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# Impact of agricultural practices on plant-available silicon

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## Abstract

Silicon (Si) is a beneficial nutrient for many plants, including major crop species. Yet, the impacts of agricultural practices on Si cycling have been hardly studied. We investigated the effects of long-term fertilizer (farmyard manure, NPK) and/or lime applications on concentrations of acetate-extractable Si ($Si_{acetate}$; i.e., potentially mobile and plant-available Si) in a Chernozem topsoil (Bad Lauchstädt, Germany). The $Si_{acetate}$ concentrations were between 122 and 292 mg Si kg$^{-1}$, and thus, larger than \`critical values\` considered to trigger Si limitation of plant growth. We found positive relationships between $Si_{acetate}$ concentrations and soil pH, which might be explained by pH-dependence of the phytolith solubility as well as of the sorption of Si to mineral surfaces. Our data suggest that differing agricultural practices affects Si fluxes and availability in soil by affecting the soil pH.

## Main text

Silicon has become widely recognised for being a crucial plant nutrient (Guntzer et al., 2012a). Important crop species, such as wheat, maize and rice, are among the so-called `Si accumulators`, i.e., plants that actively take up dissolved silicic acid (DSi) from soil solution (Ma and Yamaji, 2015). In plants, DSi precipitates forming so-called `phytoliths`, which are amorphous Si oxide bodies. Silicon supports the resistance of plants against a broad spectrum of stresses, including pests, diseases as well as abiotic stresses, such as salinity and toxic metals (Guntzer et al., 2012a).

The biogeochemical Si cycle in ecosystems is determined by in- and outputs (e.g., irrigation, drainage, percolation, plant removal) and internal transformation processes, including weathering of primary silicate minerals, formation of pedogenic secondary minerals, formation and recycling of phytoliths, and sorption of Si at mineral surfaces (Cornelis and Delvaux, 2016). Human cultivation of the landscape can cause profound alteration of the cycle. For instance, the study of Struyf et al. (2010) suggests that the transformation of forests into cultivated grassland and cropland in Europe decreased the export of Si from terrestrial ecosystems into aquatic systems due to the combined effect of altered weathering of geo-/pedogenic silicate minerals and altered recycling of phytoliths. In cropland, the Si cycle is thought to be strongly influenced by the large Si export with the harvest, which reduces the storage of relatively soluble phytoliths in topsoil (Vandevenne et al., 2012).

Most literature on Si cycling in agricultural systems has been focused on rice and sugarcane production (Haynes, 2014). This is due to their economic importance and because they are often grown on highly weathered (sub-) tropical soils low in plant-available Si. Much less research has been conducted in agroecosystems of temperate zones. Moreover, effects of common agricultural practices on Si cycling, such as application of chemical fertilizers (nitrogen, phosphorous, potassium; NPK) and liming have been hardly studied (Haynes, 2014). Here, we investigated the effects of long-term application of NPK fertilizers, lime and farmyard manure (FYM) on easily extractable and potentially plant-available Si in topsoils at a Haplic Chernozem site at Bad Lauchstädt (Sachsen-Anhalt, Germany).

The Static Fertilization Experiment at the study site was established in 1902, and represents one of the oldest long-term trials on impact of agricultural practices on ecosystems. Detailed descriptions of the site are provided in Körschens et al. (1998). Mean annual temperature and precipitation are 8.8 °C and 480 mm, respectively. The crop rotation originally included sugar beet, spring barley, potatoes and winter wheat; since 2015 sugar beet and potatoes were replaced by maize. The soil is a Haplic Chernozem formed into carbonates-containing loess. The loess is characterized by high silt contents; the major mineral is quartz. Illite is the dominant clay mineral in the topsoil, smaller quantities of kaolinite are also present; concentrations of dithionite-extractable iron (representing total pedogenic Fe oxides) in topsoil are about 40 g kg$^{-1}$ (Kleber et al., 2004). We focussed on twelve different field treatments, each applied to research plots of 10.0 m × 26.5 m = 265 m$^2$ size. The treatments include combinations of (i) three addition levels of farmyard manure (0, 20 Mg per ha since 1902, and 30 Mg per ha since 1906), (ii) two levels of NPK application (no application and varying amounts of NPK, depending on crop demand; Köppen and Eich, 1991), and (iii) two levels of lime addition (no liming and liming every fourth year since 1924).

No independent replicates of treatment plots were included when the experiment was established. We therefore divided individual plots into four subplots, and sampled one soil core (metal corer of 3.2 cm diameter; 0–30 cm soil depth) at random positions within the subplots as well as one core at the centre of the plots. The soil samples were then dried (40 °C) and sieved to <2mm for chemical analyses.

We extracted the soil samples using the acetate method as given in Sauer et al. (2006). The method extracts soluble and some of the adsorbed Si from soil ($Si_{acetate}$), i.e., Si that potentially is mobile and plant-available. Concentrations of $Si_{acetate}$ in topsoil are often positively related to the Si uptake by plants (e.g., Xu et al., 2001; Sauer et al., 2006). Briefly, 10 g of dry soil were extracted with 100 ml 0.18 M Na acetate, adjusted to pH 4, for 5 h at 40 °C. The extracts were filtered (PTFE filter; 0.45 µm) before Si measurements by inductively coupled plasma optical emission spectrometry (Ultima 2, Horiba Jobin-Yvon, Longjumeau, France). In addition, soil pH was measured potentiometrically in 0.01 M $CaCl_2$ solutions at a soil:solution ratio of 1:2.5.

The five replicated soil core samples per plot were used for statistical testing for effects of different treatments on soil properties. Moreover, we tested for correlation between pH and concentrations of $Si_{acetate}$. As data were not normally distributed (even after transformation), non-parametric statistical approaches were used, including Mann-Whitney Rank Sum tests and Spearman rank correlation. Differences were considered significant at the 0.05 probability level. Statistical analyses were conducted using SigmaPlot 11.0 (Systat Software GmbH, Erkrath, Germany).

Results showed that concentrations of $Si_{acetate}$ ranged between 122 and 292 mg Si $kg^{-1}$ soil for individual samples (Figure 1). An unambiguous interpretation of main effects of single factors (i.e., liming, NPK application, FYM manure addition) was not possible because they were not consistent for all factor combinations. Addition of lime in combination with NPK at constant FYM addition significantly increased $Si_{acetate}$ concentrations (Figure 1; see supplementary material for results of all Mann-Whitney tests). Without liming, NPK addition lowered $Si_{acetate}$ concentrations and only concomitant addition of substantial 30 t FYM again increased the Si concentrations (Figure 1, left panel). At limed plots, a comparable negative effect of NPK on the $Si_{acetate}$ concentrations at lower FYM additions was not distinctively apparent. The pH values of individual soil samples ranged between 6.2 and 7.5, and they were positively related to the concentrations of $Si_{acetate}$ (Figure 2).

The concentrations of $Si_{acetate}$ reported here are larger than `critical values` of 80 mg Si $kg^{-1}$ determined previously (Xu et al., 2001), suggesting wheat growth is not limited by Si availability at the site. They are in the range of concentrations reported in literature. For instance, in a previous study on topsoils of Southeast-Asian paddies, $Si_{acetate}$ concentrations ranged from 20 to 51 mg Si $kg^{-1}$ in Vietnam and from 141 to 322 mg Si $kg^{-1}$ in the Philippines (Klotzbücher et al., 2015). The differences between Vietnamese and Philippine soils were explained by differences in weathering status of the soils, i.e., differences in contents of weatherable silicate minerals, which potentially release plant-available Si into soil solutions. The concentrations reported here are more similar to those found for the less weathered Philippine soils developing on young volcanic parent material. These results were surprising, i.e., we expected lower concentrations of potentially mobile Si because weathering rates for most silicate minerals are low at circum-neutral pH values (e.g., Guntzer et al., 2012a; Cornelis and Delvaux, 2016), and, in line, previous work using X-ray diffraction analysis suggested that the mineral composition of the clay fraction in topsoils of non-fertilized plots hardly changed during the first ~100 years of the experiment (Kleber et al., 2004). We assume that a combination of two effects contributed to the surprisingly high $Si_{acetate}$ concentrations. First, mobilization of Si via weathering of silicate minerals might be enhanced in `hotspots` of the rhizosphere, where plant root activity acidifies soil solutions. Second, the solubility of phytoliths increases with pH (in the pH range relevant to soils) – a feature in which phytoliths differ from other important silicate minerals (e.g., Guntzer et al., 2012a) – hence, phytolith dissolution should be relatively high and a major determinant of $Si_{acetate}$ concentrations at the study site.

The pH-dependent differences in dissolution rates of phytoliths between treatments might be an explanation for the positive relationship between soil pH and $Si_{acetate}$ concentrations (Figure 2). Long-term FYM application likely enhanced phytolith input to soil but did not translate into clear effects on $Si_{acetate}$ concentrations (Figure 1). We thus assume that pH-dependent differences in phytolith solubility are more important than the quantities of FYM-derived phytolith input in determining potentially plant-availabe Si in topsoils. Future research should attempt to relate inputs and stocks of phytoliths to dynamics of Si in soil solution in order to test this assumption.

An additional reason explaining the relationship between soil pH and $Si_{acetate}$ concentrations may be that differing pH values affect mineral surfaces with variable charge sites, and thus, the sorption of silicic acid to these surfaces. Previous work suggested that Si adsorption onto iron oxides and bulk soil materials increases with pH and has a maximum at pH 9–10 (Christl et al., 2012; Haynes and Zhou, 2018). Hence, pH seems a major determinant of $Si_{acetate}$ concentrations in topsoil as it controls phytolith dissolution rates as well as the capacity of minerals to bind and retain Si.

Impacts of fertilizers and liming on Si cycling in soil have hardly been addressed so far. Guntzer et al. (2012b) found increasing Si concentrations in winter wheat due to lime addition at a Luvisol site (Broadbalk, Rothamsted). These data from another agricultural site are well in line with our findings on how pH changes affect Si mobility in topsoils. Our work underlines the prominent role of soil pH, as it suggests that these relationships occur across different agricultural sites and practices (despite of the diverse impact of the practices on soil properties). In order to improve the mechanistic understanding about how agricultural practices affect Si cycling, more research is necessary on the relative importance of factors causing the dependence of plant-available Si on soil pH, which may include pH-dependent phytolith dissolution and sorption processes.

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**Figure 1.** Concentrations of acetate-extractable Si ($Si_{acetate}$) in topsoil as a function of differential agricultural treatment (with/without liming, three levels of FYM addition and with/without NPK addition).

**Figure 2.** Relationship between pH and concentrations of acetate-extractable Si ($Si_{acetate}$) in the topsoils (data for all individual samples; 12 treatments with 5 spatial replicates per treatment; the grey line represents a trend line).

# Supplementary material

# Statistical evaluation of agricultural treatment effects on acetate-extractable Si in topsoil (Wilcoxon-Mann-Whitney-Test)

**Appendix 1.1**: Effects of liming. Codes for treatment identification are as follows: First number = liming (1 = no, 2 = yes); Second number = NPK (0 = no; 1 = yes); third number = amount of FYM application (0, 200, and 300 t ha$^{-1}$). Significant differences are depicted in bold numbers.

| Treatments | p |
|---|---|
| 1-0-0 vs. 2-0-0 | 0.310 |
| 1-1-0 vs. 2-1-0 | **0.008** |
| 1-0-200 vs. 2-0-200 | 0.548 |
| 1-1-200 vs. 2-1-200 | **0.008** |
| 1-0-300 vs. 2-1-300 | 0.151 |
| 1-1-300 vs. 2-1-300 | **0.008** |

**Appendix 1.2**: Effects of NPK. Codes for treatment identification are as follows: First number = liming (1 = no, 2 = yes); Second number = NPK (0 = no; 1 = yes); third number = amount of FYM application (0, 200, and 300 t ha$^{-1}$). Significant differences are depicted in bold numbers.

| Treatments | p |
|---|---|
| 1-0-0 vs. 1-1-0 | 0.032 |
| 1-0-200 vs. 1-1-200 | 0.222 |
| 1-0-300 vs. 1-1-300 | **0.008** |
| 2-0-0 vs. 2-1-0 | **0.008** |
| 2-0-200 vs. 2-1-200 | **0.016** |
| 2-0-300 vs. 2-1-300 | 1.000 |

**Appendix 1.3**: Effects of FYM application. Codes for treatment identification are as follows: First number = liming (1 = no, 2 = yes); Second number = NPK (0 = no; 1 = yes); third number = amount of FYM application (0, 200, and 300 t ha$^{-1}$). Significant differences are depicted in bold numbers.

| Treatments | p |
|---|---|
| 2-0-0 vs. 2-0-200 | 0.222 |
| 2-0-0 vs. 2-0-300 | 0.690 |
| 2-0-200 vs. 2-0-300 | 0.095 |
| 2-1-0 vs. 2-1-200 | 0.690 |
| 2-1-0 vs. 2-1-300 | **0.008** |
| 2-1-200 vs. 2-1-300 | **0.016** |

| | |
|---|---|
| 1-0-0 vs. 1-0-200 | 0.421 |
| 1-0-0 vs. 1-0-300 | **0.008** |
| 1-0-200 vs. 1-0-300 | 0.151 |
| 1-1-0 vs. 1-1-200 | 0.151 |
| 1-1-0 vs. 1-1-300 | **0.008** |
| 1-1-200 vs. 1-1-300 | 0.690 |