decreased in Europe (Travnikov *et al.* 2012), and in line with this, the deposition of the trace metals in the Valkea-Kotinen catchment clearly declined over the last 20 years (Ruoho-Airola *et al.* 2014). However, this decrease was not clearly reflected in lake water concentrations. Regarding element concentrations in the lake water, the response to atmospheric deposition is difficult to differentiate from other factors, such as natural catchment acidity due to organic soils and delays in the hydrological transport of the trace metals from the catchment due to their strong retention in the soil (Mannio *et al.* 1995, Tarvainen *et al.* 1997, Ukonmaanaho *et al.* 2001). Acidity particularly controls the levels of As, Cd and Zn, while organic matter controls the levels of Cr, Fe, Cu and Ni in head water lakes, and Pb, Mn and Al are affected by both factors. Humic substances act as carriers of trace metals from catchment soils to surface waters, irrespective of the source of trace metals.

According to Ukonmaanaho *et al.* (2001), the retention of total atmospheric deposition (bulk + throughfall) of Pb, Cd, Cu and Zn in

the Valkea-Kotinen catchment was $\geq 77\%$, and only 3%–26% accounted for the lake sediment. The accumulation of trace metals in the lake sediments, particularly of Hg, Pb, Cd and As, declined in recent decades, presumably reflecting the decrease in the atmospheric loading and catchment supply (Mannio 2001a, Ukonmaanaho *et al.* 2001). In agreement with this, a clear decrease in the concentration of Hg in pike was found in Lake Valkea-Kotinen between 1980 and 2002 (Verta *et al.* 2011).

In contrast to other trace elements, Al_{tot} significantly increased in 1994–2009, although acidity decreased and Al_{lab} concentration mainly remained unchanged, and therefore processes other than acidification may have controlled Al_{tot} leaching. It is known that aluminium in soil percolation water is largely controlled by the concentration of organic complexes (DOC) (e.g. Lindroos *et al.* 2011), and an increase in Al_{tot} concentration in Lake Valkea-Kotinen may have a link to the increased export of DOC from the catchment. Weathering of minerals in forest soil (like aluminium) is, inter alia, temperature-dependent (e.g. Johnson *et al.* 1994), and it has also been suggested that an increased DOC concentration in soil solution increases the weathering release of Al (Lindroos *et al.* 2003). Air temperature significantly increased and snow cover thickness decreased in the Valkea-Kotinen region, and the leaching of DOC to surface water significantly increased in Lake Valkea-Kotinen, all of which suggests an enhancement of the weathering rate of Al. The results altogether suggest that climate may be an important driver behind the observed increase in Al_{tot} .

Dissolved organic carbon

The increase in DOC and water colour in Lake Valkea-Kotinen was in agreement with earlier observations from Finland and elsewhere in Europe and North America (e.g. Vuorenmaa *et al.* 2006, Monteith *et al.* 2007, Sarkkola *et al.* 2009). Several studies have suggested that the principal driver for the regional increase of DOC concentration was the recovery from acidification, i.e. a decrease of sulphate deposition and an increase of pH in the soil, and a consequent

increase of the solubility of DOC in the soil (Evans *et al.* 2006, Vuorenmaa *et al.* 2006, de Wit *et al.* 2007, Monteith *et al.* 2007, Haaland *et al.* 2010). However, both the production and transport of DOC are strongly influenced by climate and the increases have also been linked, in part, to climatic drivers, including temperature (e.g. Freeman *et al.* 2001a, 2001b, Evans *et al.* 2006, Sarkkola *et al.* 2009), soil moisture and frequency of severe droughts (e.g. Worrall *et al.* 2004, 2006), solar radiation (e.g. Hudson *et al.* 2003), and variations in runoff and in the timing and intensity of precipitation and snowmelt (e.g. Hongve *et al.* 2004, Erlandsson *et al.* 2008). Because the different factors usually act simultaneously and in a complex way, the significance of each driver may vary between sites, regions and times (Monteith *et al.* 2007).

Although neither precipitation (Jylhä *et al.* 2014) nor runoff exhibited any long-term trend in the Valkea-Kotinen catchment, short-term fluctuations in runoff have modified the load of DOC to the lake. For example, following the drier year of 1997, DOC concentration and water colour increased in Valkea-Kotinen in 1998 with the second highest summer and autumn runoff. Concentrations of DOC were elevated again in the early 2000s due to moderate summer runoff in 2001, a very dry year in 2002 followed by a moderately wet summer in 2003 and an exceptionally wet summer in 2004, as seen also in the patterns of water colour (Arvola *et al.* 2010b). Watts *et al.* (2001) noticed that runoff-driven enhanced levels of water colour may persist for several years. A similar lag in recovery of DOC concentrations was also found in a nearby humic lake after the 2004 summer flood (Jennings *et al.* 2012).

Increased DOC concentration and water colour, and the consequent decrease in light penetration into the lake may have large ecological impacts on Lake Valkea-Kotinen, such as decreasing primary production (Arvola *et al.* 2014) and decreasing feeding efficiency and growth of perch (Rask *et al.* 2014a). Increased light attenuation in water may also strengthen the steepness of thermal stratification and raise the thermocline depth (e.g. Tanenzap *et al.* 2008).

In the future, climatic factors are likely to play an even greater role in modifying the DOC

concentration in Lake Valkea-Kotinen (Futter *et al.* 2009), due to the recent stabilisation of sulphur deposition (Skjelkvåle *et al.* 2005), and the sensitivity of the transport of DOC to projected changes in climate (Sobek *et al.* 2007, Jennings *et al.* 2010, Naden *et al.* 2010). However, the large increases in surface-water DOC concentrations in Lake Valkea-Kotinen recorded at the end of the 20th century are unlikely to continue into the future (Futter *et al.* 2009). After a few decades, climate change may result in lower runoff and drier soils, and as a result in-lake DOC concentrations may decrease due to smaller terrestrial runoff and longer water residence times (Schindler *et al.* 1996, Holmberg *et al.* 2014), suggesting greater in-lake processing of DOC.

Dissolved inorganic carbon

The low DIC concentrations in the uppermost water layer and high concentrations below the epilimnion suggest that the uptake by algae and mineralisation by bacteria (Huotari *et al.* 2009, Arvola *et al.* 2014) are the biological processes modifying DIC in Lake Valkea-Kotinen. In spring and autumn, when deep water was mixed with epilimnetic water, DIC concentrations at the surface were substantially higher than during the rest of the summer season. Increasing trends in the surface DIC concentration in July and August can be explained by increased alkalinity and higher respiration relative to primary production (Arvola *et al.* 2014), while the increase in October might be due to the later start of autumn turnover in the 2000s as compared with that in the 1990s (Jylhä *et al.* 2014). At a depth of 5 m, the increased DIC concentration suggests higher organic matter mineralisation throughout the study period, which is in accordance with the higher DOC concentration in the lake. It should be considered that because of low water pH, DIC was predominantly composed of CO₂.

Dissolved oxygen

In the 2000s, spring oxygen conditions in the hypolimnion were extremely poor, probably due to the lack of complete overturn after ice-out. A

clear spring overturn in May was only recorded in 2007, but it may also have briefly taken place in 2000 and 2002. As a result of higher spring air temperatures and earlier ice-out (Jylhä *et al.* 2014), and increase in water colour, the onset of thermal stratification took place earlier and consequently thermal stability became stronger, both factors which favoured oxygen depletion in the lower part of the water column. In favourable conditions the onset of stratification may take place within a couple of days after the ice-off (Salonen *et al.* 1984). Increased DOC and water colour led to heat absorption in shallower water layers, which means that heat is distributed across a smaller water volume, a fact also supporting more rapid and steep stratification.

Steeper thermal stratification and shallower oxic epilimnion strongly increase the bottom area that is predominantly anoxic for more than 10 months per year. If the oxycline is located at a depth of 3 m, the area of the anoxic sediment is 30%, but a 1-m shift upwards increases it by 20%. In anoxic conditions, it is likely that phosphorus stored in the sediment will be released into the water, causing eutrophication. Oxygen deficiency in the hypolimnion may have other consequences, such as the production of methyl-Hg (Verta *et al.* 2010) and its accumulation in fish (Rask *et al.* 2010), higher CH_4 fluxes into the atmosphere (Kankaala *et al.* 2006), and a thinner oxic layer may also mean changes in predator–prey relationships. Any major change in the oxygen regime may therefore have important chemical and biological consequences in small humic lakes with steep thermal and chemical stratification (Forsius *et al.* 2010).

Nitrogen and phosphorus

The increase in DIN concentrations was one of the most consistent changes during the study period, taking place since the early 1990s. This was a surprise, because nitrogen deposition declined at the same time (Ruoho-Airola *et al.* 2014). In agreement with that, nitrate concentrations generally decreased in small headwater forest lakes in Finland (Vuorenmaa and Forsius 2008), and inorganic nitrogen concentrations and exports in boreal Finnish forest streams did not

change, or showed a slight decrease in concentrations during the last 15–28 years (Sarkkola *et al.* 2012). Equally, elsewhere in Europe and North America only a few significant trends in NO_3 concentrations were detected, but concentrations were decreasing rather than increasing (Skjelkvåle *et al.* 2005, Garmo *et al.* 2011). De Wit *et al.* (2008) reported an increasing trend in NO_3 flux in a low N deposition area in a boreal stream in Norway. This trend was unlikely to have been dominated by soil N status and N deposition, but it was more related to climate variables such as changes in snow depth, winter discharge and temperature.

Studies from European forested ecosystems show a clear relationship between N deposition and N loss (e.g. Dise and Wright 1995, MacDonald *et al.* 2002), and depositions < 9–10 $\text{kg ha}^{-1} \text{yr}^{-1}$ resulted in only very little NO_3 leaching to the surface waters (e.g. Dise and Wright 1995, Wright *et al.* 2001). Thus, the annual average deposition of inorganic nitrogen ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) of ca. 4 $\text{kg ha}^{-1} \text{yr}^{-1}$ and ca. 2.5 $\text{kg ha}^{-1} \text{yr}^{-1}$, in the Valkea-Kotinen catchment in 1988–1997 and 2003–2011, respectively (Ruoho-Airola *et al.* 2014), should mean low deposition-driven risk of N leaching. Moreover, the input–output budgets of inorganic nitrogen for the Valkea-Kotinen catchment showed high net retention (> 95%) of inorganic nitrogen (Forsius *et al.* 1995, 2005, Vuorenmaa *et al.* 2012), which is in accordance with low soil water NO_3 concentrations (mean 10 $\mu\text{g l}^{-1}$ in 1989–1997; Ukonmaanaho and Starr 2002) in the catchment of Valkea-Kotinen. Additionally, the fluxes of DIN in the soil percolation water were very low and did not exhibit any consistent trend pattern during 1998–2004, indicating that the N retention capacity of the soil was not exceeded (Mustajärvi *et al.* 2008). The mean annual and spring air temperatures significantly increased. The increased temperatures in the Valkea-Kotinen region in 1990–2010 (Jylhä *et al.* 2014) may have caused increased leaching of inorganic N from the catchment through increased N mineralisation in the soil. Since inorganic N concentrations in soil solution were not increasing, the potentially increased mineralisation may have been concealed behind the decreased N deposition and possible greater uptake and accumula-

tion of N by vegetation in conditions of warmer and extended growth periods.

Since the enrichment of soils in N towards saturation in the catchment is not plausible, we suggest that the significant trend in DIN concentrations is more likely related to in-lake processes and hydrology than to the direct N deposition effect. Firstly, nutrient monitoring data with the nutrient enrichment experiments in Lake Valkea-Kotinen suggested that in the 1990s phytoplankton was limited by both P and N, but later the P limitation became proportionally more severe (Järvinen 2002, *see* Arvola *et al.* 2014). Opposite to DIN, the concentration of $\text{PO}_4\text{-P}$ in the uppermost 1 m was practically always below the detection limit (Arvola *et al.* 2014), also suggesting P limitation. The decrease in organic carbon sedimentation relative to N_{tot} and P_{tot} during the first 11 years of the study period suggests a rather dramatic change in the biogeochemistry of the major nutrients in Lake Valkea-Kotinen (Arvola *et al.* 2014). Therefore, an intriguing question is whether there was a link between the recorded decrease in C/N and C/P of the settled material and the higher lake-water $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations during late the 1990s. Both results suggest that N limitation may have decreased since the middle of 1990s, although the atmospheric deposition of N has decreased since the end of 1980s. Surveys covering oligotrophic lakes in Europe and North America (Bergström *et al.* 2005, Bergström and Jansson 2006) suggested that atmospheric deposition of N in excess of natural levels increased inorganic nitrogen concentrations, which is likely to have caused a shift from natural N limitation to P limitation. The shift from N limitation towards P limitation was found to be steepest at a relatively low N deposition level, from 2 to 5 kg ha⁻¹ yr⁻¹. An additional complication for trend assessment is the declining N deposition, which may affect the future balance between N and P limitation. Secondly, low DIN concentrations in the early 1990s may be explained by concurrently high primary production and phytoplankton biomasses (Arvola *et al.* 2014). Thirdly, hydrological conditions may modify the leaching of nitrate from the catchment. Although discharge from the catchment showed no long-term trend during the study

period, striking hydrological short-term patterns characterised the runoff. Wet years in the periods 1995–1998 and 2001–2008 with higher summer/total runoff, and the very dry year in 2009 can be distinguished in the intra- and inter-annual variations in DIN concentrations. The variability of NO_3 trends in undisturbed forested streams and lakes illustrates that control of DIN concentrations and fluxes is complicated, often apparently independent of trends in N deposition, and not thoroughly understood (e.g. Garma *et al.* 2011).

A weak dependence between DOC and $\text{N}_{\text{tot}}/\text{TON}$ in our study lake contradicts the results of studies from unmanaged boreal forest catchments, where a relatively strong correlation between stream and lake water TOC and $\text{N}_{\text{tot}}/\text{TON}$ concentrations and fluxes exists, due to the close association of organic nitrogen loss with leaching of DOC, both originating primarily from allochthonous dissolved organic matter (e.g. Kortelainen *et al.* 2006, Hessen *et al.* 2009). This pattern seems valid for comparison of single values (e.g. means for the whole study period), but when long-term trends are considered, the relationship may be weaker (e.g. Sarkkola *et al.* 2012), however, indicating the variable controls on DOC export from terrestrial catchment and complex controls of DOC and TON in lake ecosystems. An increasing DOC concentration may be caused by increased leaching of relatively undecomposed organic matter rather than highly decomposed material (Sarkkola *et al.* 2012). DOC in soil solution and surface waters in boreal forested catchments is dominated by hydrophobic acids, which are relatively resistant to decay (Starr and Ukonmaanaho 2004). Many studies have suggested that the nitrogen concentration in organic matter increases with an increased decomposition (e.g. Laiho and Laine 1994). Lake Valkea-Kotinen has a retention time of about 1 year and, in general, organic nitrogen may be affected by several in-lake processes modifying the concentrations.

P_{tot} concentration did not show any long-term trend in Lake Valkea-Kotinen, although short-term patterns were evident. One possible reason for the variability in P_{tot} concentration might be deteriorated oxygen conditions in the hypolimnion, and enhanced release of phosphorus from the sediment in the 2000s. The incom-

plete spring overturn seems to be a significant factor influencing P_{tot} concentration in the lake (Arvola *et al.* 2014). Hydrological conditions, such as wet summer in 2004 may have increased leaching of phosphorus, since DOM is considered to be a major carrier of organic P (e.g. Dillon and Molot 2005, Kortelainen *et al.* 2006). High precipitation and runoff may have reduced P-sorption by increasing solubility of phosphates that are bound to aluminium and iron oxides and amorphous minerals, and consequently may have changed iron mineralogy and destabilised sorbents in forest soils with amplified P release (e.g. Pant and Reddy 2001).

Conclusions

Our results from Lake Valkea-Kotinen verify that the international emission abatement actions for air pollutants have led to a recovery from acidification, and to a lesser extent, a decrease in trace-metal loadings. However, processes regulating S retention and release in the catchment are still not fully understood. The increase in dissolved organic carbon concentration and the brownification of lake waters may have large ecological impacts on lake ecosystems, and changing carbon dynamics in the lakes is one the key challenges in the future. Another challenge is the enrichment in nutrients due to changing in-lake processes and climate-driven conditions, which may play an important role in affecting the processes in pristine lakes. If sulphate-driven acidification continues to decrease, nitrate may become proportionally more important in affecting acidification in headwater lakes. As a whole, the annual and inter-annual variability of the results emphasise the need for a long-term approach, including a comprehensive set of physical, chemical and biological variables for detecting the impacts of changing environmental conditions. Although the effects of different, more or less randomly occurring, factors are difficult to interpret, sufficiently long and intensive data series provide the means for solutions and reasonable hypotheses to be tested experimentally or through additional measurements. The effects of climate change and changes in in-lake processes will increase data requirements, and

should be taken into account when assessing long-term surface water quality and developing future monitoring network, due to the more complex processes involved.

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