Horizontal and vertical distribution of biogenic silica in coastal and profundal sediments of the Gulf of Finland (northeastern Baltic Sea)

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We studied the distribution of biogenic silica (BSi) and other potentially bio-available Si pools (NaCl-, NaBD- and NaOH-extractable Si) in short (0–25 cm) sediment cores from estuarine, coastal and open-sea areas in the Gulf of Finland (northeastern Baltic Sea). The BSi pool (150–1200 μmol g^{-1} DM, dry matter) was the largest potentially bio-available Si pool. In a part of the studied area, the concentration of BSi increased towards the sediment surface and could be used as an indicator of eutrophication. Several profiles were uneven due to disturbances in the sediment surface layer. The concentration of BSi was higher in the eastern (> 1000 μmol g^{-1} DM) than in the western Gulf of Finland (ca. 500 μmol g^{-1} DM). Although high estuarine retention of Si occurred, its importance in the studied area was small. High local variability in BSi concentrations probably contributes to earlier found discrepancies between external load and burial of Si in the Gulf of Finland.

Introduction

Biogenic silica (BSi) is produced by aquatic organisms (primarily diatoms, but also e.g. radiolarians, testate amoebae, chrysophytes, *see* e.g. Nelson *et al*. 1995) and by many terrestrial plants (*see* Piperno 2006 for a review). The organisms take up dissolved Si (here denoted DSi; Si(OH)$_4$ or Si(OH)$_3^-$) and produce siliceous structures which consist of hydrated amorphous silica (SiO$_2$ × nH$_2$O) either as separate particles (plants: phytoliths) or as some form of shell or supportive structure (e.g. diatom frustules). Since BSi is a comparatively stable structure,

it is preserved in soil and sediment to such an extent that it can be used for paleolimnological (reviewed by Koning *et al*. 2002) or paleontological purposes (Piperno 2006). Mostly, the remains of diatoms (or phytoliths) are isolated from the surrounding media and examined microscopically to infer conditions in the past. The bulk concentration of BSi is, however, also used, as the chemical extraction of BSi is, albeit neither cheap nor rapid, more rapid and cheaper than extraction and microscopic examination of the samples (cf. Conley 1998). Bulk BSi can be used e.g. as a paleoproductivity proxy, assuming that diatoms represent a stable part of the

phytoplankton community and that the amount of their remains in the sediment is an adequate indicator of the primary production in the past (*see* Mortlock *et al*. 1991, Koning *et al*. 2002). Since primary production and carbon drawdown are interlinked (Treguer and Pondaven 2000), the BSi concentration can also be used to reconstruct past climatic conditions.

The concentration of BSi in sediments is, however, also studied to understand the cycling of Si within the water ecosystem and watershed. As a nutrient which is only essential in appreciable amounts for certain primary producers (mainly the diatoms), Si and its availability in relation to the other main nutrients (nitrogen, N, and phosphorus, P) contribute to the quality of the phytoplankton community. Shortage of Si will affect diatoms and other Si-requiring organisms, while non-Si-requiring groups — such as e.g. dinoflagellates and cyanobacteria — will receive a competitive advantage (e.g. Reynolds 1980). Although Si is a very common element in the biogeosphere, the amount of bioavailable Si in water ecosystems is limited due to the slow weathering rate of (most) silicate minerals (Lerman 1988, Hartmann *et al*. 2010). Unlike for N and P, anthropogenic activities have also rather retarded than accelerated the cycling of Si within watersheds (*see* Conley *et al*. 1993, Rahm *et al*. 1996, Humborg *et al*. 2008). The short-term cycling of Si is, in fact, largely governed by the biological cycling of Si in both the aquatic and terrestrial parts of the watershed (Conley 2002, Derry *et al*. 2005, Sommer *et al*. 2006, Struyf and Conley 2009, Cornelis *et al*. 2010a).

Many aspects of the short-term Si cycle are not yet well known, particularly in the terrestrial part of the ecosystem (*see* Sommer *et al*. 2006, Cornelis *et al*. 2010a, 2010b). While the aquatic Si cycle has been studied much longer, the reasons behind the observed decreasing trends in dissolved Si concentrations in several semi-enclosed seas and coastal areas around the world remain somewhat mysterious (Conley *et al*. 1993, Rahm *et al*. 1996, Conley *et al*. 2000, Humborg *et al*. 2004, Papush and Danielsson 2006). In the Baltic Sea, a mismatch between the calculated and observed loads and burial of Si also exists: calculations indicate that more Si is possibly buried in the sediments (as BSi)

than what is brought into the sea by rivers (as dissolved Si (DSi); Conley *et al*. 2008, Papush *et al*. 2009).

While it is relatively well known how much dissolved Si is brought into the Baltic Sea by rivers (Conley *et al*. 2000, Conley *et al*. 2008, Humborg *et al*. 2008, Papush *et al*. 2009), the dynamics of BSi have been studied much less. Some aspects of the distribution of BSi in both profundal and estuarine sediments from the Gulf of Finland have also been studied, but mostly only as a proxy for changes in the deposition of Si with time (Vaalgamaa 2004, Conley *et al*. 2008,Vaalgamaa and Conley 2008). Few studies have, however, been concerned with the horizontal variability of Si or with the retention of Si by estuaries.

Here, we studied the distribution of biogenic Si and three other, within short-term time scales potentially bioavailable Si pools (Tallberg *et al*. 2009), in short surface-sediment profiles from the Gulf of Finland (Baltic Sea) and along two estuarine gradients in the Gulf of Finland and the Archipelago Sea (northeastern Baltic Sea). Our main goals were to (1) study the retention of Si in two very different estuaries and (2) clarify whether the burial of BSi differed along horizontal gradients in the Gulf of Finland. The use of BSi as a paleo-indicator for eutrophication and the role of other Si pools in the studied sediment are also discussed. While the transport and retention of BSi by rivers — which is another potential source of error in Si budget calculations (Conley 1997) — also need to be clarified, this remained outside the scope of the present study.

Material and methods

Study area and sampling

We took sediment samples during three cruises on board r/v *Aranda*, r/v *Aurelia* and r/v *Muikku* in August and September in 2003 and 2004 from two estuaries (Paimionlahti and Ahvenkoskenlahti; Figs. 1 and 2) and from shallow and profundal sites in the open Gulf of Finland (Baltic Sea, Fig. 1). The total area of the Gulf of Finland is ca. 30 000 km² (catchment area 420 990 km²) and the average and maximum depths 37 and
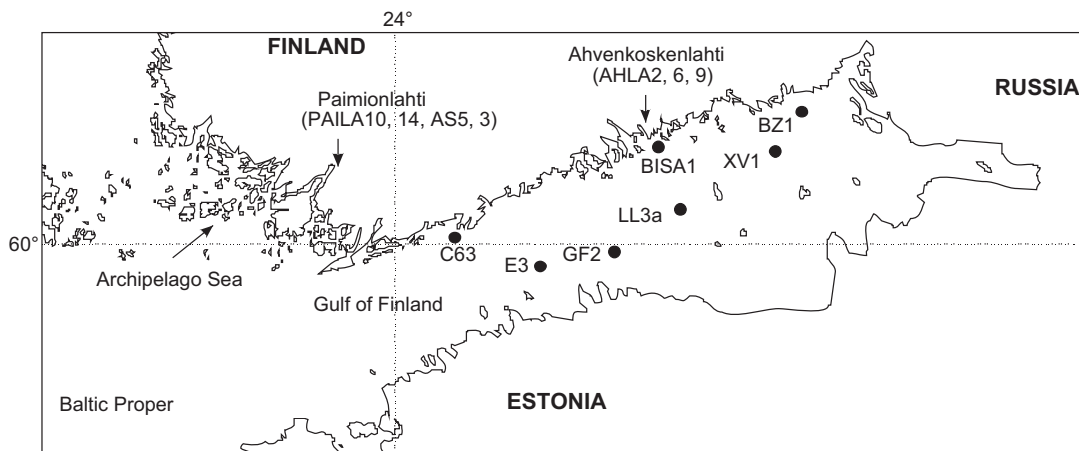
Fig. 1. The map of the study area showing locations of the sampled stations (for depths and background information, *see* Table 1).
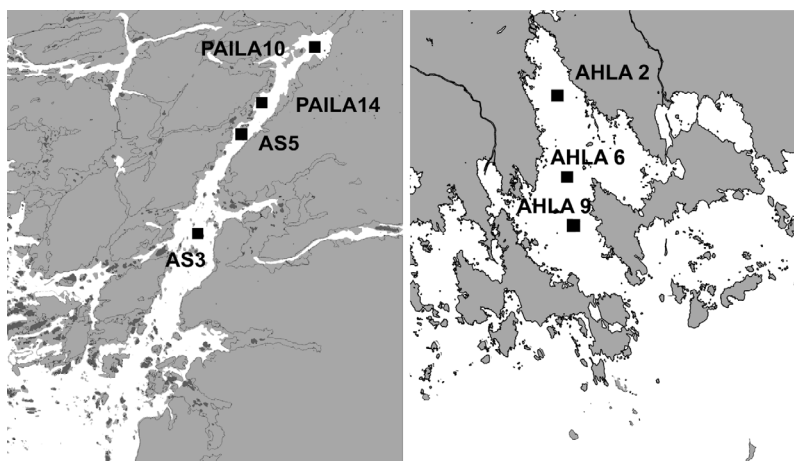

Fig. 2. The location of the sampling stations in Paimionlahti (left) and Ahvenkoskenlahti (right). Sampling depths and morphological details are given in Table 1. The maps are not to scale.

123 m, respectively; the water volume is ca. 1100 km³ (e.g. Alenius *et al*. 1998). The maximal salinity in the surface water is ca. 7 PSU with more saline water below the halocline at 60–80 m depth. Paimionlahti (area 96 km², average depth 11.6 m, theoretical hydraulic retention time ca. 5 years) is a narrow estuary of the Archipelago Sea fed by the small and turbid Paimionjoki (mean flow 0.09 m³ s⁻¹, max. turbidity 750 FNU) and a catchment of 1088 km² (Kangas *et al*. 2003, Lukkari *et al*. 2008). The catchment area consists of forests (50%), fields in agricultural use (43%), peatland (4%), and lakes (1.6%) (Ekholm 1994). The predominant soil type is clay. Ahvenkoskenlahti is a shallow

(mean depth 4.3 m) semi-enclosed estuary (52.5 km², hydraulic detention time 17 days) in the eastern Gulf of Finland mainly influenced by the western branch of the Kymijoki (mean flow 156 m³ s⁻¹). The large drainage basin of the Kymijoki (37 159 km²) is rich in lakes (18%), while the field percentage is low (mean 6.6%; Pitkänen *et al*. 1986). The small Taasianjoki (530.3 km²) also discharges into Ahvenkoskenlahti (mean flow about 5 m³ s⁻¹).

We took samples from accumulation sites (with the exception of the coastal site C63 which represents a transportation area, Lukkari *et al*. 2009b) along outward gradients in the two bays (Fig. 2) and along an easterly transect in the Gulf

of Finland, including both coastal and profundal sites (Fig. 1). The profundal sites are located in areas which were hypoxic during sampling. In Paimionlahti, we took samples from four sites (Paila10, Paila14, AS3 and AS5) and in Ahvenkoskenlahti from three sites (Ahla2, 6 and 9; Fig. 2 and Table 1). At the estuarine sampling sites, the sediment surface layer was brown (barely so at AS3), indicating the presence of Fe-oxides. In the open Gulf of Finland, we took samples from seven sites, three coastal (C63, BISA1 and BZ1) and four profundal (E3, GF2, LL3A and XV1). The coastal site BISA1 is close to the mouth of Ahvenkoskenlahti. At the coastal sites (depth 29–45 m), the oxygen concentration in the hypolimnetic water or at the sediment surface was higher than at the profundal sites (depth 58–89 m, *see* Table 1). The sediment at all sites consisted of muddy clay or clayey mud. The upper part of the sediment profiles were laminated with grey-black lamina partially disturbed by bioturbation. At the estuarine sites and coastal sites C63, BZ1 and BISA1, the sediment was generally covered by a 1–2-cm-thick brown and fluffy layer, while the sediment at the other sites was black and/or covered by white bacterial

growth. Closer descriptions of the sediment are provided by Lukkari *et al.* (2008, 2009a, 2009b).

We took samples from the uppermost sediment (0–25 cm) with a Gemax twin corer and sectioned the sediment into 1-cm-thick slices. The samples for the sequential extraction were sliced in a sub-oxic environment (under gaseous nitrogen, N_2, atmosphere) to minimize oxidation of the sediment samples and stored at +5 °C in plastic containers (sealed in N_2-filled gastight bags) until further treatment. Samples for BSi were stored at +4 or +5 °C for a few weeks in plastic containers before freeze-drying.

Analyses

We determined BSi in freeze-dried, mortar-ground sediment using a modification of the procedure by DeMaster (1981). Thirty (± 5) mg of dry sediment was weighed into polyethylene 100 ml bottles (Plastex Ltd.) and extracted with 40 ml 1% sodium carbonate (Na_2CO_3) in a +85 °C water bath for 5 hours (pH 10.6). The bottles were shaken at the start of the extraction and after 1, 2, 3 and 4 hours. At 3, 4 and 5 h, 1-ml samples for Si

Table 1. The depth, salinity, near-bottom water dissolved oxygen (O_2) at the time of sampling, sediment accumulation rate (SAR; Mattila *et al.* 2006, Lukkari 2008), and total C (TC), Fe, Mn and Al in the topmost sediment cm at the sampled stations (Lukkari *et al.* 2008, 2009a, 2009b). nd = not determined. Oxygen values marked with * were determined ca. 1 m above the sediment. GoF = Gulf of Finland.

Location	Depth (m)	Salinity (PSU)	O_2 (ml l^{-1})	SAR (g m^{-2})	TC (μmol g^{-1} DM)	Total Mn (μmol g^{-1} DM)	Total Fe (μmol g^{-1} DM)	Total Al (μmol g^{-1} DM)
Paimionlahti								
Paila10	12	nd	6*	4600	2000	13	1100	3500
Paila14	29	6.2	3	5500	2600	18	1400	3900
AS5	33	6.3	2	4700	2800	14	1100	2800
AS3	19	6.3	6	840	3000	12	950	3000
Ahvenkoskenlahti								
AHLA2	4.0	nd	6*	730	4500	10	600	2500
AHLA6	7.0	nd	4*	660	4100	12	830	2900
AHLA9	13	nd	5	1400	4400	16	810	2600
Coastal GoF								
C63	45	6.0	9*	nd	3800	13	570	2300
BISA1	29	5.7	4	990	9200	40	590	1800
BZ1	40	6.1	3	430	9200	27	470	1700
Profundal GoF								
E3	89	9.7	0.4	nd	5200	120	1100	2500
GF2F	83	9.5	1	960	6800	380	2000	2600
LL3A	63	8.2	2	330	6300	83	820	2500
XV1	58	7.0	3	330	10000	16	630	1800

analysis were taken from each bottle and diluted with 9 ml of 0.021 N HCl. The Si concentration of these samples was analyzed spectrophotometrically (blue ammonium-molybdate complex, Mullin and Riley 1955). BSi concentrations in the sediment samples were then calculated for the 3, 4 and 5 h time points using a linear regression. The analysis (mineral correction) is based on the assumption that all biogenic Si in the sediment samples dissolves during the first three hours of the extraction, while mineral-derived Si dissolves from the sample in smaller amounts at a constant rate throughout the extraction (*see* e.g. Conley 1998 for a closer description). The analysis extracts amorphous, alkaline-dissolvable forms of Si, of which biogenic remains (i.e. diatom frustules, sponge spicules, phytoliths) are normally assumed to constitute the main part.

Total aluminum (Al), phosphorus (P), iron (Fe) and manganese (Mn) was analyzed from the sediment samples using ICP-OES (TJA-25, Thermo Jarrell Ash) after combined fluoric acid (HF), aqua regia and boric acid digestion in a microwave oven (*see* Lukkari *et al.* 2007 for details). Total amounts of sediment sulfur (S), nitrogen (N) and carbon (C) were measured with a LECO CNS-2000 analyzer in the laboratory of the Pirkanmaa Regional Environment Centre.

A P-fractionation procedure (modified from Psenner *et al.* 1984 by Jensen and Thamdrup 1993 and Lukkari *et al.* 2007) was used to estimate three additional Si pools in the sediment. The applicability of the procedure for Si was tested in a separate study (Tallberg *et al.* 2009), where the two first steps of the procedure (the NaCl and NaBD extractions) proved useful for Si as well. In the P-fractionation procedure, a sample of fresh sediment with a wet weight corresponding to a dry weight of 0.5 g was extracted sequentially with (1) 0.46 M sodium chloride (NaCl) for 1h, (2) NaBD (a bicarbonate-dithionite extractant prepared by combining 0.11 M sodium bicarbonate, $NaHCO_3$ (adjusted to pH 7) with 0.11 M sodium dithionite, $Na_2S_2O_4$) for 1 h, followed by two rinses with the same NaBD reagent and (3) 0.1 M sodium hydroxide (NaOH) for 18 h, followed by one rinse with NaOH. The first step (NaCl) extracts pore water (and loosely sorbed) P (and Si), and the second step (NaBD) redox-sensitive, mainly Fe- and Mn-bound P

(and Si; Lukkari *et al.* 2007, Tallberg *et al.* 2009). The NaOH-extraction extracts P from Al oxides, possibly partly P from non-reducible Fe-oxides (Lukkari *et al.* 2007) and labile organic P, and can theoretically also be used to estimate Si bound to Al- and non-reducible Fe-oxides. Since the alkaline NaOH-extractant also extracts BSi, however, the results for Si are only indicative (Tallberg *et al.* 2009). The NaCl-extractable Si pool can, however, be assumed to represent pore-water and loosely sorbed Si and the NaBD-extractable Si pool to represent redox-sensitive Si (Tallberg *et al.* 2009).

The extractions were performed at room temperature in 100-ml polypropylene tubes on an orbital shaker table (400 rpm). All samples were extracted at a sediment-to-solution ratio of 1:100, and each step was followed by a 15-min rinsing with 0.46 M NaCl to minimize re-adsorption (Jensen and Thamdrup 1993). The extractants and rinsing solutions for each extraction step were combined into one sample for analysis. Prior to analysis, the samples from each step were centrifuged (4000 rpm, 15 min.), filtered through 0.4-μm Nuclepore polycarbonate membranes, and acidified with 4.5 M sulfuric acid (H_2SO_4). The fractionation extracts were analyzed for total dissolved P, Si, Fe, Mn and Al by ICP-OES in the laboratory of the Institute for Environmental Research at the University of Jyväskylä. A closer description of the procedure is found in Lukkari *et al.* (2007).

We calculated the accumulation or burial rate of BSi, B_{BSi} (g m^{-2} year^{-1}) as

$$B_{BSi} = C_{BSi} \times SAR \qquad (1)$$

where C_{BSi} is the the average concentration of BSi in the 0–25 cm layer (mg g^{-1} DM) and SAR is the the estimated sediment accumulation rate (g m^{-2} year^{-1}; Mattila *et al.* 2006 and Lukkari 2008).

The load of DSi (DSi$_{load}$, t year^{-1}) was calculated as

$$DSi_{load} = C_{DSi} \times Q \qquad (2)$$

where C_{DSi} (g m^{-3}) is the concentration of DSi in river water and Q is the river discharge (m^3 s^{-1}). The DSi and Q data were taken from the

HERTTA database of the Finnish Environment Institute. All available monthly averages from the 1960–2000 period were used. The areal load of DSi ($ADSi_{load}$, g m^{-2} year^{-1}), was calculated as

$$ADSi_{load} = DSi_{load}/A \qquad (3)$$

where A is the area of the receiving water body. The retention of Si (R_{Si}, %) — here defined as the Si accumulated or buried semi-permanently in the sediment — by the estuaries was calculated as:

$$R_{Si} = B_{BSi}/ADSi_{load} \times 100 \qquad (4)$$

The B_{BSi} value used here was the average for all the stations in each area.

We tested for differences in BSi concentrations as a function of sediment depth using linear regression analysis ($n = 13$). We tested the residuals for heteroscedasticity using residual plots and considered no transformations of the data necessary. These statistical analyses were made with the MS Excel (2003 SP2) Analysis ToolPak.

Results and discussion

Vertical differences in the sediment: signs of eutrophication?

The sedimentation of BSi has been widely used to infer changes in the productivity of the ecosystem, as it can be assumed that diatom production and sedimentation increases with eutrophication (Mortlock *et al*. 1991, Conley *et al*. 1993). While this is, in general, true, it should be kept in mind that eutrophication also may induce changes in the composition of the phytoplankton community: the increased production is often channeled mainly through other phytoplankton groups and may eventually at least cause a decrease in numbers of siliceous phytoplankton (Reynolds 1980, Smayda 1997). The percentage of produced BSi that is buried in the sediment (and not e.g. dissolved in the water column or at the sediment surface) is also not a constant, but varies according to environmental conditions (such as pH, ambient DSi concentration, temper-

ature; reviewed by Ragueneau *et al*. 2000). All paleoproductivity proxies are, however, subject to uncertainties, and the use of BSi is well established as reasonably reliable.

Although the studied sediment profiles were not very deep (25 cm), a eutrophication signal — i.e. increasing BSi sedimentation with time caused by anthropogenic nutrient enrichment (*see* below) — could be discerned in several parts of the studied area. At five stations (AS3, AHLA2, BISA1, C63, LL3A), the BSi concentrations increased towards the surface ($r^2 = 0.34$–0.77, $0.0001 < p < 0.0375$; Figs. 3 and 4). At four of these stations, the relatively low sediment accumulation rate (Table 1) meant that the period covered by the profiles was fairly long, 60–80 years. At these stations, BSi accumulation in the sediment seems to be a reasonably good indicator of eutrophication: anthropogenically induced eutrophication in the Baltic Sea began as early as in the early 20th century (or even earlier, *see* e.g. Rosenberg *et al*. 1990, Conley *et al*. 2002, 2008), and has not yet shown any clear signs of decreasing (Lundberg 2005). The latter is evident at the last station, BISA1, where the BSi concentration clearly increased towards the surface, although the sediment profile covered only the most recent 25 years (Fig. 4). We thus found a clearer indication of eutrophication than Olli *et al*. (2008), who studied diatom stratigraphy in a short core from the coastal western Gulf of Finland, and found very little change with depth and no clear signs of eutrophication. The larger amount of samples studied in the present case showed that eutrophication can be discerned from BSi profiles in the Gulf of Finland: areal variability in the sedimentation and possibly preservation of BSi in the sediment is clearly high, however (*see* below). Due to this variability and the uncertainties discussed below, the current data set was too small to make reliable comparisons about the eutrophication history of the different parts of the studied area.

The BSi concentration profiles were, however, not uniformly indicative of eutrophication: some of the profiles were also very uneven, and the innermost part of Paimionlahti formed an exception, where the concentration of BSi rather decreased with time towards the surface layer
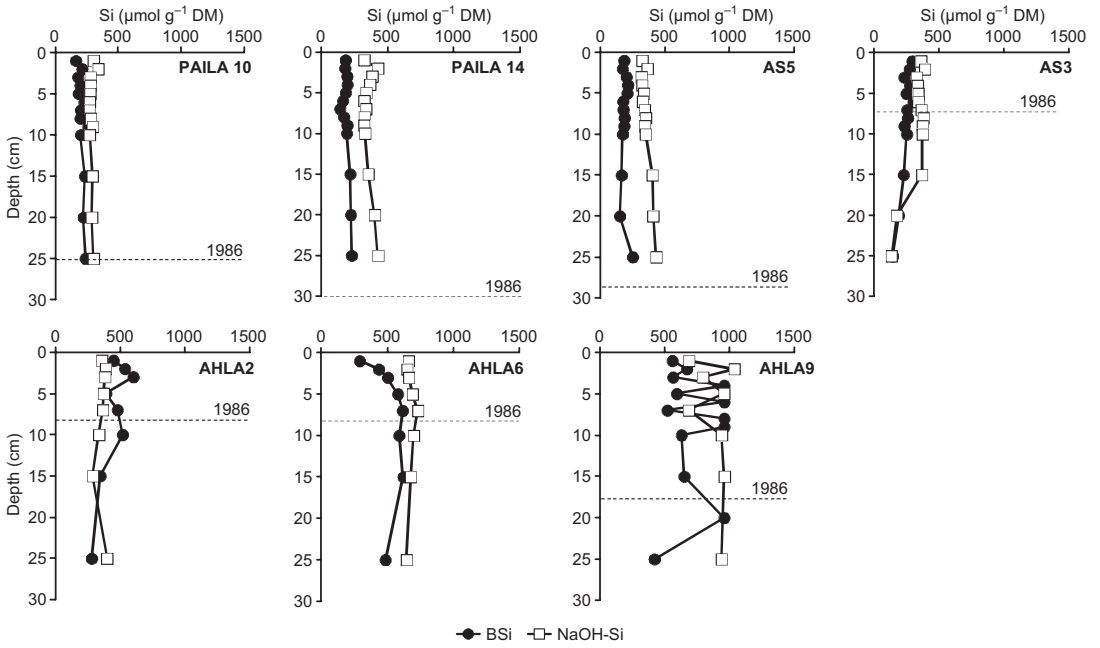
Fig. 3. Vertical distribution of biogenic silica (BSi) and NaOH-extractable Si (NaOH-Si) in the topmost 25 cm of the sediment at the sampling stations in the studied bays (PAILA and AS = Paimionlahti, AHLA = Ahvenkoskenlahti; *see* Figs. 1 and 2 for the location of the stations). The dotted line and the year 1986 indicate the approximate age of the sediment.
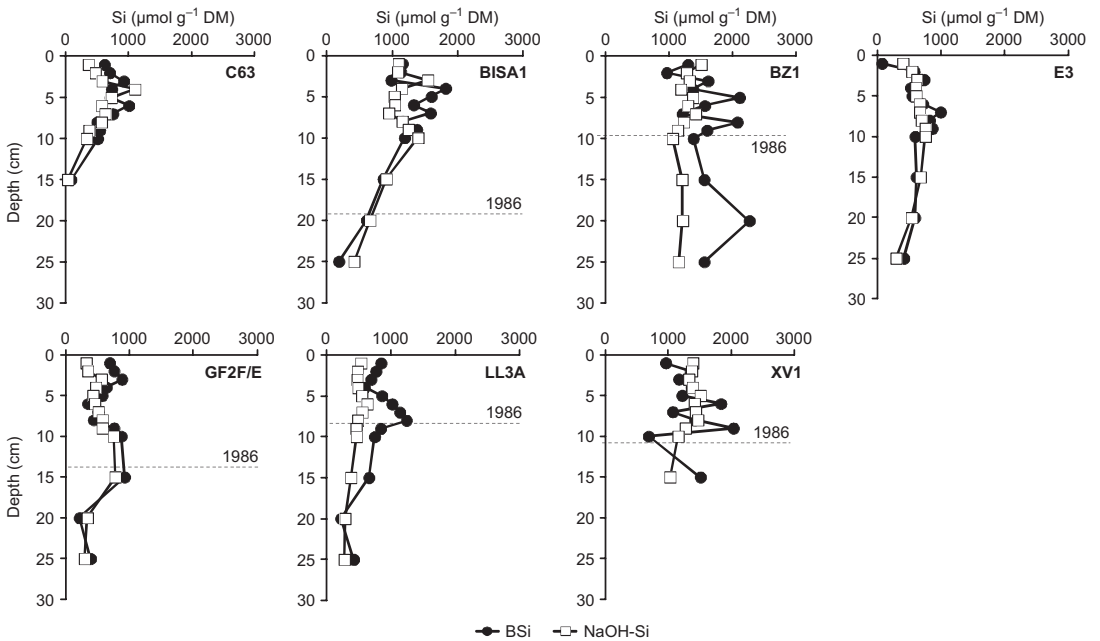

Fig. 4. Vertical distribution of biogenic silica (BSi) and NaOH-extractable Si (NaOH-Si) in the topmost 25 cm of the sediment at the sampling stations in the coastal (C63, BISA1, BZ1) and profundal (E3, GF2F, LL3A, XV1) Gulf of Finland (*see* Fig. 1 for the location of the stations). When available, the dotted line and the year 1986 indicate the approximate age of the sediment.

(from ca. 240 to 160 μmol g^{-1} DM, Fig. 3). A very slight decreasing trend in PO$_4$-P and unfiltered Si measured from the river discharging into Paimionlahti (the Finnish Environmental Institute database) indicated that this may be a true indicator of a slight decrease in the trophic state of the bay. The changes with depth were however small ($r^2 = 0.37$, $p = 0.0281$ and $r^2 = 0.48$, $p = 0.0091$).

Especially in the eastern part of the open sea area, the BSi profiles were remarkably uneven (especially stations XV1 and BZ1, Fig. 4). Several possible explanations exist. Firstly, analytical uncertainties may contribute. The analysis of BSi involves corrections for mineral interference, and is even at its best only an approximation of the true concentration (*see* Conley 1998, Koning *et al.* 2002, Sauer *et al.* 2006). Major sediment redistribution is another possible, but unlikely, explanation as the distribution of P pools in the same profiles did not show the same pattern (Lukkari *et al.* 2009a, 2009b). Another possibility is that the uneven profiles reflect actual variability in the sedimentation of BSi. The main sedimentation of diatoms (and, consequently, BSi) in the Baltic Sea normally takes place at the end of the spring bloom when nutrients are depleted, as scarcity of the main zooplankton grazers at this point of the seasonal cycle minimizes the recycling of the biomass within the pelagic ecosystem (Lignell *et al.* 1993, Heiskanen 1998, Tamelander and Heiskanen 2004). In the northwest Baltic Sea, this spring bloom is dominated by either diatoms or dinoflagellates (or by the two together) and there is considerable year-to-year variability as to which group dominates, although the exact reasons — which probably include hydrographical variations — for this are not fully known (e.g. Kononen and Niemi 1994, Wasmund and Uhlig 2003, Tamelander and Heiskanen 2004, Wasmund *et al.* 2011). It is possible that the uneven profiles reflect this year-to-year variability. The Si concentrations in the water column in e.g. the Gulf of Finland are frequently very low (even below 2 μM; Danielsson *et al.* 2008) and although Si limitation of the total primary production is unlikely at present, Si deficiency probably contributes to the dominance of dinoflagellates over diatoms in the spring and conse-

quently to cyclical variations in the sedimentation of BSi. The clearest zigzag pattern in the BSi profiles appeared near the sediment surface, and there is some evidence that dinoflagellate dominance over diatoms increased during the past decades in different parts of the Baltic Sea (Wasmund and Uhlig 2003, Pellikka *et al.* 2007, Klais *et al.* 2011, Wasmund *et al.* 2011). Dissolved Si concentrations in the water column also still show decreasing trends in all parts of the Baltic Sea except the Gulf of Bothnia (Papush and Danielsson 2006), i.e. including the Gulf of Finland.

The uneven BSi profiles at, predominantly, the eastern coastal stations, may also be due to the fact that dissolution of BSi and sorption of the released DSi varies with time due to variable conditions of e.g. redox at the sediment surface. Overall, sorption has received comparatively little attention as a factor which regulates the mobility of Si in a sediment. It may however affect the short-term mobility of the element in e.g. shallow sea-shelf areas (Gehlen and van Raaphorst 2002 with references). The small interest in these processes is partly due to methodological difficulties: it is difficult to separate and quantify the adsorbed Si fraction from the large pool of BSi (*see* e.g. Sauer *et al.* 2006, Tallberg *et al.* 2009). Studies dealing with redox-sensitive Si processes are also scarce (Sommer *et al.* 2006, Tallberg *et al.* 2009), although it has been shown that redox can affect Si dynamics in soil when iron oxides are present (Sommer *et al.* 2006) and that a redox-sensitive Si pool is released concomitantly with a redox-sensitive P pool under strongly reducing conditions such as the NaBD extraction used here (Tallberg *et al.* 2009). It should naturally always be kept in mind that all fractionation procedures provide only operationally defined estimations of elemental pools and not the true values *per se*.

At the stations where the BSi profiles were visibly uneven (e.g. XV1, BZ1, Fig. 4), the profiles of NaBD-extractable, redox-sensitive Si were also quite uneven, while the concentration of easily available NaCl-extractable Si was high at the sediment surface (> 25 μmol g^{-1} DM, Fig. 5). At stations BISA1 and to some extent BZ1 the concentration of NaCl-extractable P in the surface layer was also high (Lukkari
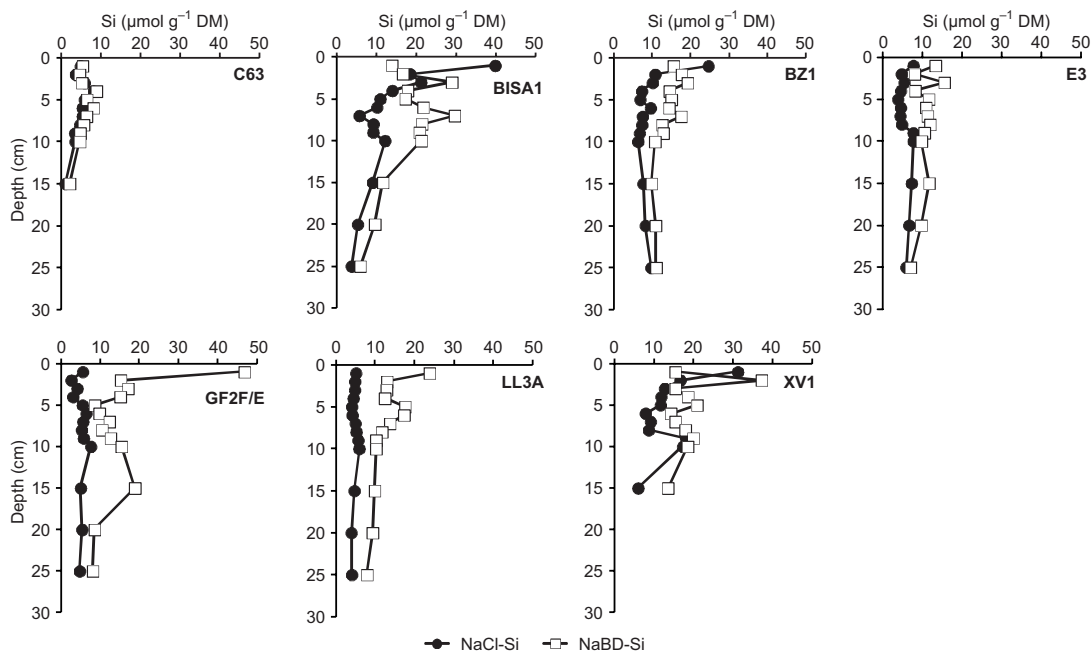
Fig. 5. Vertical distribution of NaCl- and NaBD-(dithionite)-extractable Si (NaCl-Si and NaBD-Si, respectively) in the topmost 25 cm of the sediment at the sampling stations in the coastal C63, BISA1, BZ1) and profundal (E3, GF2F, LL3A, XV1) Gulf of Finland (*see* Fig. 1 for the location of the stations).

et al. 2009b). This has been attributed to a lack of available sorption sites, possibly caused by reduction-induced dissolution of iron-oxyhydroxides during a preceding anoxic period (Lukkari *et al.* 2009b). As P and Si are adsorbed to the same sorption sites at Fe-oxyhydroxide surfaces (Hingston *et al.* 1967), the same explanation may apply to the high concentration of easily available NaCl-extractable Si at the sediment surface. At the stations concerned the surface sediment was rich in TC (Table 1), and periods of anoxia due to high decomposition of organic matter in the bottom water occur in the area (HELCOM data base).

Alternating oxic and anoxic periods may also have produced the variability in the NaBD-extractable, redox-sensitive Si profiles, and possibly in the BSi profiles as well. The influence of anoxia on the dissolution of BSi and redox-conditions on Si speciation are, however, largely unexplored subjects (but *see* Hartikainen *et al.* 1996, Sommer *et al.* 2006, Belias *et al.* 2007, Tallberg *et al.* 2009, Loucaides *et al.* 2010). The explanations we offer here for the uneven profiles may be interlinked. Inter-annual vari-

ability between diatom and dinoflagellate dominance in the water column would produce higher sedimentation of BSi in the years when diatoms dominate and consequently a higher pulse of organic matter to the sediment surface, which in turn could lead to anoxia and dissolution of Fe-oxyhydroxides. In years when dinoflagellates are dominant, the sedimentation pulses and the risk of anoxia would be smaller, as dinoflagellate cells are mainly remineralized in the surface layers (Heiskanen 1998). Spatially variable sedimentation patterns in different years, induced by annual differences in hydrographical conditions (water currents, mixing), may also have contributed.

In the GF2-basin, the concentration of redox-sensitive (NaBD-extractable) Si was exceptionally high in the sediment surface layer (47 μmol g^{-1} DM), despite the fact that the basin is situated below the halocline and poorly oxygenated, and that the measured near-bottom-water oxygen concentration was low (Table 1 and Fig. 5, Lukkari 2008). Under these conditions, the redox-sensitive compounds which are extracted by the NaBD-extraction should already have dissolved. This anomaly may have been
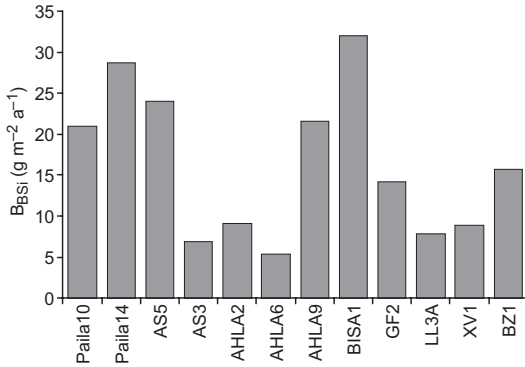
Fig. 6. Burial of biogenic Si (B_{BSi} calculated from the concentration of BSi and the sediment accumulation rate, Eq. 1) at the sampling stations for which sediment accumulation rates (Table 1, Mattila *et al.* 2006) were available.

due to partial inhibition of Fe reduction by Mn reduction (Lovley and Phillips 1988), as the sediment at the station was exceptionally rich in Mn (Table 1; Lukkari 2008). Manganese dissolves at a higher redox potential than Fe (e.g. Thamdrup *et al*. 1994) and both the concentration of total Mn (Table 1) and the NaBD-extractable Mn concentration (ca. 10 times higher than elsewhere, 150 μmol g^{-1} DM, Lukkari *et al*. 2009a) were high in the uppermost sediment centimetre at station GF2F. High concentrations of nitrate also prevailed (Lukkari 2008). These conditions may thus have prevented the dissolution of NaBD-extractable redox-sensitive Si and explain the peak at the sediment surface.

Horizontal distribution of BSi in the Gulf of Finland

The horizontal variability in the sediment BSi concentration was clear and followed an east–west gradient with high concentrations in the east (average 1000–1200, max. 2300 μmol g^{-1} DM) and lower in the west and inside the bays (average 150–500 μmol g^{-1} DM) (Figs 3 and 4). A similar pattern in the concentration of TC — which in this sea area can be used as an indicator of TOC, as the concentration of inorganic C is low (Lukkari 2008) — could be discerned (Table 1). This was expected, as the eastern Gulf of Finland is, in general, more eutrophic than its

western part (Conley *et al*. 1997, Pitkänen and Tallberg 2007). The higher concentrations of BSi in the sediment in the east were, however, partly explained by the lower sediment accumulation rates there (Table 1), i.e. the BSi in the surface sediment was deposited over a longer period. When the burial rate of BSi was calculated for the different stations (B_{BSi}, Eq. 1), the values for the eastern stations were rather low than high with some exceptions (Fig. 6). Disturbances, such as bioturbation and mechanical resuspension of the surface sediment expose larger amounts of deposited BSi to favorable circumstances for dissolution in the east (i.e. steeper concentration gradients, better oxygen diffusion etc.; Ragueneau *et al*. 2000, Dixit and van Cappelen 2002, Holstein and Hensen 2010). Visual examination of the sediment cores showed that bioturbation had occurred at several of the stations. Where the water column is frequently mixed, e.g. in the near-shore areas above the halocline in the Gulf of Finland, a significant proportion of Si needed for diatom production may thus be supplied from the sediment surface layer.

Conley *et al*. (2008) used a model to calculate a Si budget for the Baltic Sea, in which the loading of Si as DSi to the Gulf of Finland was smaller than the amount of Si that was buried in the sediment as BSi. They suggested that one significant factor in the discrepancy between the calculated load and burial of Si in the Baltic Sea is the inadvertent overestimation of the sedimentation rates of BSi caused by biased sampling of mainly places where sediment accumulates steadily. Other factors include changes in the dissolved Si stocks, and Papush *et al*. (2009) showed more recently that another probable reason is the transport of DSi into the Gulf from the Baltic Proper. We would further like to point out that in the topographically heterogeneous Gulf of Finland where the hydrographical conditions also vary, the areal variability in sediment BSi content is quite high. Together with the normally quite small number of available BSi samples, this alone produces highly variable basin-wide BSi accumulation estimates if extrapolated. If, for instance, the accumulation of BSi in the sediments of the Gulf of Finland was estimated from the samples taken in this study, the numbers would range from 170 to

960 kt year^{-1}, depending on sample location. The small-scale variability with depth of the BSi content in many of the studied sediment profiles also shows that more reliable results are probably gained by measuring BSi from a composite sample from, for example, 0–10 cm depth than from the surface sediment alone.

Estuarine retention of Si

The river load of DSi brought into the two studied bays was differently affected by the two bays with different flow regimes. The load of Si (calculated from the concentration of DSi measured from the river water) was much higher in Ahvenkoskenlahti than in Paimionlahti due to the higher discharge of the Kymijoki (166 m^3 s^{-1}, Table 2), although the concentration of DSi in the river water was higher in the Paimionjoki than in the Kymijoki (7.3 *vs*. 2.1 g m^{-3}, Table 2). Due to the very low discharge of the Paimionjoki and high sediment accumulation rate (and, consequently, calculated rate of BSi burial, 22 g m^{-2} year^{-1}) in Paimionlahti, the theoretical retention of Si in Paimionlahti bore no real relation to the DSi load (> 1000%, Table 2).

However, although the high load of DSi from the Kymijoki mostly passes through Ahvenkoskenlahti, it seems to produce a BSi burial peak outside the bay at station BISA 1 (32 g m^{-2} year^{-1}, Fig. 6). This phenomenon was not limited to BSi: the sampling site was also among the highest in sediment organic material, carbon, nitrogen and phosphorus, within the study area (Table 1 and Lukkari *et al*. 2009b). As the primary production in the Gulf of Finland is most likely limited by

either N or, in near-shore areas, possibly by P, an increase in BSi sedimentation caused by high DSi influx is unlikely to be this straightforward. For the same reason, changes in BSi sedimentation with time cannot reliably be interpreted as a function of changes in the DSi load. The peak in sedimentary BSi outside Ahvenkoskenlahti may be caused by good conditions for production, i.e. high supply of all nutrients and more stable conditions for diatom production than in the bay itself. It may also be partly due to sedimentation of BSi brought by the river, which may sediment outside the bay as the flow slows down (*see* Conley 1997) and the salinity gradient steepens. BSi is not included in the monitoring data from the rivers, as the analysis is time-consuming and expensive. A fairly high load of BSi though the Kymijoki is feasible, however, as the drainage area is quite rich in lakes (Pitkänen and Tallberg 2007) where planktonic production and consequently also production of BSi is generally higher than in running water.

The excessively high (relative to the river load) calculated burial of BSi in Paimionlahti (22 g m^{-2} year^{-1}, Table 2) may be due to several factors. The high presence of clay (and other mineral) particles in Paimionlahti may have caused an over-estimation of the amount of BSi in the sediment. Although a correction for release of mineral Si is included in the BSi analysis, the fact remains that the produced BSi concentration is only an estimate, since the mineral correction is based on the differences in solubility between mineral Si and biogenic or amorphous Si (DeMaster 1981, Conley 1998). High concentrations of minerogenic Si fractions with higher solubility will, especially in combination with

Table 2. The total DSi load into the two studied bays as calculated from the average concentration of DSi in the river water (River DSi) and the average river flow ($Q_{average}$). The areal load of DSi, ADSi$_{load}$ was calculated by dividing DSi$_{load}$ with the area of the receiving water body. The BSi burial (B_{BSi}) was calculated from the average concentration of BSi in the sediment profiles (Fig. 3) and the sediment accumulation rate (Table 1). The retention of Si, R_{Si} by the estuaries was calculated as $R_{Si} = B_{BSi}/ADSi_{load} \times 100$. The B_{BSi} value used was the average for all stations in each area. The concentrations of DSi and the Q values were taken from the Hertta database at the Finnish Environment Institute (monthly averages).

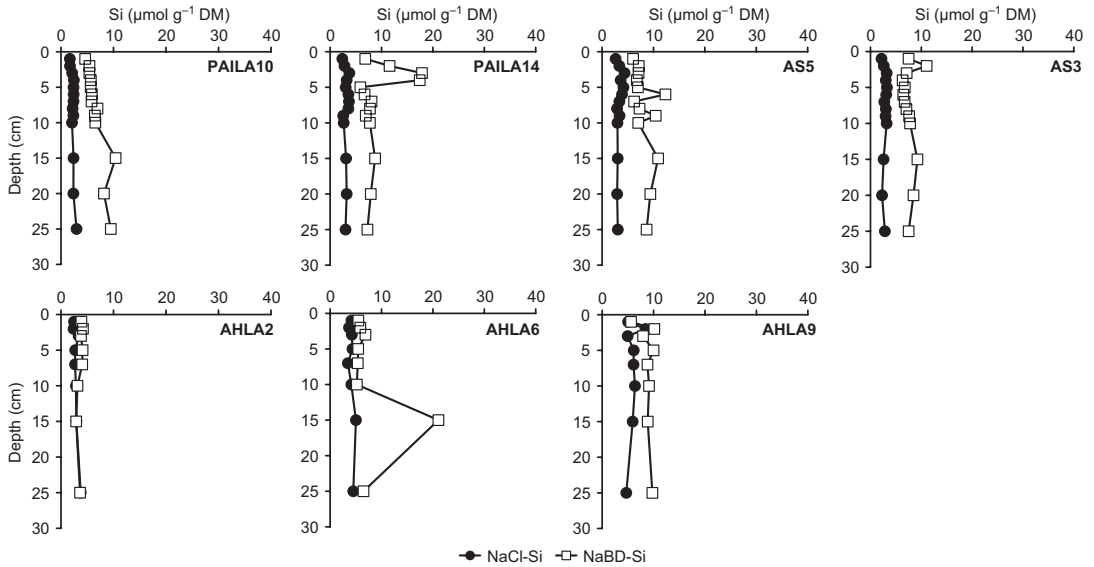|	River DSi (g m^{-3})	$Q_{average}$ (m^3 s^{-1})	DSi$_{load}$ (t year^{-1})	Area (km^2)	ADSi$_{load}$ (g m^{-2} year^{-1})	B_{BSi} (g m^{-2} year^{-1})	RSi (%)
Paimionlahti	7.3	0.09	21	96	0.22	22	10120
Ahvenkoskenlahti	2.1	166	11100	53	209	14	6

Fig. 7. Vertical distribution of NaCl- and NaBD-(dithionite)-extractable Si (NaCl-Si and NaBD-Si, respectively) in the topmost 25 cm of the sediment at the sampling stations in the studied bays (PAILA and AS = Paimionlahti, AHLA = Ahvenkoskenlahti) in the Gulf of Finland and the Archipelago Sea (*see* Figs 1 and 2 for the location of the stations).

low concentrations of BSi, produce erroneously high BSi estimates (Mortlock and Froehlich 1989, Gehlen and van Raaphorst 1993, Conley 1998, Koning *et al.* 2002, Cornelis 2010). The BSi extractant used here (1% Na_2CO_3), extracts not only BSi from aquatic organisms present in the sediment but also the dissolved, easily available Si, any (amorphous) Si adsorbed on clay and oxide surfaces, as well as some Si contained in short-range ordered silicates, such as imogolite and allophane (Mc Keague and Cline 1963a, 1963b, Cornelis 2010). The comparative reliability of the BSi extraction method in sediment studies is, partly, based on the fact that BSi derived from aquatic organisms normally dominates the potentially extractable fraction to such an extent that the error due to extraction of other fractions is negligible.

The sediment in Paimionlahti is rich in clay particles (Pitkänen and Tallberg 2007), Fe and Al (Table 1; Lukkari 2008), but the exact composition (i.e. oxide content) of the studied sediment is not known. The concentration of NaBD-extractable Si bound to reducible Fe-oxides was not especially high in Paimionlahti (5–20 μmol g^{-1} DM, Fig. 7). Some evidence for the existence of another alkaline-extractable Si fraction in addi-

tion to the BSi fraction in Paimionlahti was, however, shown by the results from the NaOH-extraction subsequent to the NaBD-extraction in the P fractionation procedure (Fig. 3). In Paimionlahti, the NaOH-extractable pool of Si was larger than the Na_2CO_3-extractable pool of BSi, whereas the reverse was in general true for the other stations (Figs 3 and 4). The NaOH extraction (0.1 M, 18 h, room temperature) can theoretically be used to estimate Si bound to oxides of non-reducible metals, although one has to keep in mind that the extraction is not designed for Si (*see* Tallberg *et al.* 2009) and that it also extracts BSi. We have earlier shown that in Fe- (and Al-) rich sediments comparatively poor in BSi such as in Paimionlahti, a larger NaOH-extractable than Na_2CO_3-extractable pool of Si indicates the existence of a substantial oxide-bound Si pool (Tallberg *et al.* 2009).

Another possible explanation for the high burial of BSi in Paimionlahti is the same as we presented above for the sedimentation peak of BSi outside Ahvenkoskenlahti; i.e. BSi brought by the river is included in the burial estimate but not in the load. In Paimionlahti, the lower flow rate of the river and the morphology of the bay distributed most of any BSi brought by the river

within the bay, while the main sedimentation event took place outside Ahvenkoskenlahti due to the higher flow rate of the Kymijoki. Further, the rate of sediment accumulation may also have been somewhat overestimated (*see* Mattila *et al.* 2006). Inflow of DSi from the sea area outside Paimionlahti is also possible.

Summary and implications

The ongoing eutrophication of the Gulf of Finland could be discerned from the studied BSi profiles. The profiles also showed that the variability in the sedimentation and possibly preservation of BSi in the sediment was high. The more detailed use of BSi as a paleoproductivity indicator in the Gulf of Finland would require a higher number of deeper cores, as the within-core variability was quite high in many of the cores and the present ones were quite short (25 cm). More BSi is found in the sediments of the more eutrophic eastern than in the western part of the Gulf, although the high differences in sedimentation rates partly obscure the differences in (BSi) production. The variability in BSi largely follows other eutrophication indicators (e.g. C), but some indications of changes in the phytoplankton spring community in especially the eastern coastal Gulf of Finland can be inferred from the profiles. The increasing frequency of years when dinoflagellates dominate the spring bloom could explain the temporally variable sedimentation of BSi shown in the sediment profiles (but *see* also below).

The uneven sediment profiles of BSi in especially the eastern coastal Gulf of Finland, may indicate either cyclic variations in the relative dominance and consequent sedimentation of diatoms in the (spring) phytoplankton community, patchy sedimentation induced by inter-annually variable hydrographical conditions, bioturbation or mechanically induced resuspension in the surface sediment layer (*see* Mattila *et al.* 2006 with references), or reactions of BSi by mineral components of the sediment, possibly induced by periodic anoxic events. It is very likely that several of these processes interact. While our data is not sufficient to determine what the main reason for the zigzag-pattern in the profiles is, it clearly

shows that a sufficient number of samples from a sufficient number of depths are needed to get reliable results on BSi sedimentation. The high spatial variability in the sediment BSi content also shows that these samples have to be taken with large areal coverage and, ideally, including small-scale replicates. This variability in BSi sediment content and sedimentation rates is likely to be one reason for the observed discrepancies between load and burial of Si in the Gulf of Finland (*see* Conley *et al.* 2008). Another factor which may influence the burial estimates is that they are based only on BSi burial, disregarding e.g. oxide-bound Si fractions in the sediment surface layer. This highlights the need for development or modification of extraction methods for sediment Si studies. Based on the current data and the analyzed Si pools, the role of other — on a short-term time scale potentially mobile — Si pools in the sediment is, however, small.

The total retention of DSi by estuarine areas in the Gulf of Finland (and the Baltic Sea) is, based on the current study, low. Although the retention capacity of Paimionlahti was high, this was due to a combination of low river flow and the morphology of the bay, which both contributed to the very high sedimentation rate. Ahvenkoskenlahti, on the other hand, retained only a small part of the DSi load due to the much higher flow of Kymijoki . While indented estuaries thus retain a large part of the DSi load brought by small rivers of moderate flow and this combination is frequent in, especially, southern Finland, most of the DSi load is brought into the Gulf of Finland and the Baltic Sea by large rivers. The three largest rivers in Finland (Kemijoki, Tornionjoki and Kymijoki) transport more than half of the Finnish load of DSi to the Baltic Sea (Humborg *et al.* 2008). The situation for the Gulf of Finland is similar: the three largest rivers Neva, Narva and Kymijoki are responsible for almost 80% of the total DSi load (Humborg *et al.* 2008).

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