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# High concentrations of amorphous, biogenic Si (BSi) in the sediment of a small high-latitude lake: implications for biogeochemical Si cycling and for the use of BSi as a paleoproxy

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**Abstract** The concentration of biogenic silica (BSi) in soils and sediments may be studied for several purposes, most notably either as a paleo-environmental proxy or to clarify the transport of weathering-derived Si within the biogeosphere. With this in mind, we explored the reasons behind the very high BSi concentration (average 250 mg Si g<sup>-1</sup> dry mass) in the sediment of a small, high-latitude lake in Finnish Lapland, Lake Kuutsjärvi, using bulk BSi and stable Si isotope analysis of major Si pools in the lake and its drainage area. The high BSi content of the sediment was relatively stable over the past few hundred years and recent changes in the food web of the lake were not clearly reflected in the data. The origin of the sedimentary BSi was not solely autochthonous diatom production: extraneous sources accounted for possibly as much as 54–88 % (isotope analysis). A main reason for the high BSi content appeared to be the transport of older deposits of diatom material from the drainage area into the current lake basin, although other factors such as good preservation conditions may have contributed. Although our results indicate that small high-latitude lakes may be hot-spots in the burial of BSi, more information is needed on the processes that affect the translocation of BSi from the drainage area to the aquatic system. Caution is advisable when past lake conditions are inferred from sedimentary BSi only.

**Keywords** Sediment · Biogenic silica · BSi · Phytolith · Lake · Stable isotopes

## Introduction

Biogenic silica (BSi) is an amorphous form of silicon (Si) constructed by a diverse number of organisms. It is primarily used as a protective shell or frustule by aquatic diatoms (*Bacillariophyceae*, cf. Hecky et al. 1973), some chrysophytes (*Chrysophyceae*), silicoflagellates (*Dictyococcales*, cf. Adjou et al. 2011), sponges (*Porifera: Demospongiae* and *Hexactinellida*, cf. Maldonado et al. 2005), or as structural support for many land plants, where BSi is precipitated in amorphous form as phytoliths (see Epstein 2001; Piperno 2006). As BSi remains are preserved relatively well in soils and sediments, and as many species produce species-specific, original structures, BSi remains are commonly used paleo-indicators in both aquatic and terrestrial environments (cf. Battarbee 1986; Piperno 2006). Bulk BSi is also used as an indicator of past aquatic productivity (see Fortin and Gajewski 2009 for a review), mostly in combination with other paleo-indicators. The Si isotopic composition of diatom BSi has also been used to infer past changes in, e.g., climate (e.g. De La Rocha et al. 1998; Opfergelt and Delmelle 2012; Hendry and Brzezinski 2014).

The production and dissolution of different forms of amorphous or biogenic Si is, however, also the main driving force behind the global short-term (non-geological) biogeochemical cycling of Si (Tréguer and De La Rocha 2013), making the occurrence of BSi in different aquatic and terrestrial environments as well as the processes affecting it important in several further ways. The importance of BSi in the biogeochemical Si cycle is based on the

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fact that although Si is one of the most common elements on Earth and is present in vast quantities in most rocks and soils, most of this lithogenic Si is structurally bound into mineral form from which it is released only through slow weathering reactions on geological time-scales (Lerman 1988). The pool of biogenic, amorphous Si cycles at a substantially faster rate, as its solubility is of a different order of magnitude than that of mineral Si (approximately  $2 \times 10^{-9}$  versus  $6 \times 10^{-14}$  mol cm<sup>2</sup> s<sup>-1</sup>, Hurd 1983; Lerman 1988).

The overall importance of the biogeochemical Si cycle is related largely to the importance of diatoms in aquatic systems. Silicon-requiring diatoms are one of the main groups of primary producers globally: i.e., they are responsible for an estimated 25–45 % of the total, global primary production, and one of the most common phytoplankton groups in most aquatic environments (Mann 1999; Tréguer and De La Rocha 2013). Due to their heavy, Si-containing frustules and their ecological preferences, most diatoms also have high sedimentation rates (Smetacek 1985). As most other groups of phytoplankton do not require Si at macronutrient levels, changes in the supply or recycling of Si to or within the aquatic environment may thus affect the structure of the aquatic phytoplankton community (e.g. Egge and Asknes 1992; Yool and Tyrrell 2003), with low availability of Si leading to dominance by other phytoplankton groups and higher availability to an increased competitive advantage for diatoms. This has important consequences for the functioning of the aquatic ecosystem and food web: the supply of Si may be what at certain times determines whether the system is dominated by high diatom biomasses and high sedimentation (export production, cf. Dugdale and Goering 1967), or a higher proportion of other phytoplankton groups (flagellates, cyanobacteria) with intensive recycling of organic material and nutrients in the pelagic system. Further, the prevalence of diatoms is also connected to the carbon (C) cycle, as the high sedimentation of diatoms and organic material with its concomitant immobilization of C (the Si or C pump, cf. Dugdale et al. 1995; Tréguer and Pondaven 2000) is a major sink for C globally.

The importance of the terrestrial bio-geosphere in the short-term cycling of Si has, on the other hand, been fully recognized only relatively recently (but see Bartoli 1983), and its relevance for the supply of Si to aquatic systems as well as the importance of Si for terrestrial plants are only beginning to be understood (Epstein 1999; Conley 2002; Cornelis et al. 2010; Struyf and Conley 2009, 2012). As, however, the annual fixation of Si into amorphous, biogenic form as phytoliths has been estimated to range between 60 and 200 Tmol a<sup>-1</sup> (Conley 2002; Laruelle et al. 2009), i.e. within the same order of magnitude as the aquatic BSi fixation (Tréguer et al. 1995; Tréguer and De

La Rocha 2013), it is clear that it is necessary to include the terrestrial aspects of the short-term Si cycle in all calculations. The aquatic aspects of the biogeochemical Si cycle are better known (Tréguer et al. 1995; Laruelle et al. 2009; Tréguer and De La Rocha 2013), but there are gaps in our knowledge of, in particular, the connections between the terrestrial and aquatic parts of the Si cycle (Struyf and Conley 2009; Dürr et al. 2011). As burial of BSi in aquatic sediments is an important drawdown mechanism for both Si and C (Tréguer and Pondaven 2000), it is important to recognize potential hotspots for this burial and the mechanisms behind it. The importance of small lakes and watersheds in the burial of Si (and C) is still largely unknown, especially in high latitude areas, despite the fact that this may be one of the regions most affected by global warming (Smol et al. 2005). Moreover, small lakes (<0.01 km<sup>2</sup>) comprise ca. 91.3 % of the number of lakes globally and cover ca 16.5 % of the total lake area (Downing et al. 2006).

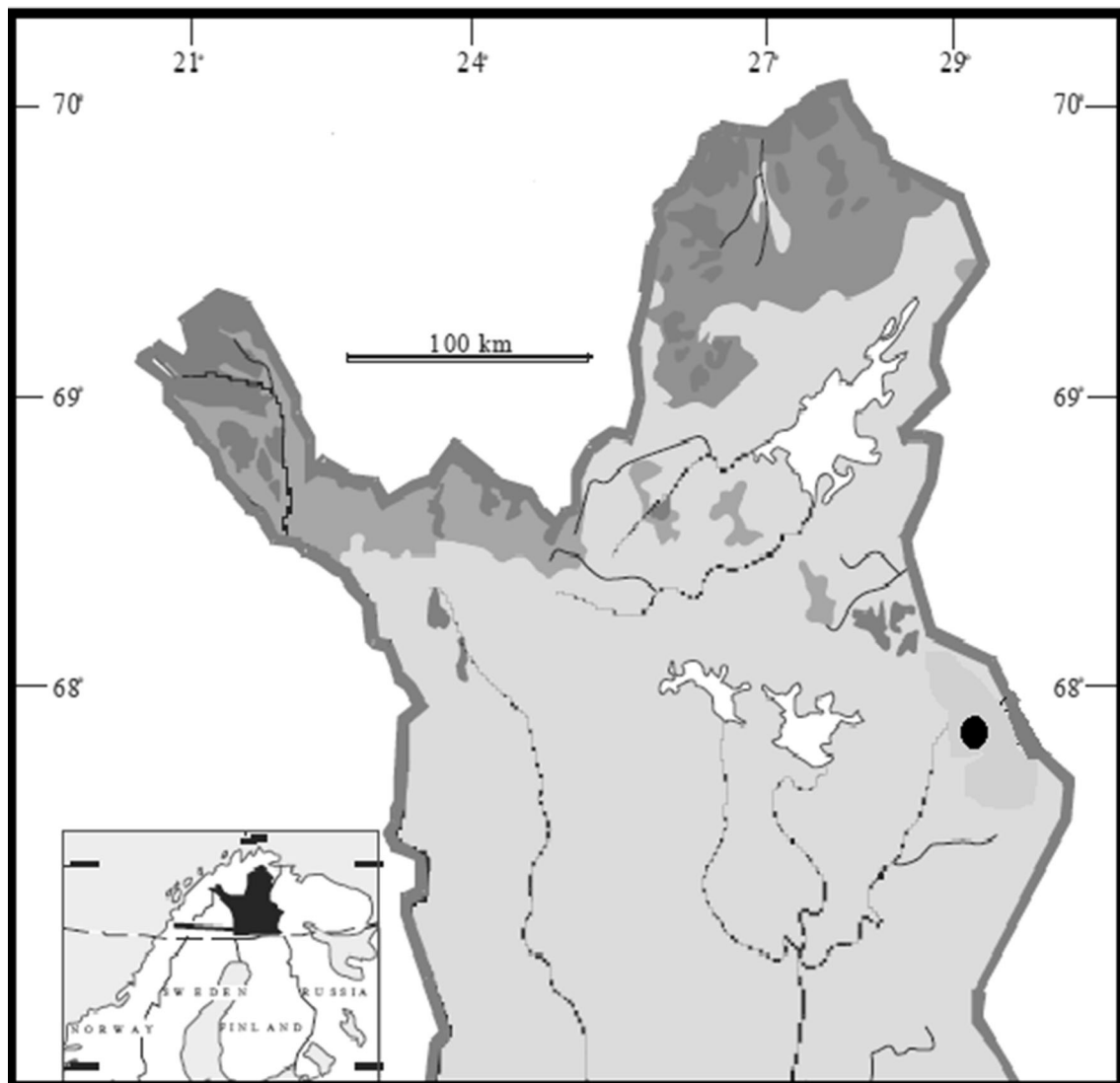
Silicon isotopes have during the past 20 years emerged as a powerful tool in, especially, marine sciences, where the <sup>30</sup>Si/<sup>28</sup>Si ratio ( $\delta^{30}\text{Si}$ ) measured from sediment BSi has been extensively used to reconstruct past conditions of e.g. productivity and climate (De La Rocha et al. 1997, 1998; Cardinal et al. 2005; Hendry et al. 2010). The method is based on the preferential incorporation of the lighter isotopes into diatom frustules during growth (De La Rocha et al. 1998). Recently, Si isotope ratios have also been used to determine the origin of Si in soil and runoff with the aid of other naturally occurring chemical and biological fractionation processes (Georg et al. 2006a; Opfergelt et al. 2008; Demarest et al. 2009; Cornelis et al. 2011).

In this study, we conducted a survey of the Si budget of a small high latitude lake. Our main goals were to (1) clarify the processes influencing the accumulation of Si in the lake sediment, using the potential of Si stable isotopes as a tracer in this context, and (2) to study the feasibility of bulk BSi measurement as a paleo-indicator of past environmental changes. Our study also provides more information about so-far insufficiently studied areas, such as the importance of high-latitude areas in Si cycling and Si transport from the terrestrial to the aquatic part of the drainage area.

## Materials and methods

### Study area

The main study lake, Lake Kuutsjärvi (67°45'N, 29°37'E; 341 m a.s.l.;  $D_{\text{max}} = 8.2$  m, surface area <1 ha) is an oligotrophic lake located in north-eastern Finland inside the Värriö Strict Nature reserve (Fig. 1). In 1967 the Värriö



**Fig. 1** The location of the study area in Finnish Lapland. The Värriö area where Lake Kuutsjärvi is found is indicated by the *black dot*

research station (University of Helsinki) was established on the lake shore and in 1982 brown trout (*Salmo trutta m. lacustris*) were introduced into the lake. The lake is situated in an area where the bedrock consists mainly of Archean gneiss and migmatites (Hirvas 1991). The soil layer is shallow (0–20 cm in sampled area) and dominated by moraine and sandy deposits (Hirvas 1991; Johansson 1995). The vegetation is primarily made up of forests dominated either by Scots pine (*Pinus sylvestris*, ca 60 % of total area) or by a combination of Norwegian spruce (*Picea abies*) with some mountain birch (*Betula pubescens subsp. tortuosa*, ca 40 %). The ground vegetation is dominated by blueberry (*Vaccinium myrtillus*), lingonberry (*Vaccinium vitis-idaea*), juniper (*Juniperus communis*), different lichen and mosses and heather (*Calluna vulgaris*). Some peatland (bog) occurs beside the lake. The lake

catchment has an area of ca 1.5 km<sup>2</sup> and contains steep hillsides of high relief.

The supplementary study lakes (here named Lakes Tippakuru, Pirunkuru and Välijärvi, Fig. 1) are situated within a few km of Lake Kuutsjärvi. The vegetation, bedrock and soil characteristics of the lakes are as described above with small deviations in e.g. vegetation coverage. Trout were also introduced into Lake Pirunkuru and Välijärvi in the 1980s, while Lake Tippakuru remained fishless.

#### Water samples

Surface (0–1 m) water samples were taken from Lake Kuutsjärvi and Lake Tippakuru using a Limnos tube sampler at two-week intervals during the ice-free period of

2010 (June 9–October 6). These samples were analyzed for total P and N, PO<sub>4</sub>-P (both 0.2 µm filtered and non-filtered), NO<sub>2</sub> + NO<sub>3</sub>-N, total Fe, chlorophyll *a* (chl *a*), dissolved organic carbon (DOC) and total organic carbon (TOC) at the laboratory of the Lapland Centre for Economic Development, Transport and the Environment using the standard methods of the Finnish Environment Institute. In addition, a water sample (0–8 m) was taken from beneath the ice cover on April 15, filtered (0.2 µm) and analysed for total Al, Fe, Mn, P, and Si using ICP-OES at the University of Helsinki. A composite water sample (0–8 m) and samples from the in- and outflows of the lakes were taken from the lake on June 10, filtered (0.2 µm) and analysed for dissolved Si (DSi) using a standard spectrophotometrical method (blue ammonium-molybdate complex, Mullin and Riley 1955). Data on DSi concentrations in lakes from Northern Finland (Lapland province, *n* = 694) were gathered from the HERTTA database at the Finnish Environment Institute. Only measurements made by spectrophotometric methods were included in order to ensure that all measurements were comparable.

#### Sediment and soil samples

Sediment samples (0–15 cm, several replicate cores) were collected at the deepest point (8 m) of Lake Kuutsjärvi in April 2010 using a gravity corer. The cores were subsampled at varying thickness (0.25, 0.5 or 1 cm) according to use and depth (see below). Approximate water content (105 °C) and organic matter content (estimated as loss on ignition, 550 °C; cf. Heiri et al. 2001) were determined at depth intervals of 0.25 cm from 0 to 7 cm sediment depth and 0.5 cm from 7 to 15 cm depth. One sediment core was dated by gamma spectrometry at the Environmental Radioactivity Laboratory, University of Liverpool, England. The analysis was done based on <sup>210</sup>Pb, <sup>226</sup>Ra, and <sup>137</sup>Cs by direct gamma assay using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby et al. 1986).

Biogenic Si content (BSi) was determined from 0–1, 1–2.5, 2.5–5, 5–10, 10–15 and 15–20 cm composite sediment samples according to DeMaster (1981). The sediment was dried (60 °C) and mortar-ground, whereafter 30 mg of dry sediment was weighed into polyethylene 100 ml bottles (Plastex Ltd) and extracted with 40 ml 1 % sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) in a +85 °C water bath for 5 h (pH 10.6) with intermittent shaking. After 3, 4 and 5 h, 1 ml samples for Si analysis were taken, diluted with 9 ml of 0.021 N HCl, and analysed for DSi (Mullin and Riley 1955). The BSi concentration of each sample was calculated as the intercept of the linear regression line through the time points based on the assumption that all BSi in the sediment samples has dissolved during the first 3 h of the

extraction, while mineral-derived Si is dissolved from the sample in smaller amounts at a constant rate throughout the extraction (see Conley 1998 or Tallberg et al. 2009 for further references and discussions on the errors involved). For comparative purposes, additional BSi surface sediment samples (0–5 cm) were taken from Lake Kuutsjärvi and from Lakes Tippakuru, Pirunkuru and Välijärvi in May 2012 using the same gravity corer and sample preparation procedure as described above. BSi was analysed from these sediment samples as above. The DSi concentration of the sediment interstitial water was determined from the Lake Kuutsjärvi sediment samples (1–2.5, 2.5–5, 5–10, 10–15 and 15–20 cm) after manual filtration through 0.2 µm polypropylene syringe filter membranes (Ø 25 mm, WWW International). DSi was determined from the interstitial water samples using the same standard spectrophotometrical method as above (Mullin and Riley 1955).

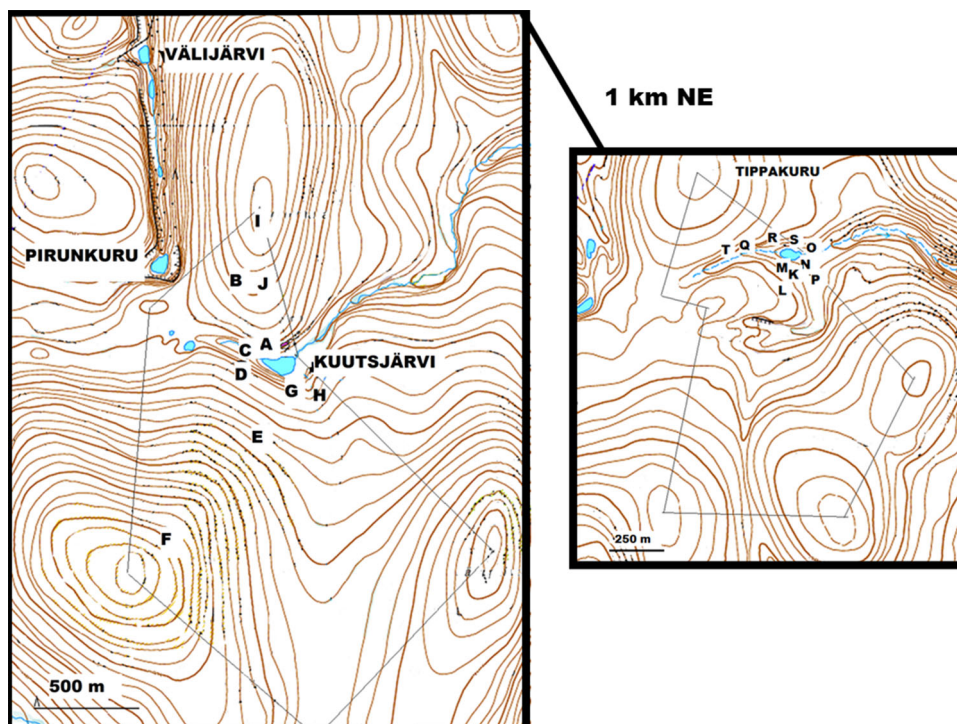
Soil samples (litter and topsoil separately) were taken from 10 sites in the Lake Kuutsjärvi and eight sites in the Lake Tippakuru catchment areas (Fig. 2). While most of the sites were dominated by pine or spruce forest they included an open, stony site from the highest point of the catchment and a swampy bog site near the lake; more details are shown in Table 1. The litter sample was collected from the top layer by hand and consisted of the previous year's litterfall. Soil samples were collected with a soil corer (diameter 2 cm) and represented a composite of the whole soil layer (total depth 5–15 cm). Five parallel samples were combined before analysis for both litter and soil samples. Biogenic Si was analysed from the composite dried (60 °C) and mortar-ground samples as above.

Slides for microscopic examination of sediment, soil and litter samples were prepared by adding 5 ml of 30 % H<sub>2</sub>O<sub>2</sub> to 0.01 g of dry material in plastic 12 ml test tubes, heating the suspension in a water bath at +80 °C for 4 h and adding a few drops of 18 % HCl. Thereafter, the samples were washed by filling the test-tubes with Milli-Q water, centrifuging for 10 min at 3,000 rpm, and decanting the liquid. This process was repeated four times. Slides were mounted using Naphrax and examined using a Zeiss microscope.

#### Stable isotope samples

A rough approximation of the Si isotope compositions of the lake water, lake inflow water, litter, soil and sediment composite samples (June samples) was made in order to investigate the origin of the sediment BSi. Stable Si isotopes analyses were made at Université catholique de Louvain in Belgium according to the method from Opfergelt et al. (2011). Briefly, soil and litter samples were ashed to remove organic matter. Then ashed samples and sediment samples were dissolved by NaOH fusion at 720 °C in

**Fig. 2** The soil and litter layer sample sites around Lake Kuutsjärvi (*left*) and Tippakuru (*right*). The approximate drainage area of Lake Kuutsjärvi and Lake Tippakuru is indicated by the *thin line* in each panel, and the location of the supplementary study lakes Pirunkuru and Välijärvi in the *left-hand* panel. The sample sites are marked with the letters A–J (Kuutsjärvi) and K–S (Tippakuru). The maps are based on data from the National Survey of Finland (09/13). The descriptions of the sites can be found in Table 1



**Table 1** The vegetation of the terrestrial sampling sites around Lakes Kuutsjärvi (A–J) and Tippakuru (K–S) and the concentration of BSi in the detritus or litter layer and in the soil (as mg Si g<sup>-1</sup> DM (dry matter), average with standard deviation in parentheses)

Sample ID (Fig. 2)	Dominant tree	Litter (mg Si g <sup>-1</sup> DM (SD))	Soil
A	Pine	0.7 (n.a.)	2.7 (n.a.)
B	Pine	1.4 (0.3)	3.0 (0.3)
C	Pine	1.0 (0.0)	3.4 (0.0)
D	Spruce	2.3 (0.2)	38 (0.6)
E	Spruce	1.6 (0.3)	3.7 (0.3)
F	Birch	1.9 (0.2)	2.8 (0.2)
G	Spruce	1.6 (0.2)	3.3 (0.0)
H	Birch	1.9 (0.1)	8.8 (0.1)
I	Pine	1.8 (0.1)	2.5 (0.5)
J	–	1.7 (0.0)	4.5 (0.2)
K	Pine	0.6 (0.1)	2.8 (0.1)
M	Spruce	1.7 (0.1)	3.0 (0.2)
N	Spruce	1.2 (0.1)	5.1 (0.2)
O	Birch	6.7 (0.2)	12 (0.2)
P	Spruce	2.5 (0.4)	8.7 (0.3)
Q	Pine	1.2 (0.2)	3.6 (0.3)
R	Pine	1.7 (0.1)	4.2 (0.3)
T	Spruce	1.0 (0.2)	1.7 (0.0)

See Fig. 2 for the exact location of the sampling sites

a silver crucible. Dissolved samples and water samples (lake water, lake inflow water, 0.2 μm filtered as above) were purified for isotopic measurements through cation

exchange resin (BioRad AG50W-X12; Georg et al. 2006b). Silicon isotope compositions were determined on a Nu Plasma MC-ICP-MS (instrument located at Université Libre de Bruxelles, Belgium), in dry plasma mode using a desolvating system Cetac AridusII, in pseudo-high (“medium”) resolution mode. The instrumental mass bias was corrected for by the sample-standard bracketing technique, and by using an external Mg doping.

The data are expressed in relative deviations of <sup>30</sup>Si/<sup>28</sup>Si ratios from NBS-28 silica sand standard using the common δ-notation (‰) where:

$$\delta^{30}\text{Si} = \left[ \left( \frac{{}^{30}\text{Si}/{}^{28}\text{Si}_{\text{sample}}}{{}^{30}\text{Si}/{}^{28}\text{Si}_{\text{NBS28}}} \right) - 1 \right] \times 1,000. \quad (1)$$

Each sample was analysed in replicates or triplicates, where each single δ-value (*n*) represents one sample run and two bracketed standard runs. Accuracy and reproducibility (δ<sup>30</sup>Si) were checked on reference material diatomite (+1.29 ± 0.12 ‰, 2SD, *n* = 6), and USGS rock standard BHVO-2 (−0.33 ± 0.10 ‰, 2SD, *n* = 2), which yielded isotope compositions indistinguishable from previously published values (Reynolds et al. 2007; Abraham et al. 2008).

The BSi extracted from the sediment was considered as BSi from phytoliths and diatoms. An isotope mass balance was used to calculate the proportion of Si from diatoms (*x*) and the proportion of Si from phytoliths (1 − *x*):

$$\delta^{30}\text{Si}_{\text{bulkBSediment}} = [\delta^{30}\text{Si}_{\text{diatom}} \times x] + [\delta^{30}\text{Si}_{\text{phytolith}} \times (1 - x)]. \quad (2)$$

The value for  $\delta^{30}\text{Si}_{\text{phytolith}}$  is assumed to be similar to the litter Si isotope composition. The value for  $\delta^{30}\text{Si}_{\text{diatom}}$  can be calculated as:

$$\delta^{30}\text{Si}_{\text{diatom}} = \delta^{30}\text{Si}_{\text{lakewater}} + {}^{30}\epsilon. \quad (3)$$

Based on the Si isotope composition of the lake water and using the isotope fractionation factor  ${}^{30}\epsilon$  associated to Si uptake by diatoms. A value of  ${}^{30}\epsilon$  at  $-1.1\text{‰}$  was determined in vitro (De La Rocha et al. 1997) and in situ (Fripiat et al. 2011) for marine diatoms, and validated in lakes (Alleman et al. 2005; Opfergelt et al. 2011).

## Results

An indication of the average water characteristics of Lakes Kuutsjärvi and Tippakuru is given in Table 2. The concentrations of total N, C (DOC and TOC), chl a and Fe were clearly lower in Kuutsjärvi than in Tippakuru, while the P ( $P_{\text{TOT}}$  and  $\text{PO}_4\text{-P}$ ) and Mn concentrations were higher in Kuutsjärvi. The average C/N ratio was 13 in Lake Kuutsjärvi and 22 in Lake Tippakuru.

The water content of the topmost sediments (average 0–15 cm) of Lake Kuutsjärvi was 89 % and the organic matter content 27 %. Based on the sediment dating, the

**Table 2** Data on the current (2010) composition of the water in Lakes Kuutsjärvi and Tippakuru

	$P_{\text{TOT}}$ ( $\mu\text{g l}^{-1}$ )	$\text{PO}_4\text{-P}$ ( $\mu\text{g l}^{-1}$ )	$N_{\text{TOT}}$ ( $\mu\text{g l}^{-1}$ )
Kuutsjärvi	21 (14–26)	10 (4.0–15)	150 (80–320)
Tippakuru	9.6 (7.0–13)	2.0 (–)	230 (110–450)
	CHLa ( $\mu\text{g l}^{-1}$ )	DOC (mg $\text{l}^{-1}$ )	TOC (mg $\text{l}^{-1}$ )
Kuutsjärvi	2.2 (0.9–2.5)	1.9 (0.9–2.5)	1.8 (0.9–2.9)
Tippakuru	3.1 (1.2–6.1)	4.5 (3.2–6.5)	4.5 (3.3–6.0)
	Fe ( $\mu\text{g l}^{-1}$ )	Al ( $\mu\text{g l}^{-1}$ ) <sup>a</sup>	Mg ( $\mu\text{g l}^{-1}$ ) <sup>a</sup>
Kuutsjärvi	11 (8.0–13)	430	740
Tippakuru	25 (10–34)	450	570
	Mn ( $\mu\text{g l}^{-1}$ ) <sup>a</sup>	Ca (mg $\text{l}^{-1}$ ) <sup>a</sup>	Si (mg $\text{l}^{-1}$ ) <sup>a</sup>
Kuutsjärvi	680	2.6	4.0
Tippakuru	530	1.9	3.8

The P, N, chl a, C and Fe values are average (min–max in parentheses) values from a total of 9 surface water (1 m) samples taken with 2–6 week intervals between April and October. The Al, and Mn values (marked with letter <sup>a</sup>) are from a single composite sample (0–8 m in Lake Kuutsjärvi, 0–6 m in Lake Tippakuru) taken in April 2010 (see text for information on measurement techniques)

sediment accumulation rate was very low ( $0.03\text{ cm year}^{-1}$ ) from the early 19th century until the beginning of the 1970s, where after it increased to around  $0.14\text{ cm year}^{-1}$  (Table 3). The building of the research station in 1967 and the introduction of trout into the lake in 1982 thus correspond to sediment depths of 2.6 and 2.8 cm, respectively. The sediment accumulation rates in Kuutsjärvi were clearly lower than in Tippakuru, where the rate was estimated as  $0.21\text{ cm year}^{-1}$  at present and  $0.04\text{ cm year}^{-1}$  in the 1850s.

The dissolved Si concentration in Lake Kuutsjärvi (composite sample) was  $4.8\text{ mg l}^{-1}$  beneath the ice in April and  $3.7\text{ mg l}^{-1}$  in June (see Table 4). The in- and outflow concentrations were 3.0 and  $3.4\text{ mg l}^{-1}$ , respectively (Table 4). The concentrations in Lake Tippakuru were slightly lower. Compared to the level of DSi in the measurements available from the water of other lakes in Finnish Lapland, the DSi concentrations of Lakes Kuutsjärvi and Tippakuru were high (in the highest 7 % of the

**Table 3** The age of the sediment and the sedimentation rate in Lakes Kuutsjärvi and Tippakuru based on  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ , and  $^{137}\text{Cs}$  by direct gamma assay according to Appleby et al. (1986); see text for details

Sediment depth (cm)	Year (AD)		Sedimentation rate (cm $\text{a}^{-1}$ )	
	Kuutsjärvi	Tippakuru	Kuutsjärvi	Tippakuru
0	2009	2010	n.a.	n.a.
0.13	n.a.	2009	n.a.	0.21
0.375	2007	n.a.	0.16	n.a.
0.625	2005	2007	0.13	0.20
1.125	2001	2004	0.1	0.14
1.625	1995	2000	0.07	0.11
2.125	1986	1995	0.05	0.09
2.625	1974	n.a.	0.04	n.a.
3.125	1962	1984	0.04	0.08
3.625	1950	1977	0.03	0.07
4.125	1933	1969	0.03	0.06
4.625	1918	1961	0.03	0.06
5.125	1905	1953	0.04	0.06
5.625	1890	1944	0.04	0.06
6.125	1878	1935	0.04	0.06
6.625	1866	1926	0.03	0.06
7.25	n.a.	1915	n.a.	0.05
7.625	1831	n.a.	0.03	n.a.
8.25	n.a.	1896	n.a.	0.05
9.25	n.a.	1876	n.a.	0.05
10.25	n.a.	1852	n.a.	0.04

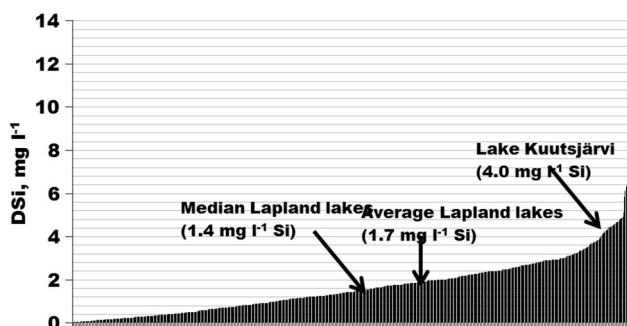
The error margin for the sedimentation rate varied between 2.2 and 8.8 %

n.a. Not available



**Table 4** The concentration of dissolved Si ( $0.2 \mu\text{m}$  filtered,  $\text{mg l}^{-1}$  Si) in the in- and outflow and in the water column (composite sample from June, see text for details) from lakes Kuutsjärvi and Tippakuru and the average concentration of BSi in the top (0–2 cm) sediment layer in lakes Kuutsjärvi, Tippakuru, Pirunkuru and Välijärvi (as  $\text{mg g}^{-1}$  DM, the  $\text{SiO}_2$  % is obtained by multiplying the respective number by 0.214)

Lake	Si, inflow ( $\text{mg l}^{-1}$ )	Si, lake ( $\text{mg l}^{-1}$ )	Si, outflow ( $\text{mg l}^{-1}$ )	BSi, 0–2 cm ( $\text{mg g}^{-1}$ DM)
Kuutsjärvi	3.0	3.7	3.4	270
Tippakuru	2.8	3.0	2.8	240
Välijärvi	n.a	n.a	n.a	170
Pirunkuru	n.a	n.a	n.a	130



**Fig. 3** The concentrations of dissolved Si (DSi, as  $\text{mg Si l}^{-1}$ ) in the water column of lakes from the Lapland province in Northern Finland from which spectrophotometrical measurements were available in the HERTTA database at the Finnish Environment Institute ( $n = 497$ ). The median and average values and the concentration measured from Lake Kuutsjärvi in this study are indicated by arrows

measurements available, Fig. 3). Some geographical correlation could be discerned in the concentrations, as high DSi concentrations were relatively frequent in the area in Eastern Lapland near Kuutsjärvi (although the available measurements were few).

The BSi concentrations in the litter layer and topsoil collected from around Lake Kuutsjärvi (Fig. 2) were, with the exception of one outlying value (sample point D,  $38 \text{ mg Si g}^{-1}$  dry mass, DM), fairly low ( $1.5$ – $8.8 \text{ mg as Si g}^{-1}$  DM; Table 1). Slightly higher concentrations were found where the share of deciduous vegetation and/or trophic state was higher and in bog-like, wetland near-shore areas (Table 1). Microscopic examination of the samples showed that diatoms were present in high numbers only in the D-site soil sample, and that intact phytoliths were relatively rare in all soil samples. The BSi data from the soil and litter samples taken around Lake Tippakuru was similar, with the highest values measured from the wetland samples.

In the Kuutsjärvi sediment, the BSi concentration was very high (average  $250 \text{ mg Si g}^{-1}$  DM,  $40$ – $60 \text{ wt\% SiO}_2$ , Fig. 4; Table 4). The concentrations in the surface sediments (0–2 cm) from the three comparison lakes near Lake

Kuutsjärvi were lower, but still high ( $130$ ,  $170$  and  $240 \text{ mg Si g}^{-1}$  DM, Table 4). The BSi concentration at  $2.5$ – $5 \text{ cm}$  depth was somewhat lower than at other depths in the  $0$ – $20 \text{ cm}$  sediment profile from Lake Kuutsjärvi, although the difference was obscured by large variability between replicates and not statistically significant. Diatoms dominated in the samples with only a few recognizable phytoliths in each, although some possibly amorphous Si without clear structure could be discerned by microscopy. The DSi concentration in the sediment interstitial water varied between  $20$  and  $25 \text{ mg l}^{-1}$  with slightly higher values in the upper part of the profile; the highest value was measured from the  $2.5$ – $5 \text{ cm}$  depth sample where the BSi concentration was lowest, but the differences between depths were small.

The  $\delta^{30}\text{Si}$  signatures measured in the different Si pools are given in Table 5. The  $\delta^{30}\text{Si}$  value of the bulk soil was  $-0.05 \text{ ‰}$ , which is consistent with a gneissic parent material generally characterized by  $\delta^{30}\text{Si}$  ratios close to  $0 \text{ ‰}$  (Savage et al. 2012). The  $\delta^{30}\text{Si}$  value of the litter at  $-0.15 \text{ ‰}$  is comparable with available litter data from the boreal forest region ( $-0.22$  to  $+0.20 \text{ ‰}$  from spruce, larch and birch; Engström et al. 2008). Lake and drainage water  $\delta^{30}\text{Si}$  values at  $+1.25$  and  $+1.37 \text{ ‰}$ , respectively, are isotopically heavier, as expected for lake water in cold regions (Opfergelt et al. 2011). The bulk sediment  $\delta^{30}\text{Si}$  value at  $-1.14 \text{ ‰}$  is isotopically lighter, which can also be expected from the contribution of isotopically lighter weathering products (secondary clay minerals, Opfergelt et al. 2010) or aged BSi (see “Discussion”).

The  $\delta^{30}\text{Si}$  value for BSi extracted from the sediment was  $-0.06 \text{ ‰}$ . This value can be assumed to contain contributions from phytoliths, diatoms and non-biogenic, amorphous Si compounds. Phytoliths are assumed to be characterized by a  $\delta^{30}\text{Si}$  value similar to the one of the litter ( $-0.15 \text{ ‰}$ ), but this has to be considered with caution, given the variability of  $\delta^{30}\text{Si}$  ratios in phytoliths among plant species (Opfergelt et al. 2008). However, the litter value ( $-0.15 \text{ ‰}$ ) seems a reasonable assumption in the

**Table 5** The Si isotope composition ( $\delta^{30}\text{Si}$ , ‰) of the sediment top layer, BSi extracted from the top sediment layer, the litter and soil layers and from the lake water and lake inflow water (see text for details)

	$\delta^{30}\text{Si}$ (‰)	SD (analytical)	SD (replicates)	N
Sediment BSi	$-0.06$	0.05	0.04	2
Sediment	$-1.14$	0.05	nd	1
Soil	$-0.05$	0.05	0.02	3
Litter	$-0.15$	0.05	0.02	2
Lake water	1.25	0.05	0.03	2
Lake inflow	1.37	0.05	0.09	2

present study, given that the phytoliths observed in the sediment samples appeared to be mainly derived from the dominant terrestrial vegetation in the area (pine, spruce and birch, data not shown), typical for the subarctic and temperate forest region. For lake BSi (diatoms), a  $\delta^{30}\text{Si}$  signature can be calculated from Eq. 3 as 0.15 ‰, assuming that the composite water sample from June used for the analysis is a representative sample of the dissolved Si source for the diatoms in the lake. Based on the above assumptions and the isotope mass balance calculation in Eq. 2, and given the analytical uncertainty on isotope measurements, we tentatively estimate that between 12 and 46 % of the BSi in the sediment originated from autochthonously produced diatoms, whereas between 54 and 88 % originated from other sources of possibly terrestrial origin.

## Discussion

### Minor changes in BSi accumulation with time

The BSi concentration in Lake Kuutsjärvi was relatively constant as a function of depth and time during the studied period, i.e. roughly the two past centuries. A slightly increasing trend with time occurred, however, from the beginning of the 19th century. This is in agreement with the trend in the organic matter concentration of the sediment, where an increase appeared at around the same time. Despite the relatively isolated and unperturbed location of the lake, such an increase in the productivity of the lake around this time follows general trends observed elsewhere in high-latitude areas (Sorvari et al. 2002; Smol et al. 2005; Thomas et al. 2008 with references). The increasing trend in BSi was slight, however, and no clear conclusions about increases in productivity can be drawn from the BSi data alone. The main perturbation in the recent history of the lake, the building of a research station at its shore in 1967, could not really be discerned in the concentration of BSi; only a very slight, insignificant decrease at 3 cm depth occurred.

### High BSi accumulation in the sediment: reasons and implications for Si cycling

The BSi concentrations in the sediment from Lake Kuutsjärvi were very high (max. 270 mg g<sup>-1</sup> Si DM, i.e. almost 60 wt% SiO<sub>2</sub>), and the almost as high concentrations measured from three lakes in the area immediately adjacent showed that the cause was not any single anomaly in Lake Kuutsjärvi. Other lakes in the high-latitude area mostly exhibit markedly lower sediment BSi concentrations, e.g. between 0.9 and 56 mg g<sup>-1</sup> Si DM in a total of

63 Canadian Arctic lakes (Fortin and Gajewski 2009), <50 mg g<sup>-1</sup> Si DM in several Alaskan lakes (Hu et al. 2001, 2003; McKay et al. 2008; Peros and Gajewski 2009), max 70 mg g<sup>-1</sup> Si DM in Lake Danntjörn, Norway (Nesje et al. 2004) and 14–47 mg g<sup>-1</sup> Si DM in Lake Haukadalvatn in Iceland (Geirsdottir et al. 2009). Although very high concentrations of BSi (>90 mg g<sup>-1</sup> Si DM) are common only in Southern Ocean sediments or geothermally influenced lakes where modern diatomites are being formed (see e.g. Theriot 1992), high BSi concentrations have also been measured in sediments from other northern areas. In e.g. another lake in Iceland, Lake Stora Viðarvatn, the modern sediment BSi concentration reached 160 mg g<sup>-1</sup> Si DM with as high values as 250 mg g<sup>-1</sup> Si DM in deeper sediments (pre-19th century, Axford et al. 2009), and in Ongoke Lake in Alaska the BSi concentrations in the sediment were estimated to be almost as high as in Lake Kuutsjärvi (100–220 mg g<sup>-1</sup> Si DM, Chipman et al. 2009). Relatively high concentrations (>120 mg g<sup>-1</sup> Si DM) have also been found in sediments from Lake CF8 on Baffin Island (Thomas et al. 2008) and from North Lake on Greenland (Axford et al. 2013). These high BSi concentrations have, in general, been attributed mainly to high autochthonous diatom production in the lakes, however, while our study revealed some other possible reasons behind the high accumulation of BSi in the Lake Kuutsjärvi sediment, i.e. inflow from the drainage area. As sediment BSi concentrations are commonly used to draw conclusions about the past (diatom) production in the water body in question, this aspect needs to be clarified.

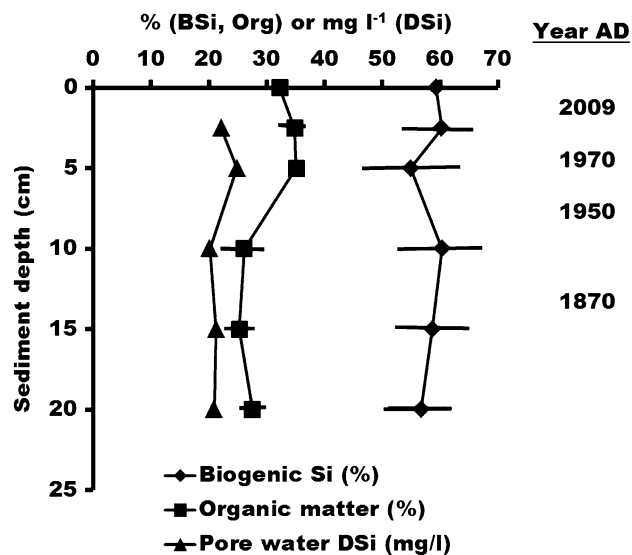
### Autochthonous diatom production?

Obviously, the most likely explanation for the high BSi concentrations in the Kuutsjärvi sediment is still high autochthonous diatom production in combination with ideal preservation conditions in the sediment. The present-day lake phytoplankton community is, however, dominated by chrysophytes, green algae and blue-green algae, with diatoms in a minor role (only sparse sightings of mainly centric diatoms, such as *Aulacoseira*). Further, although Lake Kuutsjärvi can be classified as close to mesotrophic, i.e. relatively nutrient-rich compared to many small, high-latitude lakes based on the concentration of total P in the water, all other trophic indicators available (total N, chl a) place the lake firmly in the oligotrophic category (Wetzel 2001). On the other hand, the sedimentary diatom data indicates that diatoms are much more common in the sediment from Lake Kuutsjärvi than in other lakes of similar trophic state, although the estimates are not directly quantitative (unpublished data). The benthic and/or littoral diatom populations, of which we unfortunately have no data, may also be major contributors to the BSi deposited

in the sediment, as the role of benthic communities is generally large in small, northern lakes (Rautio et al. 2011). It is also possible that the phytoplankton sampling was not frequent enough to catch all present-day planktonic diatom production. The very high BSi concentrations in the sediment are still somewhat surprising.

Good conditions for preservation may also be part of the explanation, particularly when the BSi concentration is compared to those in lakes from lower latitudes. Firstly, the ambient temperature in the studied area is low, and even more volatile organic compounds are initially preserved in the sediment (in the surface layer, the BSi and organic matter together made up 95 % of the dry matter). Secondly, two other factors may impact the preservation of BSi in the sediment favourably: the relatively high aluminium (Al) concentration in the lake and the high BSi concentration and consequently high concentration of DSi in the sediment pore water. High Al concentrations have been shown to retard BSi dissolution by a substitution process, where Al is incorporated into the BSi structure and its solubility decreases (van Bennekom et al. 1991; Dixit et al. 2001; Koning et al. 2007). Incorporation of Al into diatoms during growth (biomineralization) in Lake Kuutsjärvi could have been favoured by the relatively high Al concentration in the water column (Table 1). Inclusion of Al into decaying BSi structures in the sediment itself is also probably a more common phenomenon in all Al-rich sediments than previously realized (Dixit et al. 2001; Michalopoulos and Aller 2004; Koning et al. 2007; Loucaides et al. 2010), and may have further retarded the dissolution of the BSi structures in the sediment. In most studied cases such diagenetic reactions involving BSi and Al increase downcore as the material ages, and thus do not entirely explain the high concentrations in the very surface layer where fresh material abounds.

A similar, simpler explanation for the high concentration of BSi in the sediment which does not take into account the origin of the material is the high BSi concentration itself. The solubility of BSi is highly variable with values from 3 to 21 mg l<sup>-1</sup> Si reported (Dixit et al. 2001; Loucaides et al. 2012 with references). The concentrations of DSi in the interstitial water of the top part of the sediment profile in Lake Kuutsjärvi (21–24 mg l<sup>-1</sup>, Fig. 4) were high compared to these values and to other values measured from the uppermost layers of lake sediment profiles (Harriss 1967; Bailey-Watts 1976; Nriagu 1978; Cornwell and Banahan 1992; Parker et al. 1977; Peinerud 2000), where values above 20 mg l<sup>-1</sup> were mostly found only at 10–20 cm sediment depth. As supersaturation of the sediment interstitial water with DSi is a factor retarding further dissolution (cf. Lewin 1961; Loucaides et al. 2012), the high BSi concentration in the surface sediment will thus contribute to the further accumulation of more BSi. The



**Fig. 4** The concentration of biogenic silica (BSi, as SiO<sub>2</sub>-%, to get mg g<sup>-1</sup> Si multiply by 4.7 or see Table 4 for average), the percentage of organic matter (%) and the concentration of dissolved Si (DSi, mg l<sup>-1</sup>) in the Kuutsjärvi sediment (0–20 cm). Standard deviations are indicated by the *horizontal bars*. The age of the sediment (<sup>210</sup>Pb, <sup>226</sup>Ra, and <sup>137</sup>Cs direct gamma assay, see text for details) is indicated by the years on the *right-hand side*

two latter explanations do not explain the abundance of BSi available for preservation, however.

#### Lithogenic amorphous Si?

One reason behind the high BSi concentration in the sediment could be “contamination” by high concentrations of lithogenic, amorphous Si, but this is on the whole unlikely, as non-biogenic amorphous Si is generally formed only under relatively rare conditions of high supersaturation of Si within the soil or sediment (Drees et al. 1989) or inherited from parent materials. The separation of amorphous Si itself into fractions according to its origin is difficult (cf. Sauer et al. 2006; Siipola et al. 2013). Some attempts have been made (Kamatani 1971; Maldonado et al. 2005; Chu et al. 2011), and it has tentatively been shown that even the group or species origin of the BSi may influence dissolution rates. It is likely that significant occurrence of pedogenic, amorphous Si in the Kuutsjärvi sediments would have shown up in the extraction used. The mineral correction inherent in the extraction methodology used (cf. DeMaster 1981) is based on the separation of Si pools using their different dissolution rates, and in the present study the Si extracted in the analysis exhibited a very similar rate of dissolution, indicating a relatively homogenous source of BSi. Some mineral “contamination” by easily dissolved or adsorbed Si pools is possible, and some adsorbed Si was very likely included in the BSi

estimates, as it has proven very difficult to separate adsorbed and biogenic Si pools from each other. Such adsorbed Si pools are normally only a fraction of the BSi pool (Siipola et al. 2013) and should not be the main reason behind the high BSi concentrations observed.

#### Terrestrial impacts?

Although the isotope data should be considered as only roughly indicative due to the limited number of analysed samples, it was interesting to note that it indicated that a substantial part (more than 50 %) of the BSi in the Lake Kuutsjärvi sediment was of terrestrial origin. The impact of terrestrial vegetation on Si supply to the aquatic biogeo-sphere has been recognized as significant only fairly recently (Conley 2002), and the axiom that most translocation of Si from the watershed to water bodies takes place via runoff and consists mainly of dissolved Si, DSi, is being supplemented with new information on the role of transport of Si in amorphous and/or biogenic form. The role of BSi export from the terrestrial area is not very well known and substantial erosion has sometimes been seen as a prerequisite for the export of these fairly large particles (Cary et al. 2005). The role of terrestrial sources of BSi in high-latitude lacustrine sediments has been even more sparsely studied, but in lakes with low autochthonous production, biogenic silica produced by terrestrial vegetation from the drainage area could very well constitute a significant fraction of the BSi buried in the sediment. BSi derived directly from terrestrial vegetation in the immediate watershed is not by itself a very likely explanation for the high BSi content in the sediment in Lake Kuutsjärvi, however, as microscopic examination of the sediment samples yielded only a few clearly distinguishable phytoliths. Indistinct material of possibly amorphous or biogenic Si origin was also found when the acid-cleaned material was examined, but whether this material originated from the drainage area or the lake cannot be visually determined. Secondly, the abundance of BSi in the shallow topsoil around the lakes was not very high. The soil around Lake Kuutsjärvi (and Lake Tippakuru) mostly exhibited BSi concentrations (1.5–8.8 mg Si g<sup>-1</sup> DM) which were comparable to forested areas in central France (0.6–6.8 mg Si g<sup>-1</sup> DM, Cornelis et al. 2010) and the Kalix region in Sweden (ca 7 mg Si g<sup>-1</sup> DM Engström et al. 2008).

BSi of terrestrial origin could also have been preferentially deposited into (or, alternatively, much better preserved in) the lake during a longer period of time. The steep shorelines of the lakes and the surrounding terrain provide some support for this theory, as the lakes are also small: the movements of the ancient glaciers which covered the area caused significant erosion and local

deposition of material namely at the bottom of channels and gorges (Johansson 1995), while the steep slopes in the surrounding area have a relatively shallow soil cover. High particle transport from the watershed into the lake is thus topographically speaking feasible (see also below). Measurements of soil runoff are not available, but the available rainfall data from the region (station Kemihäärä, Kummanniiva, ca 100 km west of Lake Kuutsjärvi) show some high monthly averages (>100 mm), mainly in July about every 5 years, which may be responsible for high short-term erosion events (Korhonen and Haavanlammi 2012).

The glacial pre-history of the region also may have influenced the BSi concentrations in the sediment more directly. In the nearby (ca 100 km west) Sokli region, large deposits of old (30,000–40,000 years) diatomite and diatom gyttja have been found (Ilvonen 1973), and initial observations from a deeper (several meters) sediment core from Lake Kuutsjärvi showed distinct laminae of possibly diatom gyttja origin. The high BSi concentration in the sediment could thus be related to historical transport processes within the drainage area, where older deposits of diatom material were transported into the Kuutsjärvi valley through the relatively narrow inlet and deposited in the current lake basin and, for some of the reasons outlined above, well preserved therein (the sediment dating would, in this case, not be entirely reliable for all the sediment material). The light  $\delta^{30}\text{Si}$  signature (−1.14 ‰) of the bulk sediment BSi could thus be explained by the presence of older, allochthonous BSi. This theory would also explain why only few phytoliths were found in the sediment despite the evidence from the stable isotopes, and would also provide a possible explanation for the outlier in the BSi concentrations in the soil around Lake Kuutsjärvi, i.e. point D near the lake inflow, where 10 times as much BSi was found as in the other soil samples (38 mg Si g<sup>-1</sup> DM, Fig. 1; Table 1). This was the only soil sample where diatom remains were abundant, and this namely in the soil and not in the litter layer sample. The sampling site (D) is the only one situated near the inflow to the lake but clearly above the current water level, in a place where some part of a large inflow of material produced elsewhere would be deposited, but which should not be submerged by the present lake at any time of the year.

#### Conclusions

Perturbations in the recent history of Lake Kuutsjärvi, i.e. the building of the research station and the introduction of a predatory fish species, could only tentatively be discerned in the bulk BSi measurements from different depths in the lake sediment. The data rather indicated that the high BSi concentration in the sediment surface layer is relatively

stable and has stayed at more or less the same level over the past 2–300 years.

The main result of this study is that the high BSi concentration in Lake Kuutsjärvi sediment could be due to inflow of material from the drainage area, not necessarily only to high autochthonous (diatom) production in the lake itself. Although the mass balance based on stable Si isotope analyses was fairly rough, in combination with the other data, it indicated that a substantial part of the BSi buried in the sediment of the lake very likely was of terrestrial, not only autochthonous aquatic origin. The fundamental reasons for this remain somewhat uncertain, but it is likely that the reasons were related to historical transport processes within the drainage area, where older deposits of diatom material were transported into the current lake basin, while the transport of terrestrially produced phytolith BSi from modern terrestrial vegetation into the lake was a minor source of BSi. The predominance of a terrestrial source for the BSi in Lake Kuutsjärvi shows that bulk BSi measurements from sediments should be used with caution as indicators of past aquatic production or climatic variability without further verification (see also Chipman et al. 2009). Our results may thus help to explain why it has proven difficult to produce reliable models relating, e.g., atmospheric temperature to sediment BSi content (Fortin and Gajewski 2009). The present results also tentatively support previous findings about the importance of the drainage area as a source of potentially bioavailable Si for aquatic ecosystems, although it also raises new questions about the ultimate origin of this bioavailable Si.

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