# Impact of tree species on the distribution of amorphous silica in an acid brown soil

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## Abstract

Biogenic silica (BSi) precipitates in leaves and needles of trees and contributes to the amorphous silica fraction (ASi) in soil through litterfall. In forest ecosystem, the ubiquitous and significant ASi pool could influence the Si mass-balance at watershed scale, which plays a major in the global biogeochemical processes. Thus, an accurate quantification of the ASi pool in forest soils is a mandatory step. Here, we examined the distribution of the ASi in an acid brown soil under various tree species (Douglas fir, Black pine and European beech) established in identical soil and climate conditions. We quantified the ASi concentration in soil with alkaline extraction (Na<sub>2</sub>CO<sub>3</sub> 0.1M). The mean content of ASi in humus layer significantly decreases in the sequence (mg ASi / g): Douglas fir (14.5) > European beech (11.8) > Black pine (5.4). Tree species impacts the ASi pool in the humus layer through different uptakes of  $H_4SiO_4^{0}$  and accumulation of BSi in leaves and needles. In mineral layers, pedogenic processes could hide tree species impact on ASi concentration, which decreases from the humus layer to 15 cm depth and then progressively increases from 15 to 75 cm depth under each three species. In soil, the distribution of the ASi content seems rather influenced by translocation-dissolution, pedogenic opal formation and ASi sorption onto Fe oxides. Our data imply that forest ecosystem type impacts the stock of BSi in a soil-tree system.

# 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<sup>-1</sup> (Conley 2002), which rivals BSi production of diatoms in oceans (240 Tmol year<sup>-1</sup>) (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<sub>2</sub>O). 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 form leaves and needles through digestion at 120 °C in a concentrated HNO<sub>3</sub> (70 %) /  $H_2O_2$  (30 %) mixture.

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In this study, the alkaline solution (Na<sub>2</sub>CO<sub>3</sub> 0.1 mol  $l^{-1}$ , pH = 11.2) was applied to extract ASi in forest soil samples. 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<sub>2</sub> (mg g<sup>-1</sup>) 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

Figure 1 shows that the ASi content in the humus layer was affected by tree species. The mean content of ASi (mg SiO<sub>2</sub> g<sup>-1</sup>) 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 ASi 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.





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.

#### Conclusion

In identical soil and climate conditions, Cornelis *et al.* (2010) prove that the annual Si uptake is clearly dependent on tree species, decreasing in the sequence: Douglas fir  $(30.6\pm8.0 \text{ kg ha}^{-1} \text{ yr}^{-1}) >$  European beech  $(23.3\pm6.5 \text{ kg ha}^{-1} \text{ yr}^{-1}) >$  Black pine  $(2.3\pm0.9 \text{ kg ha}^{-1} \text{ yr}^{-1})$ . 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 ASi sorption onto Fe oxides.

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. More than 30 years after plantation, the ASi concentration in soil is influenced by the Si recycling but also by pedogenic processes. In our temperate and granitic environment, the study of the relative contribution of small ASi pool and large crystalline silicates pool on the dissolved Si need more consideration.

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