

Review article

## Review of methodologies for extracting plant-available and amorphous Si from soils and aquatic sediments

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**Abstract.** There is a variety of methodologies used in the aquatic sciences and soil sciences for extracting different forms of Si from sediments and soils. However, a comparison of the published extraction techniques is lacking. Here we review the methodologies used to extract different Si fractions from soils and sediments. Methods were classified in those to assess plant-available Si and those to extract Si from amorphous silica and allophane. Plant-available Si is supposed to comprise silicic acid in soil solution and adsorbed to soil particles. Extraction techniques for plant-available Si include extractions with water, CaCl<sub>2</sub>, acetate, acetic acid, phosphate, H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and citrate. The extractants show different capabilities to desorb silicic acid, with H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and citrate having the greater extraction potential. The most common extractants to dissolve amorphous silica from soils and aquatic sediments are NaOH and Na<sub>2</sub>CO<sub>3</sub>, but both also dissolve crystalline silicates to varying degrees. In soils moreover Tiron is used to dissolve amorphous silica, while oxalate is used to dissolve allophanes and imogolite-type materials. Most techniques analyzing for biogenic silica in aquatic environments use a correction method to identify mineral derived Si. By contrast, in the soil sciences no correction methods are used although pedologists are well aware of the overestimation of amorphous silica by the NaOH extraction, which is most commonly used to extract silica from soils. It is recommended that soil scientists begin to use the techniques developed in the aquatic sciences, since it seems impossible to extract amorphous Si from soils completely without dissolving some of the crystalline silicates.

### Introduction

Silicon (Si) is the second most common element of the earth's crust with a mean content of 28.8 wt% (Wedepohl 1995). Its special importance for global biogeochemistry results from a link to the global carbon cycle by marine organisms such as diatoms, radiolarians, and sponges (Treguer et al. 1995; Treguer and Pondaven 2000). The formation of opal in these organisms has been identified in numerous studies (e.g. Müller 2003). Relative to the state of knowledge on Si in aquatic biogeosystems, the understanding of Si pools and fluxes in terrestrial biogeosystems is lacking (Sommer et al. 2006), although a large variety of procedures for extracting Si from soils and aquatic sediments has been developed within the last 50 years. These methods were designed for various purposes and consequently dissolve different Si fractions. Earlier studies were primarily interested in the amounts of different forms of Si in soils (Hashimoto and Jackson 1960; Beckwith and Reeve 1963, 1964; Schachtschabel and Heinemann 1967). With the recognition that Si is an important element for the growth of plants (Epstein 1994; Ma 2003) especially for crops that require large amounts of Si for growth (rice, sugarcane), many methodologies have been used in recent years to evaluate plant-available Si (Datnoff et al. 2001).

Before applying any type of extraction it is essential to consider the various Si fractions which may be present in sediments and especially in soils, since weathering and mineral neo-formation processes create a greater variety of Si-fractions in soils than in sediments (Figure 1). Mineral soils develop from rocks or sediments and are mainly composed of primary crystalline silicates such as quartz, feldspars, mica, and secondary silicates, especially clay minerals (Iler 1979; Conley et al. 2005). Moreover they contain Si of

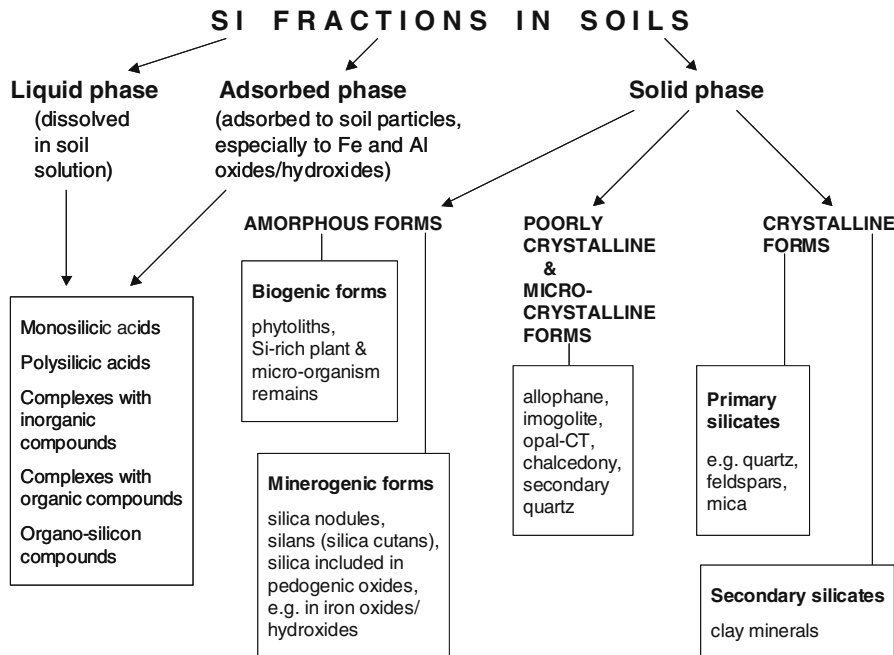


Figure 1. Classification of silicon compounds in the soil (modified from Matichencov and Bocharnikova 2001).

biogenic origin (mainly phytoliths, but sometimes diatoms and sponge spicules; Jones 1969) and pedogenic amorphous silica (Drees et al. 1989). In addition, complexes of Si with Al, Fe, heavy metals and soil organic matter occur (Matichencov and Bocharnikova 2001; Farmer et al. 2005). Silicic acid is also dissolved in soil solution with some part of the silicic acid adsorbed to soil minerals, particularly to iron and aluminium oxides/hydroxides (e.g. Beckwith and Reeve 1963, 1964; McKeague and Cline 1963a; Hansen et al. 1994; Dietzel 2002).

Dissolved silicic acid in soil solutions primarily occurs as monomeric or oligomeric silicic acid (Iler 1979). Monomeric silicic acid ( $\text{H}_4\text{SiO}_4$ ) dissociates into  $\text{H}^+ + \text{H}_3\text{SiO}_4^-$  above pH 9 and into  $2\text{H}^+ + \text{H}_2\text{SiO}_4^{2-}$  above pH 11. Oligomeric silicic acid is only stable at high concentrations of silicic acid at pH > 9 (Knight and Kinrade 2001). Moreover it occurs as a transition stage during the dissolution of minerals, which under most natural conditions is only stable for a few hours or days, before it decomposes into monomeric silicic acid (Dietzel 2000). In most soils and natural waters only undissociated monomeric silicic acid occurs (McKeague and Cline 1963b; Dietzel 2000). Alkaline soils such as Solonetz and Solonchaks also contain dissociated monomeric silicic acid.

In contrast to the well-crystalline Si-rich soil components, Si complexes and poorly or non-crystalline silica are much more difficult to assess. Various methods for extracting these Si fractions from soils have been reported in the literature. These methods were developed for different purposes. Some were intended to extract plant-available Si (e.g., Imaizumi and Yoshida 1958; Ayres 1966; Haysom and Chapman 1975), others were developed for pedogenetic studies in order to assess the formation of different Si fractions during soil development (e.g., Hashimoto and Jackson 1960; Biermans and Baert 1977; Arnseth and Turner 1988).

Our current understanding of the biogeochemistry of Si is limited by our ability to quantify the pools and fluxes of various Si fractions with different reactivities in the biogeosphere. We need to identify methodologies that are capable of quantifying various Si fractions, especially those methodologies that can be used to assess the linkages between terrestrial and aquatic biogeosystems (D.J. Conley, 2002, Working document on the measurement of biogenic silica, unpublished). While there is a large variety of different techniques used in the soil sciences and in aquatic sciences, there has been no systematic survey of the methodologies available. This review is intended to summarize and compare previously published extraction techniques

used to determine different Si fractions in soils and aquatic sediments. Measurement for total Si and for the so-called weatherable fraction of primary silicates are not treated here.

### Methods for extracting plant-available Si

The addition of Si in various forms to crops has been shown to have many beneficial effects (Datnoff et al. 2001). This has not only been shown for crops with a high demand for Si such as sugar cane and rice, but also for tomato, cucumber, and strawberry (Korndörfer and Lepsch 2001). Stimulation of photosynthesis, improvement of leaf erectness, decreased susceptibility to disease and insect damage, and alleviation of water and various mineral stresses are all important benefits of Si additions to plants (Ma et al. 2001). Therefore, several procedures to determine plant-available Si have been developed. Most of them apply an anion to replace adsorbed Si and have been tested by determining the correlations between Si analyzed in the extract and crop yield. The most common methods use  $\text{CaCl}_2$ , acetate/acetic acid or citrate (Table 1).

#### *H<sub>2</sub>O and CaCl<sub>2</sub>*

Different methodologies have been applied to soils to extract the water-soluble Si, most of them used to identify a need for Si fertilization. Schachtschabel and Heinemann (1967) developed a procedure to determine water-soluble Si in loess soils of western Germany to determine which soil properties influence the content of water-soluble Si in soils (Table 1). A  $\text{NaN}_3$  solution was used to prevent microbial activity. The amount of Si in the extract increased by 10–20% without addition of  $\text{NaN}_3$ , which was interpreted to be the result of microbial production of reducing and complexing agents, which dissolve Fe, Al, and Mn oxides, so that the Si bound in these oxides is released. Schachtschabel and Heinemann (1967) refrained from continuous shaking, because McKeague and Cline (1963b) found that shaking causes an increase in Si extracted due to abrasion.

Fox et al. (1967) and Khalid et al. (1978) shook a 1:10 soil–water suspension for 4 h to determine water-soluble Si in soils developed from basic volcanic rocks on Hawaii. The objective of their investigation was to study the response of sugar cane to calcium silicate slag fertilization (Fox et al. 1967) and the fate of applied Si during 5 years cropping (Khalid et al. 1978). Nonaka and Takahashi (1988, 1990) also used water to extract Si from soils in order to estimate the need for Si fertilization. They incubated soils at 40 °C for 1 week. The advantage of the procedures of Schachtschabel and Heinemann (1967) and Nonaka and Takahashi (1988, 1990) is that they allow an equilibration between soil and solution, however, the disadvantage is the long duration of the extraction.

Another way to determine the amounts of water-soluble silica in soils is by measuring the silica concentration directly in soil solutions. Gérard et al. (2002) analyzed Si in leaching and capillary solutions of a volcanic soil in the Beaujolais (France). The leaching soil solutions were obtained by use of zero-tension plate lysimeters and the capillary solutions with cup lysimeters connected to a suction of 600 hPa.

The weakest extractant after water is  $\text{CaCl}_2$ , which only extracts the easily soluble Si fraction (Berthelsen et al. 2001). Haysom and Chapman (1975) compared 0.01 M  $\text{CaCl}_2$ , 0.5 M ammonium acetate, and 0.005 M sulfuric acid for their ability to extract plant-available Si from soils and found that Si extracted by  $\text{CaCl}_2$  showed the highest correlation to sugar cane yield ( $r^2 = 0.82$ ).

#### *Acetate and acetic acid*

Acetic acid ( $\text{CH}_3\text{COOH}$ ) and some acetates (particularly  $\text{CH}_3\text{COO}^- \text{NH}_4^+$ ,  $\text{CH}_3\text{COO}^- \text{Na}^+$ ), are used to remove soluble Si and some of the exchangeable Si from soils. Numerous procedures applying these extractants are available in the soil sciences literature with most methodologies using a buffered acetate/acetic acid solution, however, few studies have focussed on the forms of Si extracted with acetate/acetic acid.

Table 1. Extraction procedures to determine water-soluble and adsorbed Si in soils and sediments.

Extractant	Procedure	Si fraction supposed to be extracted	Reference
H <sub>2</sub> O, 0.1% NaN <sub>3</sub> (to reduce biol. activity)	Sample:solution = 10 g:50 ml, 21 days at room temperature, manual shaking 2× per day	Water-soluble Si in soils	Schachtschabel and Heinemann (1967)
H <sub>2</sub> O	Sample:water = 10 g:100 ml (3 g:30 ml), 4 h continuous shaking	Water-soluble Si in soils	Fox et al. (1967), Khalid et al. (1978)
H <sub>2</sub> O	Sample:water = 10 g:60 ml, incubation at 40 °C for 2 weeks	Water-soluble Si in soils	Nonaka and Takahashi (1988, 1990)
H <sub>2</sub> O	Sample:water = 10 g:100 ml, 1 h shaking	Water-soluble Si in soils	Korndörfer et al. (1999)
CaCl <sub>2</sub>	0.01 M CaCl <sub>2</sub> , sample:solution = 1 g:20 ml, 16 h continuous shaking	Si present in the soil solution, the 'readily available' Si in soils	Haysom and Chapman (1975)
CaCl <sub>2</sub>	Sample:solution = 10 g:100 ml, 1 h shaking	Si present in the soil solution, the 'readily available' Si in soils	Korndörfer et al. (1999)
NaOAc and acetic acid	14.8 g NaOAc + 49.2 ml acetic acid l <sup>-1</sup> (= 0.18 M NaOAc + 0.87 M acetic acid), adjusted to pH 4, sample:solution = 10 g:100 ml, 5 h at 40 °C, occasional shaking	Soluble and some exchangeable Si in soils	Imaizumi and Yoshida (1958)
NaOAc and acetic acid	14.8 g NaOAc + 49.2 ml acetic acid l <sup>-1</sup> , adjusted to pH 4, sample:solution = 10 g:100 ml, 1 h shaking	Soluble and some exchangeable Si in soils	Korndörfer et al. (1999)
NH <sub>4</sub> OAc and acetic acid	0.5 M NH <sub>4</sub> OAc, adjusted to pH 4.5-4.8, sample:solution = 1 g:20 ml, 1 h continuous shaking	Soluble and some exchangeable Si in soils	Ayres (1966), Cheong and Halais (1970)
NH <sub>4</sub> OAc and acetic acid	0.5 M NH <sub>4</sub> OAc, adjusted to pH 4.8, sample:solution = 1 g:10 ml, 1 h continuous shaking	Soluble and some exchangeable Si in soils	Fox et al. (1967)
Acetic acid	0.5 M acetic acid, sample:solution = 1 ml:10 ml, 1 h shaking, 12 h resting	Soluble and some exchangeable Si in soils	Snyder (1991)

Acetic acid	0.5 M acetic acid, sample:solution = 1 ml:10 ml, 1 h shaking	Soluble and some exchangeable Si in soils	Korndörfer et al. (1999)
Acetic acid	0.5 M acetic acid, sample:solution = 10 ml:25 ml, overnight resting, 2 h shaking	Soluble and some exchangeable Si in soils	Snyder (2001)
Phosphate + acetate + acetic acid	0.1 M NH <sub>4</sub> OAc containing 500 ppm (0.016 M) P (as Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ), adjusted to pH 3.5 with 0.1 M acetic acid, sample:solution = 1 g:10 ml, 4 h continuous shaking	Soluble and some exchangeable Si in soils	Fox et al. (1967)
Phosphate + acetic acid	0.1 M acetic acid containing 50 ppm (0.0016 M) P (as Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ), adjusted to pH 3.5 with NH <sub>4</sub> OH, sample:solution = 1 g:10 ml, 4 h continuous shaking	Soluble and some exchangeable Si in soils	Khalid et al. (1978)
Phosphate buffer solution	(0.04 M Na <sub>2</sub> HPO <sub>4</sub> , adjusted to pH 6.2 with 0.04 M NaH <sub>2</sub> PO <sub>4</sub> ), sample:solution = 1 g:10 ml, 24 h continuous shaking	Soluble and some exchangeable Si in soils	Kato (1999, personal communication to Snyder), cited in Snyder (2001)
Citric acid	0.1 M citric acid, sample:solution = 1 g:50 ml, 2 h shaking, resting overnight, 1 h shaking	Soluble, exchangeable and specifically adsorbed Si in soils	Acquaye and Tinsley (1964)
Na citrate + NaHCO <sub>3</sub>	40 ml 0.3 M Na citrate + 10 ml 1 M NaHCO <sub>3</sub> , sample:solution = 2 g:50 ml, 5 min at 80 °C	Soluble and exchangeable Si; Si adsorbed to sesquioxide surfaces in soils	Breuer (1994)
NH <sub>4</sub> citrate	1 M NH <sub>4</sub> citrate, sample:solution = 10 g:25 ml 80 h continuous shaking	Soluble, exchangeable and specifically adsorbed Si in soils	Sauer and Burghardt (2000, 2006)
H <sub>2</sub> SO <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.02 N H <sub>2</sub> SO <sub>3</sub> containing 3 g (0.02 M) (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> l <sup>-1</sup> , sample:solution = 1 g:100 ml, 30 min continuous shaking	Soluble, exchangeable and specifically adsorbed Si	Fox et al. (1967)
H <sub>2</sub> SO <sub>4</sub>	0.005 M H <sub>2</sub> SO <sub>4</sub> , sample:solution = 1 g:200 ml, 16 h continuous shaking	Soluble, exchangeable and specifically adsorbed Si in soils	Hurney (1973)

Imaizumi and Yoshida (1958), Ayres (1966) and Wong You Cheong and Halais (1970) used buffered acetate solutions to extract plant-available Si from soils. Fox et al. (1967) used a buffered ammonium acetate solution containing 500 ppm P (as  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ). Snyder (2001) reported an acetic acid extraction, which is used at the Soil Testing Laboratory at the University of Florida Everglades Research and Education Center (EREC) as a standard method to analyze plant-available Si in soils used for rice growing. Nonaka and Takahashi (1990) found that the acetate extraction was too strong for soils previously fertilized with calcium silicates, because it dissolved some nonavailable Si from the fertilizer.

#### *Phosphate–acetic acid and phosphate buffer solution*

The phosphate anion has been used to extract adsorbed Si from soils to assess plant-available Si. Khalid et al. (1978) applied a water extract and a buffered extraction solution of phosphate and acetic acid (Table 1) to determine plant-available Si in a volcanic soil of Hawaii. They used the Si extracted by water as ‘intensity factor’ and that extracted by the phosphate buffer as ‘capacity factor’. Another phosphate extraction was introduced by Kato (personal communication cited in Snyder 2001). He found that in contrast to the acetate buffer extraction it did not overestimate the Si availability in soils previously fertilized with silicates. Snyder (2001) assumed that this is because the phosphate does not dissolve residual calcium silicate fertilizer, but displaces adsorbed silicic acid.

#### *Citrate and citric acid*

Acquaye and Tinsley (1965) used citric acid and Sauer and Burghardt (2000) citrate to estimate the amount of (unspecifically and specifically) adsorbed Si in soils. The extraction procedure of Sauer and Burghardt (2000) was based on the experiments reported by Beckwith and Reeve (1963, 1964). Beckwith and Reeve (1963) shook soil with solutions containing up to 135 ppm of monosilicic acid for 144 h. They found a significant decrease of dissolved silicic acid within the first 24 h and concluded that soils have a great ability to adsorb monosilicic acid. In subsequent experiments Beckwith and Reeve (1964) studied the release of adsorbed silicic acid from soils. They found that the release was minimal between pH 7 and 9 and increased below and above this range. To reach adsorption equilibrium, 80 h shaking was sufficient. About 0.1 and 1 M citrate solution enhanced the release of silicic acid. The authors proposed that the citrate ions occupy the sorption positions and form complexes with metal ions, which otherwise could adsorb silicic acid.

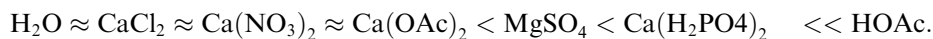
Breuer (1994) used an extraction solution consisting of 40 ml of 0.3 M Na citrate and 10 ml of 1 M  $\text{NaHCO}_3$ , and extracted 5 min at 80 °C. He found a close correlation ( $r^2 = 0.81$ ) between Si measured in this extract and Si contents in the dithionite extract (Mehra and Jackson 1960), which is commonly used in soil science to dissolve pedogenic sesquioxides. It consists of the Na citrate/ $\text{NaHCO}_3$  extraction as described above and subsequent addition of  $\text{Na}_2\text{S}_2\text{O}_4$  to reduce the Fe and Al and thus dissolve the oxides. Breuer (1994) found that Na citrate/ $\text{NaHCO}_3$  extracted about 17% of the amount of Si dissolved by the complete dithionite procedure. From this result and from the close correlation between both methods he concluded that Na citrate/ $\text{NaHCO}_3$  extracted only the Si fraction adsorbed to sesquioxide surfaces, while the dithionite extraction completely dissolved the sesquioxides, thereby releasing Si bound inside them.

#### *Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and sulfurous acid ( $\text{H}_2\text{SO}_3$ )*

Sulfuric and sulfurous acid have been used to extract the plant-available Si fraction. Fox et al. (1967) compared several methods, among them a procedure using a mixture of sulfurous acid and ammonium sulfate (see below). Hurney (1973) carried out calcium silicate fertilization studies on sugar cane in Australia and used diluted sulfuric acid to extract plant-available Si. The method was compared to five other extraction methods (see below) for plant-available Si by Berthelsen et al. (2001).

*Studies comparing different methods to extract plant-available Si from soils*

Fox et al. (1967) compared the capability of several anions to extract plant-available Si from an Oxisol of Hawaii (Figure 2). They found an increasing extraction capacity in the following order:



In addition, Fox et al. (1967) carried out extractions with water, phosphate/acetate, sulfate/sulfurous acid, and acetate/acetic acid on different soils (see Table 1 for procedures). In contrast to the first study, in most of the soils investigated phosphate extracted the greatest amount of Si, but in the case of further developed volcanic ash soils sulfate dissolved more Si (Figure 3). Acetic acid in all cases extracted less Si than phosphate and sulfate but significantly more than water. These results clearly show that the different extractants, which all are supposed to dissolve plant-available Si, do not extract exactly the same Si fraction from soils.

Korndörfer et al. (1999) evaluated four extractants for plant-available Si in fertilization experiments with upland rice (see Table 1 for methods). They used four typical soil types of Minas Gerais, Brazil, and five levels of previous fertilization with Wollastonite for each soil. Coefficients of determination between Si extracted from the soils and Si contents of the plants were  $r^2 = 0.84$  for water,  $r^2 = 0.70$  for  $\text{CaCl}_2$ ,  $r^2 = 0.88$  for acetic acid and  $r^2 = 0.69$  for acetic acid/acetate buffer.

Berthelsen et al. (2001) compared six Si extraction methods, the  $\text{CaCl}_2$ -extraction of Haysom and Chapman (1975), the acetate procedure of Wong You Cheong and Halais (1970), the acetic acid method of Snyder (1991), the phosphate/acetate extraction of Fox et al. (1967), the citric acid procedure of Acquaye and Tinsley (1965), and the sulfuric acid method of Hurney (1973). They observed that ammonium acetate,

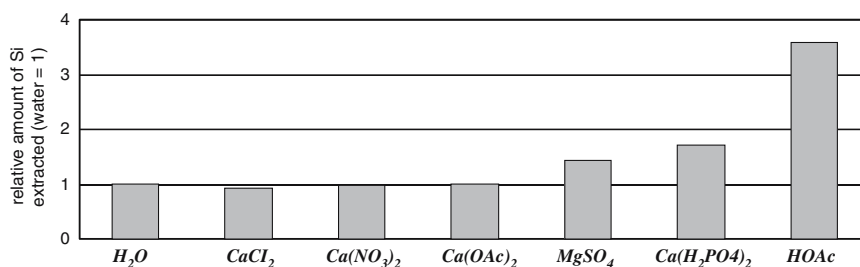


Figure 2. Relative amounts of Si measured in different extractants (concentration: 0.1 M) applied on a Hydrol Humic Latosol of Hawaii (data from Fox et al. 1967).

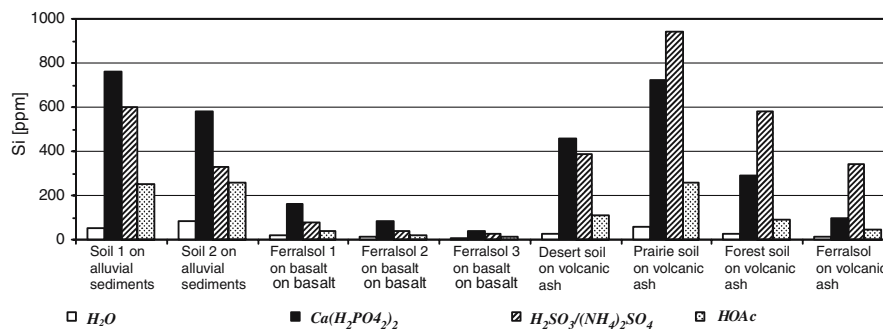


Figure 3. Comparison of amounts of Si extracted by water,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{H}_2\text{SO}_4$ , and acetic acid from different soils of Hawaii. The values for water-extractable Si are 100-fold exaggerated. The clay mineral composition of the soils on alluvial sediments is dominated by montmorillonite, that of Ferralsol 1 by kaolinite, those of Ferralsol 2 and 3 by goethite and gibbsite, and those of the soils on volcanic ashes by allophane (data from Fox et al. 1967).

acetic acid, and phosphate/acetate extracted 1, 1.5, and 3 times more Si from soils than CaCl<sub>2</sub>. Diluted sulfuric acid and citric acid dissolved 12 and 16 times, respectively, more Si than CaCl<sub>2</sub>. They suggested that CaCl<sub>2</sub> extracts the easily soluble Si, and that acetate, acetic acid, and phosphate acetate also dissolve some of exchangeable Si, while citric acid and sulfuric acid extract specifically adsorbed Si. Since the two latter extractants are very acid (pH 2) and the method of Hurney (1973) consists of 16 h continuous shaking, it must be assumed that silicates, especially clay minerals, are attacked both chemically and mechanically, so that the amounts of plant-available Si are overestimated by these methods.

De Lima Rodrigues et al. (2003) compared three Si extraction procedures, the acetic acid method used at the EREC (Snyder 2001), the acetate/acetic acid procedure of Imaizumi and Yoshida (1958), and the CaCl<sub>2</sub> extraction reported by Haysom and Chapman (1975). They found a decreasing extraction capacity in the order acetate/acetic acid > acetic acid > CaCl<sub>2</sub>. A coefficient of determination of  $r^2 = 0.33$  was found for the relation between Si measured in acetate/acetic acid and CaCl<sub>2</sub>, suggesting that the fractions extracted are overlapping but not identical. This finding supports the hypothesis that CaCl<sub>2</sub> extracts only the easily soluble Si, while acetate/acetic acid extracts some of the adsorbed Si. Si dissolved by acetic acid showed a strong relation to Si extracted by acetate/acetic acid ( $r^2 = 0.59$ ) and also to Si extracted by CaCl<sub>2</sub> ( $r^2 = 0.53$ ) suggesting that the extraction mechanism of acetic acid is between those of the two other extractants.

### Methods for extracting Si from amorphous silica, allophane, and imogolite-type materials

Alkaline wet chemical dissolution techniques, such as extraction with NaOH, a strong base, and Na<sub>2</sub>CO<sub>3</sub>, a weak base, are often used to analyze amorphous Si (ASi) in soils (Foster 1953; Follett et al. 1965), as well as amorphous biogenically derived Si (BSi) in freshwater and marine sediments (DeMaster 1979, 1981; Mortlock and Froelich 1989; Müller and Schneider 1993; Conley and Schelske 2001; Koning et al. 2002) (Table 2). These methods make use of the fact that the solubility of amorphous silica strongly increases at higher pH values (Iler 1979). One of the initial purposes of treating soil samples with NaOH was to remove amorphous substances prior to X-ray diffraction analysis in order to improve the clay mineral spectra.

Studies on BSi from aquatic environments have been very much concerned with the contribution on Si from simultaneous dissolution of mineral silicates. Significant efforts have been made to reduce this contribution. Corrections for the simultaneous dissolution of Si have been made using time course extractions or corrections using Al:Si ratios. The time course extraction was originally developed by DeMaster (1979, 1981) using 1% Na<sub>2</sub>CO<sub>3</sub> at 85 °C, over a total period of 5 h, during which the extract is sampled and analyzed several times (Figure 4). The technique is based on the observation that under these extraction conditions most BSi dissolves completely within the first 2 h of the extraction, while aluminosilicates release Si at a constant rate over the whole extraction time, which allows for the determination of BSi by extrapolating the Si release through time back to the intercept to correct for mineral dissolution (Figure 4).

#### *Sodium hydroxide (NaOH)*

NaOH extraction is the most commonly used method in soil analysis to assess ASi in soils. It is also used to extract ASi in sediments from aquatic environments (e.g. Müller and Schneider 1993; Koning et al. 2002).

#### *NaOH extractions applied to soils*

Foster (1953) used hot 0.5 M NaOH for the determination of ASi (including Si from biogenic and mineralogenic silica) and alumina in soils. This procedure has become a standard method to extract ASi in soils, although it is well known that NaOH also dissolves some part of the silicate minerals, but does not extract ASi bound in sesquioxides (e.g. Follett et al. 1965; Wada and Greenland 1970). To reduce the dissolution of silicate minerals Hashimoto and Jackson (1960), who also used 0.5 M NaOH, restricted the extraction duration to 2.5 min. Karathanasis (1989) applied a modified version of the method of Hashimoto and



Table 2. Extraction procedures to determine Si bound in amorphous silica and pedogenic oxides in soils, sediments, and suspended matter in water samples.

Extractant	Procedure	Si fraction supposed to be extracted	Reference
NH <sub>4</sub> oxalate	0.2 M NH <sub>4</sub> oxalate (ca. 700 ml), adjusted to pH 3.0 with 0.2 oxalic acid (ca. 535 ml), sample:solution = 2 g:100 ml, 1 h shaking in a dark room	Si bound in amorphous and poorly crystalline ('active') pedogenic oxides and oxy-hydroxides of Fe, Al and Mn	Tamm (1932), modified by Schwertmann (1964)
Na pyro-phosphate + NH <sub>4</sub> oxalate	Sample + 25 ml of 0.1 M Na pyrophosphate, adjusted to pH 10, wash with 10 ml of 1 M NaCl, apply 15 ml of 0.2 M NH <sub>4</sub> oxalate	Si bound in amorphous silica in lake sediments	Ewing and Nater (2002)
NaOH	0.5 M NaOH, sample:solution = 1 g:50 ml, 4 h boiling	Si bound in amorphous silica in soils	Foster (1953)
NaOH	0.5 M NaOH, 2.5 min boiling	Si in allophanes and amorphous silica in soils	Hashimoto and Jackson (1960)
NaOH	0.5 M NaOH, light fraction of coarse silt (20–50 μm), sample:solution = filter content:15 ml, 16 h at 150 °C	Phytolith Si in soils	Herbauts et al. (1994)
NaOH	0.5 M NaOH, coarse silt (20–50 μm) sample: solution = 1 g:100 ml, 20 min boiling	Phytolith Si in soils	Jones (1969)
NaOH	0.5 M NaOH, sample:solution = ≤ 100 mg:100 ml, 60–90 min at 85 °C	Biogenic silica in marine sediments	Koning et al. (2002)
NaOH	1 M NaOH, sample:solution = sample containing ≤ 10 mg SiO <sub>2</sub> :100 ml, at 85 °C, 10–20 min for plankton and sediment trap material, 40–60 min for Quaternary sediments	Biogenic silica in marine sediments and particulate matter from marine environments	Müller and Schneider (1993)
NaOH	0.2 M NaOH, sample:solution = filter content:4 ml, 10–15 min boiling, neutralization with 1 ml 0.5 M H <sub>2</sub> SO <sub>4</sub>	Biogenic silica in water	Paasche (1973), Krausse et al. (1983)
NaOH	0.2 M NaOH, sample:solution = filter content:4 ml, 40 min boiling, neutralization with 1 ml 1 M HCl	Biogenic silica in water	Ragueneau and Tréguer (1994)
NaOH	0.2 M NaOH, sample:solution = filter content:10 ml, 15 min boiling, neutralization with 10 ml 0.2 N HCl	Biogenic silica in water	Conley (2002, unpublished)
KOH + HCl	0.5 M KOH, 2.5 min boiling, centrifugation, 1 h shaking soil with 6 M HCl	Si bound in amorphous silica in soils	McKeyes et al. (1974), Karathanasis (1989)
Na <sub>2</sub> CO <sub>3</sub>	5% (0.5 M) Na <sub>2</sub> CO <sub>3</sub> , sequential extraction, sample:solution = 100 mg clay:80 ml, first cold: 16 h shaking, then hot: 2 h boiling, repeat each step until Si content in extract is low and constant	Si bound in amorphous silica in soils	Follett et al. (1965)

Table 2. Continued.

Extractant	Procedure	Si fraction supposed to be extracted	Reference
Na <sub>2</sub> CO <sub>3</sub>	5% (0.5 M) Na <sub>2</sub> CO <sub>3</sub> , sample:solution = 1 g:25 ml, agitate 10 min at 80 °C, repeat until Si content in extract is low and constant	Si bound in amorphous silica in soils	Arnseth and Turner (1988)
Na <sub>2</sub> CO <sub>3</sub>	0.5 M Na <sub>2</sub> CO <sub>3</sub> , sample:solution = 2 g:50 ml, 16 h shaking at room temperature	Si bound in amorphous silica in soils	Breuer (1994), Breuer and Herrmann (1999)
Na <sub>2</sub> CO <sub>3</sub>	0.5 M Na <sub>2</sub> CO <sub>3</sub> , sample:solution = filter content: 35 ml, 2 h at 85 °C, neutralization with 5.5 ml 6 M HCl	Biogenic silica in water	Conway et al. (1977)
Na <sub>2</sub> CO <sub>3</sub>	0.05 M Na <sub>2</sub> CO <sub>3</sub> , sample:solution = filter content: 18 ml, 2 h at 85 °C, neutralization with 0.5 M HCl to turning point of methyl orange	Biogenic silica in water	Paasche (1980)
Na <sub>2</sub> CO <sub>3</sub>	21% (2 M) Na <sub>2</sub> CO <sub>3</sub> , 4 h at 90–100 °C	Amorphous silica in marine sediments	Eggiman et al. (1980)
Na <sub>2</sub> CO <sub>3</sub>	1% (0.1 M) Na <sub>2</sub> CO <sub>3</sub> , sample:solution = 30 mg:40 ml or filter content:40 ml, 5 h shaking at 85 °C	Biogenic silica in sediments and water	DeMaster (1981, 1991), Conley (2002, unpublished), Conley and Schelske (2001)
Na <sub>2</sub> CO <sub>3</sub>	2 M Na <sub>2</sub> CO <sub>3</sub> , sample:solution = 25–200 mg:40 ml, 5 h at 85 °C, pretreatment: 5 ml 10% H <sub>2</sub> O <sub>2</sub> + 5 ml 1 N HCl, washing with 20 ml water	Biogenic silica in sediments	Mortlock and Froelich (1989)
Tiron	0.1 M Tiron (4,5-dihydroxy-1,3-benzene-disulfonic acid [disodium salt]) (pH 10.5), sample: solution = 25 mg:30 ml, 1 h at 80 °C	Si bound in amorphous silica in soils	Biermans and Baert (1977), Kodama and Ross (1991)
	Sequential extraction after iron oxide dissolution (Mehra and Jackson 1960), first with 2% (0.2 M) Na <sub>2</sub> CO <sub>3</sub> , then with 0.5 N NaOH, see text for details of procedure		Wada and Greenland (1970)

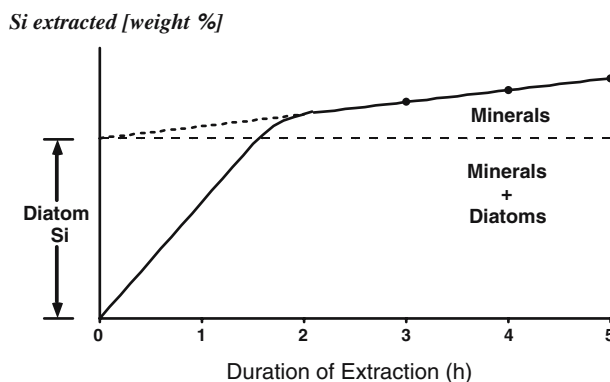


Figure 4. Hypothetical diagram of Si extraction from sediments with 1%  $\text{Na}_2\text{CO}_3$  at 85 °C. The solid line represents Si concentration in the extract as a function of time, the points depict the sampling times. The dotted lines show the extrapolation used to determine BSi (redrawn from DeMaster 1981).

Jackson (1960), using KOH instead of NaOH. After the extraction they centrifuged and shook the soil with 6 M HCl for 1 h, since McKeyes et al. (1974) showed that such alternating alkaline–acid treatment removed amorphous silica from soils more effectively.

Jones (1969) used a NaOH extraction to determine the phytolith content of soils more rapidly than by the common density separation method (Piperno 1988). He boiled soil in 0.5 N NaOH for 20 min. When the results of the extraction of 31 Illinois soils were plotted vs. the opal content determined by density separation, a coefficient of determination of  $r^2 = 0.94$  was obtained with an intercept of 3.52 mg  $\text{SiO}_2$ , which was attributed to the dissolution of quartz. Herbauts et al. (1994) criticized that Jones (1969) did not take into account that other major silicate minerals, such as feldspars and micas, in addition to quartz are dissolved during the alkaline extraction. To minimize this effect Herbauts et al. (1994) applied the NaOH extraction to only the light fraction of the coarse silt (20–50  $\mu\text{m}$ ), after dividing the coarse silt into a light (phytolith) and heavy (mineral) fraction by a series of heavy liquid separations with  $\text{ZnBr}_2$  solution adjusted to a density of 1.92  $\text{g cm}^{-3}$ . The phytoliths were digested overnight with 0.5 M NaOH at 150 °C. Phytolith Si measured was correlated to gravimetrically determined phytolith Si with  $r^2 = 0.91$ , and to phytoliths counted with  $r^2 = 0.73$ .

For technical reasons both methods (Jones 1969 and Herbauts et al. 1994) used the particle size fraction 20–50  $\mu\text{m}$ , although the fraction 5–20  $\mu\text{m}$  usually contains high amounts of phytoliths (Jones and Beavers 1964; Verma and Rust 1969; Yeck and Gray 1972). Therefore, these methods can be applied for comparison of phytolith contents of different soil samples, e.g. for paleoenvironmental reconstruction, but they cannot be used to calculate total phytolith Si as one of the Si pools in soils for the global Si cycle.

#### *NaOH extractions applied to aquatic systems and to sediments*

Paasche (1973) introduced a NaOH extraction method for BSi in suspended matter in water by filtration onto a polycarbonate filter and digestion with NaOH in a boiling water bath for 10–15 min. Paasche (1973) experimented with various strengths of base to ensure that all the diatoms were dissolved rapidly. The Paasche (1973) methodology was modified by Ragueneau and Tréguer (1994) by boiling for 40 min. After neutralization, washing and drying the sample was digested with HF at room temperature for 48 h for determination of the remaining portion of Si termed lithogenic Si (LSi). Ragueneau and Tréguer (1994) applied their NaOH extraction method to samples of different concentrations of pure quartz, illite, and kaolinite in order to determine their dissolution at increasing mineral concentrations. They found that quartz was highly resistant to NaOH attack, while the clay minerals were dissolved to a significant extent. About 13% of kaolinite and 7% of illite were dissolved during the NaOH extraction. Therefore, Ragueneau and Tréguer (1994) concluded that, depending on the clay abundance in suspended matter, a correction for the Si released from minerals during the extraction of BSi is necessary.

Müller and Schneider (1993) developed an extraction procedure to analyze BSi in sediments using 1 M NaOH at 85 °C under continuous stirring. The increase in silicic acid was continuously monitored using an autoanalyzer and a modified version of the automated molybdate-blue method of Grasshoff et al. (1983). The resulting continuous absorbance versus time plot is evaluated according to the DeMaster procedure (1981) allowing for an accurate determination of the increase in dissolution due to minerals.

Koning et al. (2002) modified the continuous leaching technique of Müller and Schneider (1993). Samples were not only measured for the silicic acid extracted with time, but a second sample split was fed into a similar autoanalyzer system to analyze simultaneously for Al, using the method of Hydes and Liss (1976). The recording of Si and Al released from the sample was used to distinguish between BSi and Si released from clay minerals, based on their different reactivity constants and Si:Al ratios.

For soils the correction method using the different kinetics of Si release from amorphous substances and clay minerals (Figure 4) is considered more suitable than the correction method by use of Si:Al ratios, since also amorphous or poorly crystalline substances comprising Si and Al may occur in soils (Veerhoff and Brümmer 1993; Strekopytov and Exley 2005), which may also be dissolved by NaOH.

### *Sodium carbonate ( $\text{Na}_2\text{CO}_3$ )*

$\text{Na}_2\text{CO}_3$  is the most commonly used methodology for the extraction of BSi in aquatic sediments (Conley 1998). In soil science it is less often used than NaOH, but nevertheless several  $\text{Na}_2\text{CO}_3$  procedures have been developed to extract ASi from soils.

#### *$\text{Na}_2\text{CO}_3$ extractions applied to soils*

Follett et al. (1965) used a 2-step  $\text{Na}_2\text{CO}_3$  extraction procedure applied to the clay fraction of soils to study the graded dissolution of particular soil clays. Soil clay samples were extracted with 5%  $\text{Na}_2\text{CO}_3$  for 16 h at room temperature. The extraction was repeated until the amounts of Si and Al extracted reached a low and practically constant level. The residue was then digested with 80 ml of 5%  $\text{Na}_2\text{CO}_3$  for 2 h on a steam bath several times, until the amounts of Si and Al in the extracts again stayed constant on a low level. This method was applied to samples of pure kaolinite, illite, montmorillonite, vermiculite, chlorite, goethite, gibbsite, quartz, silica gel, and allophane. Si and Al contents were determined in the extracts (colorimetrically) and in the untreated samples (colorimetrically after fusion with  $\text{Na}_2\text{CO}_3$ ) to calculate the proportions of Si dissolved by the different dissolution techniques. Cold  $\text{Na}_2\text{CO}_3$  dissolved 99.4% of the silica gel, 29.8% of the allophane, up to 7.4% (illite) of the clay minerals, and 0.2% of the quartz (Figure 5). After subsequent extraction with hot  $\text{Na}_2\text{CO}_3$  the silica gel was completely dissolved, and 65.6% of the allophane, up to 11.3% (illite) of the clay minerals, and 3.5% of the quartz were dissolved. NaOH extracted 78.6% of the allophane, 6% of the illite, and 10.2% of the montmorillonite.

Arnseth and Turner (1988) used 5%  $\text{Na}_2\text{CO}_3$  at 80 °C and repeated the extraction until the amounts of Si extracted stayed constant on a low level. Breuer (1994) and Breuer and Herrmann (1999) used 0.5 M  $\text{Na}_2\text{CO}_3$  and shook 16 h at room temperature. It can be assumed that the Si fractions dissolved by these two methods were similar to those extracted by the cold and hot extraction steps applied by Follett et al. (1965).

#### *$\text{Na}_2\text{CO}_3$ extractions applied to aquatic systems and sediments*

The  $\text{Na}_2\text{CO}_3$  extraction technique developed by DeMaster (1981, 1991) is one of the most widely used methods used to extract BSi from marine sediments (Conley 1998; Conley and Schelske 2001). DeMaster (1981) tested a variety of different temperatures, different base concentrations and used different materials (clay samples, diatoms, radiolarians and ASi) to examine for the best conditions to digest all of the BSi while minimizing the dissolution of Si from minerals.

Eggiman et al. (1980) used a 21% (2 M)  $\text{Na}_2\text{CO}_3$  solution to extract amorphous silica in marine sediments. They digested the samples at 90–100 °C for 4 h and used the Al contents in the extract to correct for solubilized non-amorphous silica. Mortlock and Froelich (1989) proposed a single extraction with 2 M

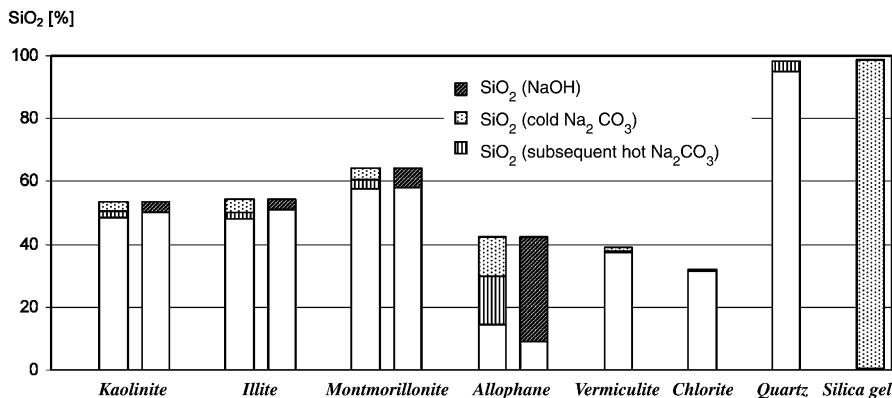


Figure 5. SiO<sub>2</sub> extracted from mineral samples by different solutions (data from Follett et al. 1965). The columns represent the total SiO<sub>2</sub> contents of the materials. The right columns for kaolinite, illite, montmorillonite, and allophane show the proportion of SiO<sub>2</sub> dissolved by NaOH. The other columns show the amounts of SiO<sub>2</sub> extracted by cold Na<sub>2</sub>CO<sub>3</sub> and subsequent hot Na<sub>2</sub>CO<sub>3</sub>.

Na<sub>2</sub>CO<sub>3</sub> at 85 °C for 5 h for determination of BSi in marine sediments without a correction for mineral dissolution. Most of the sediments analyzed by Mortlock and Froelich were in the high siliceous sediments of Antarctica and simultaneous extraction of minerals should be small relative to the large amount of amorphous silica extracted. They found by microscopic inspection of the residues after extraction that all diatoms are dissolved by this extraction, but up to 20–50% of radiolarians can still be present. Since in their sediment samples radiolarians generally represented only 2–4% of the mass of BSi the resulting underestimation of BSi is <2%. In samples, in which radiolarians represent a larger fraction of BSi, they recommended after Na<sub>2</sub>CO<sub>3</sub> extraction to wash the residual solids through a 38 or 63 μm sieve and to digest the fraction > 38 or 63 μm with 10–30 ml of 2 N NaOH at 85 °C for 5–8 h. Conway et al. (1977) used 0.5 M Na<sub>2</sub>CO<sub>3</sub> to extract BSi from water samples in a study on the biological utilization and regeneration of Si in Lake Michigan. Paasche (1980) applied 0.05 M Na<sub>2</sub>CO<sub>3</sub> to measure Si contents of different diatom species grown in laboratory culture. Since his results agreed well with those obtained by other analytical methods he concluded that the method is well suited for Si analysis in diatoms.

#### *Studies comparing the NaOH and Na<sub>2</sub>CO<sub>3</sub> extraction*

Generally, NaOH has been reported to dissolve a greater amount of minerals than Na<sub>2</sub>CO<sub>3</sub> (e.g. Eggimann et al. 1980; Paasche 1980). Follett et al. (1965) compared their 2-step Na<sub>2</sub>CO<sub>3</sub> extraction procedure to the digestion with NaOH by treating some aliquots of the same samples with 0.5 N NaOH following the method of Hashimoto and Jackson (1960). The results showed that silicic acid released from different pure clay mineral samples by subsequent cold and hot carbonate treatment varied (Figure 5). It was 9–11% of the SiO<sub>2</sub> content of the original material for kaolinite, illite, and montmorillonite and 2–4% for vermiculite, chlorite, and quartz. The authors attributed this silicic acid release to the presence of amorphous material in the minerals, because they found no evidence for mineral dissolution from X-ray, IR, or electron microscope investigation. They interpreted soil clay as ‘a continuum from completely disordered, through poorly ordered, to well crystallized material; the range of this continuum which can be extracted depends upon the reagent employed’ (Follett et al. 1965). The allophane samples released 80% of their Al<sub>2</sub>O<sub>3</sub> and more than 60% of SiO<sub>2</sub>. Silica gel released 99.4% of its SiO<sub>2</sub> during extraction with cold Na<sub>2</sub>CO<sub>3</sub>, and the remaining 0.6% during extraction with hot Na<sub>2</sub>CO<sub>3</sub>. Comparing the NaOH and Na<sub>2</sub>CO<sub>3</sub> extractions, Follett et al. (1965) found that NaOH extracted a larger amount of SiO<sub>2</sub> than Na<sub>2</sub>CO<sub>3</sub> from allophanes, but about as much or less SiO<sub>2</sub> from kaolinite, illite, and montmorillonite (Figure 5).

Wada and Greenland (1970) developed a 2-step procedure consisting of subsequent extractions with Na<sub>2</sub>CO<sub>3</sub> and NaOH. They used aliquots of 30–55 mg of the clay fraction. In a first step they extracted the

iron oxides by adding sodium citrate, sodium bicarbonate, and sodium dithionite at 80 °C for 15 min. They repeated this extraction once and washed with a mixture of sodium citrate and acetone. After this, they added 2% Na<sub>2</sub>CO<sub>3</sub> and digested the sample at 90 °C for 15 min. Finally, samples were treated with 0.5 N NaOH and heated at 90 °C for 15 min. The weight loss after each step of the procedure was determined, and infrared spectra were taken of the aliquots without treatment and after each step in order to characterize the effects of the different extractions. From the weight losses and spectra they concluded that the dithionite extraction in addition to iron oxides also dissolves 'allophane-like materials'. The carbonate-soluble materials were less well ordered than the NaOH-soluble, but both extractions did not completely dissolve allophane samples. As a general conclusion Wada and Greenland (1970) stated that 'the material dissolved by any particular treatment is primarily dependent on the initial mineral composition. Dissolution of amorphous aluminium silicates, allophanes, was only found for the clays in which they are the major constituents. Layer silicates, probably including disordered kaolin, were dissolved from the clays in which layer silicates predominated.'

Krausse et al. (1983) demonstrated that besides the type of extractant (NaOH or Na<sub>2</sub>CO<sub>3</sub>) other factors such as digestion time, temperature, pH, reagent concentration and volume also control the extent of mineral dissolution. They found that leaching samples with 0.2 M NaOH for 10–15 min at 100 °C caused a lower interference from silicate minerals and moreover was less time consuming than leaching with 0.5 or 5% Na<sub>2</sub>CO<sub>3</sub> for 2 h at 85 °C. Their time course experiments showed that the 0.2 M NaOH dissolved BSi in water samples in the Grand Traverse Bay, Lake Michigan within 11–12 min. No or little Si was leached after 15 min. Krausse et al. (1983) concluded that mineral interference was not significant compared to the quantity of BSi, but they also assumed that the extent of mineral dissolution should depend on type, quantity, and grain size of the minerals.

Conley (1998) carried out an interlaboratory comparison for BSi measurement by use of alkaline extraction methods (with Na<sub>2</sub>CO<sub>3</sub> or NaOH) in aquatic sediments. Thirty laboratories took part representing the community of aquatic scientists (paleolimnologists, paleoceanographers, limnologists, estuarine scientists and oceanographers). About 72% of the laboratories used Na<sub>2</sub>CO<sub>3</sub> as extractant solution, and 54% applied a mineral correction for calculation of the BSi contents. The Na<sub>2</sub>CO<sub>3</sub> concentrations used ranged from 0.1 M (1%) to 2 M, and NaOH concentrations ranged from 0.2 to 1 M. Sample:solution ratios ranged from 0.2 to 2.5 g l<sup>-1</sup>. The percent standard deviation of the mean was highest (67.5%) in the sample with the lowest BSi concentration, and lowest (21.2%) in the sample with the highest BSi concentration (Figure 6).

Removal of seven laboratories, whose results were > ± 1 standard deviation from the mean in at least three of the six samples, reduced variation by 30–60% of the previously determined standard deviation, so that Conley (1998) concluded that, despite the differences in the methods used, 23 of 30 laboratories analyzed BSi with acceptable precision. For most of the samples analyzed (containing no sponge spicules or radiolarians) neither the extractant (Na<sub>2</sub>CO<sub>3</sub> or NaOH) nor the procedure (DeMaster 1981, or Mortlock and Froelich 1989) were significant factors.

### *Tiron*

The aggressiveness of NaOH on clay minerals and the incomplete opal dissolution by Na<sub>2</sub>CO<sub>3</sub> led Biermans and Baert (1977) to develop another method for extraction of amorphous silica from soils using Tiron (4,5-dihydroxy-1,3-benzene-disulfonic acid [disodium salt], C<sub>6</sub>H<sub>4</sub>Na<sub>2</sub>O<sub>8</sub>S<sub>2</sub>). They carried out a series of experiments to find the optimum Tiron concentration, pH, temperature, and extraction time. Optimum extraction conditions were a Tiron concentration of 0.1 M, pH 10.5, 80 °C, and an extraction duration of 1 h. Kodama and Ross (1991) refined the method and tested its suitability on various crystalline and poorly crystalline minerals and amorphous materials. They compared the amounts of Si extracted by Tiron with those dissolved by NaOH and oxalate and found that Tiron attacks crystalline minerals to a smaller extent than NaOH, but extracts similar Si amounts from opal and obsidian as NaOH. It also dissolves similar Si amounts from allophane and imogolite as oxalate (Table 3). Therefore, the authors proposed to analyze

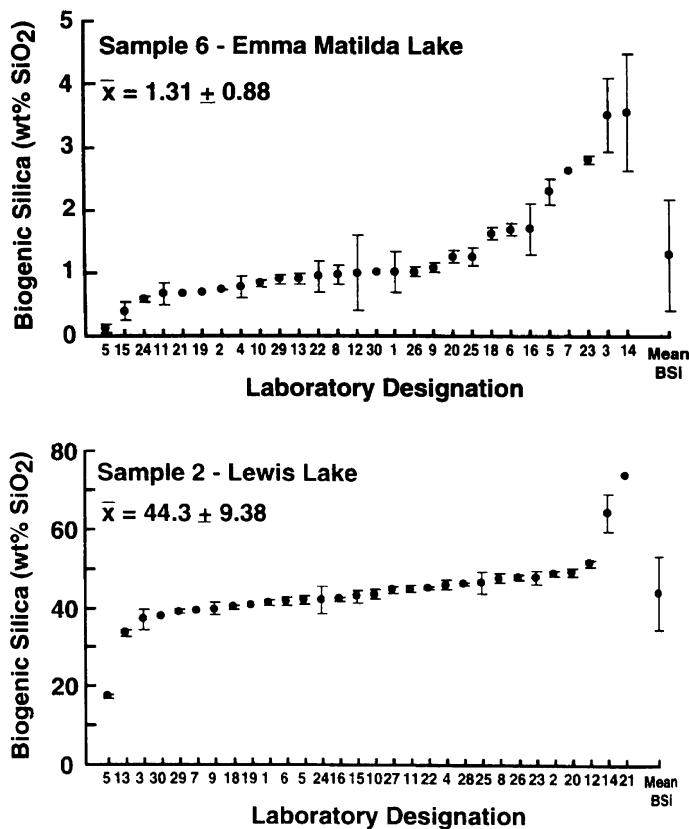


Figure 6. Results of an interlaboratory comparison of BSi measurement for the two samples with the lowest (left) and highest (right) BSi contents (please, mind different scales of y-axes) (Conley 1998).

allophane and imogolite Si by use of the oxalate extraction and amorphous Si by subtracting oxalate-soluble Si from Tiron-soluble Si. Kendrick and Graham (2004) used the Tiron extraction of Kodama and Ross (1991) in chronosequence studies to quantify pedogenic silica accumulations as an indicator for relative ages of soils.

### Oxalate

The oxalate extraction of Schwertmann (1964), which is a modification of the technique of Tamm (1932), is a standard method in soil science, which was primarily developed to determine amorphous forms of Fe and

Table 3. Comparison of amounts of Si extracted by NaOH, Tiron, and oxalate (data from Kodama and Ross 1991).

Material investigated	Si ( $\text{g kg}^{-1}$ ) dissolved by different extractants		
	NaOH	Tiron	Oxalate
Opaline silica	397	379	1
Opal, Arizona	278	38	–
Obsidian, California	73	53	–
Opal, Hawaii	43	50	–
Allophane, Japan	–	114	115
Imogolite, Japan	–	73	68

Al, and organic complexes of Fe and Al in soils, but it is also commonly used to assess the amount of Si bound in allophanes and imogolite-type materials (Simonsson et al. 1999), and seems also to dissolve zeolites (Sauer and Burghardt 2000).

Kelly et al. (1998) used the oxalate extraction to measure ASi in soils. They obtained a strong correlation between total Si and oxalate-extractable Si in pasture soils, but no such correlation from soils in a forested ecosystem. They suggested that there was a single pool of ASi in the pasture and several pools in the forest. They hypothesized that grasses, producing more phytoliths per unit weight than trees, stabilize a greater proportion of the soil silica as ASi. This interpretation is in contrast to the results of Kodama and Ross (1991), which showed that oxalate dissolves allophane and imogolite but no or very little opal (Table 3).

Ewing and Nater (2002) pretreated sediment samples with sodium pyrophosphate and then extracted with ammonium oxalate solution to detect imogolite-type materials in lake sediments. Since imogolite-type materials are typically formed in podzols, this analysis enabled them to determine the beginning of podzolization in the catchment of the lakes.

### Summary and conclusions

The extraction methods in aquatic, sedimentological and soil sciences can be subdivided according to the different purposes they have been developed for. Several procedures have been developed for agronomic purposes to evaluate the Si supply in soils and to detect the need for Si fertilization. Not all of them were intended to extract the complete amount of plant-available Si, the focus was rather on establishing extraction methods, which gave good correlations with yields. The weakest extractant used was water. Complete extraction of the water-soluble Si fraction is rather time-consuming, taking either three weeks at room temperature (Schachtschabel and Heinemann 1967) or 1 week at 40 °C (Nonaka and Takahashi 1988, 1990). Another weak extractant, only extracting the readily available Si, is CaCl<sub>2</sub>. A very high correlation was found between CaCl<sub>2</sub>-extractable Si and sugar cane yields (Haysom and Chapman 1975).

Numerous techniques have been applied to extract soluble and some exchangeable Si from soils, using different anions to desorb the exchangeable part of the Si. Most of them use a buffered acetate/acetic acid solution, some acetic acid only, and some phosphate. Several studies comparing different extraction methods for plant-available Si were carried out with partly differing results. In general it can be stated that citric acid, acetic acid, phosphate and sulfate extract more Si than acetate, nitrate, CaCl<sub>2</sub>, and water (Fox et al. 1967; Korndörfer et al. 1999; Berthelsen et al. 2001). Therefore, extraction solutions containing sulfuric acid, sulfurous acid, sulfate, citric acid, and citrate have been interpreted to extract adsorbed Si, with the different extractants desorbing various amounts of the specifically adsorbed Si fraction. Different orders of extraction capacities of the most common extractants have been obtained. Fox et al. (1967) found in two soils on alluvial sediments and three soils on basalt the following order of extraction capacities: water < acetic acid < sulfurous acid/sulfate < phosphate (Figure 3). In contrast, in three of four soils on volcanic ash, sulfurous acid/sulfate extracted more Si than phosphate. Another soil studied by Fox et al. (1967) on Hawaii released most Si during acetic acid extraction (Figure 2). Berthelsen et al. (2001) obtained a different order of extraction capacities: water = acetate < acetic acid < phosphate/acetate < sulfuric acid < citric acid. It can be concluded that the efficiency of the extractants is significantly influenced by the extraction conditions (pH, extraction duration, etc.) and the composition of the soils used (especially with regard to primary silicates, clay minerals, and amorphous components).

A critical point is that some of the methods are conducted at very low pH values, e.g. the sulfuric acid extraction of Hurney (1973) at pH 2 and the phosphate buffer methods used by Fox et al. (1967) and Khalid et al. (1978) at pH 3.5, so that it must be assumed that Si measured in these extracts is not only derived from desorption but also from silicate corrosion.

Various procedures to dissolve ASi have been developed. The most common extraction method for ASi in soil science is the NaOH extraction of Foster (1953), while in aquatic sciences both NaOH and Na<sub>2</sub>CO<sub>3</sub> are used (DeMaster 1979, 1981; Mortlock and Froelich 1989; Müller and Schneider 1993; Conley and Schelske 2001; Koning et al. 2002). The Tiron procedure, which was introduced to the soil science



community by Biermans and Baert (1977), has not been widely used compared to the NaOH extraction. The fundamental problem of quantitative ASi extraction is that it seems to be impossible to develop an extraction procedure that specifically dissolves only ASi without significantly attacking crystalline silicate minerals, especially when the amounts of silicates in the sample are high compared to the ASi contents. Therefore, many scientists working in aquatic environments use corrections for the amount of Si derived from mineral dissolution (DeMaster 1979, 1981; Müller and Schneider 1993; Conley and Schelske 2001; Koning et al. 2002). However, such correction methods, which work well in aquatic and sedimentological analysis have not yet been introduced or tested in soil science, although there are hints that they are applicable (Herrmann and Stahr 1995). A correction by use of Si:Al ratios requires constant Si:Al ratios of both, the ASi and the dissolved silicates over the extraction duration. It must be assumed that this precondition is less well fulfilled in soils than in marine sediments, because ASi in soils contains varying amounts of Al, and also clay minerals with different Si:Al ratios, which are dissolved to different extents. Therefore, the more practical way to correct for silicate dissolution is the time course extraction of Si using the different dissolution kinetics of amorphous and more crystalline Si components in soils.

Another important point to mention is that more care has to be taken concerning pH and mechanical shaking during all types of extractions (water-soluble, adsorbed, amorphous Si). Several methods operate at extremely low pH and some procedures include several hours of continuous mechanical shaking, so that it must be assumed that Si may also be released from silicates due to strong acid conditions and abrasion. The pH during extraction of soluble and exchangeable Si should be adjusted to pH 4.5–4.8 as proposed by Ayres (1966), Fox et al. (1967), and Wong You Cheong and Halais (1970) to avoid clay mineral destruction. Shaking should be kept to the minimum necessary to allow equilibration between solid and solution within a reasonable timespan, e.g. by regular short-time shaking to resuspend the samples at defined time intervals during the extraction or by continuous very slow shaking. Great care is also required during homogenization and sieving of the soil samples to avoid an increase of extracted Si caused by grinding (DeMaster 1991).

Moreover, using extraction techniques for different Si phases in soil it is important to be aware of the statement of Follett et al. (1965), who interpreted soil clay as a continuum from completely disordered to well crystallized material. Although today the knowledge about poorly crystalline clay minerals such as allophanes and imogolite has significantly improved, the core of that message is still relevant, which means that the definitions of boundaries between crystalline, poorly ordered, and amorphous phases are partly arbitrary.

Studies have shown that the ASi derived from plants (phytoliths) are ubiquitous and an important component of soils (Conley 2002, unpublished; Derry et al. 2005; Farmer et al. 2005). The storage of recyclable ASi in lake sediments has also been shown to be an important component of the mass balance in aquatic ecosystems (Conley and Schelske 2001). This review has summarized and compared a large variety of different methodologies used in the aquatic sciences and soil sciences for extracting different forms of Si from sediments and soils. In order to advance our current understanding of the global biogeochemistry of Si we need to first test and then apply the quantitative methods developed in the aquatic sciences (DeMaster 1979, 1981; Müller and Schneider 1993; Conley and Schelske 2001; Koning et al. 2002) to soil systems to investigate the importance of the soil pools of ASi to the overall mass balance in the biogeo-sphere.

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