"Impact of tree species on the distribution of alkaliextractable Si in a Cambisol"

Cornélis, Jean-Thomas ; Ranger, Jacques ; Delvaux, Bruno

Abstract

In terrestrial ecosystems, silicon (Si) uptake by higher plants induces biogenic silica (BSi) deposits in leaves, which contribute to the amorphous silica (ASi) pool in soil through litter-fall. In forests, the ASi pool, including BSi, is ubiquitous and a substantial component of soils, which might influence the Si mass-balance at watershed scale. Here, we examined the distribution of ASi pool, estimated by alkaline dissolution (alkali-extractable Si), in an acid brown soil under three common European tree species in identical soil and climate conditions in order (i) to study how the Si recycling by tree species impacts the ASi pool in soil, and (ii) to identify the different constituents of the alkali-extractable Si pool in soil. We therefore quantified the ASi concentration with alkaline extraction (Na2CO3, 0.1M), the Si adsorbed onto poorly crystalline Fe oxides by oxalate extraction and the “plant-available Si” by CaCl2 extraction. In humus layer, the alkali-extractable Si co...

Impact of tree species on the distribution of alkali-extractable Si in an acid brown soil

Jean-Thomas Cornelis[A], Hugues Titeux[A], Jacques Ranger[B] and Bruno Delvaux[A]

[A] Earth and Life Institute, Soil Science, Université Catholique de Louvain, Belgium, E-mail : jean-thomas.cornelis@uclouvain.be
[B] Biogeochemistry of forest ecosystem, INRA Centre de Nancy, France

Abstract
In terrestrial ecosystems, silicon (Si) uptake by higher plants induces biogenic silica (BSi) deposits in leaves, which contribute to the amorphous silica (ASi) pool in soil through litter-fall. In forests, the ASi pool, including BSi, is ubiquitous and a substantial component of soils, which might influence the Si mass-balance at watershed scale. Here, we examined the distribution of ASi pool, estimated by alkaline dissolution (alkali-extractable Si), in an acid brown soil under three common European tree species in identical soil and climate conditions in order (i) to study how the Si recycling by tree species impacts the ASi pool in soil, and (ii) to identify the different constituents of the alkali-extractable Si pool in soil. We therefore quantified the ASi concentration with alkaline extraction (Na_2CO_3, 0.1M), the Si adsorbed onto poorly crystalline Fe oxides by oxalate extraction and the "plant-available Si" by $CaCl_2$ extraction. In humus layer, the alkali-extractable Si concentration (mg SiO_2 g^{-1}) significantly decreases in the sequence: Douglas fir (14.5±0.65) > European beech (11.8±0.30) > Black pine (5.4±0.31). Below 15 cm soil depth, the alkali-extractable Si concentration is not significantly different between tree species. For each tree species, the alkali-extractable Si concentration in soil decreases from the humus layer to 15 cm depth and then slightly increases from 15 to 75 cm depth. Our data clearly show that tree species can impact the ASi content in topsoil (humus layer - 15 cm) through different Si uptake rates. Indeed, various Si recycling by forest vegetation imply different rates of BSi accumulation in leaves and then, different rates of BSi restitution on topsoil. In mineral layers, pedogenic processes play an important role in the ASi distribution given the alkali-extractable Si pool is mostly influenced by BSi dissolution, stable BSi preservation/translocation and secondarily by Si adsorption onto active amorphous Fe oxide surface.

Key Words
Silicon cycle, phytoliths, pedogenesis, temperate forest

Introduction
Silicon (Si), the second mass abundant element of the crustal Earth (Wedepohl, 1995), plays a major role in global biogeochemical processes. The continental cycle of Si strongly impacts the oceanic biogeochemical cycle of Si, as land-ocean fluxes contributes to more than 80% of the input of dissolved Si (DSi) in the oceans (Tréguer *et al.*, 1995). Terrestrial plants largely contribute to the DSi pool since their annual biogenic silica (BSi) production ranges from 60 to 200 Tmol $year^{-1}$ (Conley, 2002), which rivals BSi production of diatoms in oceans (240 Tmol $year^{-1}$) (Tréguer *et al.*, 1995). Besides the primary crystalline silicates and the secondary clay minerals, soil also contains an amorphous silica (ASi) fraction having both pedogenic (Wada *et al.*, 1989) and biogenic (BSi) origins (Drees *et al.*, 1989). As the solubility of ASi is an order of magnitude higher than the one of the crystalline silicate minerals (Fraysse *et al.*, 2009), amount of ASi in soils could influence the release of DSi in soil solutions and the export to the hydrosphere. An accurate quantification of the ASi pool in soils is a mandatory step to better understand the Si mass-balance at watershed scale. ASi pool in forest soil is likely impacted by tree species, because Si uptake by vegetation and return of BSi to soil are tree species-dependent (Cornelis *et*

al., 2010). However, the influence of tree species on ASi pool has not been measured yet. There is a variety of methodology used for extracting ASi from soils (Sauer *et al.*, 2006). Among them, Saccone *et al.*, (2007) prove that alkaline methods are adequate to dissolve ASi fraction in soils. Here, we isolate the impact of tree species on the distribution of ASi since soil physical and chemical properties were identical between tree plots when the experimental site was set up. Then, our study aims to evaluate the relative impact of Si recycling by forest tree species on the ASi concentration in a temperate forest soil.

Methods

The experimental site is located at Breuil-Chenue (Nièvre-Morvan, France). Over the period 2001-2006, the mean annual rainfall is 1212 mm and the mean annual temperature is 9 °C. The acid brown soil is classified as an Alumnic Cambisol (IUSS, 2006) and is developed from granite very poor in major cations (0.5% MgO, 0.6% CaO and 4.4% K_2O). The native mixed forest (oak and European beech) was clear-cutted in 1976 and replaced by monospecific plots of Douglas fir, Black pine and European beech.

Phytoliths was extracted from leaves and needles through digestion at 120 °C in a concentrated HNO_3 (70 %) / H_2O_2 (30 %) mixture.

In this study, the alkaline solution (Na_2CO_3 0.1 mol l^{-1}, pH = 11.2) was applied to extract ASi in forest soil samples (alkali-extractable Si pool). The wet alkaline method is based on the fact that the solubility of ASi is strongly enhanced at pH above 9. Corrections for the simultaneous amorphous and crystallize dissolution of Si have been made using time course extractions (DeMaster, 1981; Saccone *et al.*, 2007). Here, approximately 30 mg of dried soil (< 2 mm) was mixed in 40 ml of alkaline solution and digested at 85 °C during 5 hours. One milliliter was removed from the extraction solution after 15, 60, 120, 180, 240 and 300 minutes and was neutralized with 9 ml of 0.022 mol l^{-1} HCl. DSi was determined by ICP-AES. Under the extraction conditions, we assume that (i) most ASi dissolved completely within the first 2 hours of the extraction and (ii) alumino-silicates released Si at a constant rate over the whole extraction time. Extracted SiO_2 (mg g^{-1}) was plotted versus time and ASi concentration was estimated extrapolating the linear part to zero time (intercept value on Y-axis) following the theoretical curve to correct for continuous crystalline silicates dissolution (DeMaster, 1981; Saccone *et al.*, 2007).

Results and Discussion

Figure 1 shows that the ASi content in the humus layer was affected by tree species. The mean content of alkali-extractable Si (mg SiO_2 g^{-1}) in humus layer significantly decreased in the sequence: Douglas fir (14.5±0.65) > European beech (11.8±0.30) > Black pine (5.4±0.31). Between 0 and 7.5 cm soil depth, the content of alkali-extractable Si was significantly higher under European beech than under Douglas fir and Black pine. At the other soil depth, there was no significantly difference between tree species. The ASi distribution with depth shows very similar trend under each tree species: a decrease of the ASi pool from the humus layer to 15 cm depth and a slight increase from 15 to 75 cm depth.

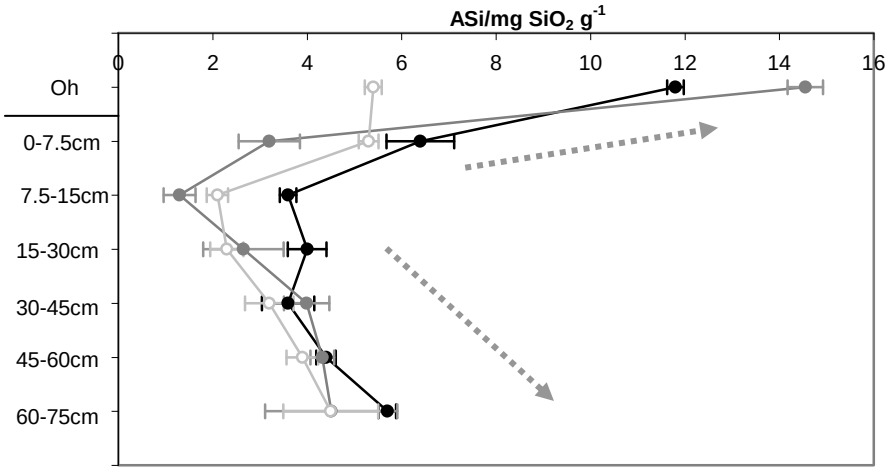

Figure 1. Mean alkali-extractable Si (estimation of ASi) concentration in humus (Oh) and soil layers, expressed as mg SiO_2 g^{-1} of dry matter.The ASi content is evaluated by wet alkaline dissolution (Na_2CO_3 0.1 mol l^{-1}) under European beech (black), Douglas fir (grey) and Black pine (white). The error bar (n = 3) represents the standard error.

In our sample, we assume that ASi pool includes biogenic and pedogenic opal as well as ASi sorption onto Fe oxides but not short-range ordered silicates such as allophane and imogolite because the acidic conditions in the humus layer (pH (H_2O) = 4 - 4.76) and the aqueous speciation of Al and Si.

In identical soil and climate conditions, Cornelis *et al.* (2010a) prove that the annual Si uptake is clearly dependent on tree species, decreasing in the sequence: Douglas fir (30.6±8.0 kg ha^{-1} yr^{-1}) > European beech (23.3±6.5 kg ha^{-1} yr^{-1}) > Black pine (2.3±0.9 kg ha^{-1} yr^{-1}). This study also reveals that, at least, 83% of the Si uptake is annually recycled on topsoil through litterfall. Thus, tree species impacts the ASi pool in organic horizons through various Si uptake and restitution on topsoil. The decrease of the ASi content between humus layer and 15 cm depth, may be due to the translocation and dissolution of phytoliths followed by root-uptake and/or leaching. Between 15 and 75 cm depth, the slight increase of the ASi content is probably due to the translocation-accumulation of stable phytoliths, precipitation of pedogenic opal and Si adsorption onto amorphous Fe oxides as revealed by acid ammonium oxalate extraction.

Conclusion

Thus, we demonstrate that tree species impacts the ASi stock in the humus layer through various Si recycling. The tree's root uptake influences the Si soil-solution equilibrium and subsequently dissolution of poorly crystalline and non crystalline inorganic soil components. Trees act both as a source (BSi restitution) and a sink (Si uptake) of dissolved Si in soil solution. In our case, the extraction of ASi from temperate forest soil samples in identical climate and soil conditions reveals that: (i) tree species impacts the BSi concentration in the humus layer through different Si recycling rates, and (ii) the alkali-extractable Si concentration in soil is influenced by the Si recycling but also by pedogenic processes such as Si adsorption onto amorphous Fe oxides. Consequently, considering the impact of tree species on the ASi fraction in humus layer, the increase of DSi leaching to the hydrosphere after deforestation (Conley *et al*., 2008) could be influenced by tree species. In our samples, the alkali-extractable Si pool mainly integrates biogenic opal (BSi) and Si adsorbed onto amorphous pedogenic Fe oxides. Consequently, the alkaline dissolution measure ASi fraction but also non-amorphous Si fraction such as 'plant-

available Si', Si adsorbed onto pedogenic oxides and Si included in short-range ordered aluminosilicates. Thus, the alkali-extractable Si pool has to be interpreted with caution depending on physico-chemical soil conditions.
In our temperate and granitic environment, it is not surprising that the small BSi pool, as compared to the large pool of crystalline silicates, does not seem to control the dissolved Si composition in forest floor leachates (Cornelis et al. 2010b)

References

Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. *Global Biogeochemical Cycles*, **16 (4)**, GB1121, doi:10.1029/2002GB001894.

Conley, D.J., Likens, G.E., Buso, D.C., Saccone, L., Bailey, S.W. & Johnson, C.E. 2008. Deforestation causes increased dissolved silicate losses in the Hubbard Brook Experimental Forest. *Global Change Biology*, **14**: 2548-2554.

Cornelis, J.-T., Ranger, J., Iserentant, A. & Delvaux, B. 2010a Tree species impact the terrestrial cycle of silicon through various uptakes. *Biogeochemistry* **97**: 231-245.

Cornelis JT, Delvaux B, Cardinal D, André L, Ranger J, Opfergelt S (2010b) Tracing the mechanisms controlling the release of dissolved silicon in forest soil solutions using Si isotopes and Ge/Si ratios. *Geochimica Et Cosmochimica Acta* **74**:3913-3924

DeMaster DJ (1981) The supply and accumulation of silica in the marine environments. *Geochimica et Cosmochimica Acta*, **45**, 1715–1732.

Drees LR, Wilding LP, Smeck NE, Sankayi AL (1989) Silica in soils: quartz and disordered silica polymorphs. In: *Minerals in Soil Environments* (eds J.B. Dixon & S.B. Weed), pp 913-974. Soil Science Society of America Book Series No. 1, Madison, WI.

Fraysse F, Pokrovsky OS, Schott J, Meunier JD (2009) Surface chemistry and reactivity of plant phytoliths in aqueous solutions. *Chemical Geology*, **258**, 197-206.

Sauer D, Saccone L, Conley DJ, Herrmann L, Sommer M (2006) Review of methodologies for extracting plant-available and amorphous Si from soils and aquatic sediments. *Biogeochemistry*, **80**, 89–108.

Saccone L, Conley DJ, Koning E, Sauer D, Sommer M, Kaczorek D, Blecker SW, Kelly EF (2007) Assessing the extraction and quantification of amorphous silica in soils of forest and grassland ecosystems. *European Journal of Soil Science*, **58**, 1446–1459.

Tréguer P, Nelson DM, Van Bennekom AJ, De Master DJ, Leynaert A, Quéguiner, B (1995) The silica balance in the world ocean: a reestimate. *Science*, **268**, 375-379

Wada K (1982) Allophane and imogolite. In: *Minerals in Soil Environments* (eds J.B. Dixon & S.B. Weed), pp. 1051-1087. Soil Science Society of America Book Series No. 1, Madison, WI.

Wedepohl KH (1995) The composition of the continental crust. *Geochimica et Cosmochimica Acta*, **59**, 1217-1232.