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Development of a method for sequential Si extraction from soils

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ABSTRACT

In this paper, we introduce a new method for sequential extraction of different silicon (Si) fractions from soils. The method has been developed based on several series of extraction experiments on well-characterized isolated soil compounds and selected soil samples. Results and implications of these test series are presented, and reasons for the choice of methods for the single steps of the sequential extraction procedure are given.

The sequential extraction method separates seven Si fractions. The first four extraction steps are performed on four replicates, which are then split into two by two replicates subjected to two different treatments in the following step. 1) The mobile Si fraction is obtained by extraction by weak electrolyte solution of $CaCl_2$. 2) Si in adsorbed silicic acid is extracted by acetic acid through anion exchange. 3) Si in soil organic matter (SOM) is released by SOM oxidation with H_2O_2. 4) Si in pedogenic oxides and hydroxides is obtained by treatment with ammonium oxalate and oxalic acid solution under UV-light. 5) In step 5 amorphous silica of biogenic and minerogenic origin is specified. This separation is done in three sub-steps: 5.1) Two samples are directly subjected to NaOH extraction to obtain the total amorphous silica fraction; 5.2) the two other samples are first subjected to bio-opal separation with sodium polytungstate; 5.3) NaOH extraction is then applied to the bio-opal samples to obtain their Si content. The difference between the amounts of Si in the extracts of sub-steps 5.1 and 5.3 is interpreted as Si from minerogenic amorphous silica forming precipitates on surfaces of mineral grains. 6) In addition, total Si concentration is either determined by fusion of sub-samples with lithium borate, dissolution in nitric acid and ICP-OES analysis or by X-ray fluorescence analysis. The share of crystalline silicates is calculated as the difference between total Si and the sum of the Si fractions obtained in extraction steps 1 to 5.

Potential drawbacks of the method include i) varying efficiency of the second extraction step, strongly depending on soil composition, ii) overestimation of Si in soil organic matter due to partial dissolution of clay minerals, pedogenic oxides and amorphous silica by H_2O_2, iii) underestimation of Si in pedogenic oxides and hydroxides due to incomplete destruction of highly crystalline pedogenic oxides or nodules.

1. Introduction

Amounts of Si in soils depend on parent material and soil type, reflecting pedogenic processes at pedon and landscape scale. They vary from less than 1 mass% Si in Histosols to up to 45 mass% Si in Podzols (Sommer et al., 2006). Si in soils most commonly occurs in quartz (Drees et al., 1989) followed by Si in primary silicates and clay minerals. In addition, various other Si compounds occur in soils that have attracted less attention in the past (Sauer et al., 2006). In general, Si released during weathering of primary silicates can be leached or consumed in the formation of secondary silicates, or it may precipitate as pedogenic silica from the soil solution (McKeague and Cline, 1963a). Silica precipitates may form amorphous coatings on mineral grains (Veerhoff and Brümmer, 1993) or mixtures with crystalline substances (Follett et al., 1965).

Si concentration in soil solution varies between 0.4 and 2000 μmol l^{-1}, depending on parent material, soil development, depth and temperature (Conley et al., 2006). Dissolved silica is usually present in marine and terrestrial environments as monomeric silicic acid (Shell, 1962). Silicic acid starts deprotonating above pH 9 (Dietzel, 2000; Wonisch et al., 2008). Dissolved silica in soil solution is part of a dynamic system; its amounts depend on mineral composition, adsorption effects, water balance, temperature and biochemical activity (Milnes and Twidale, 1983). Various organic compounds may increase or decrease silica solubility (Iler, 1979; Summerfield, 1983). Organic compounds such as low molecular weight organic acids contribute to the weathering of soil minerals through acidification and complexation (Bennett et al., 1991, 2001; Crook, 1968; Drever, 1994). Complexes of organic compounds and silica in soil solution have been identified (Matichenkov and Snyder, 1996).

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Microorganisms (bacteria, fungi, protozoa) may also affect Si-release from litter or minerals. Some microorganisms have developed mechanisms for Si-storage (biomineralization) in their bodies (Sommer et al., 2006). Thus, together with plants they are an important source of mobile Si in soils.

Silicic acid can be adsorbed to the surfaces of various soil components (Beckwith and Reeve, 1963; Dietzel and Böhme, 1997; Hansen et al., 1994; Iler, 1979; Jones and Handreck, 1963; McKeague and Cline, 1963b,c). Adsorption of monosilicic acid in soils depends on soil reaction, soil composition and the specific surface of sorbents and increases with increasing pH and specific surface area of the soil particles (Beckwith and Reeve, 1963, 1964; Cornell and Schwertmann, 1996; Gehlen and van Raaphorst, 2002; Jones and Handreck, 1963; McKeague and Cline, 1963b). Pedogenic oxides and hydroxides that are abundant in soils (Schwertmann and Taylor, 1989) play an important role in adsorption, occlusion and release of silicic acid in soils (Cornelis et al., 2010; McKeague and Cline, 1963a; Opfergelt et al., 2009).

The largest proportion of amorphous silica in most soils is represented by bio-opal (Drees et al., 1989) in form of phytoliths, siliceous sponges, diatoms and radiolarians. Some authors assume that biogenic silica is a major source of dissolved Si in soil solution (Cornelis et al., 2010; Derry et al., 2005; Miretzky et al., 2001). Alexandre et al. (1997) estimate that Si release from bio-opal is two to three times as great as that from silicate weathering. This implicates a high turnover of this fraction.

Quantification of Si pools in soils is needed for improving our understanding of biogeochemical processes involving Si in the plant–soil–soil water–groundwater system which represent a black box in global Si-cycling models so far. Such quantification requires a sequential extraction method for the various Si fractions in soils, analogous to e.g. sequential heavy metal extraction. However, a sequential extraction method has not been available so far for Si. The objective of this work was to develop such a method. For this purpose, quantitative chemical extraction methods for extracting silicon from different soil fractions were tested. Those methods that turned out most suitable were optimized and implemented as extraction steps in a sequential extraction procedure. The aim was to develop a procedure that is applicable in any ordinarily equipped soil science laboratory.

2. Materials and methods

2.1. Well-characterized soil compounds and soils used for the tests and optimization procedures

The effects of various extractants were tested on selected well-defined soil compounds (Table 1). Seven soil profiles from four different areas of SW-Germany were described and sampled to cover a range of different soils. Soils include a Cambisol and two Podzols on Triassic sandstone under forest of silver fir and Norway spruce in the northern Black Forest (Seebach area), one of the Podzols with thick eluvial horizon and one with thick illuvial horizon (on the upper and lower parts of the same slope, respectively). The climate is humid-temperate, characterized by a mean annual precipitation of 1935 mm and a mean air temperature of 6.5 °C (Sommer, 2002). The fourth soil is a Cambisol on gneiss under spruce forest (Fiedler et al., 2002) in the southern Black Forest (Wildmooswald area). The mean annual air temperature is 6 °C and annual precipitation is 1600 mm. Soils No. 5 and No. 6 are a Luvisol (plateau position) and a Calcic Regosol (shoulder position) on loess located on the same slope under woodruff beech forest in the Kraichgau region, about 2 km SW of Helmsheim. The mean annual air temperature is 9 °C and average annual precipitation is 700 mm (Bleich et al., 1990). Soil No. 7 is a Stagnosol on periglacially reworked loess, under a mixed forest of spruce, fir and beech (Ehmann, 1989) about 5 km NW of Pforzheim (Lettenbach area). The mean annual air temperature is 7 °C, and the annual precipitation is 987 mm.

The soils were sampled by horizon; the samples were air-dried and passed through a 2-mm sieve. The mineralogical composition of the clay fraction (<2 μm) was determined by X-ray diffraction analysis with Cu–Kα radiation (Siemens D 500-Diffractometer). Clay mineral percentages were calculated using the software Diffrac AT 3.3. Particle size distribution of the soil samples was determined by wet sieving (sand fractions) and pipette method (silt and clay). Soil pH was measured using a glass electrode in 0.01 M $CaCl_2$ suspensions at soil to solution ratio of 1:2.5. Bulk density was determined by the dry weight of undisturbed soil samples taken in 100 cm^3 steel cylinders. Total carbon contents were determined by CN analyzer Vario EL, Hanau (dry combustion). Soil organic carbon (SOC) was determined according DIN ISO 10694 (1996). Inorganic carbon was measured using a Scheibler apparatus (Schlichting et al., 1995). The main characteristics of the soil samples are presented in Table 2.

2.2. Methods selected and tested for the sequential Si extraction procedure

All experiments in this study were carried out using plastic vessels such as polypropylene, polyethylene or polymethyl pentene. Glass vessels were not used because Si could be released from any glassware. During extraction the samples were either shaken on a horizontal shaker only for 1 min/h (using a clock timer) or very slowly end-over-end to avoid abrasion of soil particles (McKeague and Cline, 1963b). All extractions were done on at least two replicates (4–8 replicates for adsorption–desorption experiments). Analysis of Si in the extracts was performed by ICP-OES (inductively coupled plasma

Table 1
Well-characterized soil compounds used for the tests and optimization procedure.

Substance	Characteristics	pH (H_2O)	Element analysis	Distributor
Bio-opal	From *Equisetum fluviatile*	4.4	Organic carbon = 0.9%	Obtained by the method of Bartoli and Wilding (1980)
Silica gel	Purum $SiO_2 * H_2O$	3–8	n.d.	Merck
Kaolin	60% Quartz, 40% kaolinite	3.7	Si = 29% Al = 17% Fe = 1%	CH Erbslöh
Smectite	76% Na-montmorillonite, 15% Quartz, 8% illite	10.5	Si = 28% Al = 12% Fe = 4%	CH Erbslöh
Geothite	61% Goethite, 27% quartz, 12% illite	6.2	n.d.	Sigma-Aldrich
Al-hydroxide	99% Gibbsite	9.7	n.d.	Merck
Peat	Natural, pure H3–H5	3.9	n.d.	Manna, Haug GmbH
Microcline	84% Microcline, 16% anorthite	9.4	Si = 33% Al = 13%	Dr. F. Krantz
Quartz powder	>99% Quartz	6.7	n.d.	Merck

n.d.: not determined.