Soil mineral depletion drives early Holocene lake acidification

John Boyle1*, Richard Chiverrell1, Andrew Plater1, Ian Thrasher1, Emily Bradshaw2, Hilary Birks3, and John Birks3
1School of Environmental Science, University of Liverpool, Liverpool L69 7ZT, UK
2Department of Geography, Loughborough University, Leics LE11 3TU, UK
3Department of Biology and Bjerknes Centre for Climate Research, University of Bergen, Allegaten 41, N-5007 Bergen, Norway

ABSTRACT

In recent decades, explanations for post-glacial lake acidification have focused on changing climate and biotic factors. Here we present a unique lake sediment data set combining diatom-inferred acidity reconstruction with detailed quantitative assessment of soil base dynamics that challenges this view. We show, at Kråkenes Lake in Norway, that historical development of soil mineral depletion inferred from the lake sediment record is consistent with the extent and timing of early Holocene acidification. The lake-water acidification can be fully accounted for by abiotic soil mineral depletion, suggesting a lesser role for alternative acidifying mechanisms, such as direct climate impacts and successional changes in organic acid production. There are at present few comparable data sets, but those that exist suggest similar rates of soil base depletion. As this acidification is not confined to water, abiotic mineral depletion is likely also to impact terrestrial ecosystems, and dynamic vegetation models that exclude irreversible mineral depletion will fail to capture an important element of global ecology.

INTRODUCTION

Terrestrial and aquatic ecosystems recycle their mineral nutrients (N, P, and bases such as Ca), but nevertheless losses occur and external sources are needed to maintain productivity in the long term. Nitrogen is supplied from the atmosphere or fixed biologically, but bases and P must come largely from weathering of bedrock minerals in soil, the atmospheric supply being generally low. In regions with base-poor bedrock and conditions unfavorable for weathering, typically granitic catchments from high latitudes or altitudes, mineral nutrient supply is sufficiently low today to limit ecosystem productivity. But is this impoverishment invariant, a simple function of climate and geology, or has progressive leaching of bases from the soil led to this state? In deglaciated regions across the northern hemisphere, base-poor lakes have sediment records that reveal higher pH values and productivity in the early post-glacial period (Bradshaw et al., 2000; Engstrom et al., 2000; Ford, 1990; Haworth, 1969; Jones et al., 1989; Renberg, 1990; Whitehead et al., 1989). In dispute is whether this past condition was caused primarily by climatic and biotic effects (Engstrom et al., 2000; Whitehead et al., 1989), or by transient enrichment in base derived from parent rocks as originally proposed by Salisbury (1922) and more recently by Boyle (2007). Kråkenes Lake, on the island of Vågsøy (western Norway), is typical (Fig. 1A), providing an ideal test site for the mineral-depletion hypothesis. Post-glacial acidification is recorded in its diatom record (Bradshaw et al., 2000), it has an exceptionally well-studied early Holocene sediment record (Birks et al., 2000; Birks and Birks, 2008) supplying important paleoenvironmental information (Fig. 1B), and the land surface was fully zeroed, from a mineral-weathering perspective, by glacial scour during the last glaciation. Originally ice free from ca. 14 kyr B.P., a cirque glacier occupied the upper catchment during the Younger Dryas (Mangerud et al., 1979), finally melting within a decade (Birks and Wright, 2000) of Holocene warming at 11.53 kyr B.P. (Gulliksen et al., 1998). Mineral supply to the lake, dominated during the late-glacial period by sediment from the glacier, had by the early Holocene switched to catchment

METHODS

A sediment core was collected in May 2007 to assess soil development at Kråkenes Lake. The 8.96-m-long core was taken from the terrestrialized southwestern lake arm (level was lowered in the 19th century) using a 1-m-long, 70-mm-diameter Russian corer in 10 overlapping drives. These were stored at 4 °C in plastic guttering wrapped in polythene sleeves, sliced at 10 mm intervals, and freeze dried within two weeks. Water content and loss-on-ignition (LOI) profiles were used to verify overlaps between core drives prior to further analysis.

As sediment composition is affected by particle size, the sediment was separated into particle size fractions (<20 µm and 20–36 µm).
Following sieving to remove the coarser sediment, the sub-36 µm fraction was split at 20 µm by pipette method in temperature-controlled settling tubes. The procedure was repeated three times to achieve better than 90% separation.

To assess primary rather than secondary minerals, samples were treated with NaOH to remove elements bound to organic matter, a method based on the modified Williams method (Williams et al., 1967). Concentrations were expressed as mass fraction of the pre-treatment sample mass.

The allogenic (externally derived primary soil mineral) component was analyzed for mineral elements using X-ray fluorescence analysis (XRF) and for mineralogy using X-ray diffraction (XRD). XRF analysis was performed with a Bruker S2 Ranger energy-dispersive instrument. XRF analysis was performed with a Bruker S2 Ranger energy-dispersive instrument. Loose powders were pressed lightly in sample cups with 6 µm polypropylene film, and were measured for 250 s under helium at three different tube settings. Variable alpha mass attenuation corrections were applied taking measured organic-matter concentrations into account. Calibration used a set of 15 certified reference materials. Processing the reference materials as unknowns generated root mean squared differences of better than 5% of mean for the elements used in this study. X-ray diffractograms were collected using a PANalytical X’Pert Pro MPD X-ray diffractometer. A copper X-ray tube was operated at 40 kV and 40 mA. Samples were back-loaded into cavity holders. LoI at 450 °C was measured relative to the dry weight at 105 °C (Boyle, 2004).

Core chronology was established using uniquely identifiable volcanic ash (tephra) layers (Vedde, 11.97–12.25 kyr B.P.; Saksunarvatn, 10.11–10.25 kyr B.P.; and Hekla-4, ca. 4.4 kyr B.P.) and correlation with the well-dated Kråkenes master core (Birks et al., 2000).

RESULTS AND DISCUSSION

The sediment record reveals that on deglaciation (11.5 kyr B.P.), the sediment supply comprised mainly terrigenous mineral matter, which was rapidly augmented by organic matter and biogenic silica that reached 75% of the sediment dry mass by 10 kyr B.P. Such biogenic dilution strongly impacts the lake sediment record, reducing the concentration of primary soil minerals. However, it is the assemblage, not the concentration, of primary minerals in the sediment that reflects changes in the catchment soil, and subsequent analysis refers only to the allogenic sediment fraction. XRD analysis (not shown) is inconclusive; it reveals the presence of plagioclase, amphibole, quartz, mica, chlorite, and apatite (at detection limit), but the weak signal from small samples is too noisy to constrain the subtle temporal variations. Instead, we use XRF element concentration data to quantify changes in mineral concentration. Element concentrations were normalized to Zr, a chemically resistant element, to correct for dilution by biogenic silica. For element \( \epsilon \) at depth \( d \), the normalized concentration is given by:

\[
C_{\text{norm, } \epsilon}(d) = \frac{C_{\text{norm, } \epsilon}(d)}{C_{\text{norm, Zr}}(d)} \text{ (1)}
\]

For all elements (Fig. 2), this analysis reveals decreases through time, occurring more rapidly for the finer of the two size fractions. \( P \) decreases far faster than the other elements, which all show broadly similar rates of decline. These element-concentration changes reflect a declining mineral concentration in the sediment, specifically of apatite (P), biotite (K), there being no other abundant K-bearing minerals, and plagioclase and/or hornblende (Ca), and these in turn reflect a declining mineral concentration in the soil from which the sediment particles were derived. That this decline is caused by chemical weathering is strongly supported by the fine fraction changing most rapidly and apatite, the most weatherable mineral (Guidry and Mackenzie, 2003), changing fastest.

The rates of mineral depletion observed in the sediment record can be used to estimate their mass-specific dissolution coefficients (mass fraction lost per year). The mineral depletion curves (Fig. 2) display statistically significant negative correlations of log concentration with time (zeroed at the start of the Holocene), the best-fit exponential curves yielding the mass-specific rate coefficients (yr⁻¹). These can be aggregated to determine the total base loss rate (calculating the Ca released by the apatite P depletion) from the <36 µm soil fraction (Fig. 3A), the best-fit exponential curve yielding a rate coefficient of \( 10^{-3.95} \) (95% confidence interval of \( 10^{-4.34}-10^{-3.83} \)) (Fig. 3B).

The question is whether this rate of depletion is consistent with the acidification. To quantify this, the diatom-inferred pH values must be converted into an estimate of alkalinity flux. By adopting the usual assumption that aqueous pCO₂ was 3× atmospheric (Cole et al., 1994), the alkalinity (mEq m⁻²) may be calculated from pH using published equilibrium coefficients (Stumm and Morgan, 1996). The product of this and the mean annual runoff (m yr⁻¹), calculated from precipitation and temperature using the empirical Turc equation (Turc, 1954) (Fig. 1B), provides an estimate of the alkalinity flux (mEq m⁻² yr⁻¹). A best-fit exponential curve (Fig. 3B) shows a decline in alkalinity flux with a rate coefficient of \( 10^{-4.5} \) (95% confidence interval of \( 10^{-5.13}-10^{-3.85} \)), which is within the range of depletion rates for the elements (Fig. 2). Though not identical, the decline in alkalinity export flux (Fig. 3B) and rate of total base depletion (Fig. 3A) are very similar. Indeed, given that the hydrological and soil-erosion catchments are unlikely to be
identical, the two rate estimates are remarkably similar.

This is the first time that such a comparison has been made; it shows that soil bases deplete rapidly enough to explain the acidification at this site. But, is the amount of base involved sufficient to account for the alkalinity flux? To test this, the soil base export rate is calculated using the depletion rate coefficients, and the initial composition and areal density of catchment soils. For the two particle-size fractions, both the initial soil composition and the rate coefficients can be taken from the data in Figure 2. However, quantifying the soil areal density is more difficult. The proportion of soil in fine fractions can be estimated—glacial tills in western Norway typically have 20% of their mass finer than 36 μm, and 13% finer than 20 μm (Haldorsen, 1981)—but the catchment average soil density is not known. Instead, we can apply the rate constants and compositions of Figure 2 to a range of soil areal densities, scaled according to the size-distribution data (Haldorsen, 1981) to calculate the expected base export. We can then test whether the export rates needed to account for the alkalinity flux are provided by a reasonable soil areal density. The best fit to the magnitude of the alkalinity flux (Fig. 3B, solid line) is provided by an areal soil density of 530 kg m⁻²; the predicted rate of base decline broadly agrees with the rate of decline in alkalinity flux. Corresponding with a mean soil thickness of <0.5 m, this is not an unreasonable figure, global mean soil thicknesses being on this order. Consequently, both the quantity of base export flux from catchment soils at Kråkenes Lake and the rate of its depletion by progressive chemical weathering are of the correct magnitude to explain the observed early Holocene lake acidification.

Do the observations at Kråkenes Lake have general application? A comparison is possible with data from soil chronosequences, suites of soils that have developed under similar environmental conditions but which have varying ages. Our estimated depletion rate for soil apatite (size fraction weight mean k = 10⁻⁴.⁵) is consistent with values we find by fitting curves to published soil chronosequence data from New Zealand (Walker and Syers, 1976) and Hawaii (Crews et al., 1995), yielding mass-specific dissolution coefficients of 10⁻³.⁵–10⁻⁴.⁷ and 10⁻¹.⁶–10⁻¹.⁹, respectively. For silicate minerals, there are fewer comparable data. The Hawaii soil chronosequence loses Ca, presumably mainly from plagioclase, at 10⁻⁴.⁵ yr⁻¹, based on data for the first 20 k.y. (Chadwick et al., 1999; Vitousek et al., 1997). A similar rate of 10⁻⁴.⁵ yr⁻¹ is found at the Gårdsjön experimental forest, Sweden, for modern chemical budget data (Warfvinge and Sverdrup, 1992). Our results can therefore be seen as broadly in line with data from other studies, though with greater temporal resolution and providing a continuous record, in finding a small amount of rapidly weathering apatite and large amounts of more slowly weathering aluminosilicate minerals. We can gain a mechanistic insight into which minerals contribute most to lake acidification by extrapolating from our data. The impact of the contrasting mineral properties on the base depletion signal can be calculated using, for apatite and silicate respectively, log k = −3.52 and −4.50, and initial soil concentrations of 38 and 400 eq m⁻², the latter based on average granite (Krauskopf, 1982). The apatite, despite composing just 0.38% of the parent material, supplies in the early stages almost half the base (Fig. 3C) and wholly dominates the rate of change in base supply (Fig. 3D). Indeed, declining soil apatite remains the dominant cause of acidification due to base depletion for more than 7500 yr in this example.

CONCLUSIONS

Our study, the first to use a lake sediment record to quantitatively reconstruct soil primary mineral concentration changes through the Holocene, finds progressive first-order mineral depletion at Kråkenes Lake with the rate and extent needed to explain the observed post-glacial lake acidification. This confirms the theoretical prediction of Boyle (2007), and we conclude that mineral depletion, primarily of apatite, was the main cause of acidification at Kråkenes Lake. Given that Boyle (2007) also predicted a mineral-depletion acidification for seven other published lake acidification records in Europe and North America, we suggest that the process was commonly important. Two consequences follow. First, if an abiogenic process can account for much of the post-glacial lake acidification, then a lesser role remains for alternative acidifying mechanisms, such as successional changes in production of organic acids. Conversely, if an irreversible abiogenic process is a major driver, then any ecosystem model neglecting this will poorly explain pH change in post-glacial lakes and those aspects of the flora and fauna that depend upon pH. As this acidification is not confined to water, but also impacts soil, abiogenic mineral depletion is likely also to impact terrestrial ecosystems. Therefore, dynamic vegetation models that exclude irreversible mineral depletion will fail to capture an important element of global ecology. Second, the role we show for soil apatite in controlling post-glacial lake acidification supports a direct causal link with the soil phosphorus development model of Walker and Syers (1976), which also depends upon apatite. Both phenomena result from depletion of the soil nutrient pool, which is reversible only with large-scale zeroing of surface terrain at the glacial-interglacial time scale, or with volcanic eruptions, tectonic uplift, or large-scale anthropogenic erosion of land surfaces.

ACKNOWLEDGMENTS

This work was funded by a Natural Environment Research Council grant, NE/F020732/1.

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Manuscript accepted 17 October 2012
Revised manuscript received 14 October 2012
Printed in USA