

Dissolution of Silicon from Soilless Substrates and Additives

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Abstract. Silicon (Si) is a beneficial element that is usually ample in mineral soil solution, but it is minimally bioavailable from soilless substrates. Several Si additives are commercially available, but the rate of dissolution of Si is not well-characterized. The ideal additive would steadily release bioavailable Si over the crop lifecycle. We report the long-term (120 days) dissolution of Si from soilless substrates and substrate additives. Studies involving gently agitated containers with deionized water indicated that perlite, sphagnum peat, vermiculite, and coconut coir released less than 0.03 mmol Si per liter of substrate per day. Rice hulls and wollastonite (CaSiO_3) had 7- to 130-times faster rates of dissolution in this system; therefore, they were further studied in peat-based media. Dissolution of Si from the addition of 1 g wollastonite per liter of peat peaked at day 10 at 2.1 mmol Si per liter of media per leaching event (15% by volume); then, it gradually decreased over 120 days. The peak dissolution of Si amended with 12% rice hulls was similar, but it gradually increased over time. The concentrations of nine heavy metals in plant tissue were compared with untreated control plants to determine wollastonite and steel slag. The concentration of some elements statistically increased, but all concentrations were well below the legal concentration limits of these elements for human consumption in the United States. These results indicate that both wollastonite and rice hulls steadily release Si for up to 4 months; therefore, they are good sources of Si for container-grown crops in soilless media.

After oxygen, Si is the second most abundant element in natural soils, at approximately 31% Si by weight (Epstein 1999). Although predominately found as silicon

dioxide (SiO_2) in soils, the bioavailable form for plants is known as monosilicic acid, orthosilicic acid, or silicic acid [H_4SiO_4 or $\text{Si}(\text{OH})_4$]. Ortho-silicic acid and silicic acid are forms of monosilicic acid, but these terms are used interchangeably (Laane 2018). Mineral soil solutions contain from 0.1 to 0.6 mM bioavailable monosilicic acid (Epstein 1999).

Although Si is not considered an essential plant nutrient (Epstein 1994; Epstein and Bloom 2005), some argue that Si should be redefined as “essential” because all plants accumulate Si when bioavailable (Brown et al. 2022; Epstein 1999). Some species accumulate higher concentrations of Si than macronutrients. Rice (*Oryza sativa* L.) can be up to 10% Si in dry foliar tissue (Tamai and Ma 2003). Species that accumulate high concentrations of Si are known as “Si accumulators” and are defined by having $\geq 1\%$ (10,000 $\text{mg}\cdot\text{kg}^{-1}$ dry foliar tissue) Si. Species with less than 1% Si are known as “nonaccumulators,” but most species have at least 0.1% (Epstein 1999; Tamai and Ma 2003). Often, Si is beneficial to both accumulators and nonaccumulators. Its benefits include increased tolerance to biotic and abiotic stress in both field and controlled

environment agriculture (Brown et al. 2022; Dey 2022; Verma et al. 2021).

Supplementation of Si has improved floral traits such as flower diameter, stem height, stem straightness, and stem thickness of gerbera (*Gerbera jamesonii* Bolus ex. Hooker f. ‘Acapella’) (Kamenidou et al. 2010), sunflower (*Helianthus annuus* L. ‘Ring of Fire’) (Kamenidou et al. 2008), and zinnia (*Zinnia elegans* Jacq. ‘Oklahoma Formula Mix’) (Kamenidou et al. 2009). Mattson and Leatherwood (2010) reported that multiple floriculture crops increased in height and/or dry weight with Si supplementation compared with controls, but these results were dependent on the species and cultivar. Shi et al. (2014) found that Si alleviated oxidative stress of tomato (*Solanum lycopersicum* L. ‘Houpi’, ‘Jinpeng’, ‘Oubao’, and ‘Zhongza’) seed and improved germination by approximately 15% to 20% when supplemented during drought stress compared with drought stressed seeds without Si supplementation. Jeong et al. (2012) reported that potassium silicate drenches on chrysanthemum [*Chrysanthemum × morifolium* (Ramat.) Hemsl. ‘Shinro’] reduced aphid (*Macrosiphoniella sanborni* Gillette) colonies by 40% to 57% depending on the Si treatment compared with nonsupplemented control plants. Several studies have found increased tolerance of crops to common diseases like powdery mildew [*Golovinomyces* spp. (U. Braun) V.P. Heluta] with Si supplementation (Savvas et al. 2009; Shetty et al. 2012; Tibbitts 2018).

Although studies have found benefits of supplying Si in soilless media for plant morphology and increasing biotic and abiotic resistance (Frantz et al. 2010; Voogt and Sonneveld 2001), the methods of supplying Si in media are not well-studied. There are several methods of supplying Si, including foliar sprays (Asgharipour and Mosapour 2016; Mantovani et al. 2018; Menzies et al. 1992), fertigation (Boldt and Altland 2021; Buck et al. 2010; Nikpay and Soleyman-Nejadian 2014), and media amendments (Altland et al. 2016; Boldt et al. 2018; Jayawardana et al. 2016; Sistani et al. 1997; Somapala et al. 2016). Foliar sprays are commonly used for pest or disease control because they create an effective film over the cuticle layer, but the Si does not become incorporated in the plant tissue (Li et al. 2020). However, Li et al. (2020) found that Si foliar sprays increased rice yields while reducing cadmium (Cd) uptake in the rice grains. Foliar sprays are not as effective as root-applied Si if accumulation is the goal (Dallagnol et al. 2012; Liang et al. 2005; Pilon et al. 2013). Furthermore, Si can be supplied to the root zone in containers by fertigation, but Si solubility cannot be maintained in concentrated solution in stock tanks unless the pH is adjusted to 11.2 (Fatzinger and Bugbee 2021). Media amendments can be a simpler way of supplementing Si in the root zone (Haque et al. 2019).

Commercially available Si additives include steel slag, rice hulls, diatomaceous earth, and wollastonite. Steel slag, a byproduct of the metal industry, has been investigated as a Si supplement, and it also provides magnesium and calcium (Das et al. 2020; Ito

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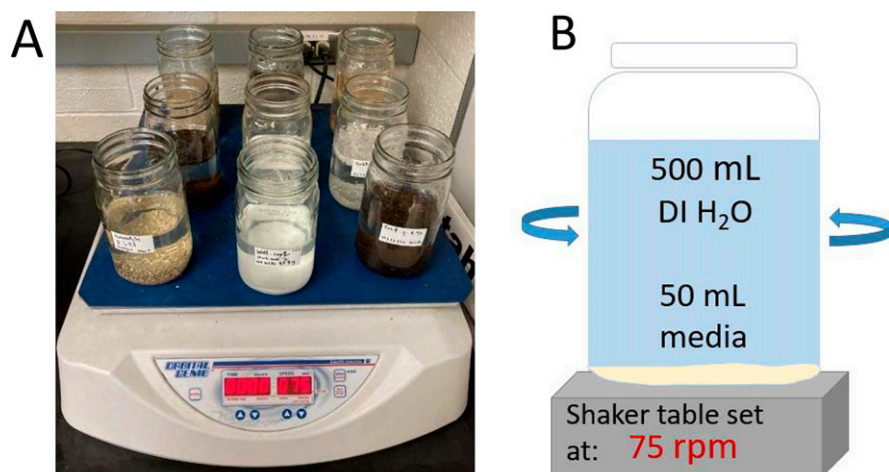


Fig. 1. Dissolution of silicon (Si) from substrates and additives were measured in glass containers. Leaching of Si from the glass was less than the detectable limits. The method shown with a photo (A) and diagram (B).

et al. 2015; Zhang et al. 2017). Frantz et al. (2010) found that steel slag had a lower release rate in water than rice hulls. Rice hulls have been used to supplement Si (Boldt et al. 2018; Frantz et al. 2010; Jayawardana et al. 2016; Sistani et al. 1997; Somapala et al. 2016), but their release rate is not well-studied. Diatomaceous earth has been used for pest control, but is not well-studied as a Si supplement (Mills-Ibibofo et al. 2019; Pati et al. 2016). Wollastonite is a naturally occurring calcium silicate mineral (CaSiO_3) that is approximately 51% SiO_2 (Vanderbilt Minerals, LLC 2018) and has shown promise as an Si amendment (Haque et al. 2019, 2020). Frantz et al. (2010) tested several steel slags, wollastonite, and parboiled rice hulls added to peat-based media for 21 d and found that rice hulls released the highest amount of Si per gram of material tested, steel slag released intermediate amounts, and wollastonite released the least amounts. However, Si release rates of these products over time are not well-characterized.

Therefore, we sought to characterize the dissolution of bioavailable Si from multiple

media components and additives over time in water and soilless substrates.

Materials and Methods

Si release rate in water. Dissolution of Si from sphagnum peatmoss (fibrous blond, ProMoss[®] III TBK; PRO-MIX, QC, Canada), coconut coir (Black Gold[®]; Sun Gro Horticulture, Agawam, MA, USA), expanded coarse perlite (Hess[®]; Hess Perlite, Malad City, ID, USA), vermiculite (horticultural coarse grade; Perlite Vermiculite Packaging Industries, Inc., North Bloomfield, OH, USA), coarse diatomaceous earth (AxisDE[®]; EP Minerals, LLC, Reno, NV, USA), powdered diatomaceous earth (Natural DE[®]; EP Minerals), parboiled rice hulls (PBH; Riceland Foods, Inc., Jonesboro, AR, USA), steel slag (Plant Tuff[®]; Edward C. Levy Corp., Dearborn, MI, USA), Ottawa sand (30–40 mesh particle size; VWR Chemicals BDH[®]; VWR International, Ottawa, ON, Canada), play sand (Sandtastik[®] Sparkling White Play Sand; Sandtastik Products Ltd., Port Colborne, ON, Canada), rock wool

(GRO-BLOCK[™]; Grodan, Roermond, the Netherlands), and wollastonite (VanSil[®] W-10; Vanderbilt Minerals, LLC, Norwalk, CT, USA) were quantified. Plant Tuff[®] was studied in four replicate jars, whereas wollastonite and rice hulls each had three replicates. The mass of 50 mL of each material was measured and added to a 1-L jar; then, it was filled to 500 mL with deionized water (Fig. 1A and B). These glass jars minimally leached Si and did not affect release rate concentrations (data not shown). Filled jars were placed uncovered on an orbital shaker (Orbital-Genie[™] Benchtop Orbital Shaker; Scientific Industries, Inc., Bohemia, NY, USA) at 75 rpm on a laboratory bench (air temperature $25 \pm 2^\circ\text{C}$).

Immediately before sampling at 7-d intervals, jars were thoroughly mixed and samples were filtered with Whatman[®] grade 1 (11 μm) cellulose filter paper (Cytiva, Marlborough, MA, USA). Solution Si concentrations were measured using a colorimeter (LaMotte[®] SMART 3 colorimeter; La Motte, Chestertown, MD, USA). The remaining solution in each jar was decanted, and the water was replaced with 450 mL deionized water for a total volume of 500 mL. Measurements of media components with steady dissolution rates of Si were ended after 60 d, and those without were continued for an additional 70 to 100 d.

Si release rate from soilless media. Wollastonite and rice hulls were further studied in soilless media. Columns were constructed using 3-inch-diameter (7.62 cm) and 10-inch-tall (25.4 cm) polyvinylchloride piping fit with a filter of landscape fabric at the bottom to achieve a media volume of 1 L (Fig. 2A and B). Columns of sphagnum peat amended with wollastonite included 1 g wollastonite, 0.75 g wetting agent (AquaGro[®] 2000 G; Aquatrols, Paulsboro, NJ, USA), and 1.23 g hydrated lime (to adjust pH to 6.0; Chemstar[®] Type S lime; Chemstar Products, Minneapolis, MN, USA) per liter of sphagnum peatmoss. Columns of sphagnum peat amended with rice hulls were prepared the same as aforementioned but included 12% rice hulls by volume



Fig. 2. A photograph of the 12 columns (1 L) used to quantify the silicon release rate in media (A) and a diagram showing leachate collection (B).

instead of wollastonite and 1.5 g hydrated lime per liter of peat to adjust the pH to 6.0.

Coconut coir is not as well-buffered as peat media; therefore, the addition of rice hulls or wollastonite was studied only to determine the change in pH over time because the release of Si was similar between media types (data not shown). Coconut coir columns amended with rice hulls comprised 12% rice hulls by volume and 0.75 g wetting agent per liter of coconut coir ($n = 3$). Wollastonite-amended columns comprised 1 g wollastonite and 0.75 g wetting agent per liter of coconut coir ($n = 3$). Coconut coir had an initial pH of 6.5 ± 0.08 ($n = 6$).

All columns were initially irrigated with 600 mL tap water (Logan, UT, USA) to settle the soilless media. The columns were subsequently leached using the pour-through method (Yeage et al. 1983) twice weekly (2–5 d between flushes) with 150, 300, or 600 mL nutrient solution for 15%, 30%, and 60% leaching fractions. Each treatment had two replicates. The nutrient solution contained $1.5 \text{ mmol} \cdot \text{L}^{-1}$ (mM) $\text{Ca}(\text{NO}_3)_2$, 2.25 mM NH_4Cl , 2 mM KNO_3 , 0.8 mM MgSO_4 , 0.35 mM HNO_3 , 3 μM MnCl_2 , 3 μM ZnCl_2 , 40 μM H_3BO_3 , 4 μM Cu-EDTA , 0.1 μM Na_2MoO_4 , and 0.1 μM NiCl_2 (pH: 6.0 ± 0.1 ; electrical conductivity: $1.2 \pm 0.06 \text{ mS} \cdot \text{cm}^{-1}$). Nutrient solution was made with reverse-osmosis water to minimize the addition of Si and was titrated with potassium hydroxide or hydrochloric acid) before irrigating to maintain pH at 6.0 ± 0.1 . Phosphorous (P) and iron (Fe) were excluded from the nutrient solution to minimize interferences with the colorimetric analysis. Leachate was collected in plastic containers until there was no residual dripping (≈ 60 min). Leachate pH (Oakton® pH electrode; Oakton Instruments, Vernon Hills, IL, USA; Hanna HI2209 Benchtop pH Meter; Hanna Instruments, Smithfield, RI, USA) was immediately measured. Silicon concentrations were measured by colorimetry.

Wollastonite pH. The dissolution of wollastonite releases two molecules of hydroxide for every molecule of Si (Eq. [1]).



Colorimetric analysis. Leachate Si concentrations were quantified colorimetrically using the heteropoly blue method (Eaton and Franson 2005) (LaMotte® silica low range test kit 3664-SC; La Motte, Chestertown, MD, USA). The silica low range test was used to achieve a higher resolution of Si in solution (Eaton and Franson 2005). Deionized water was used as a blank to account for color added by reagents, and the concentration of the blank was subtracted from the concentration of each leachate sample. A blank was made for each treatment solution every time leachates were tested. Then, samples were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) at the Utah State University Analytical Laboratory (Logan, UT, USA) to test the accuracy of colorimetric analysis. Samples were diluted using deionized water when needed.

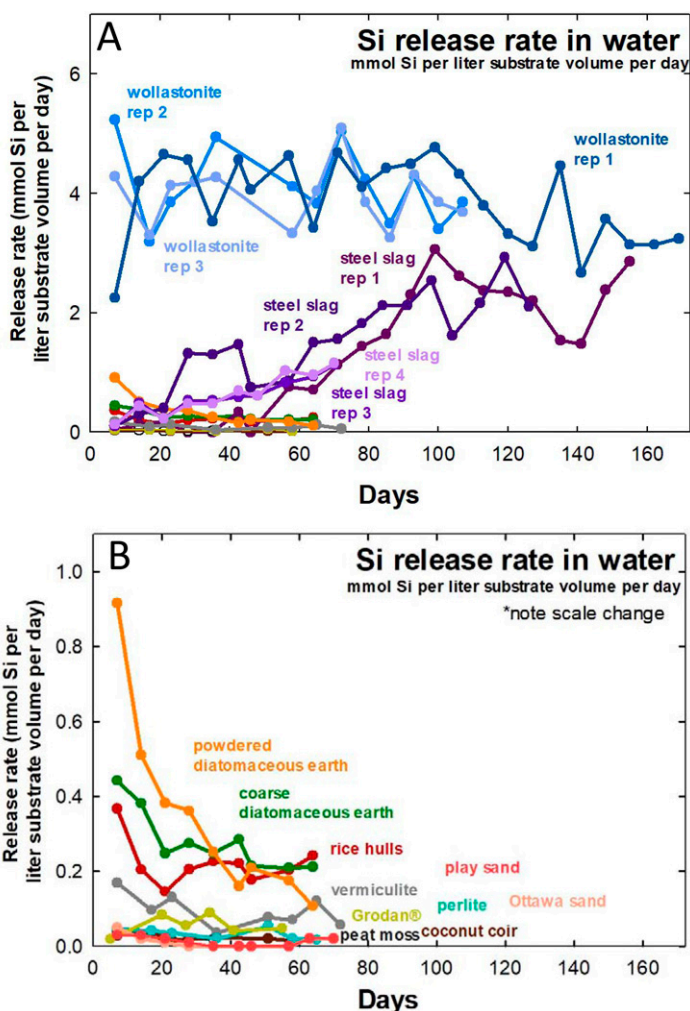


Fig. 3. Dissolution of media components or additives in water. Wollastonite (Vansil® W-10) steadily released silicon (Si) over 160 d (A). Release rates of the other media components had a 10-fold lower release rate (B). Note the 6-fold scale change. Media components other than Vansil-10 and steel slag (Plant Tuff®, Edward C. Levy Corp.) minimally released Si.

Degradation of rice hulls. One-liter glass jars filled with peat-based media were watered with tap water or a nutrient solution to quantify microbial activity. Each jar was equipped with a galvanic cell oxygen sensor (SO-110; Apogee Instruments, Logan, UT, USA) to measure the partial pressure of oxygen (O_2). Sensors were connected to

a datalogger (CR1000; Campbell Scientific, Logan, UT, USA) to record the depletion of O_2 over time, which was used to calculate respiration rate. Jars were placed in an insulated box to stabilize temperature (for system details, see Kusuma and Bugbee 2020). One jar contained peatmoss and wetting agent added at a rate of $0.75 \text{ g} \cdot \text{L}^{-1}$ peat and

Table 1. Average dissolution rates of silicon (Si)-containing products, by volume and mass, for the first 60 d. Peat moss, coconut coir, vermiculite, Grodan®, and perlite were measured until Si depletion (30–40 d). When the SD is not listed, only one replicate was evaluated.

Product	Si (mmol) released per liter of product volume per day	Si (mmol) released per kilogram of product per day
Wollastonite, Vansil 10 ($n = 3$)	4.03 ± 0.65	4.64 ± 0.37
Steel slag ($n = 4$)	0.67 ± 0.45	0.34 ± 0.14
Parboiled rice hulls ($n = 3$)	0.22 ± 0.07	1.63 ± 0.08
Powdered diatomaceous earth	0.34	0.95
Coarse diatomaceous earth	0.28	0.64
Vermiculite	0.08	0.55
Grodan®	0.04	<0.001
Play sand	0.03	0.02
Ottawa sand	0.03	0.02
Coconut coir	0.01	0.39
Perlite	0.02	0.14
Peat	0.01	0.08

moistened with tap water (Logan, UT, USA), which was applied at the same rate for all treatments. Another jar contained peatmoss with 12% rice hulls added (by volume) and wetting agent moistened with tap water. Two jars comprised the 12% rice hull and peatmoss mix with a wetting agent, but they were watered with a P-free, Si-free, and Fe-free nutrient solution. Two jars comprised the 12% rice hull and peatmoss mix with a wetting agent, but they were moistened with a complete nutrient solution using a modified 21N-2.2P-16.6K fertilizer (Peters 21-5-20 Excel; JR Peters Inc., Allentown, PA, USA) as follows: N at 120 mg·L⁻¹ with additions to increase total P to 30 mg·L⁻¹, 1 mg·L⁻¹ Cu-EDTA, 0.4 mg·L⁻¹ B, 1 mg·L⁻¹ Fe-DTPA, 21 mg·L⁻¹ S, 183 mg·L⁻¹ K, and 17 mg·L⁻¹ Si provided by AgSil® (K₂SiO₃; PQ Corp., Valley Forge, PA, USA). The nutrient solution was modified over time to optimize plant nutrition. Both nutrient solutions had a pH of 5.8 ± 0.1 and electrical conductivity of 1.3 ± 0.8 mS·cm⁻¹.

Heavy metal analysis. During a separate study by the US Department of Agriculture (Toledo, OH, USA), basil (*Ocimum basilicum* L. ‘Genovese’), which is a Si nonaccumulator, and sunflower ‘Pacino Gold’, which is a Si accumulator, were grown for 6 weeks in soilless media amended with wollastonite, steel slag, or no Si additive for heavy metal uptake analyses. Pots (diameter, 11.4 cm) were filled with a base substrate of 85 sphagnum peatmoss:15 coarse grade perlite (volume:volume; Sun Gro Horticulture) and 0.196 L·m⁻³ wetting agent (SOAX; Oasis Grower Solutions, Kent, OH, USA). It was amended with 1.17 g·L⁻¹ wollastonite (VanSil® W-10) and 1.78 kg·m⁻³ dolomitic limestone (ECOpHRST; National Lime and Stone Co., Findlay, OH, USA) with 7.12 g·L⁻¹ steel slag (PlantTuff®) and 1.48 kg·m⁻³ lime or only with 2.67 kg·m⁻³ lime. This provided ≈170 g Si per pot to the Si-amended treatments and adjusted the initial media pH to 6.0 after equilibrium for all treatments. Each treatment contained three replicates per species.

Plants were grown in a glass-glazed greenhouse from 24 Jan to 7 Mar. Supplemental irradiance was provided by high-pressure sodium lamps between 0600 and 2000 hr when benchtop ambient irradiance was less than 300 μmol·m⁻²·s⁻¹ photosynthetic photon flux density. Air temperature and photosynthetic photon flux density were measured with aspirated thermocouples and quantum sensors (MQ-200; Apogee Instruments), respectively, and recorded every 15 min using a datalogger (CR10X; Campbell Scientific). Air temperatures were 25.2 ± 1.2 °C day/21.0 ± 1.9 °C night (the mean ± SD mean daily light integral was 11.4 ± 1.3 mol·m⁻²·d⁻¹).

Plants were irrigated as needed with 15N-2.2P-12.4K (Jacks 15-5-15; JR Peters, Inc.) at a concentration of 150 mg·L⁻¹ N. At 2 and 4 weeks after transplantation, plants were provided 150 mL magnesium sulfate (1.06 g·L⁻¹ magnesium sulfate heptahydrate;

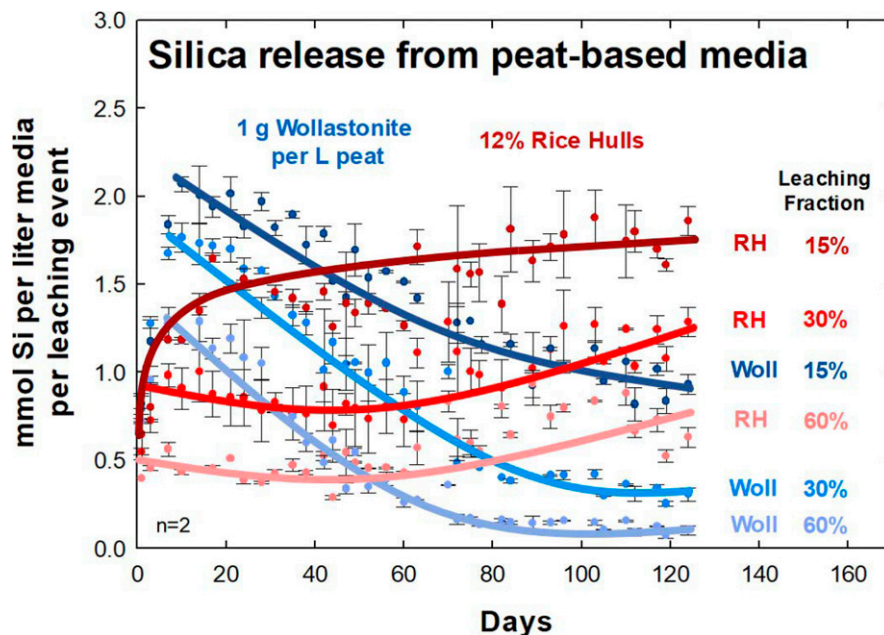


Fig. 4. Concentration of silicon (Si) in the leachate (mmol of Si per liter of media per leaching event) from peatmoss amended with wollastonite or rice hulls over 120 d. Each data point represents the average of two replicate columns, with error bars representing the SD ($n = 2$). The leachate Si concentration correlated with the leaching volume and time between leaching events. Some of the variability was associated with the time interval between leaching events, which varied from 2 to 6 d. As expected, the concentration of Si in the leachate increased with longer intervals between leaching events.

Magriculture, Giles Chemical, Waynesville, NC, USA) to optimize nutrition.

After 6 weeks, aboveground tissue was separated into leaves and stems (including inflorescences). They were dipped in acidified water (0.1 M hydrochloric acid), rinsed in 18 MΩ water, placed in paper bags, dried in a forced-air oven at 60 °C for a minimum of

5 d, and weighed to determine dry mass. Leaves were ground into a fine powder using a mortar and pestle for elemental analysis. Tissue samples were digested in nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) for the heavy metal analysis with ICP-OES at the Utah State University Analytical Laboratory.

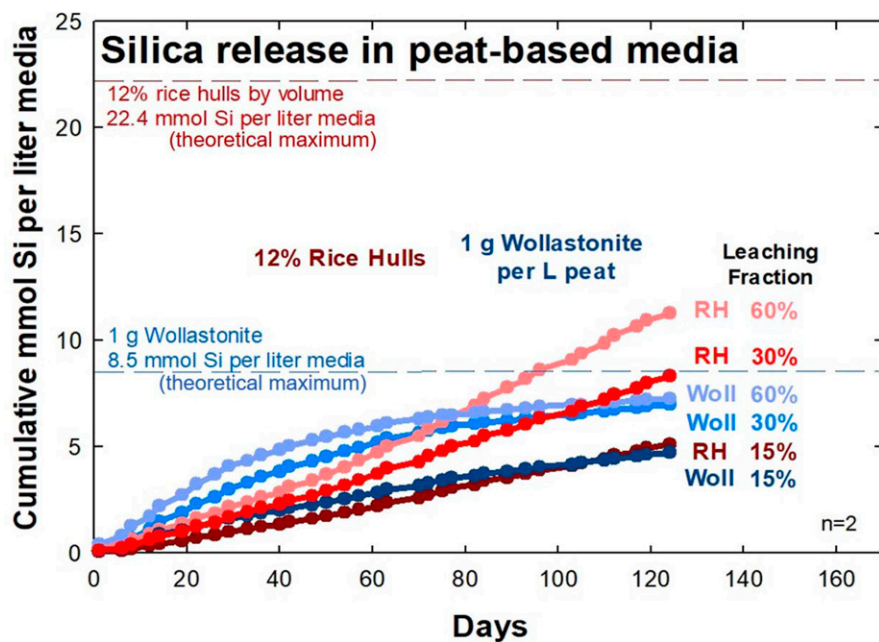


Fig. 5. Cumulative concentration of silicon (Si) released by wollastonite (1 g per liter of peat) and rice hulls (RH; 12% incorporation by volume) over time at different leaching fractions. Each data point represents the average release from two columns ($n = 2$). The dashed lines represent the theoretical maximum release of Si from each product.

Results

Si release rate in water. There were significant differences in Si release among the Si-containing substrates and additives. Wollastonite had the highest release rate of Si (4.03 ± 0.65 mmol Si per liter of wollastonite per day) over 150 d (Fig. 3A; Table 1). Peat moss, coconut coir, perlite, and sand released the least Si (≤ 0.03 mmol Si per liter of substrate per day) (Fig. 3B). Release rates per unit volume and mass are shown in Table 1.

Si release from soilless media. The Si release from peat-based media was inversely related to the leaching fraction for both rice hulls and wollastonite. Rice hull-amended peat had an average of 1.47 ± 0.27 mmol Si, 0.95 ± 0.20 mmol Si, or 0.57 ± 0.17 mmol Si per liter of media per leaching event of 15%, 30%, or 60% averaged over 120 d (Fig. 4). The leachate Si concentration from rice hulls gradually increased over time.

Conversely, wollastonite peaked at day 10; then, it decreased over time. Wollastonite-amended peat peaked at 2.1, 1.8, or 1.3 mmol Si per liter of media per leaching event of 15%, 30%, or 60%. Over 120 d, wollastonite had an average of 1.44 ± 0.40 mmol Si, 0.94 ± 0.51 mmol Si, or 0.50 ± 0.41 mmol Si per liter of media per leaching event of 15%, 30%, or 60% (Fig. 4).

Based on the mass balance analysis, the 60% leaching fraction resulted in nearly complete dissolution of wollastonite after 120 d (Fig. 5). The addition of 12% rice hulls with a 60% leaching fraction surpassed the calculated maximum concentration of Si that could be released by 1 g wollastonite per liter of peat (8.5 mM Si) at 96 d (Fig. 5). Wollastonite was depleted of Si for both the 30% and 60% leaching fractions within approximately 100 d. Both amendments released similar amounts of Si with a 15% leaching fraction (Fig. 5).

Effects of amendments on pH. Wollastonite and rice hulls increased peat-based media pH over time (Fig. 6A). Across all three leaching fractions and over 120 d, wollastonite increased the media pH approximately 0.8 units, whereas rice hulls increased the media pH approximately 1.0 unit (Fig. 6A).

Because coconut coir is less well-buffered than peat, both wollastonite and rice hulls increased media pH in 2 weeks (Fig. 6B). Wollastonite in the coconut coir-based media leached with a 15% fraction increased media pH by 1.2 units and stabilized at a pH of 7.4. Rice hulls in the coconut coir based-media with a 15% leaching fraction increased pH to and then stabilized at 6.9.

Colorimetric analysis. The colorimetric analysis results were compared with the ICP-OES analysis results to verify the accuracy of measurements. The ICP-OES Si analysis values explained 97% of the colorimetric analysis values in the leachates (Fig. 7A). There was no effect of the Si concentration on the percent error (Fig. 7B).

Degradation of rice hulls. Silicon can be released from rice hulls by both chemical dissolution and microbial degradation. Biological oxygen demand is a measurement of microbial

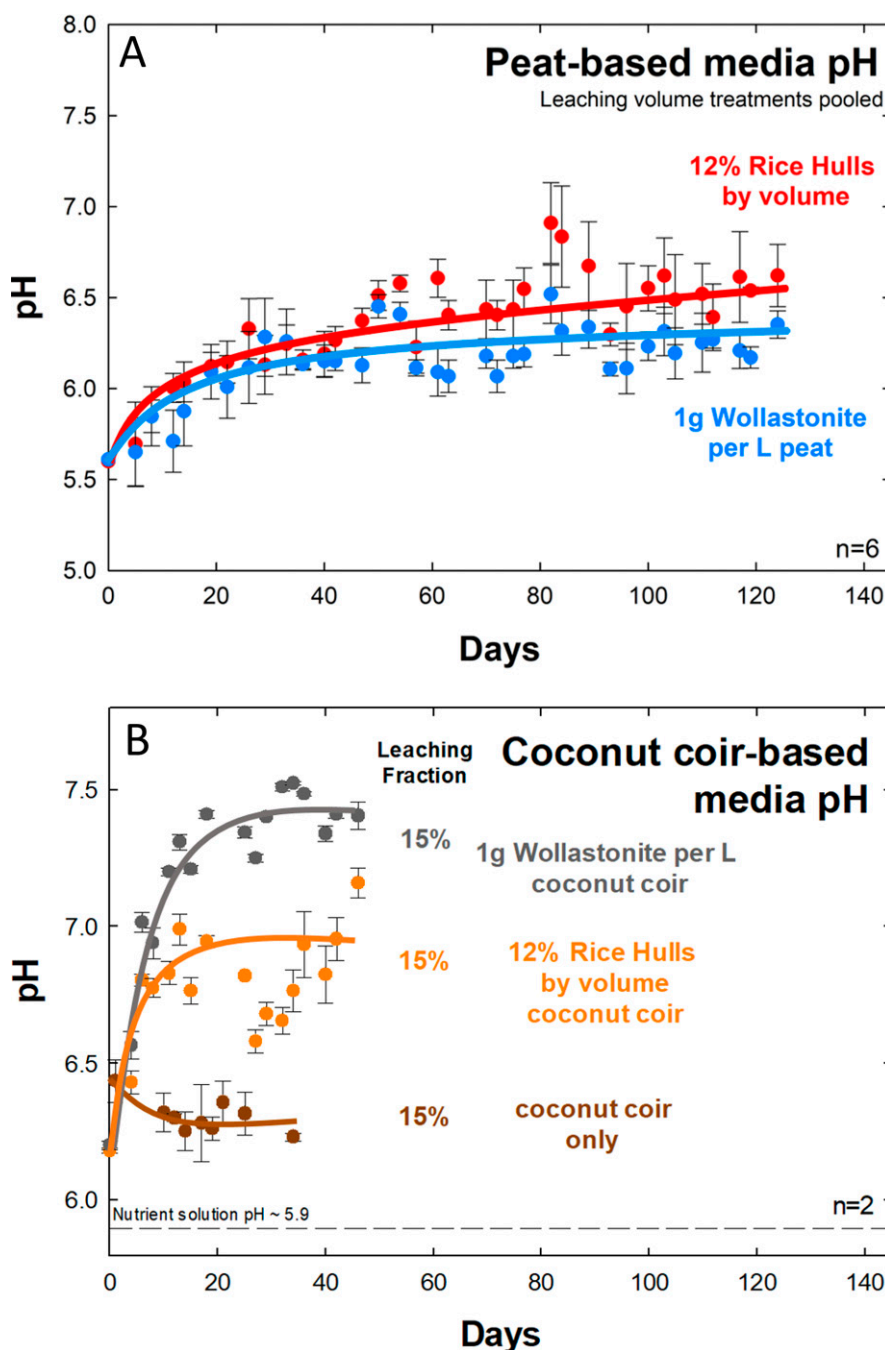


Fig. 6. The pH increased over time in both wollastonite and rice hull-amended peat (A) and coconut coir (B). Note the scale change. Nutrient solution was maintained at a pH of 5.9 ± 1.0 . Data points represent the average of the treatment (A: $n = 6$; B: $n = 2$), and error bars represent the SD. There was no effect of the leaching volume, and values were pooled for the peat-based media.

metabolism. The cumulative concentration of consumed oxygen (O_2) over 2 months increased with the increasing nutrient input (Fig. 8). As expected, peat with only tap water supported the lowest microbial metabolic rate (41.7 mmol consumed O_2 per liter of media); media with 12% rice hulls by volume was slightly higher (54.3 mmol O_2 per liter of media). The peat and rice hull mix with incomplete nutrient solution had an average cumulative consumption of 98.6 ± 4.5 mmol O_2 per liter of media (Fig. 8), whereas the media with the complete nutrient solution had the

highest cumulative microbial metabolism of 106.9 ± 12.4 mmol of consumed O_2 per liter of media.

Heavy metal analysis. The potential for plant uptake of undesirable elements is a concern for all media additives. During a separate study, nine heavy metals in leaves of basil and sunflower grown in a nonamended or wollastonite-amended peat:perlite media were analyzed. Although chromium uptake was higher in sunflower than basil, the uptake of other metals was similar between species; therefore, data from both species

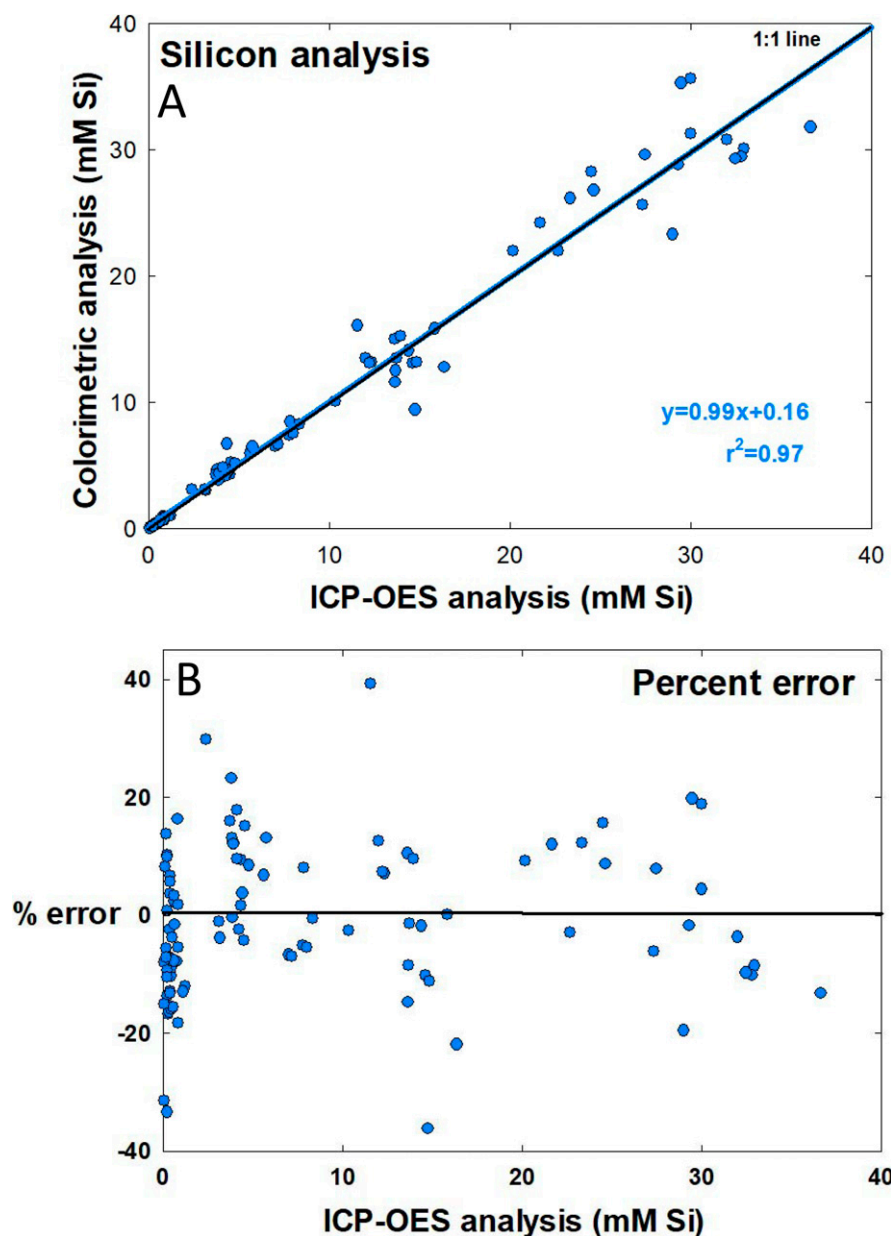


Fig. 7. Comparison of the colorimetric analysis and inductively coupled plasma optical emission spectrometry (ICP-OES) silicon (Si) analysis results ($n = 106$). Regression is shown in blue ($y = 0.99x + 0.16$; $r^2 = 0.97$) with the 1:1 line in black (A), along with the percent error. (B) Differences between measurement methods may have been caused by the time duration between sampling, sample storage temperature, and/or dilution errors. There was no difference in the percent error as the Si concentration increased.

were pooled for analysis. Aluminum, barium, cadmium, and strontium concentrations were statistically higher in leaves of plants grown in wollastonite-amended media compared with the nonamended control (Table 2).

Sunflower and basil were also grown in media amended with Plant Tuff®. Aluminum, arsenic, barium, chromium, and strontium were statistically higher in plants grown in Plant Tuff®-amended media compared with the nonamended control treatment (Table 2). However, concentrations from both additives were well below the concentration limits for human consumption in the United States.

Discussion

Si release rate in water. The ideal Si additive would have an adequate and steady-state release of Si throughout the lifecycle of a crop. Typical soilless media components minimally released Si, but media amendments significantly increased Si in water (Fig. 3A and B). Although diatomaceous earth had a rapid initial release of Si, it has a relatively high cost. Rice hulls had a low release rate in water, probably because of limited microbial metabolism in the stirred water. Steel slag slowly released a high concentration of Si, but the release was inconsistent, perhaps because of the variable particle

size. At the rate evaluated, steel slag also caused an alkaline pH of 11.3, which limits the ability of the application to maintain a suitable root zone pH. Our unpublished studies suggest that steel slag can have a higher dissolution rate in media than in water, and that the buffering capacity of a peat-based substrate can blunt the increase in pH. The $7.1 \text{ g} \cdot \text{L}^{-1}$ incorporation rate of steel slag used in the heavy metal analysis study supplied $>1.7 \text{ mmol Si}$ per liter of substrate in leachates and maintained a substrate pH less than 6.1 (data not shown). Wollastonite had the highest release of Si over 160 d during this study (Fig. 3A), but this is inconsistent with the findings of Frantz et al. (2010), who reported that rice hulls released more Si per gram than wollastonite. The particle size used by Frantz et al. (2010) was not reported; therefore, the difference between studies could be associated with particle size.

Si release rate in soilless media. For all leaching volumes, the release of Si over 120 d increased for rice hulls, whereas wollastonite peaked at day 10; then, it slowly decreased and depleted over time (Fig. 4). Rice hulls released less total Si than wollastonite until approximately day 80, but they had a higher theoretical maximum dissolution of 22.4 mmol Si per liter of peat when added at 12%. They also had longer sustained release than wollastonite (8.5 mmol Si per liter of peat) (Fig. 5). Microbial metabolism would have likely increased the degradation of rice hulls, which would be expected to release Si more rapidly (Fig. 8) (Marxen et al. 2016; Oliverio et al. 2020). This was supported by an 8% increase in consumed O_2 when the rice hull-amended media was moistened with a complete nutrient solution compared with the incomplete nutrient solution (Fig. 8). Rice hulls typically release Si biologically through degradation (Duan et al. 2021), which explains why rice hulls had a much lower release in water (Fig. 3B) than in media (Figs. 4 and 8). Because wollastonite is a mineral without carbon, the release of Si is expected to occur almost exclusively by weathering. This study used Vansil® W-10 wollastonite, which is the coarsest particle grade commercially available; however, using an even coarser grade of wollastonite may increase the longevity of Si release. A higher amount of wollastonite could be applied, but the lime would need to be adjusted to account for the effect of wollastonite on pH (Fig. 6A and B). Adjusting fertilizer additions, such as increasing the ammonium nitrogen (N) fraction, may counteract the increase of media pH if Si additives are incorporated (Cytryn et al. 2012).

Effect of media additives on pH. Silicon additives increased media pH. In peat-based media, rice hulls and wollastonite similarly increased pH (Fig. 6A), but wollastonite increased pH more than rice hulls in coconut coir-based media (Fig. 6B). The dissolution of wollastonite increases pH because every mole of monosilicic acid releases two moles of hydroxide in solution (Eq. [1]; Supplemental Fig. S9). The amount of additive should be adjusted depending on the media. Sphagnum

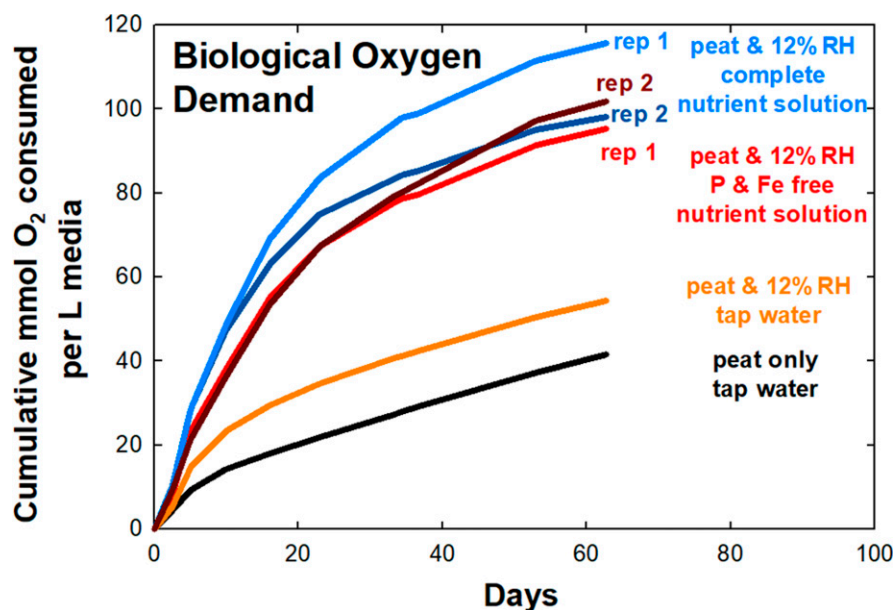


Fig. 8. Biological oxygen (O_2) demand of microbes in peat media mixes moistened with tap water ($n = 1$), 12% rice hull (RH) incorporation by volume moistened with tap water ($n = 1$), 12% RH incorporation moistened with a phosphorus (P)-free and iron (Fe)-free nutrient solution ($n = 2$), and 12% RH incorporation moistened with a complete nutrient solution ($n = 2$). The cumulative mmol of O_2 consumed per liter of media was highest in the peat and RH mix with the complete nutrient solution.

peatmoss is acidic (pH, 3.0–4.0) (Lee et al. 2021) and may not require additional lime, depending on the type and volume of wollastonite added. Coconut coir is less acidic (pH, 4.2–6.1) (Abad et al. 2002) and may not need lime to adjust the pH. It is important to note that media batches have differing pH, and recipes should be adjusted for each batch to ensure a suitable root zone environment.

Effect of the leaching fraction on the Si concentration in the root zone. The leachate volume and time between leaching influenced Si release. The greatest total amount of Si was released using a 60% leaching fraction (Figs. 5 and 6), but this volume quickly depleted Si in the root zone. The 30% leaching fraction released Si faster than the 15% leaching fraction but extended the life of the Si additive only approximately 10 d more than the 60% leaching fraction (Figs. 5 and 6). The

15% leaching fraction is a common target in containerized production because it reduces water and nutrient waste. This leaching volume maintained a steady release of Si from both amendments and extended the life of the additives (Figs. 5 and 6). Although these amendments released Si, monosilicic acid may not remain bioavailable in the root zone solution over long time periods (Schaller et al. 2021).

The irrigation rate can also affect Si dissolution. If irrigation is rapid, then channeling may occur and reduce the dissolution and bioavailability of Si (Altland 2021). These results suggest that wollastonite is a beneficial addition to soilless media mixes for crops with a lifecycle less than 4 months; however, rice hulls are suited for all crops (Fig. 5). Higher temperatures may increase the release rate of Si from either additive, but this was

not investigated during this study (Laane 2018; Schaller et al. 2021).

Potential for heavy metal contamination. Silicon amendments can supply undesired elements. The heavy metal concentrations in plant tissue grown with wollastonite and steel slag were both less than the legal concentration limits for consumption by humans and animals in the United States (Table 2) (US Food and Drug Administration 2022), but regulations vary by country. Wollastonite purity and elemental concentration might vary among manufacturers, but other wollastonite sources were not evaluated.

Potential for inhalation of fine particles during mixing. Wollastonite and hydrated lime have identical warnings regarding the inhalation danger and should be used with appropriate precautions ($5 \text{ mg} \cdot \text{m}^{-3}$ respirable dust) (Lhoist 2020; Vanderbilt Minerals, LLC 2018). The potential for airborne particles depends on the particle size; Vansil-10 is the largest particle size sold by the manufacturer.

Accuracy of the colorimetric analysis. Silicon release rates were measured during the colorimetric analysis. Phosphorous and Fe interfere with analyses (Eaton and Franson 2005); therefore, they were excluded from the nutrient solution. Elemental concentrations of Si using colorimetry were highly correlated with the ICP-OES analysis (Hansen et al. 2013) (Fig. 7A and B). The colorimetric analysis is an affordable way to measure Si in solution if interferences are not present. Although P interferes with the colorimetric test, the active uptake of P by plants should result in low P concentrations in leachates, thus minimizing this interference. Langenfeld and Bugbee (2023) showed that oxalic acid can be used to eliminate this interference. Testing for Si is inherently difficult because of the instability of monosilicic acid (Laane 2018). The temperatures and lengths of the testing samples could have introduced variability in the analytical results (Fig. 7A and B).

Calculating the leaf concentration from the root zone concentration. The uptake of bioavailable Si in plant tissue was not quantified during this study, but quantifying the

Table 2. Sunflower ($n = 3$) and basil ($n = 3$) were grown in soilless media amended with and without wollastonite or Plant Tuff[®]. Mean and SD of metal uptake are shown as the concentration in leaf tissue. Species were pooled ($n = 6$) within the amendment type because of an insignificant interaction between species apart from chromium for wollastonite. Significance was determined using $\alpha = 0.05$.

Element	Wollastonite			Plant Tuff [®]		
	(–) ($\text{mg} \cdot \text{kg}^{-1}$)	(+) ($\text{mg} \cdot \text{kg}^{-1}$)	Significance (P value)	(–) ($\text{mg} \cdot \text{kg}^{-1}$)	(+) ($\text{mg} \cdot \text{kg}^{-1}$)	Significance (P value)
Al	4.1 ± 1.6	7.3 ± 1.5	0.009	4.06 ± 1.6	10.5 ± 3.1	0.002
As	0.21 ± 0.07	0.21 ± 0.08	0.48	0.21 ± 0.07	0.34 ± 0.11	0.02
Ba	6.2 ± 0.6	7.6 ± 0.7	0.003	6.22 ± 0.62	9.73 ± 0.9	0.0001
Cd	0.15 ± 0.01	0.16 ± 0.01	0.04	0.15 ± 0.01	0.08 ± 0.02	NA ⁱⁱⁱ
Co	0.18 ± 0.06	0.24 ± 0.08	0.14	0.18 ± 0.06	0.19 ± 0.08	0.86
Cr	0.27 ± 0.04	0.32 ± 0.04	0.09	0.27 ± 0.04	0.32 ± 0.04	0.03
Pb	^{*i}	^{*i}	^{*i}	ⁱⁱ	ⁱⁱ	ⁱⁱ
Se	ⁱⁱ	ⁱⁱ	ⁱⁱ	ⁱⁱ	ⁱⁱ	ⁱⁱ
Sr	25 ± 2.5	33 ± 1.9	0.0004	25.1 ± 2.53	30 ± 2.38	0.008

ⁱ Lead (Pb) was not statistically analyzed because only one of the six replicates was above the detection limit.

ⁱⁱ Below detection limit (BDL).

ⁱⁱⁱ Significance was calculated for cadmium (Cd) in Plant Tuff[®] samples because control plant tissue had higher concentrations of Cd than Plant Tuff[®]-supplemented plant tissue.

Al = aluminum; As = arsenic; Ba = barium; Co = cobalt; Cr = chromium; Se = selenium; Sr = strontium.

concentration in the root zone can be used to calculate plant tissue Si based on water use efficiency, assuming passive uptake and mass balance principles (Eqs. [2] and [3]) (Langenfeld et al. 2022). This mass balance technique is commonly used to optimize solutions for hydroponics (Bugbee 2004; Langenfeld et al. 2022).

$$\frac{WUE \times \text{Tissue concentration}}{\text{Solution concentration needed}} \quad [2]$$

$$\frac{3 \text{ g dry mass}}{L H_2O} \times \frac{0.01 \text{ g Si}}{\text{g dry mass}} = \frac{30 \text{ mg Si}}{L H_2O} \text{ or } \frac{1.07 \text{ mmol Si}}{L H_2O} \quad [3]$$

The Si concentration in the leachate was 1 to 2 mmol/L (Fig. 5). The water use efficiency of greenhouse crops is typically 3 g dry mass per liter (Langenfeld et al. 2022). These values result in a Si tissue concentration of 1% to 2% (0.01–0.02 g Si per g dry mass) by passive uptake.

Many greenhouse and nursery crops have less than 1% Si in leaf tissues, but even these plants can accumulate high levels of Si in root tissues (Boldt et al. 2018; Boldt and Altland 2021). Si accumulating species typically have at least 1% Si in leaf tissue. Examples of horticultural crops include cucumber (*Cucumis sativas* L.) and other cucurbits, lantana (*Lantana camara* L.), phlox (*Phlox* spp. L.), sunflower, verbena (*Verbena bonariensis* L.), and zinnia (*Zinnia elegans* Jacq.) (Bold et al. 2018; Frantz et al. 2010; Ma and Yamaji 2006). Silicon is generally taken up passively with the transpiration stream, but it can be active in some species (e.g., rice and wheat) (Ma and Yamaji 2006). Species with active uptake may “mine” the media for Si and take up more than predicted by passive uptake. Chaiwong et al. (2022) demonstrated a relationship between Si concentration in the root zone and Si accumulation in rice.

A leaf tissue concentration of Si of 1% to 2% can theoretically occur with passive uptake by adding wollastonite or rice hulls to the media (Fig. 5). Amending soilless media with a steady-state-releasing Si additive can increase tolerance to abiotic and biotic stress throughout the lifecycle (Ma et al. 2001; Voogt and Sonneveld 2001).

Conclusion

The dissolution of wollastonite and par-boiled rice hulls to soluble Si was steady over 4 months in peat-based media. Wollastonite and rice hulls are similarly effective for supplying Si to crops that are grown less than 4 months, but rice hulls are better-suited for longer-term crops. Neither Si source significantly affected the heavy metal concentration in the plant tissue.

The dissolution of Si results in the release of hydroxide ions. We measured a gradual increase of 1 pH unit in peat-based media over 4 months. Minimizing this pH increase could

be achieved through the use of a more acidifying fertilizer solution with more ammonium N.

The colorimetric analysis of Si is an accurate method of quantifying Si in solution.

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