Increasing dissimilarity of water chemical compositions in a warmer climate

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[1] Understanding variability patterns of biogeochemical conditions in water is a key issue for water management strategies. Here a unique homogeneous data set of 1041 Swedish boreal lakes, sampled during three lake inventories along an 8° latitudinal temperature gradient, revealed a systematic increase in the variability of the water chemical composition between lakes with increasing temperatures. The variability pattern was consistent on a spatial and temporal scale and became especially apparent for water chemical variables showing an in-lake biological process–driven seasonality, such as nitrogen, pH, silica, and organic carbon. The degree of dissimilarity in the chemical composition between lakes was well related to the duration of the main growing and runoff season ($D_{T>0}$), both on a spatial scale (R^2 = 0.57–0.79, $P < 0.05$) and a temporal scale (R^2 = 0.99, $P < 0.05$). It is suggested that $D_{T>0}$ is a very suitable proxy to explain biogeochemical variability patterns between lakes. According to this study, a further temperature increase will result in an increased biogeochemical dissimilarity between lakes.

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1. Introduction

[2] Lake ecosystems provide a variety of essential services for human society. Their vulnerability in a warmer climate has been pointed out [*Schröter et al.*, 2005], and a tremendous number of studies are available, including a variety of review articles [*Mooij et al.*, 2005; *Ottersen et al.*, 2001; *Schindler et al.*, 1990; *Schindler* 2001]. Agreement among the studies is not always achieved, and Richard Alley (cited by *Walker* [2006, p. 804]) points out that "the rate of publications, the rate of new papers, and the rate of disagreement have multiplied amazingly." Disagreement often results from a high site-specific biogeochemical variability that is not transferable to other sites [*Davis et al.*, 1998; *Petchey et al.*, 1999; *Walther et al.*, 2002]. However, there are also examples in the literature where coherent variability patterns across large geographical regions have been detected. Here especially studies dealing with physical variables are available, describing, for example, a coherent warming of waters and a coherent earlier timing of ice break up across the Northern Hemisphere [*Gerten and Adrian*, 2002; *Magnuson et al.*, 2000].

[3] The findings of coherent variability patterns on large spatial scales are far less common for chemical and biological processes [*Anneville et al.*, 2005; *Baines et al.*, 2000; *George et al.*, 2000; *Weyhenmeyer*, 2004]. Chemical and biological variables often show a large site-specific variability, sometimes also resulting from the fact that sampling and analyzing methods are not comparable between sites and homogenous data series are missing [*Lovett et al.*, 2007]. In Sweden, which is one of the lake-richest countries in the world, homogenous data (same sampling procedure, same laboratory, and same analyzing methods) on water chemistry from more than 1000 lakes are available because of ambitious national environmental quality objectives that stipulate an intensive national freshwater monitoring program. These homogenous lake data were used to study the response of the water chemical composition to a warmer climate, both on a spatial and a temporal scale. On the basis of earlier observations that a warmer climate can result in an increased variability of meteorological variables [e.g., *Schär et al.*, 2004], I hypothesized that a warmer climate will also result in an increased variability of lake chemical variables.

2. Material and Methods

[4] In 1995, 2000, and 2005, Sweden carried out national lake inventories to identify the chemical status of its almost 100,000 lakes along 13° of latitude. From the inventories 1041 boreal lakes (more than 90% forest in the catchment area and less than 1% agriculture) were chosen that were sampled during all 3 years to evaluate spatial and temporal changes. The lakes were evenly distributed over Sweden with an approximately equal number of lakes at each latitude (Figure 1). Most of the lakes were shallow (median mean depth 4.3 m), and the lake areas varied from 0.02 to 317 km^2 with a median of 0.28 km^2. Apart from the lake morphometric data (mean lake depth and lake area), data on the catchment characteristics were available, i.e., annual mean runoff; air temperature; precipitation (average of 1961–1990); altitude;

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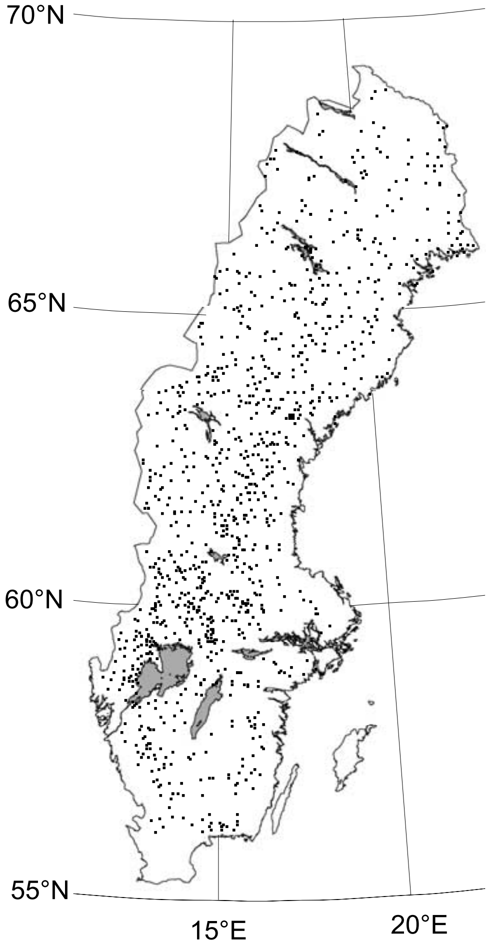

Figure 1. Map of Sweden showing the locations of the 1041 boreal lakes (solid squares).

catchment area; and percentage of water bodies, forest, sand, and mire in the catchment.

[5] The water samples were taken during autumn of each year when summer stratification had terminated and lakes experienced a complete mixture of the water column. The criteria of a fully mixed water column resulted in a start of the survey in September in the far north and in an end in December in the south. An optimum water temperature for a fully mixed water column would have been 4°C, however, because of varying weather conditions and a given sampling period of 4 months, water temperatures varied between 5.9 ± 2.1 in 1995, 7.6 ± 2.7 in 2000, and 7.0 ± 2.7 in 2005. Sampling was carried out in the middle of each lake at a depth of 0.5 m. From 1995 to 2005 surface water samples were also available from 12 out of the 1041 boreal lakes on a monthly basis (sampling in the middle of each month) from May to October, i.e., the main growing season in Sweden. The sampling and analyzing procedure was performed by one certified laboratory. Variables considered in this study were pH, alkalinity (alk), conductivity (cond), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl), sulfate (SO_4), ammonium-nitrogen (NH_4-N), nitrate-nitrogen (NO_3-N), total nitrogen (TN), total phosphorus (TP), absorbance at 420 nm of 0.45 μm filtered water in a 5-cm cuvette (color), total organic carbon (TOC), and reactive silica (Si). All analyses were done according to standard limnological methods. The data are freely available and can be downloaded at http://www.ma.slu.se.

[6] To account for meteorological conditions, complete time series of monthly mean air temperature data from 72 sites distributed all over Sweden from 1961 to 2005 were kindly received from the Swedish Meteorological and Hydrological Institute. The air temperature data were used to determine the main growing and runoff season ($D_{T>0}$). $D_{T>0}$ corresponded to the number of days when air temperatures exceed 0°C and was expressed according to the formula described by *Weyhenmeyer et al.* [2004]:

$$D_{T>0} = 365\text{d} - [(365\text{d}/\pi)\arccos(T_m/T_a)] \quad (1)$$

where T_m is the annual mean air temperature, T_a is the annual air temperature amplitude, i.e., the maximum monthly mean air temperature minus the minimum monthly mean air temperature during a year, and d are days.

[7] Since meteorological information was only available for 72 sites while lake data were available for 1041 sites, we considered region-specific patterns. For this, Sweden was divided into eight temperature regions of 1°C on the basis of average (1961–1990) annual mean air temperatures [*Raab and Vedin*, 1995]. The temperature regions ranged from ≤0 to 7°C. The temperature regions mainly reflected latitude in Sweden except of some areas in the northwest where a mountainous range forms the landscape. Each of the 1041 boreal lakes and each of the meteorological sites was attributed to a temperature region by its coordinates. The number of lakes and meteorological sites within the temperature regions was about equal.

[8] All statistical analyses were performed in JMP, version 7.0.1 [*SAS Institute, Inc.*, 2007]. In JMP, the Brown-Forsythe test was used to analyze whether variances were equal or not [*Brown and Forsythe*, 1974]. The test is appropriate for nonnormal distributed data and shows the F test from an analysis of variance in which the response is the absolute value of the difference of each observation (i.e., a water chemical variable) and the group median where a group was either a temperature region or a year. To receive a quantitative measure for the dissimilarity among lakes, the mean value of the absolute difference of each observation and the group median was used. All presented probability density functions (pdfs) are based on the kernel density estimate for each group which is a nonparametric way to smooth the data material [*SAS Institute, Inc.*, 2007]. Water chemical variables were standardized according to $x^*_i = (x_i - x_m)/s$, where x_i corresponds to the measured value of each variable, x_m corresponds to the mean value of each variable, and s corresponds to the standard deviation of each variable. This method gave 16 standardized data points for each of the 1041 boreal lakes. In this paper, these are referred to as the water chemical composition.

3. Results

[9] In analyzing the water chemical composition along a latitudinal temperature gradient over Sweden in 1995, i.e.,

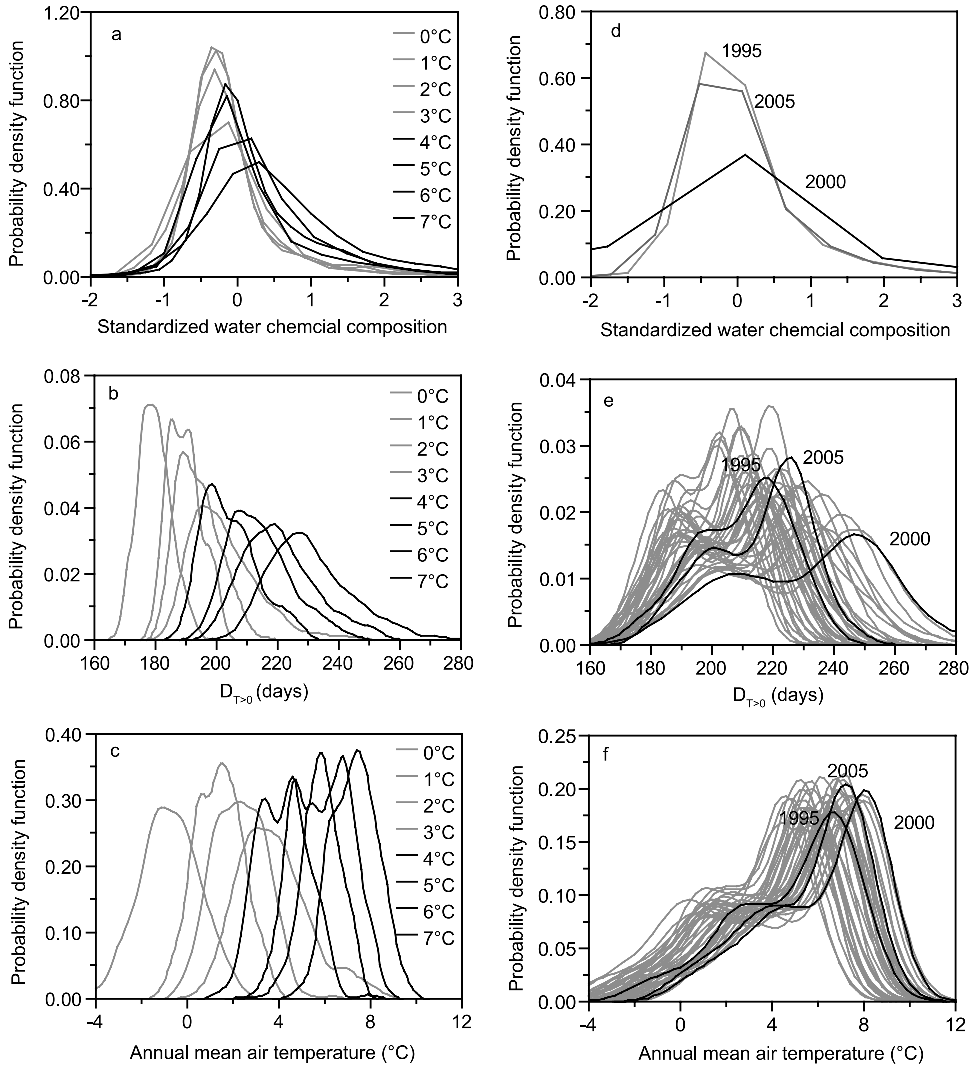

Figure 2. Probability density functions (pdf) of lake water chemistry and meteorological variables over Sweden. (a–c) Demonstration of spatial patterns. (d–f) Demonstration of temporal patterns. Figure 2a shows the pdf of the standardized water chemical composition (see section 2) for eight temperature regions in 1995. Figure 2b shows the pdf of the duration of the main growing and runoff season ($D_{T>0}$) (72 sites) for eight temperature regions from 1961 to 2005. Figure 2c shows the pdf of annual mean air temperatures (72 sites) for eight temperature regions from 1961 to 2005. Gray lines represent the colder temperature regions from 0 to 3°C, and black lines represent the warmer temperature regions from 4 to 7°C. Figure 2d shows the pdf of the standardized water chemical composition for 1995, 2000, and 2005. Figure 2e shows the pdf of $D_{T>0}$ (72 sites) from 1961 to 2005. Figure 2f shows the pdf of annual mean air temperatures (72 sites) from 1961 to 2005. Black lines in Figures 2e and 2f correspond to the years 1995, 2000, and 2005.

using the 16 standardized water chemical data for each of the 1041 boreal lakes, resulting in 16,656 data points, a clear increase in the width of the pdf of the water chemical composition was found toward warmer geographical regions (Figure 2a). Using the Brown-Forsythe test for the whole water chemical composition confirmed that the variance of the water chemical composition between the temperature regions was significantly different ($P <$ 0.0001). A wider pdf might be a result of different catchment and morphometric characteristics of the lakes toward warmer geographical regions. However, testing nine lake-specific catchment variables (annual mean runoff; air temperature; precipitation; altitude; catchment area; and percentage of water bodies, forest, sand, and mire in the catchment) and two lake variables (lake area and mean lake depth) revealed that the pdfs became smaller toward warmer geographical regions for all the tested variables. The only variable that increased its width in the pdf toward warmer regions in 1995 was the duration of the main growing and runoff season (Figure 2b) although the annual mean temperatures in 1995 showed equal widths in the pdfs toward warmer geographical regions (Figure 2c). Since the 16 water chemical variables were generally highly correlated with each other on the large spatial scale (nonparametric Spear-

Table 1. Correlation Coefficients for a Relation Between the Seasonal Cycle a Water Chemical Variable and the Seasonal Cycle of Air Temperature for 12 Swedish Lakes[a]

Lake	pH	NO_3N	Ca	Si	TN	Color	K	NH_4N	Alk	Na	Cond	SO_4	TOC	Cl	TP	Mg
Abiskojaure	−0.86	−0.02	−0.89	−0.67	−0.48	−0.42	−0.77	−0.51	−0.90	−0.73	−0.86	−0.94	−0.73	−0.52	0.57	−0.87
Allgjuttern	0.73	−0.74	−0.74	−0.46	−0.85	−0.29	0.00	−0.09	0.00	0.08	−0.20	−0.07	−0.04	−0.60	−0.73	−0.09
Brunnsjön	0.64	−0.93	0.15	−0.46	−0.15	0.97	−0.76	0.32	0.53	0.38	−0.52	−0.77	0.43	0.83	−0.37	0.06
Fiolen	0.06	−0.67	−0.80	−0.77	−0.08	−0.40	0.12	−0.13	0.58	−0.25	0.03	0.34	0.21	0.16	−0.55	−0.58
Fräcksjön	0.95	−0.70	0.05	−0.66	−0.55	−0.92	0.33	−0.35	0.37	0.98	−0.07	−0.10	0.13	0.50	0.28	−0.42
Jutsajaure	0.66	−0.52	−0.78	−0.40	0.29	−0.75	−0.57	−0.44	−0.91	−0.18	−0.54	0.29	−0.24	−0.75	0.49	−0.34
Remmarsjön	0.80	−0.94	0.38	0.25	−0.71	−0.55	−0.48	0.00	0.57	0.53	0.27	0.02	−0.53	0.66	−0.56	0.36
Rotehogstjärnen	0.86	−0.72	0.29	−0.86	0.13	−0.11	−0.84	0.72	0.63	0.71	−0.11	−0.31	−0.25	−0.05	0.16	0.09
St Skärsjön	0.93	−0.74	0.39	−0.63	−0.92	−0.73	−0.26	−0.77	0.29	0.40	0.30	−0.32	0.77	−0.09	0.58	0.16
Stensjön	0.88	−0.80	−0.45	−0.45	−0.76	−0.81	0.00	−0.90	−0.25	0.27	−0.32	0.82	−0.85	0.14	0.15	0.31
Stora Envättern	0.93	−0.70	−0.78	−0.73	0.06	−0.54	−0.17	−0.35	−0.15	0.12	0.82	−0.15	0.14	−0.06	−0.84	0.07
Övre Skärsjön	0.41	−0.69	−0.89	−0.39	−0.71	−0.40	−0.85	−0.97	0.38	0.09	−0.38	−0.46	−0.06	0.17	−0.11	−0.65
Median	0.77	−0.71	−0.60	−0.54	−0.51	−0.48	−0.37	−0.35	0.33	0.20	−0.15	−0.12	−0.05	0.04	0.02	−0.01

[a]Seasonal cycle is made of the monthly values from May to October. Seasonal cycle of air temperature is made of median values of the 72 sites. Since water chemical variables are only measured once a month with a relatively high uncertainty of each measurement, median values both for water chemistry and air temperature of the time period 1990–2005 were used, giving six data points for each correlation. For abbreviations see section 2. A high correlation coefficient, either positive or negative, indicates a clear seasonality of a variable. Taking median r values of the lakes, the degree of seasonality is highest for the variables pH, NO_3-N, Ca, Si, TN, and color.

man's ρ test for data in 1995: $P < 0.0001$ for 86% of the correlations and $P > 0.05$ for 8% of the correlations), the Brown-Forsythe test was additionally used for each individual variable, giving significant differences in the variances between the temperature regions in 1995 for NO_3-N, NH_4-N, TN, pH, Si, color, TOC, Cl, and Na ($P < 0.0001$). Of these variables NO_3-N, NH_4-N, TN, pH, Si, and color were generally best related to the seasonal cycle of air temperature (Table 1). Ca was the only variable that also showed a strong seasonality (Table 1) but no significant difference in the variances between the temperature regions in 1995 ($P > 0.05$).

[10] To test the results from the spatial scale that the pdfs of the water chemical composition might be temperature dependent and might follow the pdfs of $D_{T>0}$, a transfer from the spatial to a temporal scale was performed. In 1995, 2000, and 2005, the median annual mean air temperature for Sweden corresponded to 5.8, 7.3, and 6.5°C, respectively. According to the results from the spatial scale the widest pdf for the water chemical composition and for $D_{T>0}$ was expected in 2000,

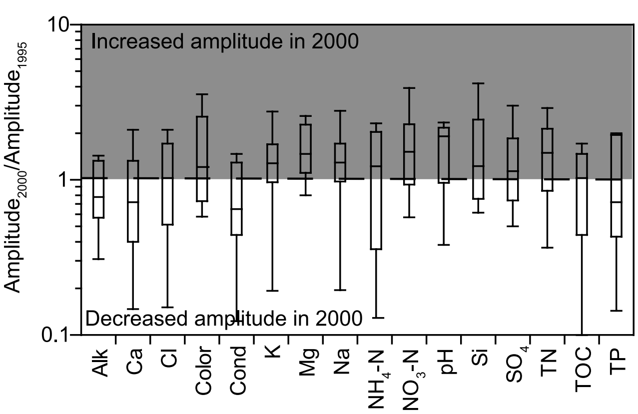

Figure 3. Changes in the annual range based on monthly values from May to October from 1995 ($Amplitude_{1995}$) to 2000 ($Amplitude_{2000}$) for 16 water chemical variables. Shown are box plots for 12 Swedish lakes. For abbreviations see section 2.

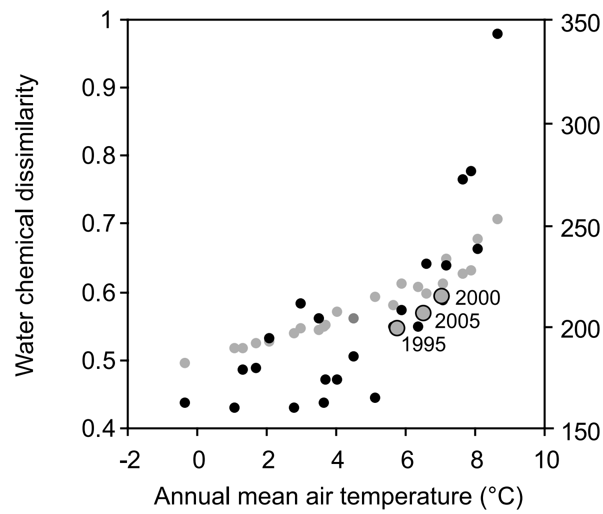

Figure 4. Relationship between the dissimilarity of the water chemical composition (standardized values of 16 variables; see section 2) between lakes and air temperatures. The dissimilarity of the water chemical composition between lakes (for definition see section 2) was determined for each of the eight temperature regions during each of the years 1995, 2000, and 2005 and related to median annual mean air temperatures for each region and each year, giving 24 data points (solid circles). Figure 4 also shows the median duration of the main growing and runoff season ($D_{T>0}$) in relation to median annual mean air temperatures for each region and each year (gray circles). Relating $D_{T>0}$ to the dissimilarity of the water chemical composition between lakes gave a significant relationship on a spatial scale for 1995 (R^2 = 0.79, $P <$ 0.01, $n = 8$), for 2000 ($R^2 = 0.69$, $P < 0.01$, $n = 8$), and for 2005 ($R^2 = 0.57$, $P < 0.05$, $n = 8$). The relation was also significant on a temporal scale by using median values for the whole of Sweden during 1995, 2000, and 2005 (large gray circles, $R^2 = 0.99$, $P < 0.05$, $n = 3$).

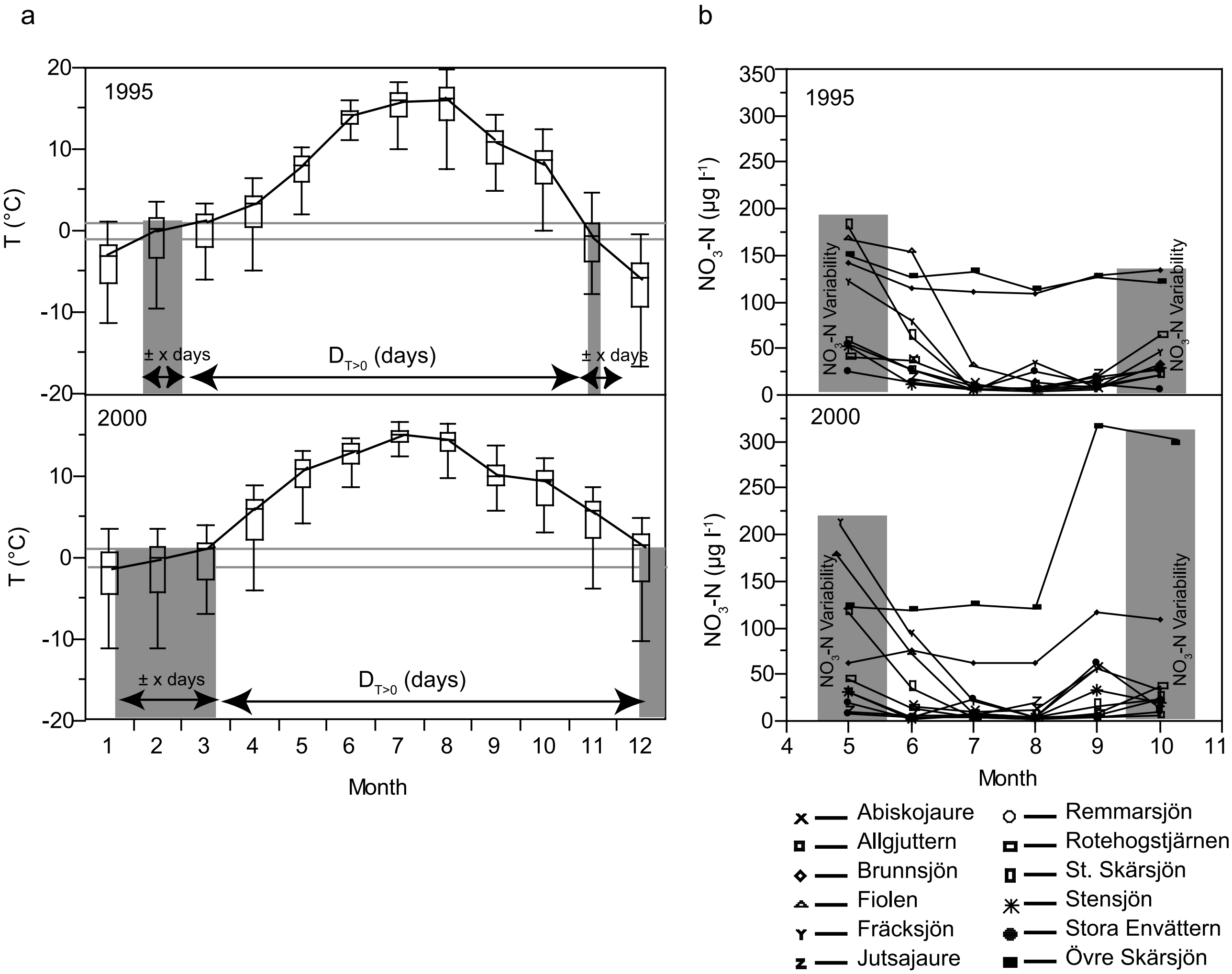

Figure 5. Annual amplitudes for air temperatures and NO_3-N concentrations during a cold year (1995) and a warm year (2000). (a) Box plots of 72 sites where median values were connected by a black line. A small air temperature amplitude that typically occurs during a warm year (e.g., 2000) causes a high variability of air temperatures around 0°C, thus of $D_{T>0}$, a large amplitude that typically occurs during a cold year (e.g., 1995) causes a low variability of $D_{T>0}$. (b) The opposite is the case for the annual amplitude of NO_3-N concentrations where a larger amplitude is observed during a warm year, giving a high variability (gray area) of NO_3-N concentrations within and between lakes during especially spring and autumn.

and the second widest one was expected in 2005. This expectation was fulfilled, both for the water chemical composition and for $D_{T>0}$ (Figures 2d and 2e), and the Brown-Forsythe test revealed highly significant differences in the variance of the water chemical composition and $D_{T>0}$ between the 3 years ($P < 0.0001$). In contrast, the width of the temperature pdf remained the same over the 3 years (Figure 2f), and the Brown-Forsythe indicated equal variances over time ($P > 0.05$).

[11] Evaluating the temporal development of the variance for each water chemical variable separately revealed that the variables that demonstrated a clear seasonality as well as significant differences in the variances between the temperature regions in 1995, i.e., NO_3-N, NH_4-N, TN, pH, Si, and color showed significantly different variances over time (Brown-Forsythe test, $P < 0.01$) while all other variables except TOC did not show significantly different variances over time (Brown-Forsythe test, $P > 0.05$). The annual amplitudes of the season-dependent variables, in particular of pH, NO_3-N, NH_4-N, Si, TN, and color were generally higher during the warm year 2000 than during the cold year 1995 (Figure 3).

[12] In order to quantify temperature-induced changes in the width of the pdf for the water chemical composition the absolute difference of each individual lake sample to the median value of the corresponding temperature region was determined, which was defined as the dissimilarity of the water chemical composition among lakes. Taking the median air temperatures for each temperature region for the years 1995, 2000, and 2005 and determining the dissimilarity of the water chemical composition between the lakes for each region and each year revealed a rapid increase in the dissimilarity between lakes with increasing air temper-

atures (Figure 4). The dissimilarity pattern of the water chemical composition between lakes along a temperature gradient was significantly related to $D_{T>0}$ both on a spatial and a temporal scale (Figure 4).

4. Discussion

[13] To increase the width of a pdf of a variable in a warmer climate can have important ramifications for adaptation and mitigation strategies [e.g., *Schär et al.*, 2004]. The results of this study indicate that a warmer climate might cause an increase in the width of the pdf of the water chemical composition, in particular of nitrogen, pH, silica, and organic carbon. The observed increase in the pdf of the water chemical composition could, however, not simply be explained by an increase in the pdf of air temperature since the air temperature pdf over Sweden remained quite constant during the time period considered (1961–2005 in Figure 2f). I suggest that changes in the width of pdfs in a warmer climate, as shown in this study, result from changing annual amplitudes. During a warm year, the annual air temperature amplitude is usually less pronounced than during a cold year, resulting in that the variability around 0°C, which defines the beginning and termination of $D_{T>0}$, increases (Figure 5a). In contrast, the annual amplitude of variables following the sine function of air temperature is often increased during warm years (Figure 3) with higher values at the beginning and the end of the year and rather similar values during summer (exemplified for NO_3-N in Figure 5b). A prolonged season also implies that lakes have more time to develop individually before another season starts. This individual development of lakes becomes apparent when comparing 1995 and 2000. In 2000 air temperatures were especially increased during September–December (Figure 5a), resulting in a later fall mixing in the southern part of Sweden. Although all 1041 lakes were fully mixed when sampled in 2000, the prolonged individual lake development until fall mixing in 2000 probably still existed during fall mixing, which might explain the observed increased width of the pdf for the water chemical composition of 1041 lakes in 2000 (Figure 2d).

[14] The clearest temperature-induced change in amplitude was noted for variables that are directly associated with in-lake biological processes, such as NO_3-N and pH. From the results, it appears that variables that in one way or another are dominated by in-lake transformations can increase their annual amplitude during warm years while variables clearly driven by processes in the catchment and not associated with in-lake biological processes do not show an increase in their annual amplitude during warm years, Ca being a good example for this kind of variable (Figure 3). An increase in the annual amplitude during a warm year results in a higher variability within and between lakes (Figure 5b). Taking nutrients as an example, a large amplitude is most likely a result of the fact that nutrient concentrations in lake waters are increased during warm winters while biological processes cause the same kind of nutrient depletion during summer as is observed during a cold year.

[15] According to the results of this study, the annual amplitudes of the in-lake process–associated variables are most likely determined by $D_{T>0}$. In Sweden, $D_{T>0}$ usually begins when the ice disappears from the lake surface. This is a critical time of the year since the timing of ice break up affects the timing of the spring phytoplankton bloom as well as the timing of the spring flood that gives an additional nutrient input into lakes with consequent changes in the biogeochemical recycling [*Straile et al.*, 2003; *Weyhenmeyer et al.*, 1999; *Weyhenmeyer*, 2004]. The ice out effect remains detectable until summer as the whole food web can be affected by an earlier timing of the spring phytoplankton bloom [*Blenckner et al.*, 2007; *Schindler et al.*, 2005; *Winder and Schindler*, 2004]. Consequently, biogeochemical variables associated with in-lake biological processes show a direct or indirect response to the timing of ice out. This kind of response gives a variety of lake variables a clear seasonal dependency. For the Swedish boreal lakes, the clearest seasonal dependency was found for the in-lake process associated variables nitrogen, pH, silica, and organic carbon (Table 1). It has earlier been documented in the literature that these variables follow a clear seasonal cycle [e.g., *Pettersson et al.*, 2003; *Wilson and Xenopoulos*, 2008]. In addition, it has earlier been observed that they are closely associated with the winter/spring situation in lakes and clearly respond to a warmer winter climate [*Blenckner et al.*, 2007; *Weyhenmeyer*, 2001; *Weyhenmeyer*, 2004]. The variability pattern of these variables followed most closely $D_{T>0}$, both on a spatial and a temporal scale, suggesting that $D_{T>0}$ is a good measure for the seasonal development of in-lake process associated variables. Further studies are recommended where the function of $D_{T>0}$ as a main driver for biogeochemical processes within lakes will be examined, especially on a temporal scale. $D_{T>0}$ has the advantage over other meteorological variables that it includes the factor time which is needed to account for season-specific processes. During each season, season-specific biogeochemical processes take place implying that a change in the duration of a season will affect the biogeochemical recycling, as suggested by, e.g., *Prowse et al.* [2006]. $D_{T>0}$ is a nonlinear function of air temperature (see equation (1)), implying that changes occur faster in warm geographical regions, giving an even more heterogeneous water chemical composition along a latitudinal temperature gradient when air temperatures increase. The results of this study are, however, probably only applicable to dimictic lakes where four seasons can clearly be distinguished.

[16] The analyses of this study, based on monthly averages, did not reveal an increasing variability of air temperatures in a warmer climate. Despite this, lake ecosystems in Sweden showed an increased dissimilarity along with increased temperatures. Taking into account that future simulations present a higher variability also for air temperatures [*Intergovernmental Panel on Climate Change* (*IPCC*), 2007a], an even more pronounced increase in the dissimilarity of the water chemical composition between lake ecosystems is expected. Such an increase will probably result in far-reaching changes in terrestrial and aquatic ecosystems, probably including changes in biodiversity. It is concluded that a further increase in the dissimilarity between ecosystems along with increasing temperatures represent a serious

challenge to adaptation and mitigation strategies outlined by the IPCC report [*IPCC*, 2007b].

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