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Natural Variability in Lake pH on Seasonal, Interannual and Decadal Time Scales: Implications for Assessment of Human Impact

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Reference values define the natural state with respect to environmental stressors and are commonly used for assessments of ecological impacts and to set restoration targets. These reference values are often treated as constants, whereas in reality they can be highly variable. Here, we study the significance of this variability for assessments of human impact on the environment, by using almost two decades of observations from 95 acid-sensitive Swedish lakes. Our approach was to first estimate the preindustrial, steady-state reference level of acid neutralization capacity (ANC) for each lake with the hydro-geochemical model MAGIC. Then the variability in pH around this “baseline” was reconstructed from the contemporary, “natural” variability in the ANC, total organic carbon (TOC) and Al-concentrations, and partial CO₂ pressure. The variability in reference pH was then examined for the period 1990–2004, on seasonal (single measurements), interannual (1-year median), and decadal (5-year median) scales. On the seasonal scale, the variability in reference pH ranged between 0.40 and 1.7. The range on the interannual time scale was up to 1.3 units and for the decadal scale up to 0.76 units. Since an anthropogenic pH decline of more than 0.4 units is deemed significant according to the Swedish Environmental Quality Criteria, this natural variability clearly needs to be accounted for when assessing acidification.

1. Introduction

Reference values are a ubiquitous but problematic feature of efforts to assess the impact of anthropogenic disturbance on the environment and establish targets for restoration. Reference values are constructed to define the “natural” state of climate, nutrient status, acidity, metals, organic contaminants, etc., and can be set for separate entities (streams, lakes, catchments), or for larger systems. They can be a direct measure of ecological status (i.e., abundance of species or biological indexes) or use a chemical criterion as a proxy.

Reference values are also an important component of some key legislation, including the EU Water Framework Directive (1), where the assessments of ecological status are based on the deviation between the present conditions and the undisturbed state. For stressors such as acidification or eutrophication, finding suitable targets is especially difficult because there is a large natural heterogeneity in acidity and nutrient status among different water bodies. Some lakes in the boreal forest zone may be naturally acidic, with pH below 5, whereas other lakes in the same region may have a natural pH over 7.5 (2). By the same token “natural” phosphorus concentrations in Europe vary from <1 to >50 µg/l (3, 4). To make relevant assessments and establish targets for restoration, as well as to promote the natural biodiversity, it is necessary to assign reference levels specific to each object.

Natural conditions, however, vary not only in space, but also in time. Taking acidity as an example it will be variable at all temporal scales, from diel to centennial. On a longer time-scale, Renberg et al. (5) showed that after thousands of years of gradual pH decline in over a dozen Swedish lakes, there was an increase from about pH 5.5 to about 6.5 between 500 B.C. and 1800 A.D. because of changes in land use practice. This type of long-term change raises the question of what is “natural”. Variability on a shorter time-scale can be exemplified by the pH-decline during spring-flood (6), where pH can be depressed naturally by up to 2 units, as a result of dilution of ANC (acid neutralizing capacity) and increasing concentrations of organic acids.

Some of the established methods for defining reference values can deal with temporal variability to some extent, such as a space-for-time substitution where the variability can be observed in the reference sites. For paleolimnological reconstructions, the temporal variability that can be resolved is limited by the resolution of the sedimentary record. However, even if we can determine the variability in the natural state to a certain degree, the issue of relating that natural variability to human impact assessment still remains. Policy should be cognizant of the fact that physical, chemical, and biological reference conditions vary on different temporal scales.

In this study, we define the temporal variability of reference values for acidification on an intermediate temporal scale, from seasonal to decadal. We then explore the implications for acidification assessments with the aim of elucidating the challenges more generally for environmental assessments based on reference conditions. In Sweden, with a long history of assessing acidification, the recommendation for estimating a stable value of acidity is to use the mean from at least three years of quarterly sampling (7). In many situations where an assessment is desired, though, such long-term data may not be available. Another reason to be cautious to this approach is that the biota is affected by shorter term fluctuations, such as “acid episodes” (8). Furthermore, the estimated reference value may not be stable, even when averaged over a longer time period, given that “natural” climatic variability associated with NAO (North Atlantic oscillation) and other global climate indices can vary on decadal scales (9). Finally, a tradeoff must be made when natural variability is averaged out because this can obscure the human influence that should be assessed. An example of this is the large decline in European acid deposition between 1990 and 2000 that has changed the acidification status in many lakes over the span of a decade (10).

It is desirable to build acidification assessments upon pH because this is the surface water acidity parameter to which biota responds most strongly (11). But it is also a parameter

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whose response to natural climatic variability is difficult to predict. The pH is dependent on ANC and DOC (dissolved organic carbon) concentrations, $p\text{CO}_2$, (partial pressure of CO_2), and aluminum complexation (12). Furthermore, the sensitivity of pH to these parameters varies across different pH intervals. To determine the variability in pH in the preindustrial state, the variability in each of these constituents has to be known, as well as how they have changed relative to the contemporary situation.

Here, we use 19 years of seasonal water chemistry observations from 95 Swedish lakes to confront the issues of variability in reference pH. We then go on to examine the implications of this variability for acidification assessments on seasonal, interannual, and decadal time scales as defined by the Swedish Environmental Quality Criteria (EQC) (11). The conceptual idea is to create time series of the reference pH using the temporal variability in water chemistry that would have existed during the preindustrial period. Because reference values often are treated as invariant in time when assessing a variety of human influences on the environment, the paper goes on to consider more generally the issue of variability in reference conditions.

2. Material and Methods

2.1. Contemporary Data. Water chemistry from 95 Swedish lakes (Figure S1, Supporting Information) has been sampled at least four times yearly, that is, once each season, between 1988 and 2006 (13). There were, in total, 9.5% missing samples in the data set. The missing samples were evenly distributed among the years and seasons, except that there were many missing values in spring (~35%) for the first six years. We considered them as having no major effect on the main results. Measurements included pH, $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, $[\text{Na}^+]$, $[\text{K}^+]$, $[\text{Cl}^-]$, $[\text{SO}_4^{2-}]$, TOC (total organic carbon), [alk] (alkalinity titrated to the end point 5.6), and $[\text{Al}]_{\text{tot}}$ (total aluminum).

2.2. Modeling of pH. The steady-state ANC and $[\text{Al}]_{\text{tot}}$ of the preindustrial reference period were taken from MAGIC hindcasts for each lake (14). Mean, “baseline” values during the reference period for other constituents of lake chemistry that influence pH (TOC and $p\text{CO}_2$) were assumed equal to their contemporary long-term means (1988–2006). The concentrations were then varied around their baselines, using observations from the contemporary variability. From this, a 19-year time series of reference pH were modeled for each lake from an ion-balance equation (eq 1) (see Supporting Information for details on pH modeling).

$$\text{ANC} = ([\text{OH}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{RCOO}^-] - [\text{H}^+] - n[\text{Al}n^+]) \quad (\text{mol/L}) \quad (1)$$

where $[\text{RCOO}^-]$ = concentration of organic anions and n = mean charge of $[\text{Al}]$. The sensitivity of the reference pH to variability in [ANC], TOC, and $p\text{CO}_2$ was examined by varying each variable while holding the other variables constant at their baseline values. The total variability in reference pH was then examined by varying all variables simultaneously. The variability in pH was determined on a seasonal (single measured values), interannual (average over 1 year), and decadal (average over 5 years) time scale. The results are presented as the range of reference pH, where the range is the difference between the 90th and the 10th percentile in the reference time series for each lake, to avoid influence from outliers.

2.3. Variability in ANC. [ANC] is calculated as the difference between strong base cations ($[\text{BC}]^*$, where * denotes correction for sea-salt deposition) and strong acid anions (equal to $[\text{SO}_4^{2-}]^*$ for preindustrial conditions) (eq S2, Supporting Information). From 1988–2006, most of the lakes were in a period of recovery from acidification with steadily decreasing concentrations of both $[\text{BC}]^*$ and $[\text{SO}_4^{2-}]^*$. In the MAGIC simulations of these lakes, trends in $[\text{BC}]^*$ and $[\text{SO}_4^{2-}]^*$

are close to linear during this period, with deviations of approximately $\pm 5 \mu\text{equiv/L}$. To estimate the natural variability of these constituents, they were detrended using Theil's slope (15) to remove the “recovery signal”. The deviation relative to the mean value is assumed to be equal for preindustrial and contemporary conditions, so the percentual deviation from the linear approximation of $[\text{BC}]^*$ and $[\text{SO}_4^{2-}]^*$ was added to the preindustrial baseline chemistry, to generate time series of the reference [ANC] for each lake (Figure S2). This natural variability in $[\text{BC}]^*$ and $[\text{SO}_4^{2-}]^*$ is primarily correlated to the hydrologic conditions (16).

2.4. Variability in TOC. The variability in TOC is influenced not only by high flows and drought (17, 18) but also by other factors, such as photodegradation (dependent on radiation intensity) (19) and primary production (20). These factors were all assumed to be directly transferable to preindustrial conditions. However, recent increases in levels of organic matter over large parts of the boreal/nemoral zone during the last decades have been documented (21). Indications are that the TOC increase can be linked to the ongoing recovery from acidification (21, 22). In that case, the baseline reference level for TOC should be constant, and higher than that seen during the study period. Therefore, TOC concentrations were detrended, using Theil's slope. The detrended time series were then used to vary pH around the baseline reference value. Because the focus of this article is on variability, we considered this acceptable, even if the exact appropriate mean level for TOC is still open to debate. TOC was used as a proxy for DOC (dissolved organic carbon, defined as that organic carbon which can pass a $0.45 \mu\text{m}$ filter). Earlier studies in Fenno-Scandia's boreal forest areas have shown that TOC and DOC differ by less than 10%, and usually less than 5%, under a variety of flow conditions (23).

2.5. Variability in $p\text{CO}_2$. $p\text{CO}_2$ is mostly dependent on the biotic respiration in the lake (24). It could, therefore, have changed if the lake underwent a change in the nutrient status since the period for which the reference state is defined, 150 years ago. The challenge is compounded by the fact that the contemporary $p\text{CO}_2$ is not measured routinely in the studied lakes. The $p\text{CO}_2$ can be modeled from the measured pH, [alk], and TOC, as long as the pH is not too low (< 5.7). Where $p\text{CO}_2$ could not be modeled acceptably, it was instead randomly estimated, from the statistical distributions of $p\text{CO}_2$ in lakes where it could be modeled for at least 90% of the observations (see Supporting Information for details regarding generated time series of $p\text{CO}_2$). Upper and lower limits for $p\text{CO}_2$ were set to prevent unrealistic values. The lower limit was set equal to equilibrium with atmospheric $p\text{CO}_2$ ($2 \times$ atmospheric pressure for winter seasons). The upper limit was set to $20 \times$ atmospheric pressure ($40 \times$ atmospheric pressure for winter seasons).

2.6. Role of Aluminum. Aluminum buffers low pH (ca., < 5.3), yielding higher, less-variable pH relative to the situation without [Al]. Considering the challenges of modeling Al-speciation under preindustrial conditions, Al-buffering was estimated from a regression of the mean-modeled Al charge as a function of pH using the WHAM model (see Supporting Information for details). The baselines for $[\text{Al}]_{\text{tot}}$ during reference concentrations were taken from the MAGIC simulations. $[\text{Al}]_{\text{tot}}$ was then varied around the baseline in the same way as $[\text{BC}]^*$ and $[\text{SO}_4^{2-}]^*$, that is, by assuming the same relative deviation from the mean value for reference and contemporary conditions, for each observation (Figure S2). It should be noted that the sensitivity of Al speciation for the reference value was not tested per se.

2.7. Synchrony and Correlations to Climate. The synchrony in how the reference values vary among the lakes was examined by calculating all the pairwise correlation coefficients for single observations, 1-year medians, and 5-year medians. Correlations between reference pH and

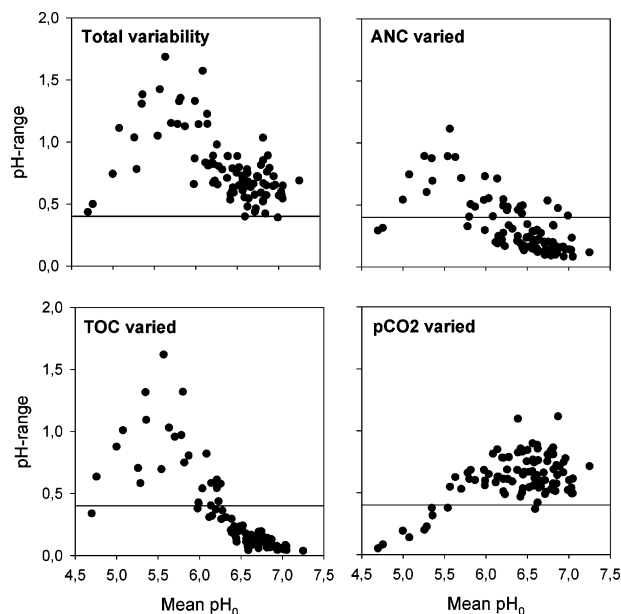


FIGURE 1. Ranges (between the 10th and 90th percentiles) for reference time series of pH, corresponding to single measured values, resulting from variability in ANC, TOC, and $p\text{CO}_2$, plotted against the mean reference pH for the 95 lakes. The limit for significant acidification ($\Delta\text{pH} > 0.4$) is shown as a reference line.

precipitation were also calculated. Monthly precipitation data were taken from nearby weather stations (distances from lakes were between 5 and 64 km).

2.8. Acidification Assessments. In the Swedish EQC, acidification assessments are built upon the parameter ΔpH , defined as the difference between the reference (pH_0) and the contemporary (pH_t) values (11). A ΔpH over 0.4 pH units is defined as significant acidification. ΔpH was calculated using both a “naturally” varying reference pH and a fixed reference pH, corresponding to the long-term mean value under “normal” hydrologic conditions.

3. Results

3.1. Variability of the Reference Level for pH. For the 95 studied lakes, the range (10–90th percentile) in reference pH yielded from modeling with varying ANC, TOC, $p\text{CO}_2$, and [Al] over a 15 year period (1990–2004) was between 0.40 and 1.7 for single measurements, with a median value of 0.72. For 1-year medians, the range was between 0.14 and 1.5 units, with a median of 0.40, and for 5-year medians, it was between 0.070 and 0.86 units, with a median value of 0.19 (Table S1, Supporting Information).

3.2. Factors Determining the Variability. **3.2.1. ANC.** With the assumptions regarding variability of $[\text{BC}]^*$ and $[\text{SO}_4^{2-}]^*$, the median range of $[\text{ANC}]_0$ (preindustrial [ANC]), 54 $\mu\text{equiv/L}$, is slightly smaller than for the contemporary and detrended [ANC] of 58 $\mu\text{equiv/L}$. For single measured values, the variability in $[\text{ANC}]_0$ yielded a range of preindustrial pH values between 0.082 and 1.1 pH units, with a median of 0.24 units. For 1-year medians, the median range was 0.17 units, and the highest range was 0.72 units, for 5-year medians the median range was 0.092 units, and the highest was 0.45 units. The variability is largest in the pH interval 5–6, but it is still considerable for both higher and lower pH (Figure 1).

3.2.2. TOC. The range of variability for detrended TOC in these lakes (5-year medians) was between 0.23 and 8.4 mg/L. If the reference level for TOC is assumed equal to the detrended, contemporary concentrations, the range in reference pH for single measured values resulting from variations in TOC was between 0.038 and 1.6 units, with a median of

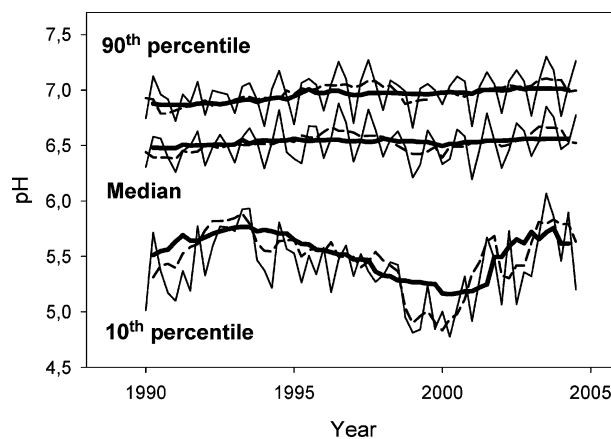


FIGURE 2. Tenth, 50th, and 90th percentile for modeled time series of reference pH in the 95 lakes, taken as 5-year medians (thick solid), 1-year medians (dashed), and single values (thin solid).

0.18 units. For 1-year medians the median range was 0.11, and the highest range was 1.0 units. For 5-year medians the median range was 0.051, and the highest range was 0.52 units. With the highest of the three pK_a -values in the triprotic model being 6.46, the effects of TOC-induced variability starts to manifest itself around this pH value, whereas it is very small for pH higher than 6.5 (below 0.1 units) (Figure 1).

3.2.3. $p\text{CO}_2$. The temporal range in EpCO_2 (excess partial CO_2 pressure) for the lakes was between 5.9 and 39 times atmospheric pressure for single values, and from 0.3 to 7.2 times atmospheric pressure for 5-year medians. The range in reference pH for single measured values resulting from variations in $p\text{CO}_2$ was between 0.051 and 1.1 units, with a median of 0.62 units. For 1-year medians, the median range was 0.33, and the highest range was 0.71 units. For 5-year medians the median range was 0.17, and the highest range was 0.63 units. The variability increases with pH and is small for pH-values below 6 (Figure 1).

In summary, the influence of the three variables ANC, TOC, and $p\text{CO}_2$ are of comparable importance, although their relative importance differs from site to site depending on the baseline reference pH (Figure 2). With a majority of the lakes (53 of 95) having mean reference pH above 6.5, $p\text{CO}_2$ is the variable that contributes most of the variability for the median lake (median range for single values = 0.62 units).

3.3. Synchrony in Variability and Correlations to Climate. At least for the seasonal variability (i.e., single measurements), there is a synchrony among the lakes in how the reference level in pH varies. For time series of single measured values, the median of all pairwise correlation coefficients for the reference pH is 0.32. The similarity decreases with the difference in mean pH. The season-to-season variability is around 0.5 units over the whole pH interval. For the decadal variability (i.e., 5-year medians), the correlation among the lakes is lower, with a median of all pairwise correlation coefficients of 0.22. For 5-year medians of reference pH, the 10th percentile varies by ~ 0.5 unit, whereas the 90th percentile of the 5-year median time series varies by less than 0.1 unit (Figure 2). One reason is that pH is more sensitive in the interval between 5 and 6, where the 10th percentile lies. Another reason is the relatively low spatiotemporal correlation for time series of $p\text{CO}_2$ (5-year medians) among the lakes (median r of all pairwise correlations = 0.31). In comparison, the median r of all pairwise correlations for 5-year median time series of reference ANC is 0.60, resulting in a higher synchrony in reference pH for lakes where ANC is more influential.

The reference pH is often negatively correlated to the precipitation on a decadal scale. There are significant negative

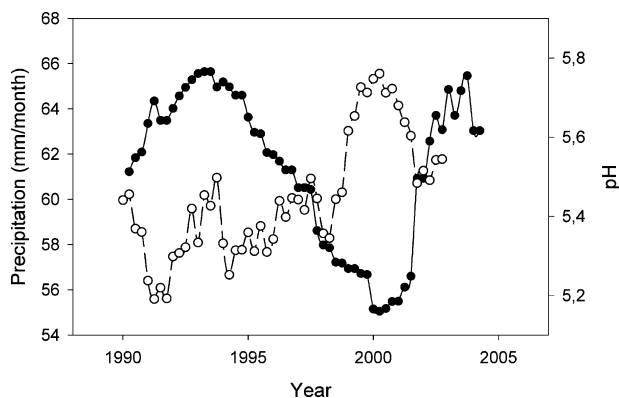


FIGURE 3. Median (for the 95 lakes) of the 5-year antecedent median precipitation (open circles, dashed line) and the 10th percentile (corresponding to the more naturally acid lakes) of the 5-year median reference pH (black circles, solid line).

correlations between 5-year medians of the reference pH and 5-year medians of precipitation for 50 of the 95 lakes (95% level of significance). This is especially the case for lakes with a lower reference pH (Figure 3). Of the 26 lakes with a mean reference pH below 6.2 (and hence mostly influenced by ANC and TOC), 19 have a significant negative correlation between 5-year medians of reference pH and precipitation (95% level of significance).

3.4. Acidification Assessments. The estimated variability in reference pH has different consequences depending on how the pH has changed since the preindustrial period (Figure 4). The lakes can be divided into three different categories:

- Lakes with a higher contemporary variability in pH than for the reference pH. This is the case for lakes where pH by acidification has moved from a stable reference interval (>6.5) to a more sensitive contemporary pH-interval (between 5 and 6). For these, the difference between using a fixed and a variable reference value is comparatively small. When assessing acidification status, the variability in ΔpH ($\text{pH}_0 - \text{pH}_i$) is large, regardless of whether the reference value is allowed to vary or not.
- Lakes with similar variability for contemporary and preindustrial conditions. This is the case for lakes that are negligible or moderately affected by acidification and, hence, are in a stable pH-interval (>6.5) during both contemporary and preindustrial conditions. For these, the variability in the reference level is very important. Acidification assessments made relative to a fixed reference value will give variable results for these lakes, whereas assessments relative to a variable reference level will be stable.
- Lakes with higher variability during preindustrial than during contemporary conditions. This is the case for naturally acidic lakes in the least stable pH-interval 5–6, which have been further acidified to a contemporary pH below 5, regulated by aluminum buffering. For these, acidification assessments will become less stable with a variable than with a fixed reference level.

4. Discussion

4.1. Implications of Variation of Reference Values for pH.

The temporal variability of reference values is often overlooked, but should be considered when determining strategies and developing methods for evaluating human impact. It can lead to errors in assessment even when using means as long as 5-years. Going longer (or perhaps even going that long) in averaging out temporal variability risks obscuring the human influences we are looking for. The problem of errors in assessment due to conflation of natural variability with human influence, however, gets worse as shorter and shorter periods are used to estimate human influence because

climatic fluctuations have such a strong influence on ANC and thus on pH. Here we have shown that if single measurements are considered, the natural variability in pH exceeds the criteria used to define significant acidification, that is, an anthropogenic pH-decline of 0.4 units, for virtually all the 95 studied lakes included in this study. Temporal variability is still a problem even with reference values corresponding to long-term (5 year) medians. Of the 95 lakes, 12 had a range in the 5-year median reference pH level of more than 0.4 pH-units. This long-term effect of precipitation on acidity is greatest in the most acid lakes (Figure 3).

Considering the variability of acidification assessments based on pH (Figure 4), a logical response would perhaps be to say that because of its complex pattern of variability, pH is not suitable as a measure of acidification and that choosing a more stable measure, such as [ANC], would facilitate more stable assessments. On the other hand, it can also be argued that the variability in pH itself is an important characteristic of the natural state for a lake, albeit more difficult to describe.

Because of the covariation in the reference pH among the studied lakes, one needs to be particularly careful when making acidification assessments on a larger spatial scale, where many objects are sampled simultaneously on one or a few occasions. Longer term data should preferably be used even if a larger population of lakes is considered, for example, an acidification assessment on a regional or national scale. If long-term data (5-year medians) are available, the covariation of the reference pH among the lakes is smaller, and the mean values of reference levels among the lakes are relatively stable, at least for higher pH-intervals (Figure 2).

4.2. Are the Reconstructed Reference Time Series

Realistic? Reconstructing water chemistry 150 years back in time is a difficult task, and most of the assumptions made regarding the variability during reference conditions are that they are equal to what is observed today. There are several uncertainties inherent in this assumption. For example, any erroneous assumptions regarding the “baseline” reference values for any of the major influences on pH would likely change the pH variability because the magnitude of variability often depends on the pH range. As for reference values for [ANC], the set of MAGIC hindcasts used in this study has proved to be consistent with paleolimnological reconstructions of preindustrial pH for 55 of the study lakes, where the same assumptions regarding baseline values for pCO_2 and TOC were used as in this study (2). Reference values for TOC could on the other hand, in the light of many recent studies (21), be expected to be higher than the contemporary concentrations. An alternative scenario was therefore examined, where the baseline for TOC concentrations was set by regression between annual means of TOC and $[\text{SO}_4^{2-}]^*$, and the baseline for reference TOC was then estimated from the reference $[\text{SO}_4^{2-}]^*$. The calculations with an alternative baseline for TOC were only carried out for lakes with a positive trend in TOC 1988–2006 (72 of 95 lakes). For these, the reference TOC rose 2.45 mg/L on average and up to 10.0 mg/L higher than contemporary concentrations. A higher reference TOC primarily changes the *mean* reference pH, but it may also change the variability for *single lakes* substantially relative to the “base-case”; the total range in reference pH (single measured values) can change by up to 0.5 units. However, in terms of minimum, median, and maximum ranges, the difference is relatively small between the different alternatives for reference TOC (Table S1).

In the lake with the largest range of pH_0 , Lake Stora Tresticklan, the reference level (5-year median) increases from 4.98 to 5.97 between 2000 and 2004. The increase in reference pH is mostly caused by an increase in the simulated ANC_0 , from 22 to 54 $\mu\text{equiv/L}$, and a decrease of TOC from 5.2 to 3.1 mg/L. This can be compared to the variability of ANC in some of the virtually unacidified lakes in the north

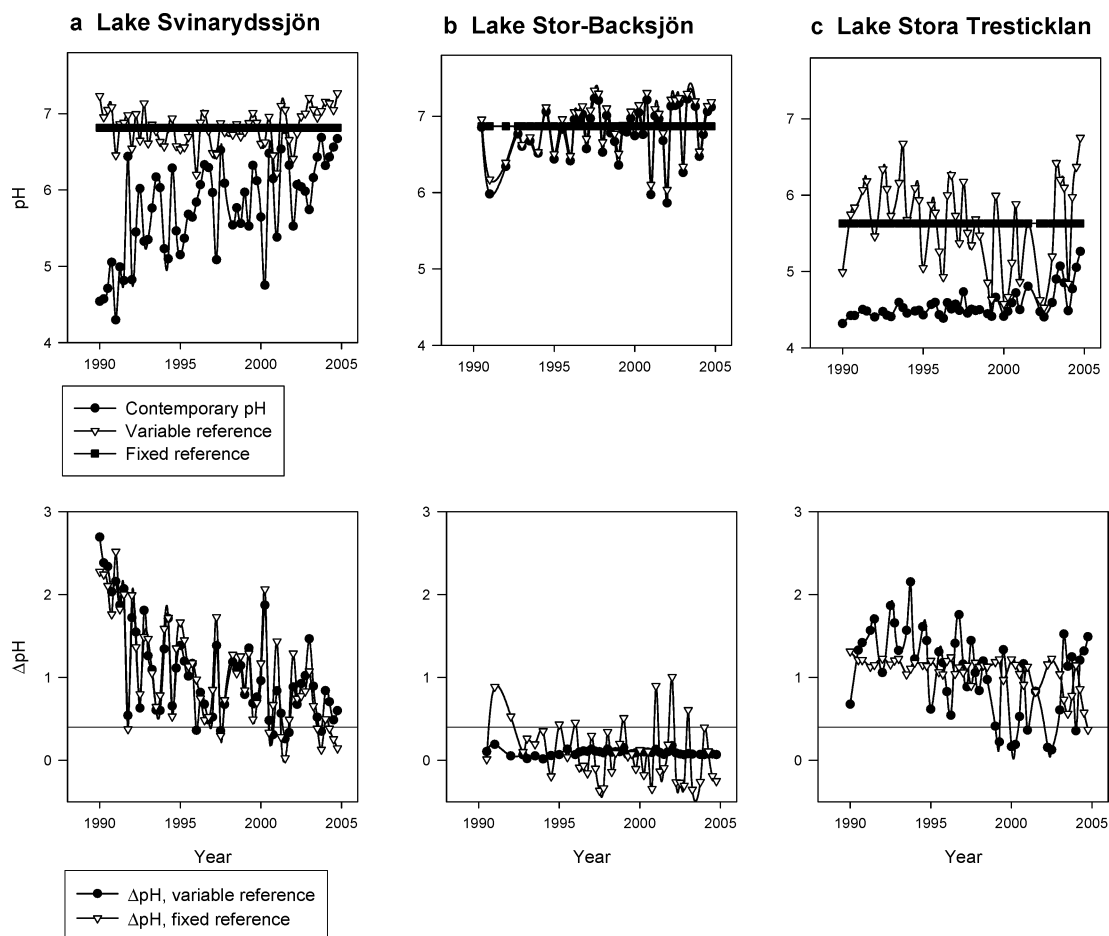


FIGURE 4. Acidification assessments of (a) Lake Svinarydssjön, (b) Lake Stor-Backsjön, and (c) Lake Stora Tresticklan. The upper panel shows time series (single values) of modeled contemporary pH (black circles), modeled time series of reference pH (open triangles), and the fixed mean reference level (black line). The lower panel shows time series of ΔpH , calculated with a variable (black circles) and a fixed (open triangles) reference level, with the limit for significant acidification ($\Delta\text{pH} > 0.4$) as a reference line.

of Sweden. Lake Njalakjaure is similar to Lake Stora Tresticklan in that it is naturally weakly buffered, and the 5-year median of ANC increased from 28 to 44 $\mu\text{equiv/L}$ from 2000 to 2004. The increase in simulated ANC_0 for Lake Stora Tresticklan is of comparable size and can thus be considered realistic.

4.3. Uncertainties in the pH Modeling. Error sources in the pH model include measurement errors, uncertainties in the dissociation of organic anions, and lack of measured pCO_2 (for pH above 6), as well as Al-speciation (pH below 5.3). Since the focus in this study is on the variability, errors in separate observations may be acceptable, as long as the range in modeled pH is similar to the measured. Indeed the range of the modeled contemporary pH is larger than the measured range (both detrended) in 65 of the 95 lakes, but the median difference is relatively small (0.06 pH units). Our modeling approach may thus exaggerate the variability in the reference value in terms of pH slightly. However, in the Swedish EQC, acidification is defined as the decline of modeled pH, that is, the same approach as used in this study.

4.4. Further Implications and Conclusions. Here, our aim has been to describe and exemplify how (1) “natural, pristine” conditions are constantly changing, (2) the difficulties in defining a varying “undisturbed state”, and (3) the policy implications of temporal variability in the reference values. This study has focused on the variability for an intermediate time scale, from seasonal to decadal variation. In so far as these variations are driven by “natural” fluctuations in climate, they are “reversible”. Climate change may

make some of these changes “irreversible”, for example by dilution effects on ANC through changed patterns in runoff or increased TOC because of higher temperatures (25). Policy makers then need to decide whether reference conditions are fixed to the conditions during the preindustrial era or adjusted to include anthropogenic effects on climate.

Variability on an intermediate time scale as described in this paper needs to be acknowledged when planning strategies for environmental monitoring programs and defining criteria for human influence. Assessment errors resulting from ignoring temporal variability in reference conditions get worse as shorter and shorter periods are used to estimate reference values. On a more fundamental level, the structure of natural temporal variability may itself be a feature of ecosystems that can be changed by human influence. While this is clearly recognized in a few issues such as the effect of regulation of river flows with dams (26), it is implicitly ignored in any assessments where reference conditions are time invariant, no matter how much consideration is given to the spatial variability in reference conditions. The spatial variation has also received much more attention than the temporal variability, even though spatial variability also has implications too important to be ignored (27). We hope that this paper’s examination of the relatively complex structure of temporal variability in pH and its causes has demonstrated that the temporal dimension must be included in environmental assessment.

Acknowledgments

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Supporting Information Available

pH modeling, reference time series generation, and mean charge of Al_{tot} estimation, table summarizing the variability in pre-industrial pH, and figures showing the locations of the 95 lakes studied and how the reference time series of $[BC]^*$ were generated. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) EU Water Framework Directive, Establishing a Framework for Community Action in the Field of Water Policy. In Official Journal (OJ L 327), 2000; Vol. Directive 2000/60/EC.
- (2) Erlandsson, M.; Bishop, K.; Fölster, J.; Guhren, M.; Korsman, T.; Kronnas, V.; Moldan, F. A comparison of MAGIC and paleolimnological predictions of preindustrial pH for 55 Swedish lakes. *Environ. Sci. Technol.* **2008**, *42* (1), 43–48.
- (3) de Jonge, V. N.; Elliott, M.; Orive, E. Causes, historical development, effects and future challenges of a common environmental problem: eutrophication. *Hydrobiologia* **2002**, *475* (1), 1–19.
- (4) Wilander, A.; Fölster, J. *Sjöinventeringen 2005—En Synoptisk Vattenkemisk Undersökning Av Sveriges Sjöar*; Rapport 2007: 16; Department of Environmental Assessment: Uppsala, Sweden, 2007.
- (5) Renberg, I.; Korsman, T.; Birks, H. J. B. Prehistoric increases in the pH of acid-sensitive Swedish lakes caused by land-use changes. *Nature* **1993**, *362* (6423), 824–827.
- (6) Buffam, I.; Laudon, H.; Temnerud, J.; Morth, C. M.; Bishop, K. Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network. *J. Geophys. Res.—Biogeosci.* **2007**, *112*.
- (7) SEPA. *Environmental Quality Criteria—Lakes and Watercourses*; Report 5050; Swedish Environmental Protection Agency: Kalmar, Sweden, 2000.
- (8) Ormerod, S. J.; Boole, P.; Mccahon, C. P.; Weatherley, N. S.; Pascoe, D.; Edwards, R. W. Short-term experimental acidification of a Welsh stream—Comparing the biological effects of hydrogen ions and aluminum. *Freshwater Biol.* **1987**, *17* (2), 341–356.
- (9) Hurrell, J. W.; VanLoon, H. Decadal variations in climate associated with the north Atlantic oscillation. *Clim. Change* **1997**, *36* (3–4), 301–326.
- (10) Fölster, J.; Wilander, A. Recovery from acidification in Swedish forest streams. *Environ. Pollut.* **2002**, *117* (3), 379–389.
- (11) Fölster, J.; Andrén, C.; Bishop, K.; Buffam, I.; Cory, N.; Goedkoop, W.; Holmgren, K.; Johnson, R.; Laudon, H.; Wilander, A. A novel environmental quality criterion for acidification in Swedish lakes—An application of studies on the relationship between biota and water chemistry. *Water, Air, Soil Pollut.* **2007**, *7*, 331–338.
- (12) Köhler, S.; Laudon, H.; Wilander, A.; Bishop, K. Estimating organic acid dissociation in natural surface waters using total alkalinity and TOC. *Water Res.* **2000**, *34* (5), 1425–1434.
- (13) SLU. Analysmetoder. Available at <http://info1.ma.slu.se/db.html>. (accessed 18 Feb 2008).
- (14) Moldan, F.; Kronnas, V.; Wilander, A.; Karlun, E.; Cosby, B. J. Modelling acidification and recovery of Swedish lakes. *Water, Air, Soil Pollut.* **2004**, *4*, 139–160.
- (15) Helsel, D. R.; Hirsch, R. M., Statistical methods in water resources. In *Studies in Environmental Science*, Elsevier Science B.V.: Amsterdam, 1992; Vol. 49, pp 266–267.
- (16) Laudon, H.; Bishop, K. H. Quantifying sources of acid neutralisation capacity depression during spring flood episodes in Northern Sweden. *Environ. Pollut.* **1999**, *105* (3), 427–435.
- (17) Erlandsson, M.; Buffam, I.; Fölster, J.; Laudon, H.; Temnerud, J.; Weyhenmeyer, G. A.; Bishop, K. 35 years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. *Global Change Biol.* **2008**.
- (18) Clark, J. M.; Chapman, P. J.; Adamson, J. K.; Lane, S. N. Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. *Global Change Biol.* **2005**, *11* (5), 791–809.
- (19) Bertilsson, S.; Tranvik, L. J. Photochemical transformation of dissolved organic matter in lakes. *Limnol. Oceanogr.* **2000**, *45* (4), 753–762.
- (20) Berggren, M.; Laudon, H.; Jansson, M. Landscape regulation of bacterial growth efficiency in boreal freshwaters. *Global Biogeochem. Cycles* **2007**, *21* (4), GB4002.
- (21) Monteith, D. T.; Stoddard, J. L.; Evans, C. D.; de Wit, H. A.; Forsius, M.; Hogasen, T.; Wilander, A.; Skjelkvale, B. L.; Jeffries, D. S.; Vuorenmaa, J.; Keller, B.; Kopacek, J.; Vesely, J. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* **2007**, *450* (7169), 537–540.
- (22) Evans, C. D.; Monteith, D. T.; Cooper, D. M. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environ. Pollut.* **2005**, *137* (1), 55–71.
- (23) Gadmar, T. C.; Vogt, R. D.; Osterhus, B. The merits of the high-temperature combustion method for determining the amount of natural organic carbon in surface freshwater samples. *Int. J. Environ. Anal. Chem.* **2002**, *82* (7), 451–461.
- (24) Rantakari, M.; Kortelainen, P. Interannual variation and climatic regulation of the CO₂ emission from large boreal lakes. *Global Change Biol.* **2005**, *11* (8), 1368–1380.
- (25) Freeman, C.; Evans, C. D.; Monteith, D. T.; Reynolds, B.; Fenner, N. Export of organic carbon from peat soils. *Nature* **2001**, *412* (6849), 785–785.
- (26) Nilsson, C.; Berggren, K. Alterations of riparian ecosystems caused by river regulation. *Bioscience* **2000**, *50* (9), 783–792.
- (27) Bishop, K. H. Liming of acid surface waters in northern Sweden: Questions of geographical variation and the precautionary principle. *Trans. Inst. Br. Geographers* **1997**, *22* (1), 49–60.

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