

Acid rain — a strong external driver that has suppressed water colour variability between lakes

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Received 4 Apr. 2017, final version received 24 Jan. 2018, accepted 24 Jan. 2018

Riise G., Müller R.A., Haaland S. & Weyhenmeyer G.A. 2018: Acid rain — a strong external driver that has suppressed water colour variability between lakes. *Boreal Env. Res.* 23: 69–81.

Increasing water colour observed in lakes in the northern hemisphere is frequently explained by several factors, including the decrease in acid deposition, climate change and recently increased concentrations of Fe. As the anthropogenic sulphate deposition levels off, pressure from an external lake quality driver with regional coverage declines. To investigate the impact of acid rain reduction on lake colour variability, we examined 25 lakes in a lake-district of southeastern Norway by analyzing atmospheric deposition, climate and water chemistry data from 1983 to 2012. We observed a marked shift in lake colour after the wet year 2000, probably triggered by a flush of water that has lifted the base line for lake colour to a higher level. Lakes had synchronous temporal trends of many water quality variables, such as conductivity and several major ions. Our data suggest that this is a response to reduced acid deposition. In contrast, lake colour and colour related variables such as Fe and TOC, showed moderate to low coherence. We propose that declined pressure from a strong external driver promotes the importance of climate variability and local catchment specific processes, giving rise to increased colour variability between lakes with time.

Introduction

Along with declined acid deposition, Scandinavian surface waters have recovered from anthropogenic acidification since the mid 1970s, leading to significant changes in ionic composition and dissolved organic matter (DOM) (Riise *et al.* 2001, Folster and Wilander 2002, Skjelkvale *et al.* 2007). Less acid rain has enhanced the mobilization of DOM in surficial organic horizons (Sawicka *et al.* 2016), due to increased charge density of humic substances and reduced ionic

strength (De Wit *et al.* 2007). Reduced loss of catchment derived ions (Likens and Buso 2012, Hessen *et al.* 2016) has decreased the electrolyte content in the receiving lakes, which may promote increased stability of organic colloids and enhanced colour in soft water lakes (Thurman 1985).

Apart from atmospheric precipitation chemistry, terrestrial export of DOM is closely related to the precipitation and runoff pattern (Hongve *et al.* 2004, Erlandsson *et al.* 2008) as well as catchment properties such as vegetation cover

(Finstad *et al.* 2016). From these it follows that climate and land use/catchment characteristics become increasingly important as key drivers for DOM, when anthropogenic sulphate deposition levels off. To what extent pressure from a strong external driver has suppressed DOM variability among lakes is a central question in the future prediction of lake quality development, having both ecological and societal implications concerning biodiversity and drinking water treatability.

There is frequently a close relationship between lake colour and concentration of dissolved organic carbon (DOC) in boreal forest lakes. However, the increase in lake colour has been more extensive than for DOC (Hongve *et al.* 2004). Increased iron (Fe) concentration as a water colour source (Xiao *et al.* 2015) was suggested to be one of the reasons for the observed deviation between DOC and lake colour (Kritzberg and Ekstrom 2012, Weyhenmeyer *et al.* 2014). Lake colour variability might, therefore, be closely related to Fe mobilization/retention processes in the catchment, such as reactivity of precipitation agents (e.g. Fe/Al sulphates), flow and redox conditions.

During long-term studies, lake dynamics often vary in time and space depending on internal and external variables. Following Magnusson *et al.* (2006) coherence (or synchrony) is defined as the degree to which different lakes behave similarly through time. External physical variables, operating at a regional scale (e.g. climatic, atmospheric variables), generally result in higher coherence than chemical variables (Magnuson *et al.* 2006). For lake water colour, Pace and Cole (2002) report a moderate coherence, based on sampling data from 20 lakes in northern Michigan (MI, USA). However, coherence between individual drivers for lake colour is rarely discussed. As the anthropogenic sulphate driver levels off, other drivers for lake colour become increasingly dominant, which will subsequently affect temporal variability patterns and transfer of colour trends to unmonitored lakes.

In this study, we investigated lake colour and its drivers in 24 lakes from 1983 to 2012. In addition, monitoring data from a drinking water source was included. All lakes are located in the boreal lake-district of Østmarka in southeast-

ern Norway. The Østmarka lake-district has a homogenous catchment land cover and bedrock structure which supports a uniform direction of long-term temporal trends (Temnerud *et al.* 2014). Accordingly, temporal patterns within the Østmarka lake-district should be representative for boreal forest catchments with relatively thin, organic matter rich soils on crystalline bedrock. Previous studies in this lake-district showed that increased water colour was related to a changed atmospheric deposition chemistry (Haaland *et al.* 2010) and increased precipitation (Hongve *et al.* 2004). Since anthropogenic sulfate deposition has strongly declined over the past decade, there is an urgent need to re-evaluate water colour trends and their drivers. This study represents the same area as Hongve *et al.* (2004), but a longer time series. We suggest that the removal of excessive amounts of SO_4^{2-} , known to flocculate organic matter in company with Fe or Al, will (1) promote the terrestrial transport of organic matter and (2) decrease the aggregation and settling rate in lakes due to increased colloidal stability with decreased ionic strength. As a consequence, we hypothesize that the importance of lake-specific catchment characteristics for lake water colour will increase, with the subsequent reduced coherence in water colour between lakes. To test our hypotheses, we performed trend and coherence analyses. Coherences are determined by statistical correlations between time series of the same variable on pairs of lakes.

Material and methods

Lake-district

The studied lakes are located within the Østmarka lake-district (59°50'N, 11°00'E) near Oslo, Norway (Fig. 1). The district is a pristine forest area mainly used for recreational purposes. It extends over 135 km² and holds numerous lakes, of which 24 are sampled regularly by the Norwegian University of Life Sciences. The lakes vary from 0.6 to 79 ha in size (mean = 17.8 ha) at an elevation of 163 to 279 m a.s.l. (mean = 221 m a.s.l.). In addition, Oslo Municipality Water and Sewerage Authority has measured raw water colour at weekly

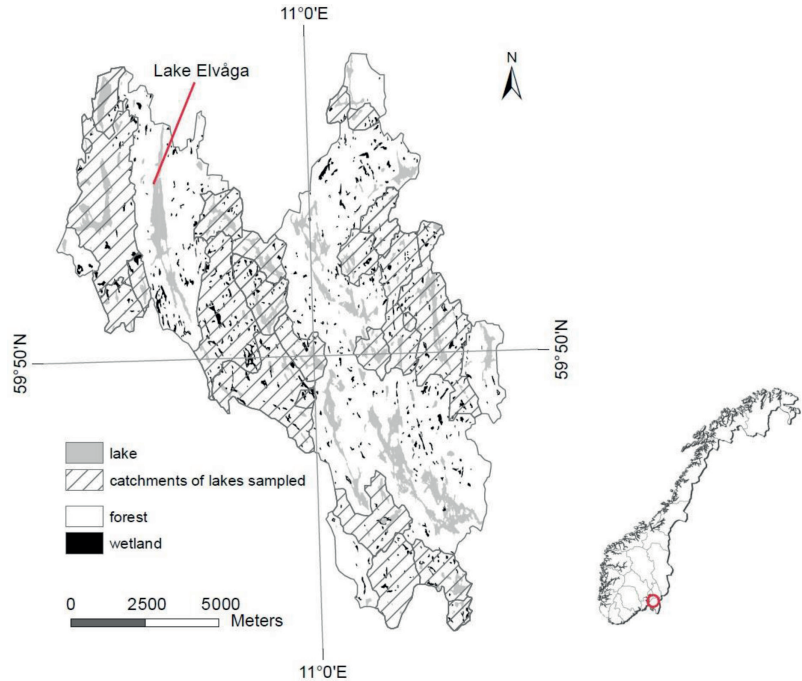


Fig. 1. The Østmarka Lake-district (59°50' N, 11°00' E), showing catchments of the 24 sampled lakes (gridded). Forests, wetlands, lakes, and the Lake Elvåga are indicated. Location of the district is circled on the map of Norway.

intervals and pH and conductivity at monthly intervals in the mixed zone of Lake Elvåga during the ice free season (April–November) from 1983–2015. The bedrock consists of granites and gneisses, with bare rock or thin covers of glacial deposits, although the latter is somewhat more extensive below the marine limit. The marine limit in the Oslo area is about 220 m a.s.l. All lakes are nutrient poor with low turbidity.

Long-term normalized (1961–1990) mean annual precipitation, from an adjacent meteorological station (Oslo-Blindern), is 763 mm yr⁻¹, ranging from 531–1173 mm yr⁻¹ during the study period (Fig. 2). Long-term mean annual air temperature is 5.7 °C (<https://www.met.no/en/free-meteorological-data/Open-source-code>). The Lake-district is situated close to the Oslofjord, hence with distinct atmospheric inputs of sea-salt. Annual variations in surface water chemistry are strongly regulated by precipitation and surface water runoff (Hongve *et al.* 2004).

Lake and catchment morphometrics were quantified from digital terrain models (DTM) and landcover data, both available with a 10 m raster grid from Norwegian mapping authorities (<http://kartverket.no/geonorge>) (Table 1). Forest is clearly dominant landcover type in the catch-

ments (mean = 93%), while open wetlands are present in some catchments (mean = 4.6%). The yearly lake water retention time (WRT) for each lake was estimated based on average lake depth (m), monthly precipitation amounts from the sampling year up to the sampling date, assuming a uniform rainfall distribution (mm yr⁻¹), and an evapotranspiration efficiency of 50% which is typical for the area (Beldring *et al.* 2002). In addition, long-term mean water retention times (WRT_{1961–1990}) were estimated for each lake, based on the long-term mean annual precipitation amounts (1961–1990).

Water sampling and laboratory analyses

Water samples were collected at depth of 0.5 m during the circulation period in late autumn in 1983, 1996, 1997, 2000, 2001, 2004, 2005, and then yearly from 2007 to 2012 (Fig. 2). To extend the number of sampling years, especially prior to the year 2000, results from a drinking water source within the Østmarka Lake-district, Lake Elvåga, were included (Fig. 1). Methods for the lake water survey are described in Hongve *et al.* 2004. Water colour was measured spectrophoto-

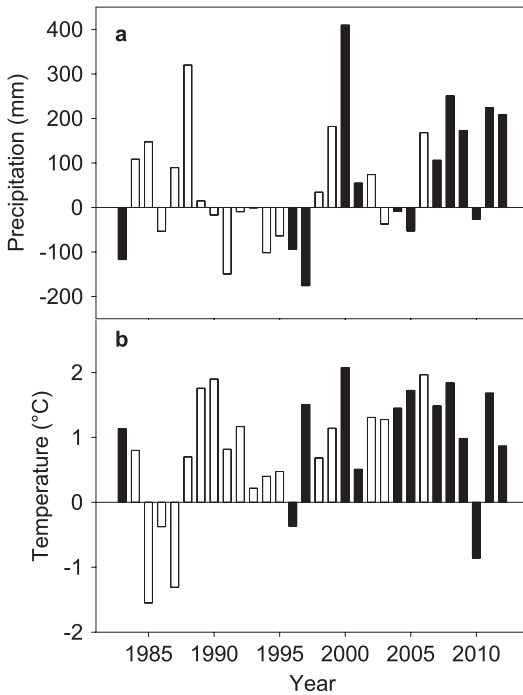


Fig. 2. Deviations of (a) annual precipitation (1983–2012), and (b) annual mean air temperatures from the long-term annual means of 763 mm yr⁻¹ and 5.7 °C. Adapted after Hongve *et al.* (2004). Dark bars represent sampling years.

metrically at 410 nm (EN-ISO 7887, 2011) and converted into units of colour (mg Pt l⁻¹). Hongve *et al.* (2004) report that differences between total organic carbon (TOC) concentrations quantified

Table 1. Lake and catchment morphometry in the lake-district.

	Mean	Range
Lake		
Area (LA) (ha)	17.8	0.6–79.1
Volume (LV) (Mm ³)	2.02	0.02–11.07
Depth (LD) (m)	8.6	2.4–22.3
Elevation (z) (m a.s.l.)	221	163–279
Catchment area (CA) (km ²)	2.9	0.1–10.6
LA/CA (%)	7.9	0.2–26.1
Water retention		
time (WRT)* (years)	1.24	< 0.1–12.1
Catchment cover (%)		
Forest	93.3	83.5–99.9
Wetlands	4.6	0.0–17.0
Lakes	2.1	0.0–8.0

* Mean WRT for the period 1961–1990.

on unfiltered and filtered samples inside the lake-district were non-significant. TOC concentrations reported in this study can, therefore, be considered a proxy for DOC concentrations. In addition to TOC and colour, 15 other physical/chemical variables were analyzed (Table 2).

Trend analysis

For trend analyses we used the non-parametric Mann-Kendall trend test, which also gives a quantitative measure of changes over time as a Theil slope (Helsel and Hirsh 1992). We performed trend analyses on Lake-district means for 17 variables during 1983–2012. Lake-district means are here defined as the mean of the 24 lakes sampled within the same sampling year. We used this approach to make our study comparable to time series analyses run by Hongve *et al.* (2004), who addressed a similar dataset but over a much shorter time period, i.e. only 5 years during 1983–2001. In addition to the temporal development of the lake-district means, we reran the trend analyses for the 17 variables for each lake individually,

Table 2. Mean and range of 17 lake water chemical variables, based on 24 lakes sampled during 13 sampling years (1983–2012). The ranges for the water chemical variables are based on lake specific means (lake means) calculated for each lake ($n = 24$) separately. Means for water chemical variables are based on all samples taken ($n = 312$).

	Mean	Range
pH	6.2	5.0–7.0
Conductivity (mS m ⁻¹)	3.0	2.4–5.8
Ca ²⁺ (mg l ⁻¹)	2.6	1.6–6.2
Mg ²⁺ (mg l ⁻¹)	0.6	0.4–1.1
Na ⁺ (mg l ⁻¹)	1.8	1.5–2.1
K ⁺ (mg l ⁻¹)	0.3	0.2–0.5
NH ₄ ⁺ (mg l ⁻¹)	0.03	0.01–0.10
SO ₄ ²⁻ (mg l ⁻¹)	3.8	2.8–9.8
Cl ⁻ (mg l ⁻¹)	2.5	2.1–3.1
Alkalinity (mmol l ⁻¹)	0.08	0.04–0.22
NO ₃ ⁻ (mg l ⁻¹)	0.48	0.27–0.63
TOC (mg l ⁻¹)	6.8	1.9–14.5
Colour (Pt mg l ⁻¹)	49	3–128
Fe (mg l ⁻¹)	0.22	0.01–0.48
Mn (mg l ⁻¹)	0.03	< 0.01–0.07
Al (mg l ⁻¹)	0.15	0.01–0.41
Si (mg l ⁻¹)	1.32	0.18–2.14

giving us a total of 408 time series. Trend significance was considered at $p < 0.05$ and $p < 0.01$. The Mann-Kendall trend tests were performed using a macro (SK-Theil) developed at the Swedish University of Agricultural Sciences (SLU).

Coherence analysis

In addition to trend analyses, for each variable we calculated the inter-annual coherence among lakes. The coherence analysis was based on a Person product moment correlation for each variable and each possible combination of lake pairs ($n = 276$). Coefficient of determination (Person's r^2) was calculated to evaluate the proportion of shared variance. As an example, if TOC concentrations in lakes A and B were high in one year, low in the next year, and so forth, a high r^2 was reached for the lake pair (A-B). A negative relation could also result in a high r^2 . Conversely, if TOC concentrations in lake A did not relate to values obtained in lake B, a low r^2 would be the result. In this study, each r^2 was based on data pairs from the 13 years sampled, 1983–2012. For each variable ($n = 17$), coherence categories were assigned using the median r^2 statistics from the 276 possible lake pairs. Coherence categories were defined as very low (median $r^2 = 0.00–0.19$), low (median $r^2 = 0.20–0.39$), moderate (median $r^2 = 0.40–0.59$), high (median $r^2 = 0.60–0.79$), and very high (median $r^2 = 0.80–1.00$), following the classification by Magnusson *et al.* (2006). In addition, we considered significance for each linear correlation at $p < 0.05$. Water retention time (WRT) was not considered a variable in the coherence analysis, due to the assumption of spatially uniform precipitation amounts for the whole lake-district. The coherence analysis was run using the software JMP® 10.0 (SAS Institute, Inc., Cary, NC, USA).

Partial least square regression models

Using water-chemical, lake, and catchment-morphometric data (predictor variables; Tables 1 and 2), in addition to climate variables on annual precipitation and annual mean air temperature, we built partial least square (PLS) regression

models. Here, inter-annual variability in lake water colour was the single respondent variable (colour models). The PLS colour models were built using the software SIMCA-P (UMETRICS AB, Umeå, Sweden). We reduced the skewness in variable distributions, by applying a logarithmic transformation where necessary, prior to the SIMCA-P test (sTest). Each PLS colour model was reduced to two components that resulted in two-dimensional variable projections. The influence of individual predictor variables on the projections (VIP) was estimated in SIMCA-P. Following suggestions from SIMCA-P, predictor variables with $VIP > 1$ were considered influential variables and used to compare and interpret PLS models that were built as follows: A first PLS model was built from absolute values (PLS-A). A second PLS model was built using standardized values (PLS-Z). The standardization was done to remove differences in variability and means between lakes (Quinn and Keough 2002):

$$z_v = \frac{x_v - \mu_{(v,L)}}{SD_{(v,L)}} \quad (1)$$

where z_v is the standardized score (z -score) for a measurement, x_v , of a water-chemical variable, v , measured in lake L , and $\mu_{(v,L)}$ and $SD_{(v,L)}$ are the long-term lake mean and the standard deviation around the mean for the water-chemical variable, v , measured in lake L . Using the standardized PLS-Z model, we aimed to disclose different temporal developments for individual lakes. We reran the PLS-Z model after removing samples from the early years 1983, 1996 and 1997, to account for the strong shift in colour drivers that occurred after the especially wet year 2000 (Fig. 2).

Results

Long-term trends

The overall water chemistry of the lakes within the lake-district is typical for boreal lakes, i.e. low ionic strength and pH (Table 2). Comparing the differences in water chemistry between lakes ($n = 24$), however, we observed greater variability, in particular for TOC concentrations (1.9 to 14.5 mg l⁻¹), water colour (3 to 128 mg Pt l⁻¹), and $WRT_{1961-1990}$ (< 0.1 to 12.1 yrs) (Table 1).

Trends in lake district means (1983–2012) showed a significant decline in the lakes' concentration of major anions (SO_4^{2-} and Cl^-), and the majority of base cations (Ca^{2+} , Mg^{2+} , K^+) concurrently with decreased deposition of SO_4^{2-} (Figs. 3 and 4). In contrast, Lake-district means in water colour ($p < 0.05$) and Fe ($p < 0.01$) increased, while TOC concentrations and H⁺ did not change over time ($p = 0.05$ and $p = 0.90$, respectively).

Despite great ranges in several water-chemical variables (Table 2), trend analyses for each individual lake time series ($n = 408$), were, generally, rather consistent. There were significant decreases in conductivity, Cl^- , and SO_4^{2-} , for 23, 22, and all 24 lakes, respectively (Fig. 4). Significant, decreasing trends were also frequent for the base cations calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+). Conversely, colour, Fe, and TOC showed significant increases in 16, 14, and 8 of the sampled lakes, respectively. Significant increases in alkalinity occurred in 6 lakes. Most remarkably, temporal trends for pH were not apparent in any of the 24 lakes sampled or in Lake Elvåga (Fig. 4). Considering the entire water-chemical dataset, opposing temporal trends for the same water-chemical variable ($p < 0.05$) were not observed, with one exception, i.e. Al (Fig. 4).

Based on multivariate analyses (Table 3), the initial colour model explained 84.1% of the overall variability in colour for the full dataset (PLS-A). A model strength of $Q^2_{(\text{cum})} = 83.3\%$, comparable to the explained variability, indicated

that the model was robust. Samples clustered by lakes, with the clear water lakes Lutvann (TOC $< 3 \text{ mg l}^{-1}$, colour $< 7 \text{ mg Pt l}^{-1}$), Nøklevann (TOC $< 6 \text{ mg l}^{-1}$, colour $< 45 \text{ mg Pt l}^{-1}$), Blåtjern (TOC $< 5 \text{ mg l}^{-1}$, colour $< 30 \text{ mg Pt l}^{-1}$), and the humic lake Bonntjern (TOC $> 10 \text{ mg l}^{-1}$, colour $> 70 \text{ mg Pt l}^{-1}$) at the outer ends. The most influential drivers of colour (VIP > 1.2) were TOC, followed by Fe, Al, and silicon (Si), then pH and WRT. Other influential variables (VIP > 1) included SO_4^{2-} and a series of WRT related lake-morphometric parameters (Table 1). Accounting for the strong differences in concentration levels between lakes, the z -score colour model (PLZ-Z) disclosed a development towards higher colour levels with time. The model explained 74.4% of the variability in colour z -scores. A model strength of $Q^2_{(\text{cum})} = 71.5\%$ indicated, in a similar way as for the PLS-A model, that the PLZ-Z model was robust. The most influential drivers for the colour z -scores were TOC, followed by conductivity. Other influential variables (VIP > 1) included SO_4^{2-} and Cl^- , yearly precipitation amounts, WRT and Fe, and ions linked to soil weathering (Ca^{2+} , Mg^{2+} , Si). In accordance with the results from trend analyses, pH did not rank among influential variables for the temporal development of the lake suite or Lake Elvåga (Table 3 and Fig. 5).

Shifting drivers for lake colour

The colour level fluctuations were modest, as

Table 3. Partial least squares (PLS) models for lake water colour. r^2 denotes the shared variance of linear correlation, Q^2 the model strength and VIP the influence of individual predictor variables. The PLS-A model was built using all 27 predictors, i.e. those listed in Tables 1 and 2, annual water retention time (WRT) estimates, and annual precipitation (Prec.). WRT_{1961–1990} estimates were not included. For the two PLS-Z models, 9 static lake and catchment morphological predictors were excluded. The PLS-A, and the first PLS-Z model include observations from a total of 309 samples each (1983–2012). The second PLS-Z model includes a total of 239 samples (2000–2012).

Model	Period	Performance		Most influential variables			Other influential variables	
		r^2	Q^2	VIP > 1.4	VIP > 1.2	VIP < 1.2	VIP > 1.0	VIP < 1.0
PLS-A (abs)	1983–2012	0.841	0.833	TOC, Fe, Al, Si	pH	WRT	SO_4^{2-}	LD, LV, LA, CA
PLS-Z (z-score)	1983–2012	0.744	0.715	TOC	–	Cond.	Ca^{2+} , Cl^- , Si, SO_4^{2-} , Fe	WRT, Prec.
PLS-Z (z-score)	2000–2012	0.616	0.566	TOC	pH		Ca^{2+} , Mg^{2+} , Fe, Al	Cond.

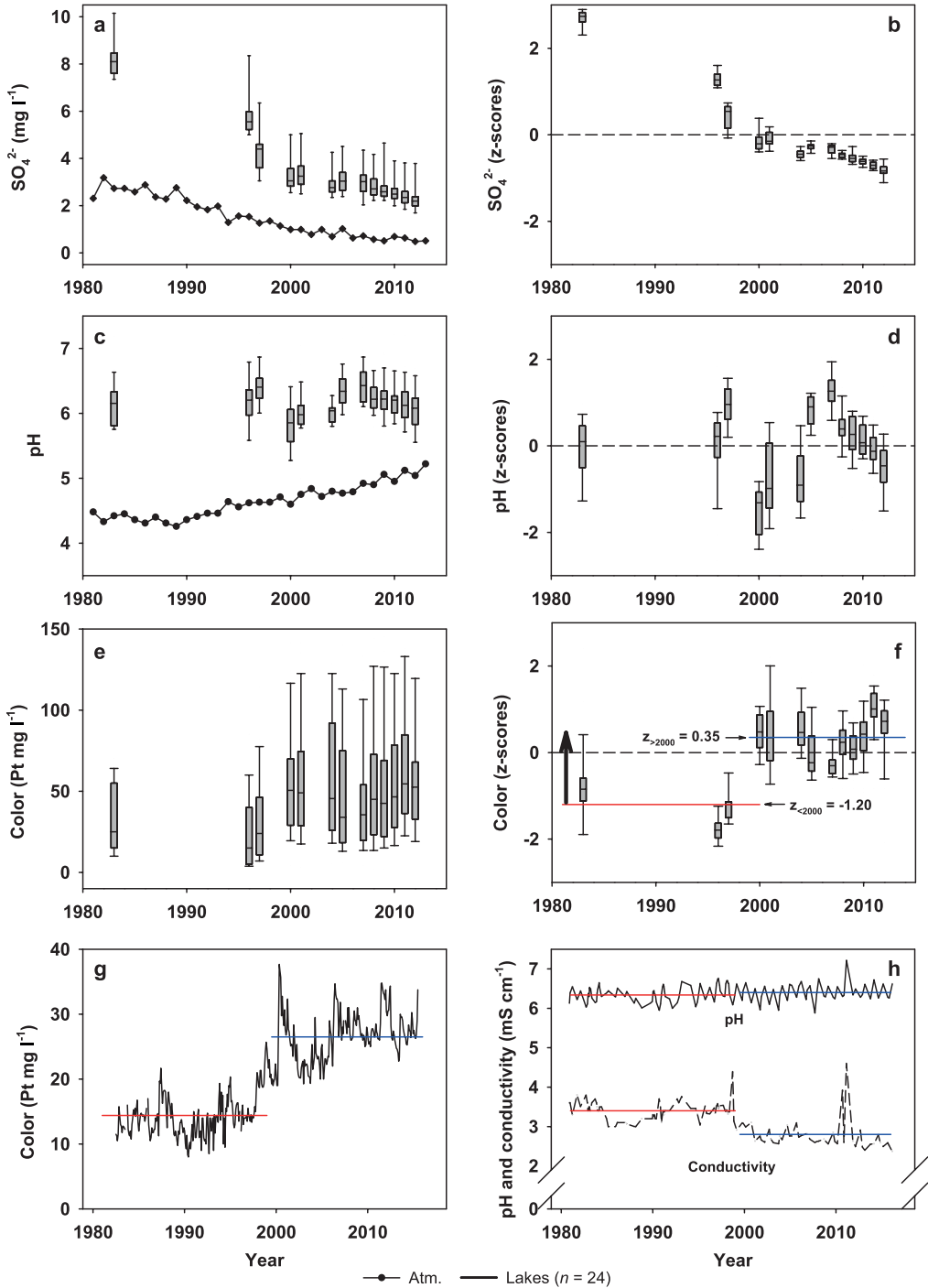


Fig. 3. Time series of lake district median, and 50% and 90% quantile ranges of (a and b) sulfate (SO_4^{2-}), (c and d) pH, and (e and f) colour. Absolute values are in the left panels and standardized values (z-scores) in the right. Annual volume weighted mean values for SO_4^{2-} in a and pH in precipitation in c are presented with black diamonds and dots, respectively. The black arrow in (f) indicates the shift in base line for colour after the year 2000, where small arrows show average z-score values prior to and after the year 2000. Monthly means of colour (g), pH and conductivity (h) in Lake Elvåga, a drinking water source for the Oslo municipality. Red and blue lines indicate the means for the years 1983–1999 and 1998–2015, respectively.

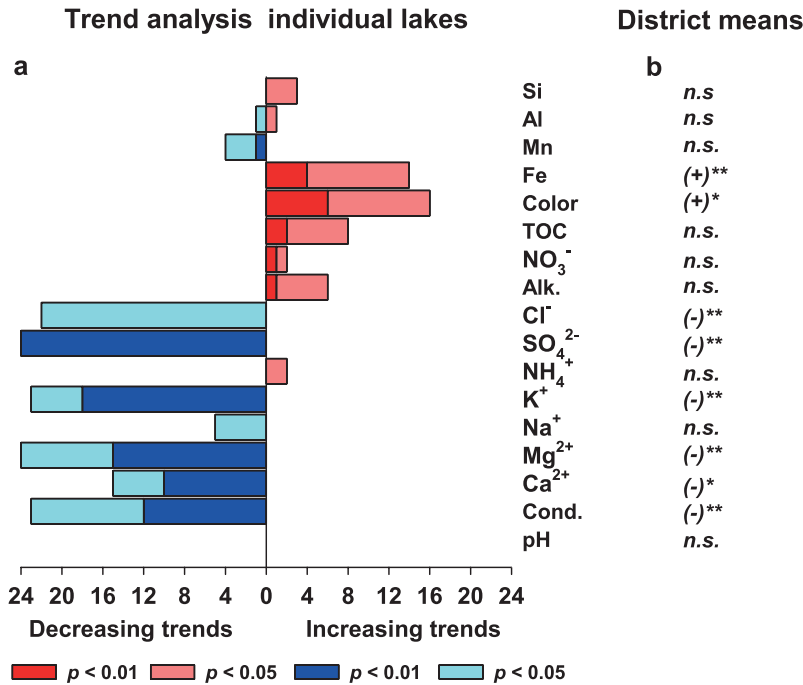


Fig. 4. (a) Count of lakes with significantly increasing (red) and decreasing trends (blue). Significance was considered at $p < 0.05$ (light colour code) and $p < 0.01$ (dark colour code). (b) Trend analysis of Lake-district means with indications of non-significant (*n.s.*), significantly positive (+), and negative (-) trends. Significance levels $p < 0.05$ and $p < 0.01$ are denoted with (*) and (**). The significances were assessed by the Mann-Kendall method.

observed for the drinking water source Lake Elvåga, since the early 1980s and until the late 1990s. Thereafter, colour has increased steadily with a marked peak in the wet year 2000 (Fig. 3g). In the year 2000, the area received 400 mm more precipitation than the normal period. This year was the wettest year for the time period addressed in this study (Fig. 2). For Lake Elvåga, we observed a clear shift in lake colour after the year 2000, where water colour varied around a higher base level (Fig. 3g). For the Lake suite ($n = 24$), the year 2000 also represented a change as the colour z -scores shifted from a negative (below mean) z -score of -1.20 to a positive (above mean) z -score of $+0.35$ that described a new reference for samples taken in subsequent years (Fig. 3f). The magnitude of the shift towards increased colour, was largest in lakes with short WRT, high TOC, low alkalinity and low pH. Rerunning the PLS-Z colour model for samples collected in the time period 2000–2012, TOC (VIP > 1.4) and pH (VIP > 1.2) ranked again among most influential variables (Table 3). The relationship between colour and TOC was positive, while the relationship between colour and pH was negative.

Coherence analyses

Among the 24 lakes sampled, the temporal water quality coherence varied strongly between the different water-chemical variables (Table 4). High temporal coherence was found for conductivity, SO_4^{2-} and Cl^- . Coherence differed, however, for individual base cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+). A high coherence was found for Mg^{2+} and K^+ , whereas a low to moderate coherence was seen for Ca^{2+} and Na^+ . Coherence for Fe and TOC was low. Colour showed a moderate coherence for the majority of lake pairs, with a median r^2 of 0.43, and a significant year-to-year correlation for 158 of 276 lake pairs (57.2%). Alkalinity showed low to moderate coherence. Lake pH also showed low to moderate coherence with significant year-to-year correlations for 160 of 276 lake pairs (58.0%).

Discussion

Long term colour development

Declining acid deposition rates have significantly

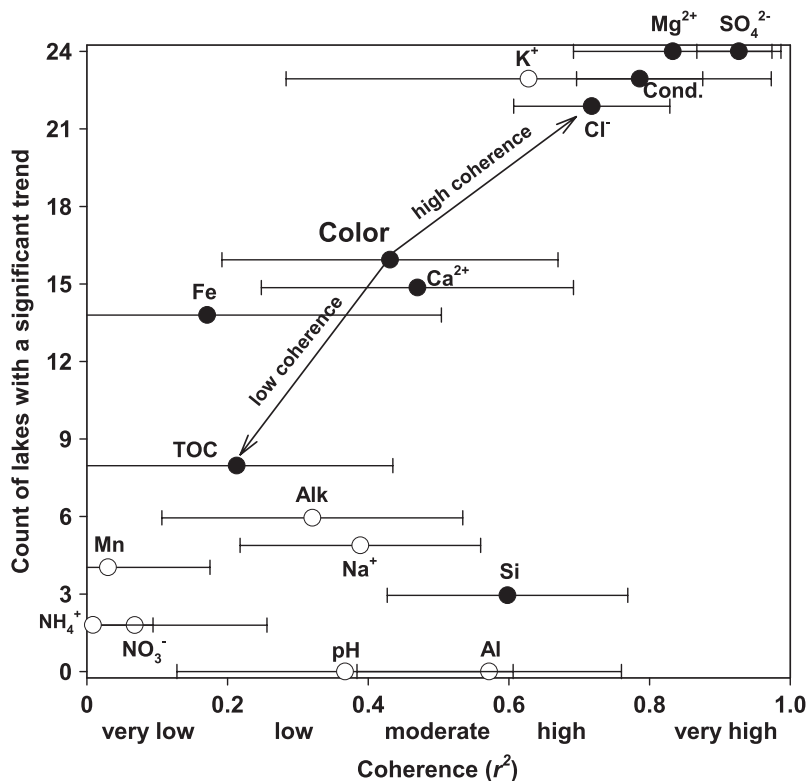


Fig. 5. Coherence (r^2) in temporal trends of water chemical variables (median, whiskers indicating 50% data range) against the number of lakes with significant trends (positive or negative, $p < 0.05$). Important drivers for colour have dark grey symbols, and the two most influential drivers, TOC and conductivity, are pointed with arrows.

Table 4. Coherence analyses for the sampled lakes ($n = 24$), and for each water chemical variable. Median and range for the shared variance, and number of lake pairs with significant covariance are presented. The r^2 statistics were obtained from a linear correlation analysis, which were run for each possible combination of lake pairs (years 1983–2012, 276 pairs). The median r^2 was used to assign the chemical variables to a coherence category, applying classification limits defined by Magnusson *et al.* (2006).

	Pairwise linear correlation (r^2)		Significant pairs	Coherence category
	Median	Range		
pH	0.37	0.00–0.88	160 (58%)	Low
Conductivity	0.79	0.12–1.00	269 (97.5%)	High
Ca ²⁺	0.47	0.00–0.86	190 (68.8%)	Moderate
Mg ²⁺	0.83	0.27–1.00	275 (99.6%)	Very high
Na ⁺	0.39	0.00–0.96	176 (63.8)	Low
K ⁺	0.63	0.00–0.96	227 (82.2%)	High
NH ₄ ⁺	0.01	0.00–0.79	27 (9.4%)	Very low
SO ₄ ²⁻	0.93	0.64–1.00	276 (100%)	Very high
Cl ⁻	0.72	0.12–0.98	267 (96.7%)	High
Alk.	0.32	0.00–0.94	136 (49.3%)	Low
NO ₃ ⁻	0.07	0.00–0.86	54 (19.6%)	Very low
TOC	0.21	0.00–0.88	99 (35.9%)	Low
Colour	0.43	0.00–0.96	158 (57.2%)	Moderate
Fe	0.17	0.00–0.85	116 (42%)	Very low
Mn	0.03	0.00–0.74	36 (13%)	Very low
Al	0.57	0.00–0.98	170 (61.6%)	Moderate
Si	0.59	0.00–0.96	188 (68.1%)	Moderate

changed the SO_4^{2-} concentration in all lakes from 1983–2012 (Figs. 3 and 4). While SO_4^{2-} was the dominant anion, in the Østmarka lake-district, during the “acid rain period”, presently SO_4^{2-} accounts for < 30% of the major anions, next to HCO_3^- and Cl (Riise *et al.* 2001). Thus, a clear shift in the anionic composition has occurred, due to reduced anthropogenic SO_4^{2-} deposition. For the same time period, lake colour has increased significantly in 16 out of 24 lakes in this study (Figs. 3 and 4). Along with the steady decline in anthropogenic SO_4^{2-} deposition, the contents of major cations and conductivity have also decreased (Fig. 4). Decreased soil weathering rates and reduced exchange rates with H^+ in the soil found by Sawicka *et al.* (2016), are a reasonable explanation to the reduced input of ions to the lakes. The investigated lakes have, in general, low ionic concentrations, and are very sensitive to changes in the input and output of ions, which can contribute to large changes in ionic strength. Inter particle forces that control colloidal stability, depend on repulsive electrostatic interactions, which are stronger in low ionic compared to high ionic solutions (Drever 1982). Dilution of aqueous solutions can, therefore, increase the stability of organic colloids (Thurman 1985), and be an important driver for the observed colour increase in the lakes.

pH has also been proposed as an important driver for the observed colour increase (De Wit *et al.* 2007), since the excess of the electrical charge (the Zeta potential) between the interfaces of organic colloids is pH dependent. If all particles in suspension have a high negative or positive Zeta potential then they will tend to repel each other, and there will no tendency to flocculate (e.g. Morales *et al.* 2013). However, the pH has not changed significantly in the Lake-district during the acid recovery period (Fig. 3), so the impact of this driver is probably small. Minor changes in acid sensitive elements such as Al and Mn (Fig. 4) also support the lack of pH changes in the Østmarka area.

Concurrently, with reduced acid deposition and conductivity, the trend analysis showed increasing values for Fe with time. Enhanced levels of Fe, can be a result of increased transport of Fe in association with organic matter. Trends for each time series ($n = 408$), showed

that colour (16 of 24 lakes) increased twice as frequently as for TOC (8 of 24 lakes). Increased delivery of light absorbing Fe to lakes (14 of 24 lakes) may partly explain this deviation between development in colour and TOC, and is in agreement with observations from boreal areas in Sweden, where decreased acid deposition on soils has mobilized Fe (Ekstrom *et al.* 2011, Kritzberg and Ekstrom 2012).

With Al being the only exception, we observed significant ($p < 0.05$) positive or negative trends for all other water-chemical variables (Fig. 4). The consistent long term trends in hydrochemistry observed for the Lake-district of Østmarka supports impact from an external driver with a regional pattern, i.e. acid rain. This is also in line with acid rain recovery results reported for other lakes and streams distributed across e.g. the UK, (Monteith *et al.* 2014) and Sweden (Futter *et al.* 2014).

Recovery from acid rain – shift in terrestrial delivery of organic matter

Although there was a coherent lake colour response with time, colour variability among lakes was much higher than variability across years (PLS-A). In other words, concentration differences between lakes were more pronounced than long-term colour trends and shifts. Export of coloured organic matter from boreal catchment is known to vary in time and space (Klavins *et al.* 2012, Raike *et al.* 2012). Variations in central predictors, such as WRT, vegetation cover, slope, and elevation, shown to be of importance for system variability in lake-districts (Sadro *et al.* 2012), are most likely responsible for this lake colour variability. However, once strong concentration differences between lakes are accounted for (z -scores), a strong shift towards a general higher colour concentration after the wet year 2000 became strikingly clear (Fig. 3f). Such environmental shifts can be a common mode for long-term temporal trends (Magnuson *et al.* 2006), where gradual changes in a driver might have little effect until a threshold is reached (Scheffer and Carpenter 2003). The wet year of 2000 may have triggered a shift, by initiating a flush of water that moved the lake colour into a

higher level (Fig. 3). For the more recent time period, 2000–2012, we no longer find a significant influence of the acid atmospheric deposition variables on lake colour (Table 3).

Combining results for long-term trends and coherence analysis showed that variables with high degree of coherence had significant trends in most of the lakes (Fig. 5). These variables are linked to acid deposition, both through direct atmospheric deposition of ions and subsequent changes in mineral weathering and ion exchange reaction (conductivity, SO_4^{2-} , Cl^- , K^+ , Mg^{2+}). In contrast, variables with moderate to very low coherence and less number of lakes have significant trends are the most influential colour variables in the PLS-A model, TOC, Fe, Al, Si and pH (Fig. 5, Table 3). According to the PLS-Z colour model, SO_4^{2-} was no longer an influencing chemical variable for colour in the period 2000–2012 compared to the period 1983–2000 (Table 3). There has also been a shift from conductivity as the most influential physical variable for colour in 1983–2012 (in addition to TOC), to pH in 2000–2012 (Table 3). This suggests a decreasing impact of an external driver, i.e. acid rain, that suppress variability to local catchment specific drivers that promote larger variability between lakes after the year 2000. All of the most important colour variables, TOC, Fe, Al, Si and pH, are related to terrestrial input to lakes, and they show moderate to low coherence and a high variability between the lakes (Fig. 5). Depending on landscape characteristics regulating water flow, soil organic matter, buffer capacity and redox conditions, the lake colour will, therefore, vary. Paleolimnological studies from one of the studied lakes in the area shows minimum accumulation of organic matter during the anthropogenic sulphur peak in the 1970s, and enhanced accumulation of organic matter both prior to and after this period (Isidorova *et al.* 2016). Thus, the present increase in lake colour is necessarily not a new phenomenon, but rather a reversal to natural, high-DOC conditions (Evans *et al.* 2012). However, as both DOM and Fe are strongly linked to catchment processes and climate, it is still to be seen if changes in climate might promote changes in lake colour (*see discussion below*).

Climate driven variability

For the whole survey period, precipitation was found to be an important driver for lake colour (Table 3), and no strong dilution of DOM during elevated rainfall and runoff periods was observed. This is consistent with a forest dominated ecosystem with relatively low (< 5%) abundance of wetlands (Laudon *et al.* 2011). Flushing of the organic rich top layers and respective runoff to lakes can induce high DOM concentrations, high colour, and lower pH during wetter years (Kortelainen and Mannio 1988, Hongve *et al.* 2004), which is in agreement with our data (Fig. 3). Runoff conditions might also affect DOM's affinity for Fe, as years with high annual precipitation have significantly higher Fe/TOC ratios compared to years with normal to low annual precipitation (Fig. 6). During high flow periods, particularly the high molecular weight fraction (> 10 kDa) of organic matter will be transported into surface waters (Riise *et al.* 1994), a size fraction that extensively associates with Fe (Riise 1999), and consequently increases the colour of water.

However, even though wetter years, generally, lead to higher colour concentrations within the lake-district (Hongve *et al.* 2004), the impact has become more extensive in recent years. An example is the comparable wet years of 1988 (1083 mm) and 2000 (1173 mm): colour peak in Lake Elvåga was much higher in 2000 compared to the year 1988 (Fig. 3g). Thus, similar high flow periods transport more DOM at present years as compared to the acid rain period, probably due to the removal of an external retention factor (i.e. anthropogenic sulphur deposition). Precipitation at present derives much lower concentrations of ions in runoff from catchment soils compared to the “acid rain” period, promoting an increased stability of DOM colloids in water. After the year 2000, the area has generally received higher precipitation than the normal period 1960–1990 (Fig. 2), resulting in a somewhat skewed distribution in the number of wet to dry years. Because of that, runoff of DOM has generally been high after the year 2000, but less affected by variations in precipitation (Table 3).

Water chemical variables, related to catchment weathering and runoff (such as conductiv-

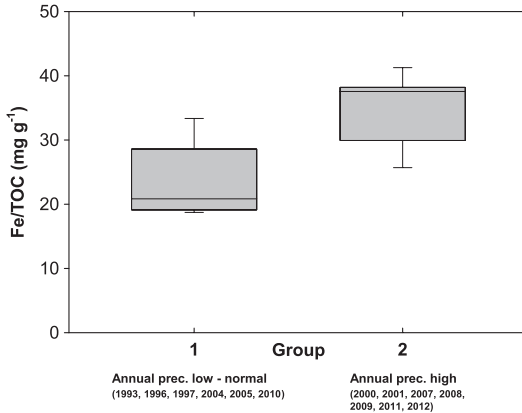


Fig. 6. Fe/TOC (mg g^{-1}) in years with low to normal (Group 1) or higher precipitation (Group 2) than the long-term mean. The boxes and whiskers show median and 50% and 90% quantile ranges.

ity, pH, TOC, Fe and Al), have been important lake colour drivers since the year 2000 (Table 3). From this it follows that specific catchment characteristics, such as position in the landscape (up or downstream lakes), soil and vegetation cover, all play an important role in the coupling between weather conditions (precipitation and temperature) and lake colour response. High sulphate deposition has been a stabilizing factor for DOM and colour, and a wetter and less acid future seems to increase the temporal variability, but decrease coherence in colour between lakes. In addition, the predicted increase in temperature will speed up the rate of biological processes, which might imply greater importance of biological variables that frequently show low coherence. This is consistent with Weyhenmeyer (2009) who shows increasing dissimilarity in water chemical composition in a warmer climate.

Conclusions

After the decline in acid rain, impact from a strong external driver has been reduced. Climate driven variability regulating the coupling between catchment and runoff quality has become a stronger and more important driver for lake colour within the Østmarka lake-district. Since DOM and Fe at present are more controlled by variations in climate than during the acid rain period, differences between catchment

and lake characteristics such as soil cover, water saturation and lake water retention time promote more pronounced differences in lake colour. This has resulted in a decreased temporal synchrony in lake colour development between lakes. A wetter future, with little or no influence from acid rain components, will likely strengthen the importance of catchment soil characteristics, and decrease the temporal synchrony of lake colour development within a boreal lake district such as Østmarka.

Acknowledgements: This work developed within the research framework “The Colour of Water”. Direct financial support was received from the Swedish Research Council (VR) and the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS). Our work profited from research frameworks established by the Norwegian Research Council (Norklima ECCO), NordForsk (CRAICC, DOMQUA), and Norsk Vann (NOMiNOR). We would like to thank Johnny Kristiansen (Norwegian University of Life Sciences) and Per Kristian Lunde (Oslo University Hospital) for excellent field assistance. The Norwegian Agency for Public Management, eGovernment (Difi), Oslo Municipality Water and Sewerage Authority and the Norwegian Institute for Air Research (NILU) are acknowledged for the provided data. We would also like to thank anonymous reviewers for useful comments, and Marcia Kyle and Thomas Rohrlack (Norwegian University of Life Sciences) for valuable corrections and discussions.

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