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Factors controlling Si export from soils: A soil column approach

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ABSTRACT

The release of dissolved silicon (DSi) from A and B horizons was investigated with leaching tests on unsaturated columns. As forest A horizons have larger biogenic Si (BSi) pools than arable lands, we compared the Si release from a forest and a cropland from the same geographical region developed on a Luvisol in Belgium and a Cambisol in Sweden. The A horizons released a quickly dissolving Si fraction in contrast to the B horizons, which did contain no or only little amounts of BSi and released lower Si concentrations. Our experiments show that Si export from forest soils is high because of the presence of a large reservoir of soluble BSi as well as due to the acidity of the soil ($pH < 4$). Leaching at two different water fluxes revealed that export in forest soils was transport controlled while cropland soils were in equilibrium.

1. Introduction

Dissolved Si export from terrestrial catchments has long been thought to be fully controlled by chemical weathering processes (Garrels and Mackenzie, 1967). However, it is now clear that the dissolution of soluble, non-crystalline silica particles present in soils does affect Si export (Derry et al., 2005; Sommer et al., 2006; Street-perrott and Barker, 2008). Part of this non-crystalline Si is of biological origin (BSi). BSi is formed when dissolved Si, primarily derived from the weathering of silicate minerals, passes through plants which form phytoliths. The presence of a BSi reservoir affects Si cycling in soils. The dissolution of non-crystalline Si is controlled by the same chemical soil water parameters (pH, base cations (BC)) controlling the dissolution of silicates (Dove, 1995; Dove et al., 2008) but experiments have shown that BSi solubility (1.8 mM Si) can be up to 17 times higher than that of quartz (0.10–0.25 mM Si) (Fraysse et al., 2006). The BSi solubility varies depending on the Si/Al ratio, the surface area of the BSi and the water content of the soil (Bartoli, 1985; Bartoli and Wilding, 1980), as well as phytolith morphology and association with organic matter (Watteau and Villemin, 2001). The accumulation of BSi in the terrestrial realm modulates the final Si export from the land to the ocean. As terrestrial ecosystems have been heavily disturbed by human activities over the last centuries, the steady-state principle of Si delivery towards oceans is now being questioned (Frings et al., 2014). This concept has become known as the "ecosystem Si filter" (Struyf and Conley, 2012).

Biogenic Si is not the only form of non-crystalline Si present in soils. Dissolved Si flowing through the soil profile can also reprecipitate as amorphous or poorly crystalline Si phases (Chadwick et al., 1987; Doucet et al., 2001) recognized as precursors for secondary clays (Dixon and Weed, 1989), or adsorb on Al- and Fe-(hydr)oxides deeper in the soil profile (Beckwith and Reeve, 1963; McKeague and Cline, 1963). These fractions are grouped under the name "pedogenic Si" (PSi). This PSi fraction occurs typically in deeper soil layers, and appears to be more reactive than BSi during alkaline extraction experiments (Barão et al., 2014). Outside the lab environment little data is available on the solubility of the PSi fraction in soils and the importance of its contribution to the Si export towards rivers. White et al. (2012) used Ge:Si ratios to trace controls on pore-water Si levels. They suggested a seasonal control of PSi on pore-water DSi levels through the formation and dissolution of poorly-crystalline Si fractions, exemplifying its potential importance. The total quantity of both types of Si combined (BSi and PSi) can be measured through alkaline extraction (DeMaster, 1981; Sauer et al., 2006). We will refer to it using its procedural term: alkaline extractable Si (AlkExSi) as proposed by Barão et al. (2014).

Silicate weathering reactions consume CO_2 from the atmosphere and convert it to bicarbonate in river and groundwater (Cochran and Berner, 1996; Lucas, 2001). The chemical composition of natural water, particularly its DSi concentration, is therefore often considered as a good indicator of the mineral weathering rate (Garrels and

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Mackenzie, 1967; Oliva et al., 2003). Plants are recognized to change soil physical properties by binding fine particles and disintegrating bedrock, which consequently changes surface areas and enhances silicate weathering (Drever, 1994). They also generate weathering agents such as acidic organic root exudates and recycle soluble cations (Kelly et al., 1998) and affect soil pH by producing H-protons and CO_2 (Hinsinger et al., 2001). Cochran & Berner (1996) demonstrated that chemical denudation rates for basalt covered by plants were ten times higher than for bare basalts, which were only colonized by microbial communities. Experiments showed that the presence of plants on basaltic rock could increase the release rates of Si by a factor of 2 (Hinsinger et al., 2001). Field weathering rates were two and three times higher for soils respectively covered with birch and conifers than for bare soils (Moulton et al., 2000).

However, silicate weathering is not only surface reaction controlled. Maher (2010) suggested that weathering in most granitic sediments is transport-controlled, i.e. dependent of fluid residence time and fluid flow rates. Dominant factors in transport-controlled weathering are fluid flow, pH and mineral solubility, whereas surface area and mineral kinetics are less important (Maher, 2010). Plant root distribution determines water uptake (Jackson et al., 2000) from the soil and thereby affects the importance of different flowpaths and water residence time. Consequently, a change in vegetation may also impact transport-controlled weathering.

Given the strong interactions between plants and the Si cycle, it can be expected that land use changes such as deforestation can significantly alter catchment scale Si fluxes, a hypothesis which was confirmed by recent empirical studies (Carey and Fulweiler, 2011; Conley, 2002). Struyf et al. (2010) found a positive relationship between the presence of forests in a catchment and DSi export. In their conceptual model, they introduced, alongside the above described effects on weathering, also the potential role of a larger AlkExSi (BSi + PSi) pool in forested systems as a source for enhanced Si delivery. In their model, the initial rapid leaching of the present AlkExSi pool increases Si delivery in the first decennia following deforestation, but over a centennial scale the reduced BSi replenishment due to crop harvesting leads to a lowered Si delivery (Keller et al., 2012; Vandevenne et al., 2012). The alteration of Si fluxes from the land to the water after deforestation or land use change may not only have significant effects on the productivity and composition of aquatic ecosystems but may also affect the biological CO_2 pump in the oceans. The latter is directly related to the ocean's primary productivity, which is strongly controlled by Si consuming plankton, i.e. diatoms (Carey and Fulweiler, 2011; Conley et al., 2008; Laruelle et al., 2009; Struyf et al., 2010).

Although several studies have confirmed that the size of AlkExSi pool in soils depends on land use and land management (Clymans et al., 2011, Guntzer et al., 2011, Keller et al., 2012, Vandevenne et al., 2012), few studies so far focused on the role of the different fractions in the AlkExSi pool in soils in controlling the actual Si release (Cornelis et al., 2010, Cornelis et al., 2014, White et al., 2012). Pore-water samples collected in the field can only be used to a limited extent to assess controls on AlkExSi solubility. First, it is hard to control the complexity of the natural hydrological system in the field as water fluxes, pore water chemistry, and more specifically pH and chemical saturation state can vary locally (Neal, 1997) due to soil heterogeneity and vadose zone processes (Neal, 1996). Secondly, while DSi concentrations can effectively be measured, it is much more difficult to determine the contribution of the different possible sources to the total DSi flux.

Laboratory column studies can overcome these objections to some degree as water fluxes and water composition can be controlled for different horizons separated in different columns. Thus, one can gain insight in the origin of the DSi. The aim of this study is to use such column studies (i) to test the hypothesis that the size of the AlkExSi pool, here coincident with the land use component, influences Si release, and (ii) to assess the contribution of BSi and PSi dissolution to the Si export. We performed leaching experiments on soil samples from the A and B horizons (to investigate the effect of the AlkExSi pool composition) collected at a forest and arable site (to investigate the effect of the size of the AlkExSi pool). The samples were collected from two land use gradients with contrasting parent material to explore the reproducibility of results: Luvisols developed on loess from Belgium, and Cambisols developed in glacial till overlaying a granite bedrock from Sweden. Thus, this study is a first step to verify the validity of the hypothesis that Si delivery depends on the size and speciation of the AlkExSi pool in soils.

2. Material and methods

2.1. Study sites and background data

Our study used soil samples from two land use gradients developed on different parent materials in temperate regions. The first location is in the Belgian Loam Belt and has a temperate climate with long-term mean annual precipitation of about 760 mm and a mean January and July temperature lying respectively between 3 °C and 4 °C and between 17 °C and 18 °C. Samples were collected from hillslopes in a catchment under forested (Meerdaal forest, f_{lv} site, 50°48′N, 4°40′E) and in a catchment under high-intensity arable land use (Ganspoel, c_{lv} site, 50°48′N, 4°35′E) (Vandevenne et al., submitted for publication). Soils in both catchments were Luvisols developed on eolian loess deposits (Van Ranst et al., 1982). Soil pits were dug for soil sampling per horizon while samples for analysis were taken by coring (Tables 1 and 2, Vandevenne and Barão et al. submitted).

In Sweden, samples were taken through coring in a catchment under continuous forest (Siggaboda, f_{cb} site, 56°27′N, 14°12′E) as well as one under arable land use (Råshult, c_{cb} site, 56°36′N, 14°11′E) (Barão et al., 2014, Clymans et al., 2011). This agricultural site is different from the Belgian site as it is located in a cultural reserve where traditional, low-intensity tillage (without chemical fertilization) is practiced and a two to three year ley is used between crops. Agricultural intensity at Råshult is therefore clearly lower in comparison to the Ganspoel site. The mean annual precipitation is ca. 700 mm yr^{-1} and January and July temperatures vary respectively between −2 °C and −3 °C and between 15 °C and 16 °C. The Swedish soils developed on sandy till underlain by granitic bedrock and were classified as Cambisols. The Cambisol soil samples were collected through coring in flat areas. A detailed description of the study area and the sampling technique was presented in Clymans et al. (2011). Soil samples used for our experiment came from a replica taken next to the corings used for soil analysis (Tables 1 and 2, Clymans et al., 2011, Barão et al., 2014). Throughout the study we indicated our sites with acronyms (f_{lv}, c_{lv} for the forested and cropland site on Luvisol in Belgium and f_{cb}, c_{cb} for the forested and cropland site on Cambisol in Sweden, respectively), specific horizons are indicated by a letter preceding this acronym (e.g. Af_{cb} for the A horizon developed under forest cover in the Cambisol).

Selected soil samples have previously been analyzed and described in detail (see Barão et al., 2014, Clymans et al., 2011, Vandevenne et al., submitted for publication). Basic soil property data including soil pH, texture, soil organic carbon content, oxalate extracted Al and Fe for the selected samples are reported in Table 1. Soil pH was determined in a $CaCl_2$ solution (0.01 M) and measured with a glass electrode (Table 1) while soil organic carbon content was measured with Walkley and Black (1934) titrations (Table 1). The grain size distribution reflects the difference in parent material between the Luvisol and the Cambisol. The sandy Cambisols are more acidic and contain higher contents of SOC in comparison to the Luvisols. The forested Cambisol has higher SOC contents and lower soil pH compared to its arable counterpart. A comparable pattern is found for the Luvisol. In both cases SOC decreases with depth, while soil pH increases.

Table 2 summarizes the results of the alkaline (Total AlkExSi, mg Si g^{-1} − BSi & PSi), oxalate ($Si_{oxalate}$) results for the selected samples. The AlkExSi contents (mg Si g^{-1}) were quantified with the continuous