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Silicon Availability from Chemically Diverse Fertilizers and Secondary Raw Materials

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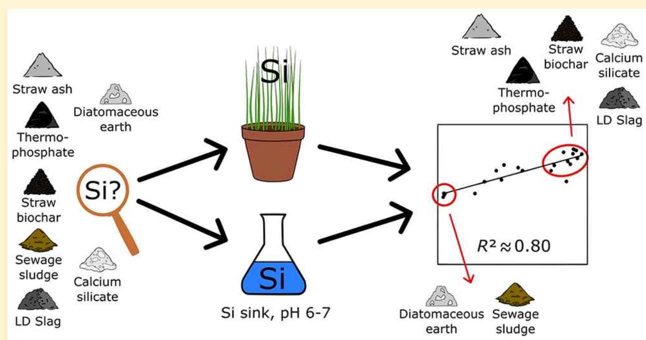
Supporting Information

ABSTRACT: Crops may require Si fertilization to sustain yields. Potential Si fertilizers include industrial byproducts (e.g., steel slags), mined minerals ($CaSiO_3$), 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 extracted by several common Si fertilizer tests: 5-day extraction in Na_2CO_3-NH_4NO_3, 0.5 mol L^{-1} HCl, and Resin extraction. In addition, we tested a novel sink extraction approach for $Si(OH)_4^0$ 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 $Si(OH)_4^0$ 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),[1] 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 (per our own unpublished results). Growing interest in the role of Si in agriculture requires improved PAS thresholds for Si application[5] 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 SiO_2, are an important Si pool in the biogeochemical Si cycle, and their importance for PAS increases with soil weathering stage,[2] so that the recycling of Si-rich crop residues such as straw can be crucial to sustain soil fertility.[1,11] 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.[16,17] Diatomaceous earth (DE), which contains diatom

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