Increasing silicon concentrations in Bohemian Forest lakes

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Abstract

Long-term trends of dissolved silicon (Si) concentrations in five glacial lakes in the Bohemian Forest, Czech Republic, recovering from acidification show higher mobility of Si from the soil to surface waters despite lower atmospheric deposition of acids. Si increased by 0.95 to 1.95 µmol yr^{-1} (36 to 51%) from 1986–2004 and with increasing pH. A change in soil solution conditions because of a sharp decrease in acidic deposition has led to marked decline in Al mobility and to considerable decreases in dissolved Al, especially Al^{3+}. The increase in Si may be related to: (1) unblocking of the inhibitory effect of dissolved Al on weathering of aluminosilicates, (2) biogenic opal (phytoliths) dissolving faster, and/or (3) lower Si precipitation as secondary aluminosilicates in soil. The change in Al speciation on the dissolution rate of biogenic silica is critical. A lack of change in Si at sites outside central Europe may be explained by small or no decline in mobility of dissolved Al. The effect of a long-term increase in temperature was probably minor.

Keywords: acidification, aluminium, Bohemian Forest, lake, phytoliths, silicon, silica, silicic acid, temperature

Introduction

Changes in silicon (Si) concentrations and fluxes of Si from terrestrial systems may reflect changes in chemical weathering. On a geological time scale of millions of years, changes in weathering rates affect the CO_2 concentration in the atmosphere through weathering of silicate minerals and transfer of CO_2 from the atmosphere to the lithosphere, primarily as $CaCO_3$ (Berner, 1994; Conley , 2002). Silicic acid may moderate Al toxicity in acidic soil (Lumsdon and Farmer, 1995; Hodson and Sangster, 1999; Exley *et al*., 2002) and the biological availability of phosphorus in the presence of aluminium (Exley *et al*., 1993; Kopácek *et al*., 2000; Krivtsov *et al*., 2000). Si may inhibit Al-induced reduction of bioavailable phosphorus by binding Al preferentially. Short-term variability of Si concentrations in streams relates to hydrology (Johnson *et al*., 1969), season (Norton *et al*., 1999; Gèrard *et al*., 2002; Soulsby *et al*., 2001) and diatom utilisation (Clarke, 2003).

The chemical weathering of silicate minerals is the primary source of Si in the environment (Oliva *et al*., 2003; White

and Blum, 1995) but biogenic silica (BSi = phytoliths + diatoms fossils) may be the principal immediate source of Si in soil solution (Farmer *et al*., 2005). Si is not conservative during weathering. Vegetation causes higher soil acidity through the production of organic acids and elevated carbonic acid (Marchetto *et al*., 1995), both of which accelerate chemical weathering. Plants play a major role in the recycling of soluble silica. Vegetation produces phytoliths, which return Si to soil with litter (Bartoli and Wilding, 1980; Conley, 2002; Farmer, 2005). Soils may have several percent of phytoliths. Wood species produce a high proportion of phytoliths containing Al (Cartelli *et al*., 2002). Dissolution rates of phytoliths may vary by 1–2 orders of magnitude, depending on coatings and Al concentration (Iler, 1973; Van Bennekom *et al*., 1989). Lake sediment contains up to tens of percent of diatoms and sponge spicules (Clarke, 2003). Interstitial water of lake sediment is enriched with dissolved Si that diffuses back into water (House *et al*., 2000; Rickert *et al*., 2002), increasing Si in the water column in the lake. In streams and lakes, dissolved Si

originates considerably from the dissolution of biogenic silica (Farmer *et al.*, 2005). Determination of Ge/Si ratios (Derry *et al.*, 2005) enables determination of the relative contribution of two main sources of Si (BSi and non-biogenic (soil minerals)) to Si cycling.

Here, 18-year trends in Si concentrations in five lakes and their principal inlets in the Bohemian Forest, Czech Republic, have been examined. This central European area has been recovering rapidly from atmospheric acidification (Veselý *et al.*, 1998a; Kopácek *et al.*, 2001) with a subsequent decrease in dissolved Al in streams and lakes (Veselý *et al.*, 1998b) and is experiencing a significant increase in average annual air temperature (Kettle *et al.*, 2003; Veselý *et al.*, 2003). The effects of increased temperature and decreased Al concentrations on the long-term increases of Si concentrations have also been evaluated.

Sites and Methods

Small lakes of glacial origin (Plešné, Certovo, Cerné, and Prášilské) are situated in the Bohemian Forest of the south-western Czech Republic between 13°11′ and 13°52′ E, and 48°47′ and 49°11′ N at elevations of 1008 to 1090 m a.s.l. Their water residence times are less than 20 months. Bedrock is granite in the Plešné Lake catchment and predominantly schist in the catchments of the other lakes (Veselý, 1994). Soils are acidic (pH_{CaCl2} of 2.5–4.5) and shallow (< 0.2 m deep) leptosol or < 0.5 m deep spodo-dystric cambisol and podzol. Base saturation is low (9–15 %) (Kopácek *et al.*, 2002). All but the Prášilské catchment are forested with 90 to 150-year old Norway spruce. During the present monitoring, the Prášilské catchment was ~50 % deforested by gales and bark beetle infestation.

Lake water samples were collected each year from the epilimnion of each lake and a principal inlet to the lake near the end of July and in the second half of October. Four to six water samples were collected during each sampling. Numerical average concentrations for each sampling were used for this analysis. During thermal stratification in July, samples were also collected from four to six depths in each lake between the surface and bottom at the deepest points in the lake and volume-weighted mean lake concentrations were calculated using known bathymetry. Seventeen inlets to Certovo, Plešné and Cerné lakes were sampled approximately monthly from 1997 to 2003.

Analytical methods are described in Veselý *et al.* (1998a) and Kopácek *et al.* (2000) and were identical throughout the study. Total Si and Al in lakes were determined by ICP-OES, and dissolved Si by the molybdate-blue technique in filtered (0.45 μm) lake samples. The difference between total Si and *in situ* dialyzable Si (in true solution) in lake samples

was ≤ 10%. Labile (ionic) aluminium (Al_i) was determined according to Driscoll (1984) and Dougan and Wilson (1974).

Data on air temperature and precipitation at Churánov station (at 1118 m a.s.l. among the lakes in the Bohemian Forest) were from the Czech Hydrometeorological Institute. Bulk precipitation during the 12-month period preceding lake sampling ranged from 846 mm (1991/92) to 1661 mm (2001/02) at Churánov site with no significant trend over the study period. Changes in ground temperature, caused by increasing air temperature, were calculated; air temperature is a crude but reasonable surrogate for soil temperature (Velbel, 1993). The mean air temperatures of the individual hydrological years observed since 1961 at Churánov were used as a forcing function at the ground surface. Negative values of monthly air temperature averages were substituted by 0 °C for calculation due to snow insulation of bedrock in winter. Subsurface temperatures at several depths and times were calculated according to Lewis (1992) using values of thermal conductivity of 1.0×10^{-6} m^{-2} s^{-1} and 1.3×10^{-6} m^{-2} s^{-1} for mica schist and granites, respectively.

Results

LONG-TERM TRENDS IN SI CONCENTRATIONS

Mean concentrations of Si in the lakes ranged from 51 to 99 μmol L^{-1}. The highest was Plešné Lake, situated on coarse-grained granite. Increasing Si concentrations occurred in all the lakes (Figs.1 and 2) and in many inlets. The rate of Si increase in lakes ranges from 0.95 to 1.95 μmol L^{-1} yr^{-1} between 1986 and 2004, a relative increase of 36 to 51% in 18 years. The Si increase in lakes and tributaries was more pronounced between 1994 and 2001 (see Cerné in Fig. 1). Concentrations of Si in lakes and residuals of Si, ΔSi, from a linear increase with time, do not relate directly ($p<0.05$) to average air temperature or precipitation volume in the year preceding sampling. Concentrations of Si in the principal inlets were generally higher and increased from 2.14 to 3.48 μmol L^{-1} yr^{-1}, i.e. faster than in lake water (Fig.1). Because concentrations of Si in precipitation are < 3.3 μmol Si L^{-1}, the source of the Si increase must be terrestrial.

Concentrations of Si were regularly lower in weakly acidified, shallow Laka Lake in summer (Fig. 2) when surface warming supports Si and NO_3 depletion by phytoplankton and uptake of Si from soil solutions by vegetation (Farmer *et al.*, 2005; Soulsby *et al.*, 2001). This seasonal variation occurs only in this lake and is superimposed on the long-term increase of Si concentrations observed for both the July and October sampling (Fig. 2).
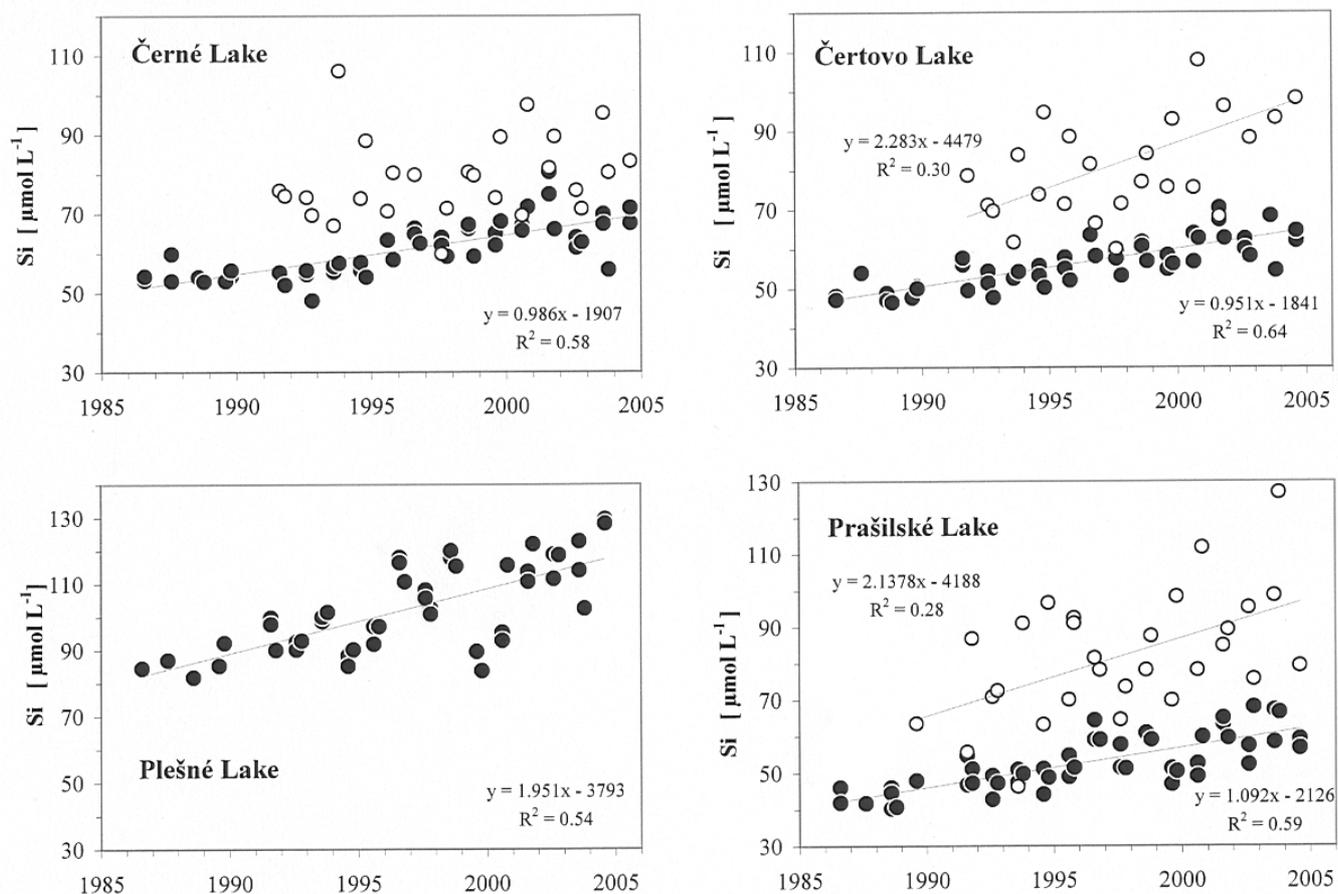
Fig.1. *Concentrations of Si in the Bohemian Forest lakes and main inlets from 1986–2004.* ● *– the average concentrations of Si for lakes in July and October;* ○ *– Si in main inlet; dotted lines = regression; an inlet to Cerné Lake was only main inlet to lakes without a significant (p<0.05) increase in Si concentration.*
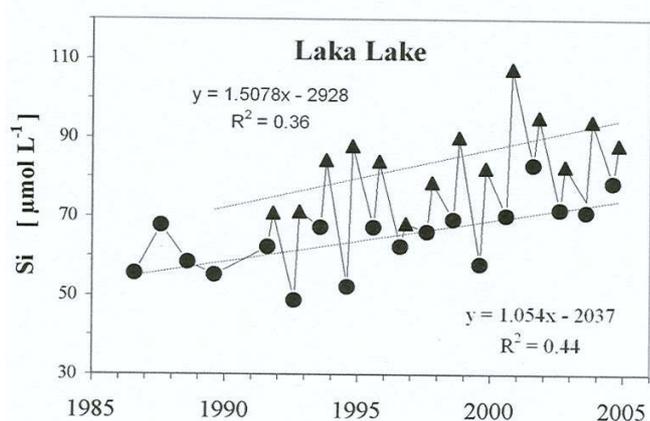

Fig.2. *Concentrations of Si in Laka Lake from 1986–2004.*
The average concentrations of Si are presented separately for July (●) and October (▲); the autumn concentrations were regularly higher in the lake suggesting seasonal variability in Si concentration in this weakly acidic and shallow lake. However, Si concentrations have increased both in summer and autumn.

Concentrations of total Al (Al_T) were relatively low (< 10 µmol L^{-1}) and Al was mostly bound to dissolved organic matter in Laka Lake due to a higher mean pH (pH ~5.7). In the four more acidified lakes, Si and Al_T were negatively related (Fig. 3). In these lakes, Al concentrations were related to concentrations of strong acid anions (SAA = sulphate + nitrate + chloride), i.e. to acidic atmospheric deposition (Veselý *et al.*, 2003; Veselý *et al.*, 1998b). The Si concentrations were negatively related to SAA.

The linear Si–Al relationship (Fig. 3) probably represents a connection between Si concentration and atmospheric deposition of acids and Al may be an intermediate (Van Bennekom *et al.*, 1989). The logarithm of Si concentration increased with the pH in the four strongly acidified lakes (e.g. Prášilské Lake, Fig. 4a). The relative increase in Si, $\Delta Si / Si$, defined as the ratio between the change in Si concentration and mean Si concentration over the study period, ranged between 0.016 and 0.023 yr^{-1}. $\Delta Si / Si$ probably increases with mean pH in weakly acid lake water
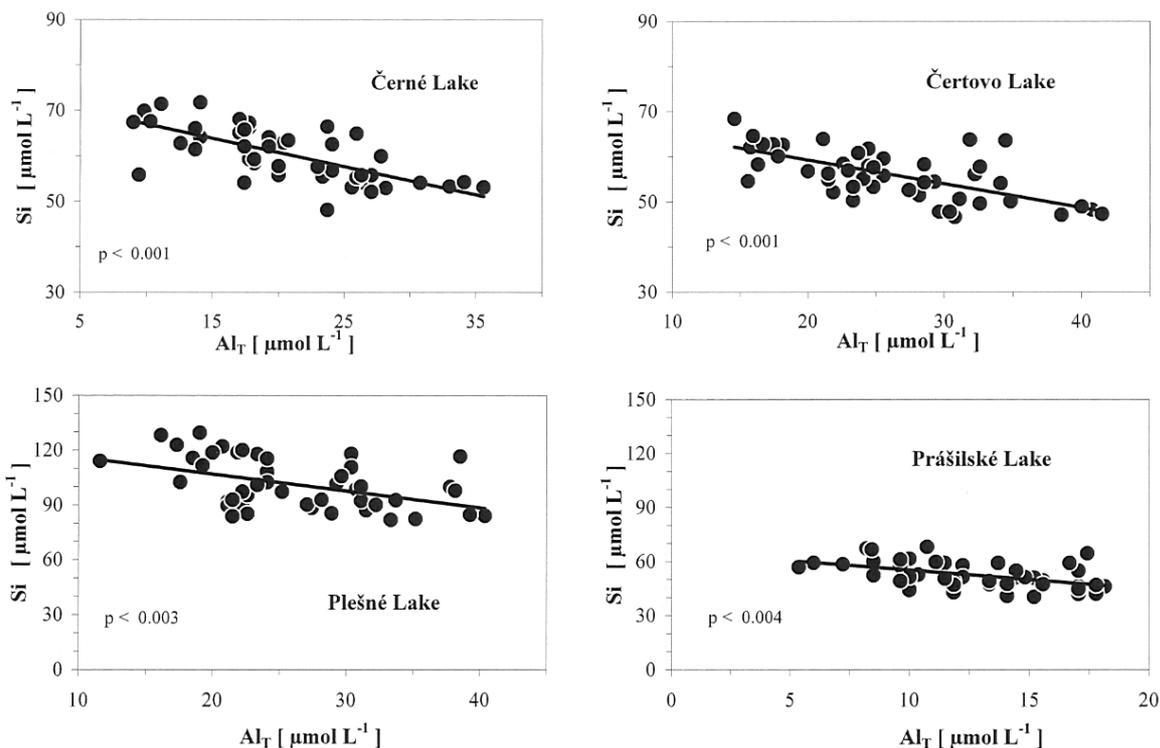
Fig. 3. *Relationships between Si and Al_T in formerly highly acidified lakes from 1986–2004. Strong inter-relation between Si and Al concentrations suggests they are regularly related.*
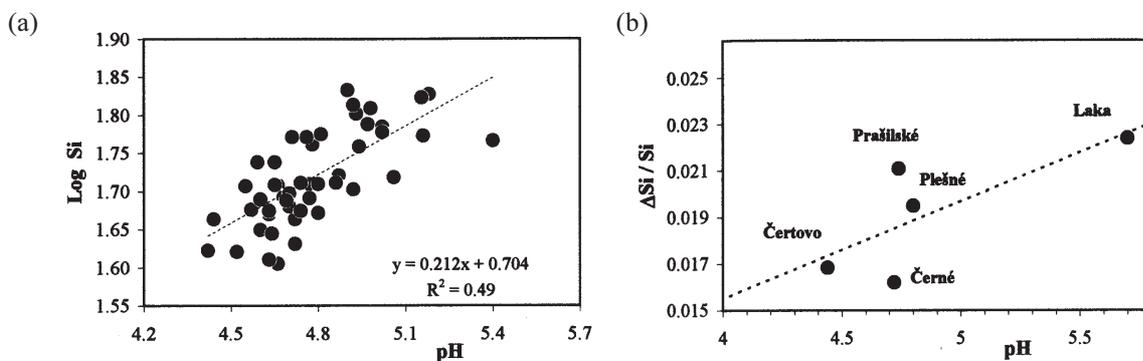

Fig. 4 *(a) Relationship between Log Si and pH in Prášilské Lake from1986–2004. Concentrations of Log Si have increased with pH suggesting that the process behind the Si increase in the lakes is dependent on the acid-base status in the catchment. (b) Relationship between relative increase of Si ($\Delta Si / Si$) and pH.*

(Fig. 4b). The processes controlling change of Si in lake water are pH-dependent (Fig. 4). However, the present results, surprisingly, show higher mobility of Si with increasing pH and in spite of lower deposition of acids.

Short-term variability of Si in streams

Daily and seasonal fluctuations in stream chemistry are dependent on many processes, especially mixing of base- and storm-flow. In most of the inlets to the lakes,

concentrations of Si decreased exponentially with increasing discharge (Q) (Fig. 5a). Decreases in solute concentrations with runoff are commonly attributed to dilution of base flow chemistry by storm- or melt-water. To separate short-term chemical effects from hydrological control in tributaries, residuals of Si were calculated from a linear regression of Si against log Q. Residuals, ΔSi, for nine of the 17 streams sampled from 1997 to 2003 were negatively related (p< 0.05) to stream water temperature (Fig. 5b). At higher stream water temperatures, Si concentrations tended to be below
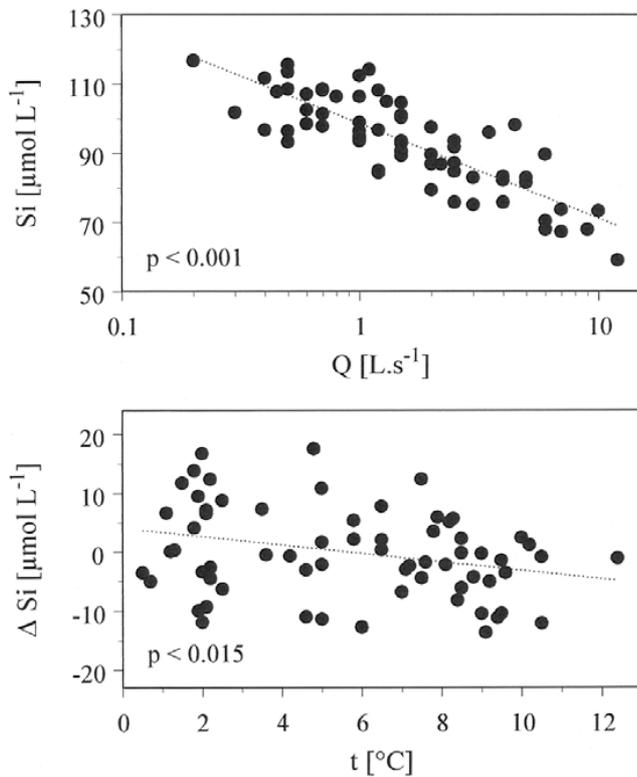
Fig. 5 (*a*) *Relationship between Si and log discharge (Q) from lake tributaries. Concentrations of Si decreased exponentially with discharge in most tributaries. (b) Residuals of Si, (ΔSi), from linear regression of Si with log Q were generally more negative at higher temperature. To separate temperature from hydrological effects, residuals of Si, (ΔSi), from a linear regression of Si against log Q were calculated at higher stream water temperatures, Si concentrations tend to be below the regression line in most of streams. The likely cause is increased plant uptake of Si from soil solution during the growing season.*

the Si/Log Q regression line in most of the streams. This suggests uptake of Si by vegetation at higher seasonal temperatures.

Discussion

Acidification of the lakes peaked in the mid-1980s (Vrba *et al.*, 2003; Kopácek *et al.*, 2001; Veselý *et al.*, 1998a). From 1986 to 2004, Si has increased, Na has remained relatively constant and concentrations of all other major solutes have decreased. Strong decrease of the SAA in water was compensated mostly by reduction of inorganic (labile) Al (Veselý *et al.*, 1998b; Kopácek *et al.*, 2000). The decline in inorganic Al was enhanced by climate warming (Veselý *et al.*, 2003).

The concentrations of Si in the five lakes increased by 36 to 51% between the summers of 1986 and 2004. Repeated regional surveys of freshwaters in the Czech Republic and

small catchment monitoring (Hruška *et al.*, 2002) showed that the increase in Si concentration is a general phenomenon for mountainous-forested areas in that period. Concentrations of Si have increased also in lakes of the Alps (Sommaruga-Wögrath *et al.*, 1997; Rogora *et al.*, 2003), and in northern-Italian rivers (Mossello *et al.*, 2000). In contrast, volume-weighted concentrations of Si in the Hubbard Brook Experimental Forest stream water show no long-term trend over the 1965–1987 period (Driscoll *et al.*, 1989). Si was unchanged in a pair of acidifying streams at the Bear Brook Watershed in Maine for the period 1987–2003 (Norton *et al.*, 1999). Therefore, there are regional differences in long-term trends in Si concentrations. Two hypotheses have been explored to explain the long-term increase observed in Si concentrations in the Czech Republic:

1. *Effect of temperature (climate warming).* The increase of Si in lakes of the Alps was accompanied by an increase in base cations that was explained by an increase in the rate of weathering induced by climate warming (Sommaruga-Wögrath *et al.*, 1997). The present study is in an area of warming (Weber *et al.*, 1997; Schär *et al.*, 2004) and a negative effect of temperature on Al concentrations in the same lakes has been observed. While the solubility of BSi and weathering rate increase with temperature, the solubility of the secondary aluminosilicates decreases. Consequently, the possible effects of increasing temperature on Si concentrations have been evaluated.

Average weathering rates of minerals depend on temperature according to the Arrhenius law (White and Blum, 1995):

$$K_w (T) = K^o_w \exp(-E_a/RT) \qquad (1)$$

where K_w is the rate constant (mol ha^{-1} yr^{-1}) at temperature T (K degrees), K^o_w is its value at a given reference temperature, E_a is apparent activation energy of the reaction and R is the gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}). Average air temperature in the year preceding water sampling ranged from 3.28 to 5.75 °C in the Bohemian Forest and increased irregularly during the 18-years of observation (Kettle *et al.*, 2003; Veselý *et al.*, 2003). Long-term warming proceeds slowly from soil into bedrock where temperature change lags behind air temperature change substantially. Calculated theoretical change in subsurface (bedrock) temperature with depth over the period 2004 to 1986 was about 0.7, 0.45, and ~ 0.35 °C at depths of 0, 10 and 20 m respectively. From Eqn.1 for E_a = 69 kJ mol^{-1} (White and Blum, 1995) a warming theoretically increases the weathering rate by about 8, 5, and 4% at depths of 0, 10 and 20 m, respectively.

Concentrations of Si in the lakes have increased substantially more.

Dissolution of amorphous (biogenic) silica also increases with temperature. The change in equilibrium solubility of BSi caused by long-term temperature change over the period studied can be calculated from

$$Ln \; (K_{T1}/K_{T0}) = -\Delta H_r^o/R \; [1/T_1 - 1/T_o] \qquad (2)$$

where ΔH_r^o is the standard heat of dissolution for the reaction, R is the gas constant, T_1 and T_0 are temperatures in K degrees at the beginning and end of the study. The effect of a temperature increase of ~0.7 °C on the solubility of amorphous silica and phytoliths suggests an increase in Si of only about 2% for standard heats of dissolution, $\Delta H_r^o = 15$ (amorphous silica) and 22 (phytoliths) kJ mol^{-1} (Farmer *et al.*, 2005; Gustafsson *et al.*, 2001). Increased temperature also enhances evapotranspiration and vegetative cycling of Si. More frequent soil drying (Simonsson *et al.*, 1999) and less frequent soil freezing (Dietzel, 2005) may also contribute to an increase in Si in freshwater. Nevertheless, combined temperature effects cannot explain the relative increase in Si observed in the lakes. Lastly, the dissolution of forest phytoliths is independent of pH at values below 6 (Bartoli and Wilding, 1980) but the process behind the increase in Si in lakes is pH-related.

2. *Decrease in Al mobility.* Atmospheric acidic deposition has decreased sharply (Kopácek and Veselý, 2005), the pH of lake waters has increased (Fig.4a) and, consequently, the mobility of Al decreased substantially. Si is negatively related to Al (Fig. 3). The relative change in Si, (ΔSi / Si), may increase with mean pH of lake water in the range 4.4 to 5.7 as well as log Si concentrations with increasing pH (Fig.4). The process behind the long-term increase in Si is more obvious at higher pH in weakly acidic environments where dissolved Al concentrations become especially low. Concentrations of Al$_T$ have decreased 60 to 75% from initial values of 41 to 18 μmol L^{-1} and concentrations (activity) of Al^{3+} even more. Three alternative hypotheses are proposed:

(a) less Si may be precipitated in soil as secondary aluminosilicates (Doucet *et al.*, 2001; Exley *et al.*, 2002), because of lower amounts of Al dissolved in the soil solution. Silica that previously was precipitated as secondary aluminosilicates may remain free, increasing Si in soil solutions, streams and lake water;

(b) lower Al mobility means lower incorporation of Al into and adsorption onto BSi (phytoliths and diatoms). Aluminium on these phases dramatically slows down BSi dissolution (Iler, 1973; Bartoli and Wilding, 1980;

Van Bennekom *et al.*, 1989; Dixit *et al.*, 2001; Rickert *et al.*, 2002). Al-free BSi dissolution kinetics may be much faster;

(c) lower dissolved Al means less restricted weathering (Chou and Wollast, 1985; Gèrard *et al.*, 1998). Above certain Al concentrations, rates of dissolution of aluminosilicates at constant pH exhibit a negative dependence on dissolved Al (e.g. Oelkers *et al.*, 1994). However, primary weathering should be related to pH negatively, in that Si should increase with decreasing pH; this is not what is observed. Precipitation of most secondary aluminosilicates increases with temperature. Therefore, from all the above options, the kinetic effect of Al speciation on the dissolution rate of BSi, the solubility of which is independent of pH below 6 (Bartoli and Wilding, 1980) is preferred. The increase in Si is dependent on pH due to an acid-base limitation of Al solubility and migration in a weakly acidic environment.

Conclusion

Silica concentrations in five Czech lakes have increased despite lower acid deposition. This behaviour of Si is paradoxical because weathering (the primary source of Si) should accelerate in more acidic environments. Yet, it seems that a sharp decrease in soil Al mobility and dissolved Al increases the rate of biogenic silica dissolution. Concentrations of ionic Al decreased, primarily because of a reduction in atmospheric deposition of acids coupled with increased soil water pH and secondarily because of temperature increases. If correct, the effect will decline as Al^{3+} concentration becomes so low that the dissolution rate of BSi becomes independent of free Al concentration as is the case in many parts of the world. Climate warming adds to the decrease in Al. The change in Si concentration in lakes was kinetically rather than thermodynamically induced.

Acknowledgements

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