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GEOCHEMICAL IMPACTS ON THE RELEASE OF SILICON WITHIN ENTIRE WATERSHEDS

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ACADEMIC DISSERTATION

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ABSTRACT

This thesis focused on the bioreactive pools of silicon (Si) in sediments and phenomena affecting Si release from sediments. There are several potentially mobile pools of Si in sediment, e.g. biogenic Si (BSi), dissolved Si, and adsorbed Si (AdSi). These various Si pools make the investigation of a single pool challenging because of the interference caused by other Si pools. To evaluate the impact different Si pools have on the Si cycle of water ecosystems, it is important to have reliable estimates of the pool sizes. In this thesis, a Bayesian probability model was successfully created to separate two pools of Si, AdSi, and BSi in a catchment area in Southern Finland. The potential correlation between AdSi and BSi was studied to determine whether the size of the AdSi pool could be inferred from the total Si pool (AdSi + BSi). Bayesian inference was also successfully utilized for the explicit separation of different sources of variation caused by measurement imprecision and inter-sample variation. Clear differences were observed between the studied AdSi and BSi pools. The potential error caused by simultaneous extraction of AdSi in BSi determinations was also quantified.

The role of land use and vegetation surrounding the catchment areas where the sampling took place were also taken into account and discussed in this thesis. The land use surrounding the sampling area was seen to affect the amount of different Si species in sediments. Erosion and nutrient leaching can have large effects on the BSi speciation in water and sediments. The role of phytoliths, amorphous silica originating from plants, was seen as an important Si species to be taken into account in future research and modeling.

This thesis also approached the effects of anoxia on Si release from sediments. Although the effects of anoxia on the adsorption and release of adsorbed phosphorus (P) have been studied frequently, the effects on AdSi are commonly ignored despite their similarities as anionic ligands. Because of these similarities, the same processes that affect adsorbed P and its release could therefore affect Si and its release. This assumption was addressed in this thesis and the effects of anoxia on AdSi dynamics in surface sediments were explored by two separate experiments: a sequential extraction for the effects of anoxia on different AdSi fractions and a longer-term release dynamics experiment. The study areas were a small catchment area in Siuntio and the Vantaa River estuary in Southern Finland.

Our study showed that anoxia does affect the release of Si. It did not however enhance the release of Si in loosely bound and reducible-Fe fractions, contrary to the a priori assumption based on the known mechanisms for P release upon reduction of Fe. Silicon also appeared to be released more slowly under anoxic than oxic conditions in most of the studied sediments.

From an ecological or water-protection perspective, the results indicated that anoxia can both increase and decrease Si mobilization. The results were, however, far from clear-cut and more studies are clearly needed to unravel the behaviour of Si under anoxic conditions.

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CONTENTS

List of original publications and participation	8
Symbols and abbreviations	9
1 Introduction.....	10
1.1 Background and motivation of the thesis.....	10
1.2 Bayesian inference	13
2 Objectives of the research.....	14
3 Materials and methods	15
3.1 Study areas	15
3.2 Laboratory methods.....	16
3.2.1 Acid oxalate extraction and organic matter.....	16
3.2.2 Biogenic Si extractions	17
3.2.3 Sequential extraction (III)	17
3.2.4 The release dynamics experiment (III)	18
3.2.5 Elemental analysis	18
3.3 Statistical analysis.....	18
3.4 Bayesian probabilistic model (I).....	19
3.4.1 Model description	19
3.4.2 Prior distributions.....	20
3.4.3 Measurement variation models and the goodness of fit	21
3.4.4 Posterior computation.....	22
4 Results and discussion.....	23
4.1 Assessing the uncertainty in silicon extractions through Bayesian inference (I)	23

4.1.1	The sources of uncertainty and the posterior distributions of BSI, TSi and AdSi.....	24
4.1.2	Quantification of the measurement error	26
4.2	Reactions of potentially mobile Si pools in sediment (II, III)	29
4.2.1	Variation in bio-reactive Si pools under different environments (II, III)	29
4.2.2	The effect of sedimentary anoxia on Si release (III)	30
5	Concluding remarks	37

LIST OF ORIGINAL PUBLICATIONS AND PARTICIPATION

This thesis is based on the following publications:

- I Siipola, V., Mäntyniemi, S., Lehtimäki, M., Tallberg, P., 2013. Separating biogenic and adsorbed pools of silicon in sediments using Bayesian inference. *Silicon*, 5, 53-65.
- II Lehtimäki, M., Tallberg, P., Siipola, V., 2013. Seasonal dynamics of amorphous silica in Vantaa River estuary. *Silicon*, 5, 35-51.
- III Siipola, V., Lehtimäki, M., Tallberg, P., 2015. The effects of anoxia on Si dynamics in sediments. *Journal of Soils and Sediments*, 16, 266-279.

The publications are referred to in the text by their roman numerals.

The author's contribution:

- I and III The author was responsible for the experimental work and writing of the articles. S. Mäntyniemi contributed on writing the Bayesian statistics section of the article, other co-authors contributed to the planning of the studies and to the revision of the manuscripts.
- II The author participated in the planning of the study and in the experimental work, minor contribution on writing of the article.

SYMBOLS AND ABBREVIATIONS

$\pi_k^{(A)}$	The true concentrations of AdSi in a sampling site k
$\pi_k^{(B)}$	The true concentrations of BSi in a sampling site k
μ_A	The median of AdSi in the study area
μ_B	The median BSi in the study area
ν_A	Coefficient of variation (CV: standard deviation divided by mean) of AdSi
ν_B	Coefficient of variation (CV: standard deviation divided by mean) of BSi
ρ	Correlation coefficient
α	Measurement standard deviation
β	Measurement coefficient of variation
γ	Ratio of variance and true concentration
$\sigma_{k,M}^{(A)2}$	The sampling site specific variance of ln-transformed measurements of AdSi
$\sigma_{k,N}^{(T)2}$	The sampling site specific variance of ln-transformed measurements of TSi
AdSi	Adsorbed Si
BSi	Biogenic Si ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$)
TSi	“total” Si = (AdSi + BSi)
DSi	Dissolved Si
MQ	Milli-Q water
ICP-OES	Inductively coupled plasma optical emission spectrometer
NaBD	Sodium dithionate
SE	Sequential extraction
RDE	Release dynamics experiment
OM	Organic matter
MCMC	Markov chain Monte Carlo
BMA	Bayesian model averaging
CV	Coefficient of variation
PI	Probability interval. Contains the true value of the parameter with the chosen probability.

1 INTRODUCTION

1.1 BACKGROUND AND MOTIVATION OF THE THESIS

The importance of the global biogeochemical silicon (Si) cycle largely rises from the fact that Si is a macronutrient for the phytoplankton called diatoms (Bacillariophyta). Diatoms are one of the most common phytoplankton groups and they compete for nutrients, such as phosphorus (P) and nitrogen (N), with other, possibly harmful or toxic, phytoplankton groups. This competition affects not only the eutrophication state but also the food webs of water ecosystems (Spilling et al. 2010, Humborg et al. 2000). The Si cycle is also linked to the carbon cycle as significant amounts of carbon are buried in the sediments in diatom form (Tréguer et al. 2000).

The Si cycle in the Baltic Sea has been thoroughly investigated during the last decades, especially after the observation that the amounts of dissolved Si have been decreasing during the 20th century (Rahm et al. 1996, Humborg et al. 2000, Humborg et al. 2006, Conley et al. 2008, Papush et al. 2009, Tallberg et al. 2009, Tallberg et al. 2012, Tallberg et al. 2013). The Si concentration decrease may have had an effect on abundance changes in different phytoplankton species, such as the increase of dinoflagellates at the expense of diatoms (Spilling 2007, Klais et al. 2011) and possibly on the mass blooms of blue-green algae (cyanobacteria) that started in the 1990s. Changes that have occurred in the Si loads and in the uncertainties concerning calculated Si budgets are still in need of further investigation. This is especially the case for the origin of biogenic Si (BSi), which is amorphous Si ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) bound by living organisms in water, sediments, and soil, and the proportion of this pool in the potentially biologically available Si budget. This information would clarify whether changes in the watersheds and the water body itself or chemical (e.g. weathering, sorption) or biological (accumulation of BSi in plants and water organisms) processes have caused the reductions in the Baltic Si concentrations. This information is needed to plan possible remediation measures correctly.

Although Si is the second most abundant element on the Earth, the bioavailability of Si is limited due to the slow weathering rate of most silicate minerals (Lerman 1988, Hartmann et al. 2010). Therefore, in both terrestrial and aquatic watersheds, the short-term cycling of Si is mainly governed by the biological cycling of Si (Conley et al. 1993, Rahm et al. 1996, Humborg et al. 2008). This cycling consists of the burial and dissolution of BSi in soils and sediments, followed by the uptake of dissolved Si (DSi) by aquatic organisms and plants. The BSi produced by plants are called phytoliths (Piperno 2006), which can be produced by both aquatic and terrestrial plants. In aquatic environments, the Si cycle is mainly governed by diatom BSi, whereas in terrestrial environments plant phytoliths are the main source

of BSi driving the Si cycle (see e.g. Stryuf and Conley 2009). The amorphous BSi structures of diatoms and phytoliths are resistant to decomposition and can be preserved in soils and sediments for time periods long enough to be used for paleo-indicator purposes (Koning et al. 2002, Piperno 2006, Tallberg 2015). Terrestrial BSi can also be found in sediments, as phytoliths are transported through topsoil erosion to watercourses (Piperno 2006, Cary et al. 2005, Fabres et al. 2008).

The naturally occurring Si pools can be roughly divided into three groups (e.g. review by Sauer et al. (2006)). The first group is the immediately available, soluble Si pool, which includes DSi (i.e. ortho-silicic acid, H_4SiO_4 , dissolved Si) and loosely adsorbed Si species. The second group is the readily soluble pool of amorphous silica consisting of biogenic silica and of Si bound to poorly crystalline constituents and weakly-ordered sesquioxides. The third group is mineral Si. The use of nomenclature and extraction methods within each group is wide, and this often makes comparison of results difficult. The separation of the different Si fractions is also difficult, as the range of variables to be taken into account is wide. These variables include the physical and chemical characteristics (e.g. soil/sediment, the existence of diatoms/phytoliths, the amount of oxide surfaces and pH) of the sample (see e.g. Sauer et al. 2006).

To determine the source of BSi in river water and Si bound to sediment particles and how easily this Si becomes available for diatoms and other Si-requiring organisms, the biogenic fraction needs to be separated from the more easily released adsorbed and amorphous Si fractions. For instance, it has been shown that sandy sediments, which are usually taken to be quite inert, can release substantial amounts of DSi (Tallberg et al. 2013). Studying the importance of this phenomenon is challenging, as separating different Si fractions from sediments and soils using chemical extraction methods is difficult (see e.g. Tallberg et al 2009). The widely used and well defined extraction methods for BSi are known to dissolve some Si minerals (DeMaster 1981, Barão et al. 2015). Accordingly, it is reasonable to assume that adsorbed Si (AdSi) is also released, causing overestimation of the BSi result. Research on this simultaneous AdSi release is scarce. Recent studies have concluded that AdSi and poorly crystalline forms of Si are co-extracted with Na_2CO_3 (Cornelis et al. 2011, Barão et al. 2015a, Barão et al. 2015b). In this thesis, a novel approach using Bayesian inference for distinguishing between the AdSi and BSi pools is presented in article I and introduced separately in the following section.

The vegetation surrounding the sampling site plays a vital role determining the amount of different Si species. If the erosion of the top soil in the catchment is high, amorphous Si and BSi in sediments can contain considerable amounts of phytoliths (Cary et al. 2005, Piperno 2006, Stryuf et al. 2009). Land use changes and related human activities may influence phytolith mobilization from soils if these activities enhance, for instance, the erosion sensitivity of the land surface (Woodward and Foster 1997, Walling

1999). High rainfall events may mobilize high amounts of particulate matter transporting phytoliths to watercourses through top soil erosion due to decreased vegetative cover (Cary et al. 2005, Piperno 2006, Fabres et al. 2008). Deforestation may also decrease the Si delivery to rivers as deforestation leads to removal of amorphous Si from the soil through erosion, decreased vegetation water consumption, and increased water fluxes promoting leaching (Struyf et al. 2010). Crop harvesting and repeated soil disturbance also prevents the replenishment of the amorphous Si stock. The role of land use regarding the transport and sizes of different Si pools is addressed in article **II**.

Anoxia is known to have many negative effects in waters. These include P release from sediments and its impact on eutrophication, but also detrimental effects on e.g. benthic fauna and other organisms (Zillén et al. 2008). Evidence exists on the connection between anoxic/hypoxic conditions and increased availability of DSi (Hartikainen et al. 1996, Bauerfeind and Bodungen 2006, Belias et al. 2007, Lukkari et al. 2007b, Papush et al. 2009, Danielsson 2014), but the reasons for this connection are unclear. Research on Si reactions under anoxia in sediment is quite limited (Hartikainen et al. 1996, Lukkari et al. 2007b, Loucaides et al. 2010), although Si shows several similarities to P as an anionic ligand (Hingston et al. 1967, Hartikainen et al. 1996). Si may e.g. affect P adsorption and release in sediments through competition for adsorption sites. Hartikainen et al. (1996) found that anoxia increased the Si concentration in sediment pore water only slightly compared to that of P. Lukkari et al. (2007) studied the effect of N₂-shielding of reduced sediment samples on different fractions of P and found total DSi from the redox-sensitive fraction to be slightly higher in the unshielded samples, suggesting the release of Fe-bound Si. A recent study by Ekeröth et al. (2016) found reduced Si fluxes from anoxic Baltic Sea sediments after bottom water oxygenation, which was explained by scavenging by iron oxides sorbents in the surficial sediment. Lehtimäki et al. (2016) studied the role of microbial activity in the dissolution of BSi and found higher dissolution of BSi under hypoxic conditions if microbial activity remained uninhibited.

One of the less known Si-related phenomena are the effects Si can have on iron oxide crystallization (Weber Jr. and Stumm 1965, Meng and Letterman 1993, Mayer and Jarrell 2000, Piispanen and Sallanko 2011). DSi can inhibit the Ostwald ripening (re-crystallization) and coagulation of iron oxides, leading to the formation of ferrihydrite instead of more crystallized Fe oxides, such as goethite or lepidocrocite. Si can also form mixed Fe-Si oxides if Fe oxidizes in the presence of Si. This process can thereby increase the sediment's P adsorption capacity by increasing the amount of available adsorption sites (see e.g. Mayer and Jarrell 2000). The interactions between Fe and Si in sediments have not been studied extensively. Furthermore, the Si effect is also usually excluded when P adsorption and release under anoxic conditions is studied. This thesis addresses these questions in article **III**.

1.2 BAYESIAN INFERENCE

Bayesian inference handles uncertain knowledge in a consistent and transparent way. Bayesian inference involves expressing existing knowledge about the variables of interest in the form of probability distributions and then updating these distributions with new data. The probability distributions are called prior and posterior distributions, referring to the distributions of knowledge before obtaining the actual data set and to the distributions after the update, respectively. Scientific learning is formalized as the obtained posterior distribution then serves as prior for the following dataset (Jaynes 2003).

Formalization of the data interpretation follows from expressing conditional knowledge about the observations before seeing them. The analyst then builds a conditional probability distribution for the data to be observed based on the knowledge about the natural phenomenon and the processes affecting them. Interpretation of the observed data is then performed using the conditional distribution, which forms the likelihood function for the parameters of interest. The posterior distribution is then proportional to the product of the prior distribution and the likelihood function.

In recent years, the use of Bayesian inference has gained increasing interest in the field of environmental chemistry. Bayesian inference has been used to reevaluate lake P models with improvements in six of the seven models tested (Cheng et al. 2010), in a P-runoff study focusing on different P fertilizer application methods (Burkitt et al. 2011), in a study on the effects of different liquid/solid ratios in multiple batch extractions of soil contaminants (Iden et al. 2008), and in estimating the annual regeneration rates of total P and N for different land uses in Tasmania to assist stakeholder management decisions (Broad and Corkrey 2011). The interest in using Bayesian inference is probably due to its ability to account for underlying uncertainties, which makes modeling of highly uncertain natural phenomena more reliable and realistic.

As described in article I, Bayesian inference provides direct statements of uncertainty about the parameters of interest, based on observed data and scientific knowledge accumulated prior to collecting the dataset (Jaynes 2003, O'Hagan 2011). The use of hierarchical models is also increasing in all areas of natural sciences, due to the efficiency and consistency of these models in pooling information from multiple sources (Hilborn and Liermann 1998, Gelman 2003, Gelman et al. 2003). In this thesis, one of the main interests with the model in article I was the separation and reduction of sampling error, which was accomplished by using a hierarchical model.

2 OBJECTIVES OF THE RESEARCH

The aim of this dissertation was to provide insights into the relative abundance of different potentially bioavailable Si pools in two boreal watersheds and into the changes occurring in these pools under different oxygen conditions. The research questions were approached by development and use of suitable extraction schemes for different Si species in sediments and by Bayesian probabilistic modeling, which was used to separate the AdSi and BSi pools of Si and to estimate the error caused by AdSi on the BSi results.

The research questions were:

1. Is it possible to use Bayesian probabilistic modeling to distinguish between AdSi and BSi pools in sediments (**I**)? Is there a correlation between the AdSi and biogenic sediment Si pools? What are the sources of variation regarding the measurements of AdSi and BSi?
2. Does sampling area (e.g. vegetation, land use) have an effect on the potentially mobile Si pools in sediments (**II**)?
3. Does increased reduction of Fe due to anoxia increase the release of Si from sediments (**III**)? What are the time scales involved in the release of Si?

3 MATERIALS AND METHODS

3.1 STUDY AREAS

The study areas used were a small catchment in Siuntio (figure 1) ($60^{\circ}04.75' - 60^{\circ}09.20'N$ and $24^{\circ}17.25' - 24^{\circ}19.80'E$) (**I**, **III**) and the Vantaa River estuary (a map can be found in article II) (**II**, **III**), located in Southern Finland. Sampling locations in Siuntio consisted of 18 sampling sites. AdSi concentration was determined from 10 sites and BSi from all 18 sites. Sampling locations were the lakes Lappträsk, Långträsk, Rudträsk, Vikträsk, Stora Bladträsk, Lilla Bladträsk, and small streams connected to the lakes. One site was located in the receiving sea estuary in Pikkalanlahti Bay. The lakes are very shallow ($<2 - 5$ m), only lake Vikträsk is deeper (17 m). The surrounding area around the lakes is mainly coniferous and mixed forest. There are also agricultural field areas next to Lake Vikträsk and River Pikkalanjoki.

Water samples from the Vantaa River were collected from four sampling points: Vantaa River ($24^{\circ}59.003'E$, $60^{\circ}13.478'N$), Vantaa River mouth ($24^{\circ}59.032'E$, $60^{\circ}12.818'N$), Mustikkamaa ($24^{\circ}59.093'E$, $60^{\circ}11.173'N$), and Naurissalmi ($25^{\circ}1.038'E$, $60^{\circ}11.433'N$). Vantaa River estuary sediment samples were collected from Vantaa River, Vantaa River mouth, Naurissalmi, and Vanhankaupunginlahti ($24^{\circ}59.411'E$, $60^{\circ}12.032'N$). An additional dataset was used for the Bayesian study (**I**) to construct the prior distribution needed for the model. The dataset consisted of data collected from 4 sampling points in the River Paimionjoki estuary (sampling area $60^{\circ}13.27' - 60^{\circ}22.14'N$ and $22^{\circ}25.98' - 22^{\circ}34.18'E$) and 3 sampling points in the River Kymijoki estuary (sampling area $60^{\circ}24.12' - 60^{\circ}27.31'N$ and $26^{\circ}28.60' - 26^{\circ}29.73'E$; Lukkari et al. 2007a, Lukkari et al. 2007b, Lukkari 2008).

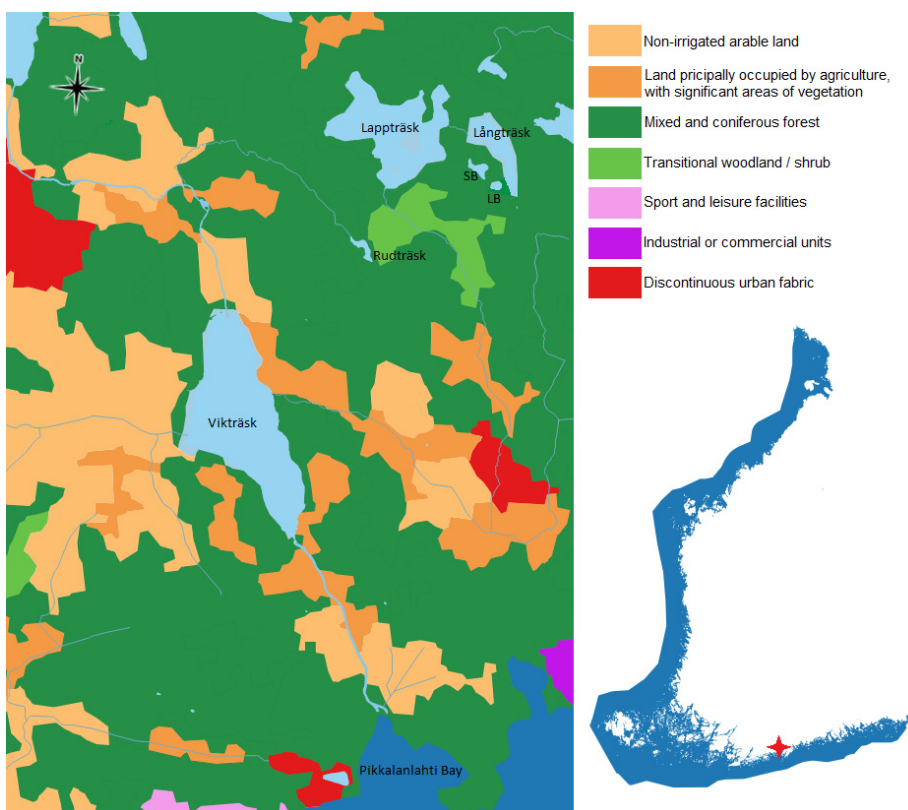


Figure 1 Landuse map of the sampling area in Siuntio, Finland. SB = Stora Bladträsk; LB = Lilla Bladträsk. Scale 1:43 000. Source: *Lapio-map application/SYKE* (http://www.syke.fi/en-US/Open_information/Spatial_datasets). Map drawn with QGIS-software (<http://www.qgis.org/fi/site/>)

3.2 LABORATORY METHODS

3.2.1 ACID OXALATE EXTRACTION AND ORGANIC MATTER

An acid oxalate extraction was used for the AdSi, P, Fe, and Al (**I**, **II**, **III**). Oxalate-extracted concentrations were compared to the results of the other extraction experiments. The oxalate extraction was conducted using 1 g of sample shaken in 60 ml of 0.2 M acid ammonium oxalate (pH 3) for 16 h in room temperature on a rotary shaker at 300 rpm (Schwertmann 1964, Jackson et al. 1986). The samples were shielded from light during the extraction. OM was estimated as loss on ignition using a temperature of 550°C for 2 h (Standard SFS 3008 1990) (**I**).

3.2.2 BIOGENIC SI EXTRACTIONS

For the determination of BSi, wet alkaline digestions were used. Water samples were pre-filtered through 2 µm or 25 µm porosity ashless filter papers, after which the pre-filtered water was passed through 0.2 µm polycarbonate membranes. The filters were dried at 60°C and the OM removed with concentrated HNO₃ digestion at 100°C. The filters were then extracted with 0.2 M NaOH at 100°C for 40 minutes (Ragueneau et al. 2005) (II). Total dissolution of the particular matter samples was executed by HF digestion (2.9 M, 48 h). Sediment BSi was extracted with 1% Na₂CO₃ at 85°C in a water bath (DeMaster 1981) (I, II, III). Subsamples (1 ml) were drawn after 3, 4, and 5 hours, after which 9 ml of 0.021 N HCl was added to dilute and neutralize the samples.

The methods were selected on basis of best suitability for the sample types. The NaOH method by Ragueneau is designed especially for the determination of BSi in suspended matter in water. This method corrects the mineral inference caused by lithogenic Si by using Si:Al ratios. The DeMaster's Na₂CO₃ method is commonly used for sediments, as it also corrects the dissolution of mineral Si in the results.

3.2.3 SEQUENTIAL EXTRACTION (III)

The purpose of the sequential extraction (SE) was to explore how anoxia affects the release of different AdSi fractions in sediments. The experiment was performed using 7 different sediment samples, of which 4 were collected from a catchment area in Siuntio and 2 from the brackish water of Vanhankaupunginlahti Bay (VKL) outside Helsinki in the Baltic Sea. One sample was a lake sediment reference material (LKSD-2, CCRMP). From Siuntio, 3 of the samples were surface sediment samples (topmost 1 cm, from small lakes and ponds) and one sample was collected from a small brook. From VKL, one of the samples was a composite sample taken from 2 to 15 cm depth and one surface sample (topmost 1 cm). The samples were selected so that they had varying Al/Fe-oxide ratios (mol/mol), forming a wide range from 0.29 to 5.5. A description of the sediment samples can be found in article III.

The SE sediment samples were first dried at 60°C (except for the already dry reference material) and passed through a 0.45 mm sieve. The experiment was conducted under oxic and anoxic conditions. In the anoxic part of the experiment, the extraction solutions were first bubbled with N₂ to remove dissolved O₂. The SE sequence used is graphically presented in figure 2. All extractions were performed with a solid:solution ratio of 1:100 at room temperature. For the anoxic samples, a N₂ glove box (max 3% O₂) was used. The pH was adjusted with NaOH or HCl as necessary. The extracts were filtered through 0.2 µm polycarbonate membranes prior to analysis with

ICP-OES (Thermo iCap, Cambridge, UK). The original scope of the extraction method is to separate different species of P: water and NaCl extract loosely sorbed, NaBD redox-sensitive Fe- and Mn-bound, NaOH Al-bound and HCl apatite-bound P. The applicability for Si is somewhat limited, as NaOH also dissolved BSi and HCl mostly mineral Si. Therefore, the main focus in this experiment was on the first three fractions. The sediment samples were washed with 0.46 M NaCl after each step to avoid tailing and to ensure that each step was completed before proceeding to the next.

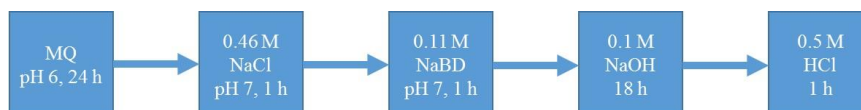


Figure 2 Extraction scheme of the sequential extraction experiment

3.2.4 THE RELEASE DYNAMICS EXPERIMENT (III)

The release dynamics experiment (RDE) was used to examine the long-term release of AdSi. The dry sediment samples were mixed with MQ water (pH 6) and left standing, except for 1 h shaking on a rotary shaker (300 rpm) prior to sampling. The experiment lasted for 28 days and subsamples were drawn with a syringe 1, 2, 3, 4, 7, 10, 14, and 28 days from the start of the experiment and filtered through 0.2 μm syringe filters. The day 28 samples of the RDE were used to detect possible formation of Fe-Si colloids and were also analyzed unfiltered.

3.2.5 ELEMENTAL ANALYSIS

Elemental analysis (Si, P, Fe, Al) of the samples was performed with Thermo iCap ICP-OES (Cambridge, UK) (**I**, **II**, **III**). Spectrophotometric determinations were used for Si in the RDE experiment and for some BSi samples (**II**), using the molybdene blue method at a wavelength of 815 nm (Mullin and Riley 1955) (**III**).

3.3 STATISTICAL ANALYSIS

In the Bayesian modeling of article **I**, OpenBugs-software was used for the Markov chain Monte Carlo (MCMC) simulations (Lunn et al. 2000). The statistical analyses in article **II** were performed using PASW Statistics 18. Analysis of variance (GLM) was followed by Bonferroni post hoc testing. The

analysis was performed to discover the differences in ASi and DSi loads of Vantaa River between different seasons and also the impact of sampling time and sampling point on the ASi and DSi concentrations in the river particulate matter and sediment. Post-hoc tests were used to avoid increasing the probability of type I error, as the analysis consisted of multiple simultaneous hypothesis testing. A 5% significance level was used in all the analyses. For nonparametric and parametric correlations, Spearman and Pearson correlations were used, respectively. Statistical analysis in article **III** was performed with the R software (R Core Team 2013). The statistical test used was the nonparametric two-sample Kolmogorov-Smirnov test (K-S test) (Chakravarti et al. 1967), which compares two empirical sample distributions against null hypothesis that they originate from the same continuous distribution. The test, which was performed at 5% significance level, was selected on the grounds that it does not require data to be normally distributed and is also sensitive to differences in location and scale of the empirical distributions.

3.4 BAYESIAN PROBABILISTIC MODEL (I)

3.4.1 MODEL DESCRIPTION

The problem assessed with the Bayesian modeling was the simultaneous and unavoidable extraction of AdSi as BSi, which is extracted due to the dissolution of mineral surfaces to which Si is adsorbed. Simultaneous extraction of two Si pools creates overestimation of the other. Furthermore, there are other sources of error, such as measurement error and the heterogeneity of the sampling sites, which also create uncertainty in the results and need to be assessed. The created model was a full probability model that separates the two Si pools (AdSi and BSi) and makes an inference about their joint variation within the studied area. The model also isolates variation between and within the sampling sites. Variation within the sampling sites (measurement errors) was tested with three hypothetical model structures. The modeled data consisted of 10 sampling sites with 33 observations for AdSi and 18 sampling sites with 58 observations for BSi collected from a small catchment area in Siuntio in Southern Finland.

The created model is graphically presented in figure 3. An assumption of exchangeability between sampling sites (all sampling sites were a priori treated indistinguishable from one another) was used for the pairs of true concentrations of AdSi (A) and BSi (B) $(\pi_k^{(A)}, \pi_k^{(B)})$. Therefore, the modeled pairs of the true concentrations were treated as conditionally independent draws from a common probability distribution whose parameters are

uncertain (de Finetti 1975). A bivariate log-normal distribution was chosen to best reflect the distribution of all studied sampling sites, if a large number of sites were sampled from the study area. Therefore, the marginal distributions of $\pi_k^{(A)}$ and $\pi_k^{(B)}$ were also log-normal.

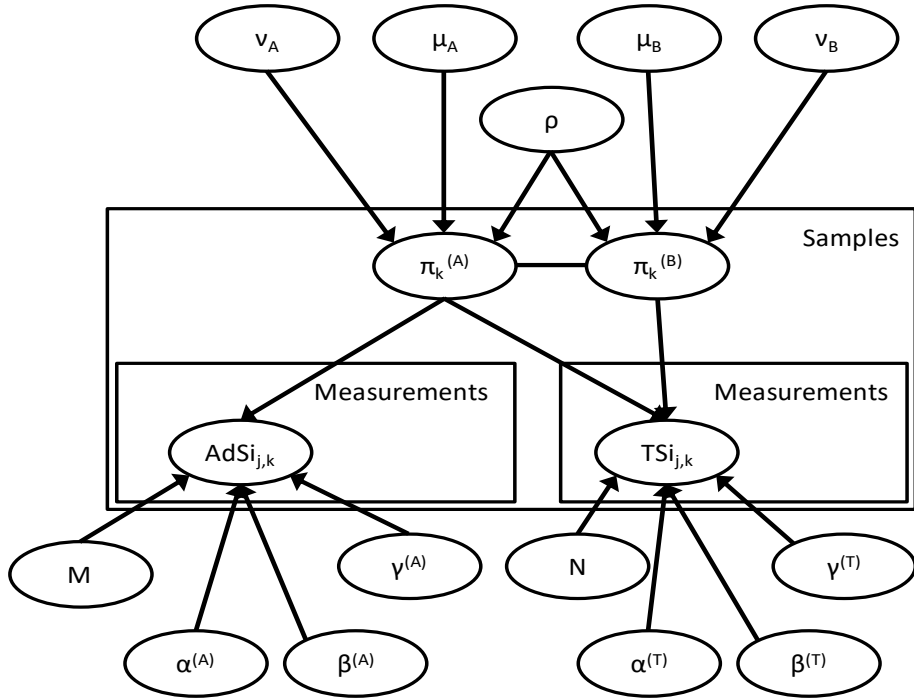


Figure 3 Graphical model of the probability model used to infer the concentration of BSi. $\pi_k^{(A)}$ and $\pi_k^{(B)}$ = the true concentrations of AdSi (A) and BSi (B) in a sampling site k ; $TSi_k = (\text{AdSi} + \text{BSi})$ = the extracted BSi concentration in a sampling site k ; μ_A and μ_B = medians of AdSi and BSi in the study area; v_A and v_B = coefficients of variation (CV: SD/mean) of AdSi and BSi; ρ = correlation coefficient describing the joint variation of $(\ln(\pi_k^{(A)}), \ln(\pi_k^{(B)}))$; M and N = model indicator variables; α , β , and γ = measurement standard deviation, measurement coefficient of variation, and the ratio between measurement variance and true concentration, respectively.

3.4.2 PRIOR DISTRIBUTIONS

An important part of Bayesian modeling is the formulation of prior knowledge into appropriate prior distributions to be used in the model. In this process both expert opinions and existing knowledge can be used. In the study in article I, expert opinion was mainly used in the selection of the prior data, which came from an area that is closely related to the studied sampling site e.g. the prior data sediment samples were collected near the modeled area and extracted for Si and other elements. The selected probability

distributions were also chosen based on the type of data to be modeled (e.g. concentrations cannot be negative) and literature. The prior data was then processed by frequentist statistics to produce the limits for the prior distributions that were selected.

The prior distributions were derived using a dataset from a previous study concerning chemical characteristics of Baltic Sea sediments (Lukkari 2008). The prior dataset consisted of extraction results for Si obtained by a SE scheme commonly used for P extraction. The data consisted of 7 sampling sites, each of which contained 8-10 samples from depths of 0 to 20 cm (a total of 76 samples). The sum of the NaCl and NaBD extractions were chosen to form the prior distribution of AdSi, and the BSi results were used for the BSi prior distribution formation. With the prior data, the BSi was taken to consist only of BSi. However, the actual modeled measurements of BSi (denoted as TSi) were taken to be the sums (AdSi + BSi). Log-normal and uniform distributions were selected for the prior parameters. The specific parameter values and detailed information on the prior construction is provided in article I.

3.4.3 MEASUREMENT VARIATION MODELS AND THE GOODNESS OF FIT

Three measurement variation models were used to isolate the between sampling site variation from the within sampling site variation and to account for the uncertainty regarding variance structures of the AdSi and BSi extraction methods. Exchangeability was again assumed within sampling sites with all measurements of TSi and AdSi. Log-normal distribution was also again chosen to describe the measurement variation, since the true underlying concentrations within each sampling site cannot be negative. The actual measurement processes were assumed to be unbiased. With the first error model, the largest errors would take place when the true concentration is small and hence the dominant source of error would be the extraction method. The second model assumed increasing standard deviation with increasing true concentration, which implies multiplicative errors. In the third error model, the measurement variance was assumed to increase linearly with the true concentration. This kind of model structure may result if the concentration is highly clustered in the sample (Lindén and Mäntyniemi 2011). Bayesian model averaging (BMA), which treats all models as alternative hypothesis about the studied phenomenon and bases all inference on their weighed mixture instead of picking the one “best” model, was used in the model evaluation (Hoeting 1999). As there was uncertainty about the proper error model for both AdSi and TSi, uninformative priors were assigned to them. Detailed information of the error models and the accompanying priors can be found in article I.

The goodness of model fit was checked using Bayesian p values (Gelman et al. 1996). The assumption of log-normality of AdSi and BSi variation within the study area and the goodness of fit of the variance structures assumed for AdSi and TSi measurement processes were verified.

3.4.4 POSTERIOR COMPUTATION

To obtain the posterior distributions, a numerical approximation method was needed; an MCMC simulation was used. In MCMC, a large sample of random values are drawn from the posterior distributions, after which descriptive statistics of the large sample can be used to approximate the respective features of the posterior distribution (Gilks et al. 1996). The precision was measured by Monte Carlo error, which was kept under 5% by increasing the MCMC sample size until the desired precision was obtained. Carlin and Chip method was used within the MCMC simulation to estimate the posterior probabilities of the different model structures (Carlin and Chib 1995). To ensure the convergence of the simulations, a minimum burn-in of 1000 iterations and Gelman-Rubin convergence diagnostics (Gelman and Rubin 1992) was used.

4 RESULTS AND DISCUSSION

4.1 ASSESSING THE UNCERTAINTY IN SILICON EXTRACTIONS THROUGH BAYESIAN INFERENCE (I)

The extraction of Si becomes challenging if different Si pools need to be separated, as there is no way of knowing how much overlap there is between the different pools or extraction steps if SEs are used (Tallberg et al. 2009). The simultaneous dissolution of different AdSi species makes the interpretation of the results difficult (Sauer et al. 2006). In addition, the multitude of different extraction methods used for the different pools makes comparison of the Si concentrations challenging (Fox et al. 1967, Jensen and Thamdrup 1993, Barbosa-Filho et al. 2001, de Lima Rodrigues et al. 2003, Saccone et al. 2007, Tallberg et al. 2009). Sediment oxide composition, the amount of OM, particle size, time, temperature, extraction solution, and oxygen conditions are some of factors that affect the results and create uncertainty.

In the study of the effects of anoxia on Si release (III), uncertainty caused by overlap was addressed by rinsing the samples with NaCl prior the next extraction step. While this procedure was probably quite sufficient for the loosely bound fraction extracted by water and NaCl, the use of the next, stronger solution, most likely extracts some of the Si left from the previous step and also some from the forthcoming steps. The use of oxalate for the Al- and Fe oxide-bound Si also releases the loosely bound, water extractable Si. The extraction of BSi uses strongly alkaline solutions that dissolve not only the BSi, but also some of the mineral structure as well, and thereby also AdSi (DeMaster 1981, Cornelis et al. 2011). This overlap between BSi and AdSi pools was assessed in our studies by Bayesian statistical modeling (I). The model was successfully able to separate the biogenic and adsorbed pools of Si and to identify the sources of within-site uncertainty regarding the two pools. The mean error caused by AdSi on the extraction of TSi (AdSi + BSi) was 7.4%. The mean concentrations of AdSi and BSi were 0.49 and 29 mg g⁻¹, respectively. Detailed results are presented in table 1.

Table 1 Posterior results of the model. π = marginal distribution of AdSi (A) or BSi (B); u = coefficient of variation AdSi (A) or BSi (B); μ = Median of AdSi (A) or BSi (B); ρ = correlation coefficient; SD = standard deviation; PI = probability interval. All results are in mg g⁻¹, except for the u and ρ , which are unitless.

	Mean	SD	MC-error	2.5 % PI	Median	97.5 % PI
π (A)	0.49	0.78	0.002	0.04	0.29	2.1
Mean AdSi	0.49	0.19	0.001	0.25	0.45	0.96
μ (A)	0.30	0.09	0.0004	0.16	0.29	0.51
π (B)	28	85	0.26	0.8	11	154
Mean BSi	29	15	0.07	13	25	65
μ (B)	12	3.7	0.02	6	11	20
TSi	29	85	0.26	1.2	12	154
v (A)	1.26	0.40	0.4	0.75	1.18	2.27
v (B)	2.26	1.07	0.009	1.13	2.00	4.99
Ratio AdSi/TSi	0.074	0.126	0.001	0.0008	0.025	0.481
ρ	-0.137	0.225	0.001	-0.550	-0.146	0.316

4.1.1 THE SOURCES OF UNCERTAINTY AND THE POSTERIOR DISTRIBUTIONS OF BSi, TSi AND ADSI

Clear differences between AdSi and TSi were found (see table 2). Model structure 1 (sd independent of concentration) was found to be the most likely source of variation for AdSi ($p = 0.95$). The result indicated that the uncertainty involved in AdSi measurement is strongly linked to the extraction method and small concentrations, which can be 100 times smaller than that of BSi. Detecting small concentrations is demanding, as there are multiple factors that can affect the results, such as purity of solutions, accuracy of the chemical analysis and, in the case of AdSi, dissolution of diatoms during the extraction. It is reasonable to assume that some amount of reactive BSi is always included in the AdSi results if there are diatoms or phytoliths present in the sample. For the model, a pre-examination of BSi dissolution was conducted with ammonium oxalate, which was the solution used in the AdSi extractions. The results indicated a negligible amount of BSi (4 mg Si/g diatoms) to dissolution. There is, of course, also some error in the prior extraction data used for AdSi; the BSi dissolution in the extraction solution of the prior data (NaCl and NaBD) was not tested. The uncertainty concerning the prior data was taken into account in the limits of prior distributions. For AdSi, there was also a 5% probability to model 3 (linear increase of variance), which caused some error by concentrations clustering. The results were otherwise clear. For TSi, the

probabilities were divided by model 2 (linear increase of sd) ($p = 0.113$) and model 3 ($p = 0.886$), which suggests the main source of variation for TSi to be the clustering of the BSi concentrations. The model 2 result also indicated multiplicative error sources, which are more difficult to identify.

Table 2 *The resulting probabilities of Bayesian model averaging*

	<i>Sd independent of concentration</i>	<i>Linear increase of standard deviation</i>	<i>Linear increase of variance</i>
AdSi	0.954	0	0.046
TSi	0.0004	0.113	0.886

The predictive posterior distributions of AdSi, BSi, and TSi for a new randomly chosen sampling site (figure 4) reflect the results of the BMA. Log-normal distributions are skewed distributions where the degree of skewness depends on the standard deviation; larger sd causes a higher degree of skewness and the means are larger than the medians. The degree of skewness and long tails of the obtained posterior distributions reflect a wide range of concentrations, which was supported by the large areal CVs (v in table 1). The wide range of concentrations also causes the distance between mean and median to be quite large. These results reflect the heterogeneous sampling area consisting of various types of water bodies from small streams to the receiving sea estuary. Better accuracy could have been achieved with a larger prior dataset or a larger amount of observed data, as there were only 10 sampling sites where both AdSi and TSi were measured. The information received from those sites was then used to estimate the amounts of AdSi and BSi in the remaining sites where only TSi was measured.

The AdSi distributions resembled the BSi and TSi distributions. The variation caused by the sampling area was, however, much smaller. For instance, the areal CV (v_A) was about half that of BSi. The extraction method was recognized through the different variance structures to be the main source of variation with AdSi. Even though the areal AdSi variation was smaller than the BSi variation, the probability intervals (PI) of mean and median were quite wide because of the small dataset.

The heterogeneous sampling area probably contributed to the larger median of the BSi posterior distribution (12 mg g^{-1}) than the prior distribution (6.5 mg g^{-1}), as the extracted amounts varied from 0.8 up to 89 mg g^{-1} . The 95% PI, which contain the true value of the parameters with 0.95 probability, were also quite wide for all parameters. More accurate estimations could have been achieved if more prior information were available or if more data was collected. With BSi, the variation through heterogeneous sampling area is much larger due to the natural variation in

the occurrence of diatoms in different water bodies combined with the diatom frustule clustering effect. Furthermore, the BSi in sediments can also contain phytoliths and sponge spicules, all of which have slightly different solubilities (Conley and Schelske 1993, Fraysse et al. 2006). In article II, these different forms were found spatially unevenly distributed in the sediments and the samples contained a lot of phytoliths. The study in article II concentrated on the Vantaa river area, where the phytoliths originated from grasses, as there is minimal forest. The sampling area in Siuntio is forested and large amount of pine needles, for instance, can accumulate in the water. Therefore, one reason for the wide distribution and clustering of BSi can be the nature and erosion susceptibility of the surrounding land. The findings from article II strongly support the model structure 3 for TSi.

When the model-estimated mean concentrations were compared to the corresponding means of observations, there was a larger deviation from the line of unity (meaning the observed and estimated results are exactly the same) with BSi than with AdSi. The same phenomenon also occurred with AdSi but it was not as pronounced, since the measurement error with AdSi was smaller and therefore the observations had higher weight. Also, when the point estimates of the observed AdSi, BSi, and TSi were compared with the corresponding predictive posterior distributions, BSi and TSi again had larger uncertainty regarding the true concentration than AdSi. The model estimated this underlying uncertainty and it was taken into account in the posterior results.

The results of this study are relevant only in the studied area. However, these results can also be used as prior information for similar study areas elsewhere. The uncertainties in the posterior distributions were quite large, but can be reduced by using the obtained distributions as prior information and updating the model with new data. As the sources of error were also identified, even a single determination per sampling site is sufficient enough to determine the posterior distributions.

4.1.2 QUANTIFICATION OF THE MEASUREMENT ERROR

The Bayesian model estimated the error caused by AdSi in the TSi results to range from 0.08 to 48%, with a mean and median of 7.4 and 2.5%, respectively. Two reasons were identified as possible reasons for such a wide range of AdSi/TSi ratios. Firstly, a high amount of OM can result in higher TSi concentrations due to phytolith BSi from plants, therefore causing reduced ratios. With the observed model data, the phytolith and diatom BSi was not separated and formed a joint pool of BSi. However, in study II phytoliths were found abundantly in the samples, especially in the VKL samples that were also used in the model. A second reason is the high amount of oxides combined with low OM and BSi concentrations. Clayey

sediments, for instance, can contain high amounts of oxides and thus high AdSi levels. If the location is low in BSi, the ratio can be quite high. Nevertheless, the ratio showed non-negligible error on the TSi extraction.

There remains high uncertainty regarding the correlation between AdSi and BSi. The high uncertainty in the results causing the wide range of PIs was probably partly due to the small amount of AdSi-BSi-pairs and uncertainty about their true concentration, and the lack of one important species of Si (DSi) in the model. The model estimated that the mean correlation between AdSi and BSi was negative, although the 95% PI did reach the positive side. The correlation was a priori expected to rather be positive than negative, as the more BSi is dissolved, the more DSi there is in the sediment pore water to adsorb onto sediment particles. In the model, the BSi modeled was undissolved diatom or phytolith BSi in the sediments. It is not known how much of the dissolvable BSi in the sediment is adsorbed on particle surfaces. A much stronger correlation would have likely been achieved if the correlation had been calculated for AdSi-DSi pairs. The study of the seasonal dynamics in Vantaa river estuary showed that the water DSi loads exceeded the amorphous Si loads at all times (**II**). Therefore, the inclusion of DSi in the Bayesian model would have provided important information and thereby reduced the uncertainty of the results. For this study, the sediment DSi concentrations were, however, not measured.

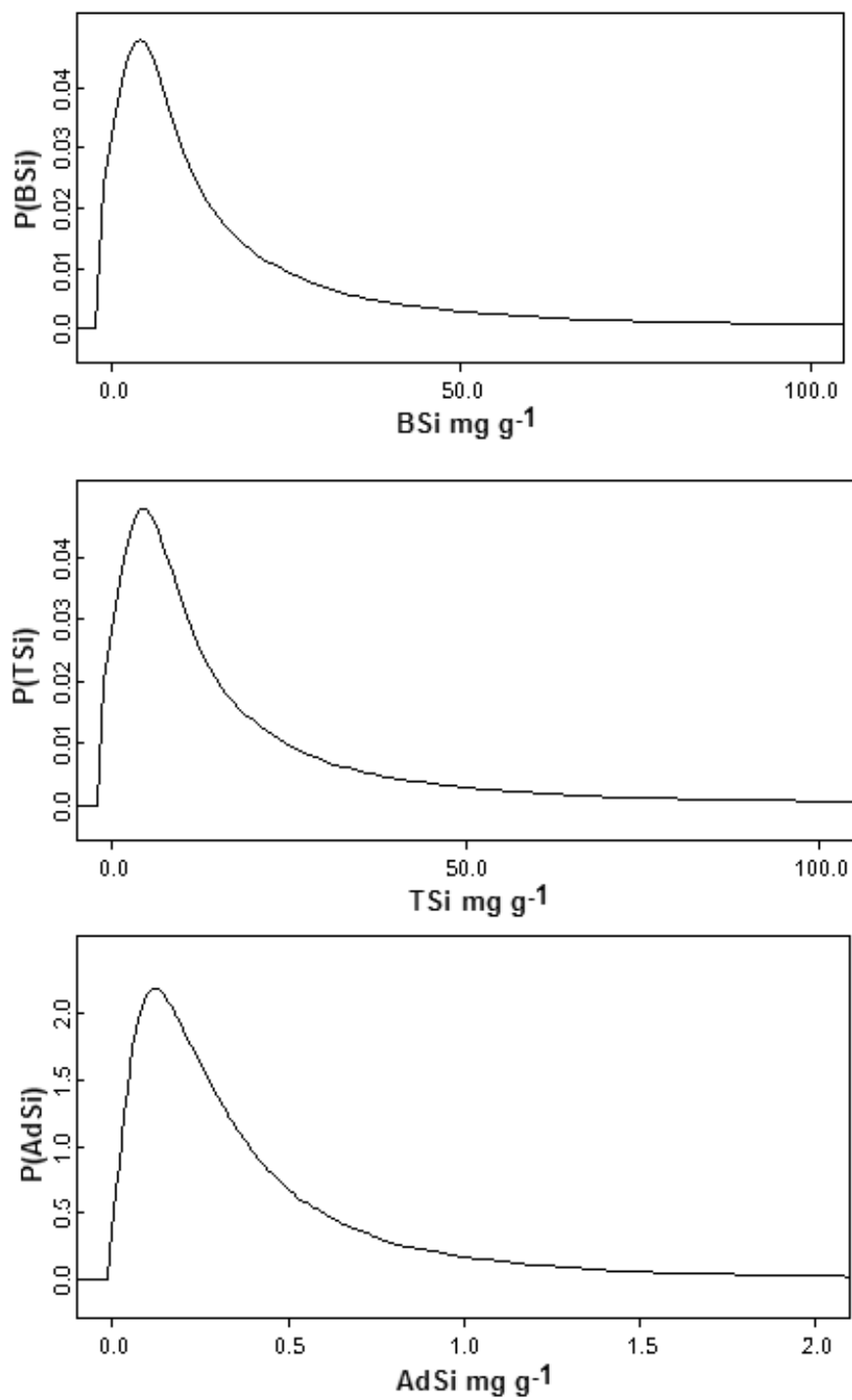


Figure 4 The predictive probability distributions of BSi, TSi, and AdSi

4.2 REACTIONS OF POTENTIALLY MOBILE SI POOLS IN SEDIMENT (II, III)

4.2.1 VARIATION IN BIO-REACTIVE SI POOLS UNDER DIFFERENT ENVIRONMENTS (II, III)

The variation and amount of different Si species in sediments is, apart from the sediment composition itself, dependent also on the season and the surrounding land area. The sediment sampling areas in studies **I** and **II** differ from each other. The Bayesian study sampling area (**I**) in Siuntio is a highly-forested environment and the Vantaa river area (**II**) is urban with agriculture and clayey soils. Article **II**, which focused on the seasonal dynamics of amorphous Si in Vantaa river area, found clear dependencies regarding the season, distance from river mouth, and the amorphous Si load coming from land on the Si concentrations in the water and sediments. Peak DSi and BSi loads were found in spring and autumn due to the high discharge of the river. This seasonal effect was caused by the combined effect of snow melting and flooding and the spring and autumn diatom blooms.

Although diatoms were the most abundant phytoplankton group in the estuary in article **II**, the diatom concentration did not correlate with the amorphous silica concentration. This indicated that most of the total amorphous silica measured from the water throughout the estuary was likely to be allochthonous Si imported by the river. The BSi and AdSi concentrations were highest in the river mouth surface sediments. Phytoliths occurred abundantly in the samples, reflecting the effect of land use in the drainage area. The Vantaa river area is, due to intensive agriculture, susceptible to erosion and nutrient leaching to the river. The phytoliths were confirmed to mainly be graminoids, which are derived from grass-dominated areas. The amount of OM and BSi was much higher in the Siuntio samples (apart from one brook sediment). The Siuntio sample BSi was not separated into diatom and phytolith BSi, but when the high OM contents are taken into account, it is reasonable to assume that phytoliths were also present in the Siuntio sediment samples.

The composition of the bioreactive pools is also affected by the particle size distribution of the sediment. Clayey sediments with predominantly small-sized particles can contain high amounts of hydrated oxide surfaces, which can increase the ability of sediment to readsorb DSi (Hallmark et al. 1982, Aston 1983). The samples in article **II** and the VKL samples in article **III** were clayey with small particles. The VKL samples were dominated by <0.006 mm particles (85-98%), while for the Siuntio samples the same fraction was maximally 57%. Detailed information on the sediment compositions can be found in article **II**.

The size of the AdSi pool in the surface sediments of Vantaa River mouth (**III**) was seen as large enough to affect the bioreactive pool within the estuary. This is because sorption-desorption reactions of DSi from oxide

surfaces can, through a buffering mechanism, regulate the amount of sediment-released DSi (Gehlen and Van Raaphorst 2002). The amount of DSi removed from the estuary through adsorption to particulate matter was seen to be limited to a few percent of the total DSi concentration (Aston 1980, Shen et al. 2008). There is very little evidence for the particular matter DSi removal regarding estuarine environments, although adsorption-desorption reactions have been shown to affect the short-term mobility of DSi in shallow shelf seas (Gehlen and Van Raaphorst 2002).

4.2.2 THE EFFECT OF SEDIMENTARY ANOXIA ON SI RELEASE (III)

The effect of anoxia was studied in article (III) in two separate experiments. In the SE experiment, sediments were sequentially extracted with different solutions to find the anoxia effect on differently bound Si species. A clear influence was seen regarding the oxidation state of the sediments. The results of the first two extractions of SE (water and NaCl), which focused on the loosely sorbed Si species of the sediments, showed that all sediments released less Si under anoxic than oxic conditions (table 3). The correlations between Si-Fe (0.78) and Si-Al (0.51) under oxic conditions indicated Fe and Al oxides as the source of the Si release. Under anoxic conditions, the respective correlations diminished to practically zero. Minor anoxic events at the sediment surface would thus rather diminish than increase the release of Si.

The next extraction (NaBD), which simulated lower redox conditions, showed similar results as water and NaCl with less Si release under anoxic conditions. The NaBD extraction did, however, result in higher Si-Fe correlations under both oxic (0.74) and anoxic (0.82) conditions. Si-Al correlations under both conditions were weak and negative (oxic -0.17; anoxic -0.25), which was reasonable and expected as Al is not a redox-sensitive element. The amount of Fe released was substantially increased under anoxic conditions, which was also expected as Fe dissolves when it is reduced from Fe³⁺ to Fe²⁺. The correlations strongly indicated that the Si extracted with NaBD was indeed Fe oxide bound. Therefore, it was surprising that the released amount of Si did not increase under anoxia as Fe oxides clearly dissolved more efficiently due to the highly reduced conditions. Apart from two samples, the sediments contained more water-extractable, loosely sorbed Si than redox-sensitive Fe oxide-bound Si.

Resorption behavior of Si

Previous studies of Si(OH)₄ sorption have shown strong adsorption affinity of Si for Fe oxides. However, under anoxic conditions the reduced Fe dissolves and therefore provides fewer adsorption sites for Si (Gehlen and Van Raaphorst 2002). In such circumstances, Al oxides can begin to play a bigger

role as adsorbing surfaces, as Al oxides are much less affected by anoxia and can serve as resorption sites for the released species. DSi also has a tendency to polymerize on sediment surfaces (Iler 1979). One of the indications of such resorption was the lower Al concentrations under anoxic conditions in the water, NaCl, and NaBD fractions (table 3). A low amount of available resorption sites (Al-oxides) and a large amount of Fe-adsorbed redox-sensitive Si was therefore seen as a possible explanation for the higher amount of Si released under anoxic conditions. Some support was found from sample S1, which had high concentration of Al-oxides. However, despite having large concentrations of oxalate-extractable Si, this sample still released the smallest amounts of Si. Further support was seen with sample S5, which had a low Al oxide concentration and high release of Si, while having second lowest amount of oxalate-extractable Si. The lack of resorption sites provided by Al oxides may therefore keep the released Si in solution. The amount of Al oxides clearly affects the net effect of anoxia on Si mobilization in sediments, instead of the mere amount of redox-sensitive Si released.

Another influential factor on the adsorptive capability of the sediments is the Si effect on Fe crystallization. Fe crystallization in the presence of Si increases the sediment surface area by preventing highly crystalline oxides (e.g. goethite) from forming during Fe²⁺ oxidation to Fe³⁺ (Weber Jr. and Stumm 1965). Si resorption may increase as the surface area increases due to the dominance of ferrihydrites, as ferrihydrite formed in the presence of Si is a stable oxidation product (Schwertmann and Thalmann 1976, Mayer and Jarrell 1996). The timespan of the experiment was, however, probably too short for any meaningful recrystallization to occur.

These reactions of Si under changing redox conditions have not received much attention in the field of Si research, even if they are also important regarding the cycling of P. While an increase in ferrihydrite formation may immobilize P due to the Si effect on Fe crystallization, a larger Si retention on oxide surfaces under anoxic conditions may, on the other hand, occupy adsorption sites suitable for P and increase its release and thereby add to the eutrophication of waters.

Al- and non-reducible bound Si

The main pools of AdSi are found in the loosely bound and redox-sensitive Fe-bound fractions. Still, there are other pools where AdSi can be found, namely the Al oxide and non-reducible Fe pools. These pools were investigated through the NaOH and HCl extractions of the SE experiment. It is known, however, that the suitability of these extractions is problematic since NaOH, for instance, can also dissolve BSi (Koning et al. 2002) and HCl dissolves mineral Si. The results in study II also show that the VKL samples used in the anoxia study contained considerable amounts of phytoliths,

which can also contribute to the BSi load. The NaOH extraction was the only step where Si concentrations were larger under anoxic conditions. Some Al dissolution was detected, which might explain the Si results to some extent.

This increased Al oxide dissolution was seen as support for the theory of resorption, as explained in the previous section. It was also interesting to note that the first enhanced release of Si under anoxic conditions occurred in the extraction part without reducing agents and not in the strongly reducing NaBD extraction, where extensive Fe dissolution occurred under anoxic conditions. The results of the NaOH extraction were consistent with previous studies suggesting larger dissolution of BSi under anoxia due to accelerated dissolution of diatom-protective coatings (Belias et al. 2007, Papush et al. 2009, Danielsson 2014). In a recent study by Lehtimäki et al. (2016), the release of DSi from both natural and cultured diatoms was highest under hypoxic conditions when microbes were present during the incubation. When cultured diatoms were mixed with sediment, the highest Si release also occurred under hypoxic conditions. From sediment without (added) diatoms, the maximum share of released Si was, however, not affected by oxygen conditions or microbial activity. Although the release rate was slower under hypoxic conditions in the beginning of their experiment, substantial amounts of DSi was released immediately after the incubation started. Our results, therefore, tentatively support both earlier and recent findings where anoxia has been indicated as a factor that increases the dissolution of BSi.

The HCl extraction mostly dissolved mineral Si, as not much AdSi was left on the sediment surfaces after the previous extraction steps; the correlations between Si and Al (0.93) and Fe (0.96) support this conclusion. As with the NaOH extraction, the HCl-extracted Si concentrations under anoxic conditions were larger than under oxic conditions. Some enhancement in the mineral dissolution may have occurred due to anoxic conditions. This conclusion was supported by previous results, where anoxia combined with acidity was found to enhance the first stage of ferrololysis (Brinkman 1970, Van Ranst and De Coninck 2002). In the first stage of ferrololysis, the reduced Fe displaces Al on silicate surfaces and mineral Si is released.

Table 3 The results of the sequential extraction under oxic (O₂) and anoxic (N₂) conditions

	Si H ₂ O		Si NaCl		Si NaBD		Si NaOH		Si HCl	
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
S1	85	60	9.2	0	38	0	2797	3794	1887	2561
S2	96	60	9.1	0	50	36	6108	11266	1245	1632
S3	112	74	15	0	283	308	7402	8471	1916	2545
S4	189	151	18	6.9	115	110	9765	9931	2874	3539
S5	23	19	5.7	0	94	28	881	924	260	342
S6	76	43	7.0	0	36	0	8300	9152	532	668
S7	92	66	8.2	0	46	18	9632	11101	1017	980
	P H ₂ O		P NaCl		P NaBD		P NaOH		P HCl	
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
S1	63	45	6.6	1.1	185	176	514	565	344	434
S2	17	2.3	5.0	0	138	67	658	806	131	97
S3	14	2.5	5.7	0	257	327	396	364	509	636
S4	35	23	6.0	0	131	360	266	254	320	257
S5	7.4	0	2.8	0	75	49	101	38	171	213
S6	26	9.3	4.0	0	63	18	366	331	33	41
S7	12	0	4.0	0	81	56	811	1157	57	41
	Al H ₂ O		Al NaCl		Al NaBD		Al NaOH		Al HCl	
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
S1	12	0	5.3	0	11	0	2919	3792	1671	4031
S2	23	3.3	8.4	0	27	0	4352	5922	1771	4395
S3	4.7	0	1.0	0	28	0	1891	2037	1484	3698
S4	21	0	0	0	0	0	3383	3551	2712	4232
S5	26	11	24	19	64	41	782	812	235	414
S6	68	29	33	13	54	3.4	4391	4735	541	787
S7	53	21	30	27	70	44	9172	9254	1364	3229
	Fe H ₂ O		Fe NaCl		Fe NaBD		Fe NaOH		Fe HCl	
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
S1	20	22	2.6	0	946	1795	145	26	2745	7162
S2	12	27	25	34	1405	2291	293	759	1350	4900
S3	18	13	10	1.7	4474	8911	355	187	4009	10242
S4	29	47	6.8	17	894	5169	9.4	21	4662	9035
S5	26	76	58	118	3710	6662	76	40	377	1515
S6	8.7	8.4	20	22	430	597	114	105	389	2547
S7	17	20	30	60	2023	2646	717	908	960	1448

The effect of time on the release of Si

Even though the SE experiment uncovered some of the behavior of different Si pools under oxic and anoxic conditions, the situation in the experiment was “forced” as, for instance, the strong reducing conditions achieved with NaBD do not exist in nature. In nature, easily extractable pools play the most important role and time is an important factor as well. In addition, the release in nature is not as rapid as in the SE experiment. Therefore, an RDE was conducted to study the effect of time combined with the two conditions (oxic and anoxic) on the release of Si.

The RDE did show time-dependent Si release. The beginning of the experiment showed the same release pattern as with the SE experiment, as the release of Si was higher under oxic conditions. As the experiment progressed, the results under both conditions started to approach each other. By day 28, almost all samples had released approximately equal amounts of Si (figure 5). Only one sample released statistically significantly more Si under oxic conditions throughout the experiment. Two samples released statistically significantly more Si under anoxic conditions. The higher release under anoxic conditions appeared to be caused by the relatively high reserves of both easily available and NaOH-extractable Si. Release of easily available (Fe-oxide-bound) Si, dissolution of BSi, or both could thus have been involved in the higher release under anoxia. The higher release under oxic conditions may have been caused by the fact that the sample (S5) was a brook sediment, collected from an environment that should be adapted to oxygenated conditions (e.g. running water). In the SE experiment, sample S5 had the highest NaBD-Si yield (21%) under oxic conditions when compared to the oxalate extraction results. Sample S5 also contained a low amount of BSi, as opposed to the samples releasing more Si under anoxic conditions.

Differences in the release rates under different oxygen conditions were also found. When comparing the time until the RDE release reached the Si concentrations obtained from the water and NaCl extractions, the release under anoxic conditions was slower. The experiment setups were different (e.g. shaking times were 1 h prior to sampling in RDE vs. 24 h in SE), which limits the comparability to some extent. The duration of the RDE experiment was also long enough for some BSi dissolution to occur, which could explain the higher results under anoxic conditions to some extent, as the released Si may have originated from both the BSi and AdSi pools. This assumption is also supported by the study of Lehtimäki et al. (2016), who found the diatom BSi dissolution rate under hypoxic conditions to be slower than under oxic conditions. They also found higher diatom dissolution under hypoxic conditions, especially if microbial activity remained uninhibited.

The day 28 samples of the RDE experiment were also used to examine the possible formation of colloidal Si particles by a filtration experiment (0.2 μm filters). As the reduced Fe^{2+} is oxidized back to Fe^{3+} in the presence of Si with samples having a high enough Si/Fe-ratio (preferably above 0.36, no effect if the ratio is below 0.1), colloidal mixed oxides can be formed (Mayer and

Jarrell 1996, Mayer and Jarrell 2000). This formation of new oxides could increase the adsorption of Si. The same phenomenon has been found to occur under anoxic conditions for P due to the formation of Fe⁺²-P complexes (Patrick Jr. and Khalid 1974, Holford and Patrick Jr. 1979, Manahan 1994, Roden and Edmonds 1997). Samples in our study had ratios ranging from 0.11 to 0.45. The results showed decreasing Fe concentrations under oxic conditions after filtering, which could indicate entrapment of insoluble Fe complexes in the filters. This could explain the cases where the anoxic Si results were higher than the oxic ones, as oxic conditions favor colloid formation and therefore trap Fe-bound Si colloids in the filters in larger amounts. For the RDE experiment, this colloid formation could have been one factor influencing the results. For the SE experiment, however, this was unlikely as the extraction times were too short for any substantial colloid formation to happen.

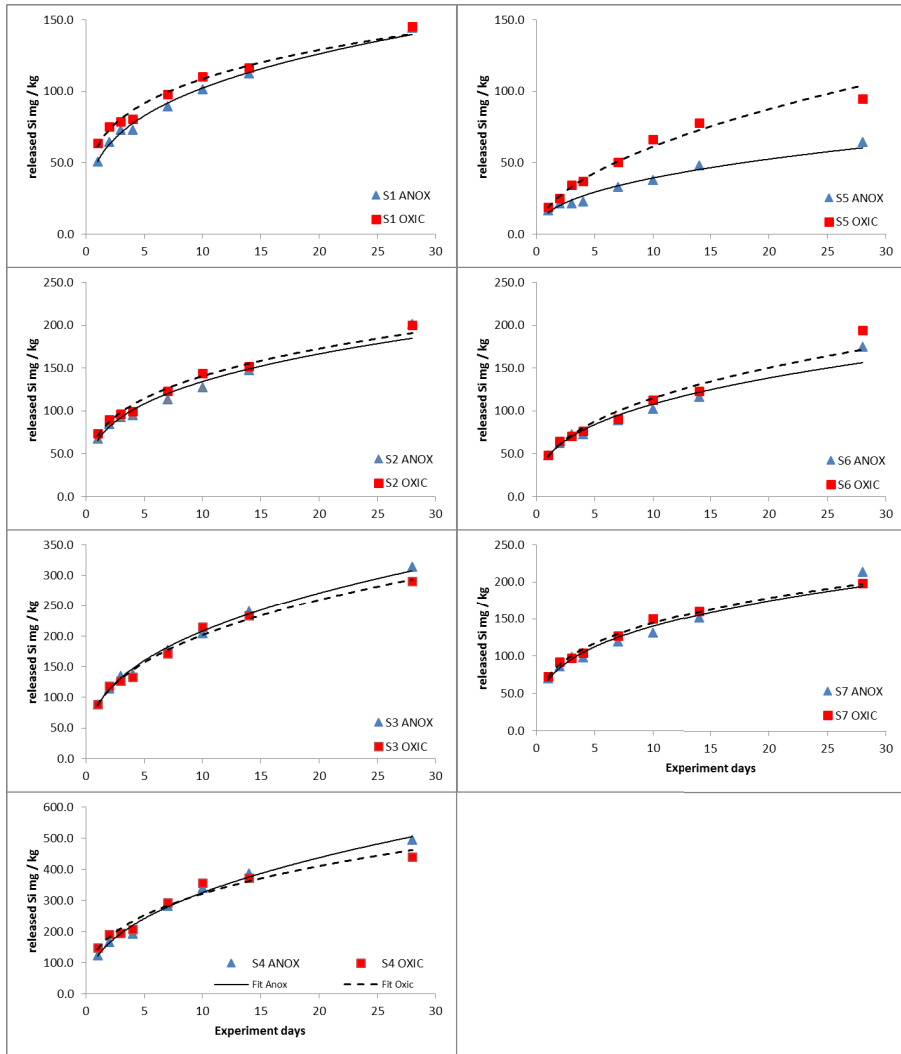


Figure 5 The results of the release dynamics experiment. The fitted formula was $f(x) = a \cdot x^b$. The solid line is the fitted curve from the oxidic experiment and the dashed line is the corresponding curve from the anoxic experiment.

5 CONCLUDING REMARKS

This thesis focused on the bio-reactive pools of Si in sediments and on phenomena affecting Si release from sediments. One of the research topics was to create a model to separate the AdSi and BSi using Bayesian probabilistic modeling (I). The results showed that the measurement error could be successfully separated from the spatial variation for AdSi and TSi, while accounting for the uncertainty regarding measurement variance structures. However, the correlation between the AdSi and BSi pools could not be determined. Reliable conclusions of the AdSi pool size cannot be made from the size of the BSi pool alone. The co-extraction of AdSi causes, however, error in the extraction results of BSi. A rough estimate could be derived of the amount of AdSi from the TSi extraction in the Siuntio catchment. In future research, the formulation of the prior distributions could be improved by performing a meta-analysis of other relevant datasets. Also, incorporation of DSi in the model is important as it plays a vital role in the interactions of different Si pools. Even further, a more spatial perspective could provide more insight into the processes controlling the amounts of AdSi and BSi found in sediments. This could include the lateral movement of BSi species from land to water, the movements of DSi along the rivers, and the distance between the sampling sites.

The land use surrounding the sampling area affects the amount of different Si species in sediments. Erosion and nutrient leaching can have large effects on the BSi speciation in water and sediments. Diatoms were found to be the most abundant phytoplankton group in the Vantaa River estuary, but phytoliths were also abundantly present in the sediments, reflecting the land use of the Vantaa River drainage area. The results of article II clearly support the results of the created Bayesian model, as a spatially uneven distribution of different BSi forms (diatom, phytolith, sponge spicule) and clear spatial dependence of BSi concentrations were detected. More investigation is clearly needed to elucidate the importance of phytoliths.

The effects of anoxia on Si release from sediments were also studied with a SE and with a longer-term RDE (III). Anoxia did not enhance the release of AdSi from the loosely bound and reducible Fe fractions as was a priori assumed. Several reasons for this unexpected behavior were discussed, of which resorption on Al oxides was seen as the most reasonable explanation. The results did, however, support recent findings by Lehtimäki et al. (2016), where the dissolution of BSi may increase under anoxic or hypoxic conditions. Si was released more slowly under anoxic than oxic conditions in most of the studied sediments, and some indications of Fe-Si colloid formation was detected. Both phenomena, especially colloid formation, require further research to identify their role(s) in the complex chemistry of

Si in nature. The anoxia experiments strongly indicated that Al oxides play a larger role in the release of AdSi than has, perhaps, been acknowledged before. Al oxides could be one factor explaining the different behaviors of Si and P. The role of Al oxides on Si adsorption, not only in sediments but also in soils where the same oxide surfaces control the adsorption of Si as in sediments, definitely deserves further research.

From an ecological point of view, the results highlight the importance of the Si cycle in ecosystems. For instance, BSi in the form of diatom frustules and phytoliths sink to the bottom sediments of rivers, lakes, and sea. These forms of BSi thus create a transport vector of atmospheric CO₂, linking the Si cycle tightly to the carbon cycle (see e.g. Tréguer and Pondaven 2000) and thereby to the phenomena affecting global warming. Si is also tightly linked to eutrophication processes, as it affects the release of P from sediments as a competing adsorptive anion having both negative and positive effects. Negative effects include inhibition of P adsorption in sediments due to (re)sorption on oxide surfaces, while positive effects include inducement of increased sediment surface area through prevention of Ostwald ripening and thereby increased potential P adsorption. It is clear that making accurate estimations of different Si pool sizes is highly important. It is important to understand Si chemistry in sediments and soils and to develop and update suitable extraction methods for the different Si pools. We need to recognize that natural and methodological sources create uncertainty in the results and that the creation of new methods in modeling that account for all the recognized underlying uncertainty is a good tool for a better and more realistic understanding of this element. Silicon is, after all, the second most abundant element on Earth and exceeded only by oxygen.

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