Silicon Availability from Chemically Diverse Fertilizers and Secondary Raw Materials

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ABSTRACT: Crops may require Si fertilization to sustain yields. Potential Si fertilizers include industrial byproducts (e.g., steel slags), mined minerals (CaSiO₃), fused Ca-Mg-phosphates, biochar, ash, diatomaceous earth, and municipal sewage sludge. To date, no extraction method was shown to accurately predict plant availability of Si from such chemically diverse Si fertilizers. We tested a wide range of products in greenhouse experiments and related the plant Si content to Si extraction in Na₂CO₃-NH₄NO₃, 0.5 mol L⁻¹ HCl, and Resin extraction. In addition, we tested a novel sink extraction approach for Si(OH)₄ that utilizes a dialysis membrane filled with ferrihydrite (“Iron Bag”). Wheat straw biochars and ash exhibited equivalent or marginally higher Si solubility and availability compared to wheat straw. Thermo-chemically treated municipal sewage sludge, as well as diatomaceous earth, did not release substantial amounts of Si. The Resin and the Iron Bag extraction methods gave the best results to predict plant availability of Si. These methods better reproduce the conditions of fertilizer dissolution in soil and around the root by (1) buffering the pH close to neutral and (2) extracting the dissolved Si(OH)₄ with ferrihydrite (Iron Bag method) for maximum quantitative extraction.

INTRODUCTION

Although not considered an essential plant nutrient, Si has positive effects on plant health, particularly resistance to biotic and abiotic stress.¹ Silicon deficiency is of concern in tropical regions where Si accumulators such as rice or sugar cane are grown, and soil plant-available Si (PAS) may be low in highly weathered soils.² In temperate regions, too, some of the major crops are Si accumulators (mainly cereals and grasses but also soybean, sugar beet, and tomato),³ and there are concerns about negative impacts of intensive agricultural practices on PAS.³,⁴ Recently, we identified a substantial proportion of Austrian agricultural topsoils to be very low in PAS, indicating that in addition, part of the temperate zone soils may require Si management and fertilization (for our own unpublished results). Growing interest in the role of Si in agriculture requires improved PAS thresholds for Si application⁵ and the characterization of PAS in potential Si fertilizers.⁶−⁸

Steel slags from blast oven furnaces (BOF slag) or from Linz–Donawitz converters (LD-slag) are major potential sources for Si fertilizer production and, therefore, have received attention in fertilizer testing.⁶,⁷,⁹,¹⁰ Phytoliths, i.e. plant-borne amorphous SiO₂, are an important Si pool in the biogeochemical Si cycle, and their importance for PAS increases with soil weathering stage,¹¹ so that the recycling of Si-rich crop residues such as straw can be crucial to sustain soil fertility.¹¹ Plant biomass can be directly recycled to the field with crop residues or after straw and stubble incineration, which remains a common practice in several parts of the world (for example, in Asia).¹² However, biomass often undergoes a cascade of agro-industrial uses before returning to the field in the form of manure, biogas slurry, compost, ash, etc. Studies have shown that straw incineration at low temperature (up to 400–500 °C) could increase straw Si solubility,¹³ but that at higher temperatures (600–900 °C), Si solubility strongly decreases due to crystallization.¹³−¹⁵ Pyrolysis is an alternative to incineration and is increasingly seen as a value adding process. Biochar from (phytolith-rich) Miscanthus was found to be a good source of plant-available Si.¹⁶ Diatomaceous earth (DE), which contains diatom...
frustules (cell walls) consisting of amorphous SiO₂, is another emerging fertilizer source (e.g., AgriPower Australia Ltd.). Furthermore, municipal sewage sludge (MSS) may also contain significant amounts of Si and has been suggested as a potential source for recycling biological Si. New thermochemical treatments of MSS such as the Ash-Dec process⁹ aim at increasing P bioavailability but their effect on Si mobilization has not yet been studied.

Common extraction techniques for Si fertilizers are based on quasi-equilibrium in water, neutral, acidic, or alkaline aqueous solutions or on induced solubilization with organic ligands such as citrate. A 5-day extraction with Na₂CO₃ and NH₄NO₃, and a pH-buffered H₂O₂ extraction protocol were among the best predictors (R² between 0.6 and 0.7) of Si availability to plants, being clearly superior to, e.g., 0.5 mol L⁻¹ HCl, 0.5 mol L⁻¹ acetate, and 5% citric acid.⁵,¹⁹ The 5-day Na₂CO₃-NH₄NO₃ extraction was validated in a single-laboratory study for testing solid Si fertilizers with Si concentrations up to 84 mg g⁻¹.¹⁰ However, testing different industrial byproducts (mainly steel slags), Haynes et al. concluded that no single fertilizer extraction technique could predict Si availability from Si fertilizers. Moreover, Zellner et al. extracted a wide range of products (including slags and biochars) with the 5-day Na₂CO₃-NH₄NO₃ method and obtained only a poor correlation with plant uptake (R² = 0.46). Hence, none of the available methods satisfactorily predicts Si bioavailability from the increasing range of potential Si sources, i.e., not only Ca- and Mg-silicates but also products based on plant Si (phytoliths), or DE as an emerging Si fertilizer.

Duboc et al. showed that an ion-sink technique based on a dialysis membrane tube filled with ferricydrate (referred to as “Iron Bag”; IB) was very well suited to assess the P availability from very contrasting recycling fertilizers. In brief, the method is based on a zero-sink created through adsorption of phosphate on the ferricydrate. After a given extraction time (a few days to weeks), the ferricydrate is retrieved, dissolved with concentrated H₂SO₄ and analyzed for P. Silicic acid, (a few days to weeks), the ferricydrate is retrieved, dissolved and rinsed with type I water after each bath.

For all analyses (fertilizer, soil, and plant extractions or digestions), we used laboratory water type I (18 MΩ cm⁻¹) and plastic vessels that were either new or washed successively in a 5% HNO₃, and in a 0.1 mol L⁻¹ NaOH bath for ≥5 h each and rinsed with type I water after each bath.

Characteristics of Fertilizers and Soil. Sample Description. Tested products are listed in detail in Table S1. They included the following: (1) municipal sewage sludge (MSS) and ash (MSSA) and their respective conversion products (AshDec-Na, pyrolysis, and hydrothermal treatments), (2) diatomaceous earth (DE), (3) one untreated LD slag and four LD slags amended with MSSA in their slag stage as phosphorus source, (4) (4) wheat straw with its respective biochars and ash (Str, Str-BC, and Str-Ash), (5) a commercial, fused Ca—Mg—P fertilizer (ThermoPhos), and (6) several reference materials (sodium metasilicate, Na₂SiO₃; SiO₂; fumed SiO₂ and calcium metasilicate, CaSiO₃). Additionally, mixed samples were produced from these individual substances to obtain fertilizer materials with intermediate Si solubility so as to fill the gap in the regression obtained with plant uptake in the first pot experiment, which consisted of two clusters (see EXP 1 with Secale cereale in Figure 4). Mixing ratio were chosen on the basis of the known solubilities of the different components with the Iron Bag extraction method (see the method descriptions below) and was therefore primarily designed to fill the gap in the Iron Bag regression.

The total Si in the materials (except straw) was determined by X-ray fluorescence spectrometry (XRFs), which was carried out on fused beads (precalcined sample powder, 1:10 with LiTB plus LiMB (66:34) flux) using a sequential XRF spectrometer PANalytical PW2404. Sample preparation by fusion with a flux enables the analysis of wide range element concentrations and improved mathematical corrections of the sample matrices’ influences, thus it was the preferred procedure in this case. See the Supporting Information for more details. The total Si in straw was determined using a molybdate blue colorimetric assay after oven-induced digestion (both methods are described below).

Sample Preparation. All fertilizers were milled to <200 μm in a vibratory ball mill (Retsch MM 200) using stainless steel grinding equipment. Individual milling steps were limited to a maximum of 3 min. After each milling step, the sample was sieved, and the fraction retained in the sieve was milled again. To not discard any fraction, this process was repeated until all material passed through the 200 μm sieve.

Soil Selection. Given raising interest in plant Si nutrition in temperate regions we used a soil from Sigmundsherberg, Lower Austria, a carbonate-free soil with a pH in H₂O (1:2.5, w/v; <2 mm fraction) of 6.05 ± 0.17, and pH of a saturated soil paste of 6.96 ± 0.41 (<4 mm fraction as used in pot experiments). CaCl₂-extractable Si²⁵ was 13.1 ± 0.8 mg Si kg⁻¹. The soil was selected on the basis of a screening of 270 agricultural topsoils in Austria because its CaCl₂-extractable Si concentration falls within the lower 10% of the concentration range covered and is also clearly below the band of upper limits of Si deficiency (20–45 mg Si kg⁻¹) reported in the literature.²⁵–²⁸

Pot Experiments. The two pot experiments were conducted in a greenhouse to estimate plant availability of Si from the fertilizer materials. Experiment 1 (EXP 1) was conducted with S. cereale L. (var. “Amilo”) with four replicates per treatment and experiment 2 (EXP 2) with Lolium perenne (var. “Grasslands NUI”) in triplicate. S. cereale, a common crop in temperate regions, was chosen for EXP 1 because it is a common arable crop belonging to the Poaceae family with a known accumulation potential for Si.²⁶ L. perenne, a wide-spread grassland species and animal feed, was chosen for EXP 2 due to its even larger Si concentration in shoots according to a dose response trial that was run in parallel to EXP 1 (see below and Figure S1). Using two different crop species is deemed to increase the validity and relevance of our
conclusions. A total of 1 kg of soil was added to each pot, and the finely ground fertilizer was thoroughly mixed at a rate of 75 and 150 mg Si (kg dry soil)$^{-1}$ in EXP 1 and EXP 2, respectively. The first rate was chosen to cover the range of fertilization of macronutrients, which show similar shoot concentrations as Si in graminaceous species. We increased the Si addition rate in EXP 2 based on a dose–response trial run in parallel to EXP 1, showing a linear increase of Si uptake by both species between 0 to 160 mg Si (kg dry soil)$^{-1}$ in EXP 1 and EXP 2, respectively. The same CAS no. (9002-29-3) as Amberlite IRC-50, which was used by Kato and Owa.9

**Si Solubility in the Fertilizer Materials.** For all extraction procedures, samples were weighted directly into the extraction vial on an analytical scale with a precision of ±0.1 mg. After extraction, all samples (except the Iron Bag method) were filtered through Munktell 14/N folded filter paper and analyzed for their Si concentration using a molybdate blue colorimetric assay (see below).

Fertilizer extractions were replicated 3–9 times to better assess their reproducibility and precision. Some replications were done in different batches with several days to months of interval and different operators.

**Quasi-Equilibrium Si-Extraction Methods from Fertilizers.** We performed five different fertilizer extractions. The benchmarks were H$_2$O with Amberlite GC50 (termed “Resin”) and the 5-day extraction with Na$_2$CO$_3$–NH$_4$NO$_3$ (“5-day”) because both were found to better predict Si plant availability than other methods in recent studies. We also extracted with 0.5 mol L$^{-1}$ NH$_4$F was added, and the solution was brought to 50 mL with type I water.

### Table 1. Characteristics of the Quasi-Equilibrium Fertilizer Extractions

<table>
<thead>
<tr>
<th>Extraction name</th>
<th>Solution(s)</th>
<th>Sample weight (mg)</th>
<th>Extraction volume and [vial size]</th>
<th>Extraction time and speed</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>0.2 mol L$^{-1}$ NaOH</td>
<td>75</td>
<td>30 mL [50 mL]</td>
<td>120 h, 5 rpm overhead</td>
<td>Georgiadis et al.$^3$</td>
</tr>
<tr>
<td>HCl</td>
<td>0.5 mol L$^{-1}$ HCl</td>
<td>100</td>
<td>15 mL [20 mL]</td>
<td>1 h, 20 rpm overhead</td>
<td>Haynes et al.$^{7}$</td>
</tr>
<tr>
<td>5-day</td>
<td>0.094 mol L$^{-1}$ Na$_2$CO$_3$ plus 0.2 mol L$^{-1}$ NH$_4$NO$_3$ (1:1)</td>
<td>70</td>
<td>35 mL plus 35 mL [100 mL]</td>
<td>1 h, 20 rpm overhead plus 5 days of resting</td>
<td>Sebastian et al.$^{10}$</td>
</tr>
<tr>
<td>Resin</td>
<td>H$_2$O plus 100 mg Amberlite CG50$^9$</td>
<td>40</td>
<td>80 mL [100 mL]</td>
<td>96 h, 7 rpm overhead</td>
<td>Kato and Owa.$^9$</td>
</tr>
<tr>
<td>MOPS</td>
<td>30 mmol L$^{-1}$ 3-morpholinopropane-1-sulfonic acid, pH 7</td>
<td>40</td>
<td>80 mL [100 mL]</td>
<td>96 h, 7 rpm overhead</td>
<td></td>
</tr>
</tbody>
</table>

**The same CAS no. (9002-29-3) as Amberlite IRC-50, which was used by Kato and Owa.**

Depletion-Induced Si Solubilization from Fertilizers (Iron Bag Method). We used a sink method that employs iron oxide slurry-filled dialysis membranes for measuring water-soluble fertilizer Si quantitatively. It was initially developed by Freese et al.$^{33}$ for soil Si extraction and adopted successfully by Duboc et al.$^{20}$ for quantitatively extracting P from a range of P fertilizers. Briefly, an iron bag consists of ca. 28 cm long visking dialysis tubing (12 000–14 000 Da MWCO; ø, 15.9 mm; width when flat, 25 mm) filled with 20 mL of a ferricydride suspension (ca. 6.9 g Fe L$^{-1}$). The iron bags are placed in a fertilizer suspension and are gently agitated during the extraction period. The working principle of IB extraction is that Si is bound on the ferricydride contained in the membrane bag, thereby lowering the solution Si concentration, which, in turn, promotes the desorption and dissolution of fertilizer Si. Further details about Iron Bag preparation are described in Duboc et al.$^{20}$

We evaluated the performance of the Iron Bag technique using different approaches, including Si sorption experiments.
from solutions containing varied concentrations of Si in the absence and presence of P and by comparison of a 7-day one-step IB extraction with the cumulative amount of Si obtained in 3 subsequent steps after 42 days. The methods and results of the evaluation experiments are shown in the Supporting Information, indicating that the method is not limited by the capacity of the iron bags.

The amount of fertilizer weighed into 250 mL containers varied, according to their Si content and expected solubility, between 20 mg (e.g., SiO2 Fumed) to 120 mg (low Si content, straw) but was 30 mg in most cases. Then, 150 mL of a 30 mmol L\(^{-1}\) MOPS buffer, adjusted to the pH of a saturated paste of our test soil (pH = 7), were added. One iron bag was added per container, and the containers were placed on an overhead shaker and were shaken at 5 rpm.

The extraction proceeded for 6 weeks, during which the iron bags were removed and replaced once (after 15 days) or twice (after 7 and 21 days) before final sampling 42 days after the start of the extraction. A single replacement after 15 days was sufficient in most cases to reach maximal Si extraction except for fumed SiO\(_2\). Particles adhering to the surface of the membrane were washed back into the bottle with type I water, and care was taken to avoid contamination of the ferrihydrite sample by cleaning the membrane with tissue paper before opening it. After opening, the ferrihydrite slurry was transferred into 100 mL vials, and the membrane was further washed with type I water to collect all the ferrihydrite. A total of 1 mL of 96% H\(_2\)SO\(_4\) was added to dissolve the ferrihydrite, and afterward, the solution was diluted to 0.25 mol L\(^{-1}\) H\(_2\)SO\(_4\). Samples were analyzed for their Si concentration using a molybdate blue colorimetric assay (see below).

**Si Availability in Fertilized Soil.** We expected to obtain the closest relation of plant Si uptake and fertilizer Si solubility by incubating the fertilizer material with the soil used in the plant uptake experiment, as it is the fertilizer–soil interaction that determines Si availability. Although this assay is impossible to do in fertilizer testing procedures, as the soil to be fertilized is unknown, we included it as a benchmark for our bioavailability study.

A total of 100 grams of 4 mm sieved, air-dried soil was weighed into 250 mL plastic vessels (a single vessel for each fertilizer). Fertilizer was added to 150 mg Si (kg dry soil\(^{-1}\)) (as in EXP 2) and mixed homogeneously with the soil. Type I water was added to reach 70% of WHC and shaken again for homogenization. Then, the vessels were covered with parafilm and incubated at 25°C for 8 days. After the incubation, the soil was oven-dried for 48 h at 50°C and sieved to <2 mm. Si availability in the soil samples was determined in 0.01 mol L\(^{-1}\) CaCl\(_2\) extracts:25 3 g of soil was mixed with 30 mL of solution and placed on an overhead shaker at 5 rpm for 18 h (instead of 16 h in the published method). After filtering, the extracts were analyzed for their Si concentration using a molybdate blue colorimetric assay (see below).

**Colorimetric Measurement of Si (Molybdate Blue).** The staining procedure was performed with reagent solutions (acidified molybdate, tartaric acid, and reducing agent) prepared according to Morrison and Wilson34 and Webber and Wilson.35 Timing of the reactions was according to Morrison and Wilson.34 More details about dilutions and volumes of reactants are given in Table S2.

**Data Evaluation.** Data evaluation and figures were done with the software R, version 3.5.136 following data entry and preparation on spreadsheet. Results of fertilizer extraction are given as mean plus or minus \(u\), where \(u\) represents the propagated uncertainty, which includes (1) an analytical uncertainty of 3% and (2) the repeatability and reproducibility uncertainty of 3%.

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**Figure 1.** Biomass and Si concentration (mean plus standard deviation, SD) in shoots of Secale cereale (EXP 1, \(n = 4\)) and Lolium perenne (EXP 2, \(n = 3\)). Different letters above bars indicate significantly different groups (Tukey HSD, \(\alpha = 0.05\)).
Figure 2. Silicon extracted from fertilizer by the five extraction methods in percent of total Si. Data plotted as mean plus $\mu$ ($n = 3−9$ measurements except Iron Bag for AshDec-Na and SiO$_2$: $n = 1$ and 2, respectively). Values above bars give the percentage of total Si extracted. Light-gray bars (AshDec-Na, DE-2, and Stz) are products that were not used in the pot experiments. To ease reading of the multi-panel figure, the first two characters of fertilizer names are printed below each panel.
assessed through replicated extractions. Results of plant experiments are expressed as mean plus or minus the standard deviation (SD).

When multiple groups were compared, the analysis of variance was performed from summary data, i.e. mean, standard deviation and sample size with the function aovSufficient (package HH). A Tukey HSD post hoc test at $\alpha = 0.05$ was performed with the function TukeyHSD, while letters for significant groups were produced with the function multcompLetters (package multcompView).

Linear fitting for plant shoot Si content versus Si extracted from fertilizer was done with the function lm. The control receiving no Si was considered as a sample in all scatter plots and linear fits and considered equivalent to applying a fertilizer without any extractable Si. Root mean squared deviation (RMSD) was calculated as:

$$\text{RMSD} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n}}$$

where $y_i$ and $\hat{y}_i$ are the observed and fitted shoot Si content, respectively.

**RESULTS AND DISCUSSION**

**Plant Shoot Biomass and Si Concentration.** We observed considerable, significant differences in plant Si concentration between fertilizers (Figure 1), whereas plant shoot biomass (7.04 and 5.56 grams per pot in EXP 1 and EXP 2, respectively) was not significantly affected by Si fertilization treatment. Overall, plant Si concentration in treatments fertilized with products DE-1, MSSA, SiO2, and fumed SiO2 as well as some mixtures thereof (Mix-1B and Mix-3B) did not differ from the control. In contrast, treatments LD-1 to LD-5, Na2SiO3, Str-Ash, Str-BC 700, ThermoP, and CaSiO3 resulted in the highest plant Si contents. Lack of fertilizer effect on plant biomass either means (1) that no significant stress occurred, which could have been alleviated by improved Si nutrition or (2) that Si supply from the soil was adequate without fertilization despite the relatively low PAS content (13.1 mg Si kg$^{-1}$ in CaCl$_2$). Tissue Si concentration ranged from 1.97 to 3.52 mg Si g$^{-1}$ in S. cereale and from 3.51 to 6.12 mg Si g$^{-1}$ in L. perenne. This is roughly comparable with published values for those species.

**Comparison of Si Extractions.** Fertilizer Si Extraction by Quasi-Equilibrium and Sink Methods. Overall, the IB method extracted more Si from most samples compared with other extractions, often approaching 100% of total Si (Figure 2). Although extraction time was longer for IB than for the other extraction methods, Figure S3 shows that on average, close to 90% of the cumulated IB-extractable Si was already extracted after 7 days, indicating a stronger sink than provided by the 5-day, Resin, and MOPS methods, respectively. This result is similar to the results for P extracted by IBs in Duboc et al., i.e. that the major proportion of “water-insoluble” compounds readily solubilized when the dissolved species were continuously removed from the solution by the strong sink. Among others, the case of SiO2 fumed (13.9 versus 82% of total Si extracted in MOPS and IB, respectively) is exemplary of the specific effect of the ferrihydrite sink, with pH being equal in both extractions.

As expected, the NaOH and HCl extractions showed a clearly opposing extraction behavior (Figure 2): most Ca–Mg silicates (LD samples, and, to a lesser extent, CaSiO3 and ThermoP) were soluble in HCl, but not in NaOH, while the contrary was observed for samples containing amorphous SiO2, such as Str-BC 400 and 700, and the SiO2 samples. The DE samples were expected to be highly soluble in the NaOH extract, but this was not confirmed. The Na2SiO3 sample was 100% soluble in all extracts except HCl (ca. 50%).

The results of Resin and MOPS extractions were very similar except for SiO2 fumed, Str, and Str-derived samples. These extractions had identical solid-to-liquid ratios and extraction periods, while the pH was slightly higher in MOPS than in Resin (7 versus 6 to 6.5 depending on the fertilizer). This suggests that the pH of the extraction solution is the major parameter controlling the Si dissolution in these extracts. Therefore, Amberlite mainly controls Si extraction by buffering the pH, while cation complexation and associated co-dissolution of Si does not contribute strongly to dissolution.

The HCl extraction was the least reproducible extraction (see large error bars in Figure 2); this could be due to the short
Silicon Extraction from Fertilized Soil. Silicon extracted from soil by the CaCl₂ extraction ranged from 14.6 to 57.5 mg Si kg⁻¹ (Figure 3). Given that 20–45 mg Si kg⁻¹ has been reported as upper limit of Si deficiency, albeit with most studies having been conducted on rice and sugar cane, the majority of fertilizers (exceptions were AshDec-Na, DE-1 and -2, MSSA, SiO₂, and SiO₂ fumed) raised the PAS level to >20 mg Si kg⁻¹ (Figure 3). The rate of Si addition for the CaCl₂ extraction experiment was 150 mg Si kg⁻¹, as used in EXP 2.

Suitability of Extractions to Predict Fertilizer PAS. When plant Si content was plotted against the proportion of fertilizer Si extracted by the different methods (Figure 4) the IB, Resin and MOPS extraction methods stand out as prediction tools for fertilizer PAS: with RMSD between 1.4 and 2.3 and R² between 0.73 and 0.90, these methods provide better predictions of fertilizer Si availability than the other methods (RMSD between 3.1 and 4.5 and R² between 0.04 and 0.52). As expected, the best fit was obtained by the CaCl₂ extraction of fertilized soil (Figure 4, gray panel) as it samples Si according to its dissolution behavior in the experimental soil without modifying pH and has been established as a reliable indicator for soil PAS for rice and sugar cane in studies involving various fertilizers’ and soils’ extraction time (1 h), which may not allow for equilibrium to be reached.

pH strongly affects fertilizer dissolution (see the HCl versus NaOH extractions in Figure 2), and it is expected that maintaining the pH of the extraction solution close to that of a soil (roughly between 5.5 and 8 in most agricultural soils) would result in a better estimate of fertilizer Si plant availability. With the Resin method, Kato and Owa emphasized pH buffering as a major reason for the better correlation of this extraction method with plant Si uptake compared with unbuffered (H₂O) or strongly acidic (HCl) extractions. However, they also mentioned that cation adsorption by Amberlite might enhance Si solubilization through cation depletion in the extraction solution; indeed, in most soils, similar processes would occur, with cations tending to be adsorbed onto exchange sites. As mentioned above, our results for Resin were similar to those of MOPS (Figure 2) in which only a pH buffer was added, suggesting that cation binding is not an important process in the Resin extraction.

Plant Available Si in Major Product Categories. Mineral Si Fertilizers and LD Slags. By-products of the steel industry are often investigated for PAS because they have long been known as potential Si-fertilizers. Our data confirm the high Si solubility (soil incubation in Figure 3 and IB extraction in Figure 2) as well as plant availability (Figure 1) from LD slags, which is close to 100% according to IB extraction. Similarly high IB extractability (and plant availability) was obtained for the commercial Si fertilizer ThermOp and the reference CaSiO₃. Results for these two materials also demonstrate the poor performance of the 5-day and HCl extractions, according to which these products would be classified as low PAS fertilizers (Figure 2).

Straw, Biochar, and Ash. According to the IB extraction (Figure 2), the soil incubation (Figure 3), and the plant experiment, (Figure 1), the proportion of PAS in straw biochars and straw ash was equivalent. Iron Bag extractability of Si (Figure 2) was 80–90% of total Si in biochars and ash (Str-BC 400, Str-BC 700, and Str-Ash) and 70% in Str. Xiao et al. reported a marked increase in Si solubility (sum of 28 successive CaCl₂ extractions) in rice straw biochars produced at intermediate temperatures (350 and 500 °C) as compared to rice straw, while at higher temperatures (pyrolysis at 700 °C and ash from combustion at 900 °C), Si solubilities...
decreased markedly. However, their results were presented as soluble Si concentration (mg Si g⁻¹) without correcting for the increasing total Si concentration in the biochar and combustion products. As shown in Table S3, the soluble Si fraction either remained unchanged or steadily decreased with increasing treatment temperature. The soluble Si fraction from biochars (28–57% of total Si) was also lower than with IB in our study.

The high Si solubility from Str-Ash in our study is in contradiction with previous studies in which high combustion temperatures (600–900 °C) strongly reduced Si solubility. The main difference is that we combusted the straw for only 15 min (instead of 3–6 h in the other studies), which was likely too short for Si crystallization to occur. We chose a shorter combustion time to obtain results that are more relevant to what would happen during field incineration of crop residues, in which temperature is expected to drop soon after the combustion is finished. Our data suggest that incineration in the field may not cause a major decrease in straw Si solubility.

**Diatomaceous Earth.** Diatomaceous earth has not been studied extensively as a Si fertilizer, and the available data show rather contrasting results. Diatomaceous earth was found to increase soil solution Si on the short-term (only at 30 days but not at other sampling times) in an alkaline and an acidic soil and to increase plant Si uptake and yield, although the effect was often dependent on soil pH and texture. In another study, Seyffert and Ferndorf did not measure an increase of Si after addition of DE, neither in soil pore solution nor in the crop biomass. Moreover, Sandhya et al. could not establish the presence of an amorphous Si fraction (which would originate from diatom frustules) in the commercial DE used in their study, and they attributed the better growth and Si uptake in DE-amended treatments to increased water retention. In an isotope dilution study, Riottes et al. found only a marginal contribution of DE fertilizer to the Si uptake of rice.

In the present study, we did not include a commercial DE fertilizer. DE-1 and DE-2 were commercialized as hygiene products for animal husbandry and household (e.g., pest control). However, considering the inconsistent results with commercial fertilizer products in literature, the very low solubility of DE in all but the strongly alkaline NaOH extraction (Figure 2), and the absence of an effect on soil PAS (Figure 3) is not surprising in our study. The solubility in the NaOH extraction solution indicates the presence of an amorphous fraction, but the products may mainly consist of other silicates, as in the case of Sandhya et al. Given the sparse data, DE fertilizers should be further studied in the future to better understand the reasons for presence, or absence, of effects on soil PAS and plant yield.

**Municipal Sewage Sludge.** All MSS-based samples exhibited only marginal release of Si (Figure 1). Given that most biological Si (phytoliths) is concentrated in non-edible plant parts, biogenic Si fractions in municipal wastewater can be expected to be low. Moreover, because they are quite soluble, phytoliths would tend to dissolve in wastewater.

Part of the dissolved Si (of geogenic and biogenic origin) should get adsorbed and immobilized on Fe-oxihydroxides during P removal in the wastewater treatment plant. The fact that the NaOH extraction of MSSA solubilized 20% of total Si (Figure 2) may indicate that some Si is adsorbed on Fe-oxides in this sample. The AshDec process (thermo chemical treatment of MSS or MSSA under reducing conditions with addition of Na₂SO₄) did not mobilize Si as it does for P (Figure 2). Similarly, only minor amounts of Si (0.26 to 1.07 mg Si g⁻¹) were extracted by IB from a MSS and its pyrolysis and hydrothermal conversion products (samples MSS, MSS-BC 500, MSS-BC 700, MSS-HC; see Table S4). Although total Si was not determined for these products, IB-extractable Si is so low that no fertilizer value can be expected. Our results also answer the question raised by Vandevenne et al. as to whether MSS could represent a substantial or relevant pool of biological Si for recycling.

**Implications for Si Fertilizer Testing, Fertilization, and Agro-Municipal Si Cycling.** In terms of testing fertilizer PAS, we conclude that where a wide range of Si sources is being compared, pH-buffered aqueous extraction methods (Resin and MOPS) are better suited than other established quasi-equilibrium extractions (5-day, HCl). While these methods are well-suited for routine analysis, the more laborious sink extraction method (Iron Bag) is another effective tool, particularly for maximum quantitative extraction of the PAS fraction. In particular, we have highlighted that products with a high content of PAS such as Str-Ash, ThermoP, and CaSiO₃ would have been considered medium-to-low PAS fertilizers according to the MOPS, Resin, and 5-day extractions. The implications are highly relevant, and we believe that the Iron Bag extraction can improve Si fertilizer characterization, particularly in the context of research and development. These methods should be compared in further experiments to understand which one performs best under various conditions (i.e., different types of soils, crops, and fertilizers).

Regarding the agro-municipal cycling of Si, neither straw pyrolysis nor combustion is likely to have a negative impact on Si cycling besides enhancing solubilization due to the destruction of plant fiber and cell walls. Silicon recycling through MSS and its conversion products does not seem to be an option given their very low extractable Si content. We found no evidence that DE provides PAS, and some previous studies with soil incubation of commercial DE fertilizers also failed to do so, such that the relationship between composition and PAS release from DE fertilizers should be better assessed in the future. The amendment of (P-enriched) LD slag can be beneficial, although the long-term effects of Cr and V accumulation need to be considered in determining application rates.

**Associated Content**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b06597.

Additional details on fertilizer sample descriptions, X-ray fluorescence spectrometry method details; Si dose response trials, Iron Bag method assessment for Si absorption, modifications to the oven-induced digestion, Si colorimetric method details, and biochar and municipal sewage sludge and conversion products results.[PDF]

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Notes

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