Aqueous Potassium Silicate

Crops

Focus questions requested by the NOSB

1. What is the fate of potassium silicate on the plant leaf surface? When sprayed, potassium silicate dries on the leaves. What happens to it there? Does it stay in that form for several days and act as a barrier? Does it transform and become absorbed into the plant as silicic acid? Does it re-dissolve and run off to the ground in rains?

Fate of potassium silicate when sprayed on leaves

When dried, strongly alkaline aqueous sprays of potassium silicate (K_2SiO_3) (CAS No. 1312-76-1) leave a finely powdered layer of potassium silicate crystals on the leaf surface. Acidic or neutral sprays of potassium silicate aqueous solutions leave a residue consisting of dried silicic acid (H_4SiO_4) (CAS No. 7699-41-4), amorphous silica (SiO_2) (CAS No. 7631-86-9), and salt crystals of the acid used (e.g., phosphoric or citric acid) to acidify the alkaline potassium silicate (Knight & Kinrade, 2001; PQ, 2006). Acids that have been used to neutralize or acidify alkaline potassium silicate solutions include phosphoric acid (Menzies et al., 1992; Bowen et al., 1992; Rodrigues et al., 2009; Rodrigues et al., 2010), citric acid (Certis, 2017; PQ, 2002), and hydrochloric acid (Liang et al., 2005).

Once dried, the various chemical species stay in that form on the leaf until they are washed off by rainfall or by sprinklers. Chemical changes in dried residues as they sit on the leaf have not been reported in the literature surveyed here (Laane, 2018; Liang et al., 2015; Datnoff et al., 2001). However, changes could occur if the leaf was sprayed by acids or bases or other chemical reagents.

The dried sprays are likely to produce a barrier preventing pathogen attack (Liang et al., 2005: Menzies et al., 1992; Rodrigues et al., 2009; Guével et al., 2007). Whether or not silicic acid is absorbed by the leaf depends on the plant species. It is not appreciably absorbed by:

- grape leaves (Bowen et al., 1992)
- cucumber (Liang et al., 2005)
- melon (Dallagnol et al., 2020)
- wheat (Guével et al., 2007)
- rice (Buck et al., 2008; Rezende et al., 2009)

Silicic acid may have limited absorption through the leaf in:

- soybeans (Rodrigues et al., 2009)
- beans (Rodrigues et al., 2010)
- tomatoes (Chien & Huang, 2022)
- strawberry (Xiao et al., 2022)

Limited absorption gives a layer of silica just beneath the leaf cuticle (Rodrigues et al., 2009). The basis for these conclusions comes from published research on potassium silicate sprays for disease prevention, and the research is summarized below.

Composition of potassium silicate sprays

The fate of potassium silicate (K_2SiO_3) aqueous sprays on the surface of the plant leaf depends on the chemical species in solution. The chemical species in solution depend on the concentration of potassium silicate and the pH of the solution (see Figure 1, below). When potassium silicate is dissolved in water, the solution is strongly alkaline—often about pH 11-12 (Certis, 2020). The fundamental silicate ion is a tetrahedron, with silicon at the center and oxygen at the corners (Knight & Kinrade, 2001). This is the monosilicate ion that predominates in dilute solutions. Only monosilicates can provide bioavailable silica to plants (Laane, 2018). As the solution concentration increases, the silicate ion polymerizes, forming at least 22 different shapes, including monomers, dimers, higher polymers, cyclic silicate ions, and other variations (Knight & Kinrade, 2001).

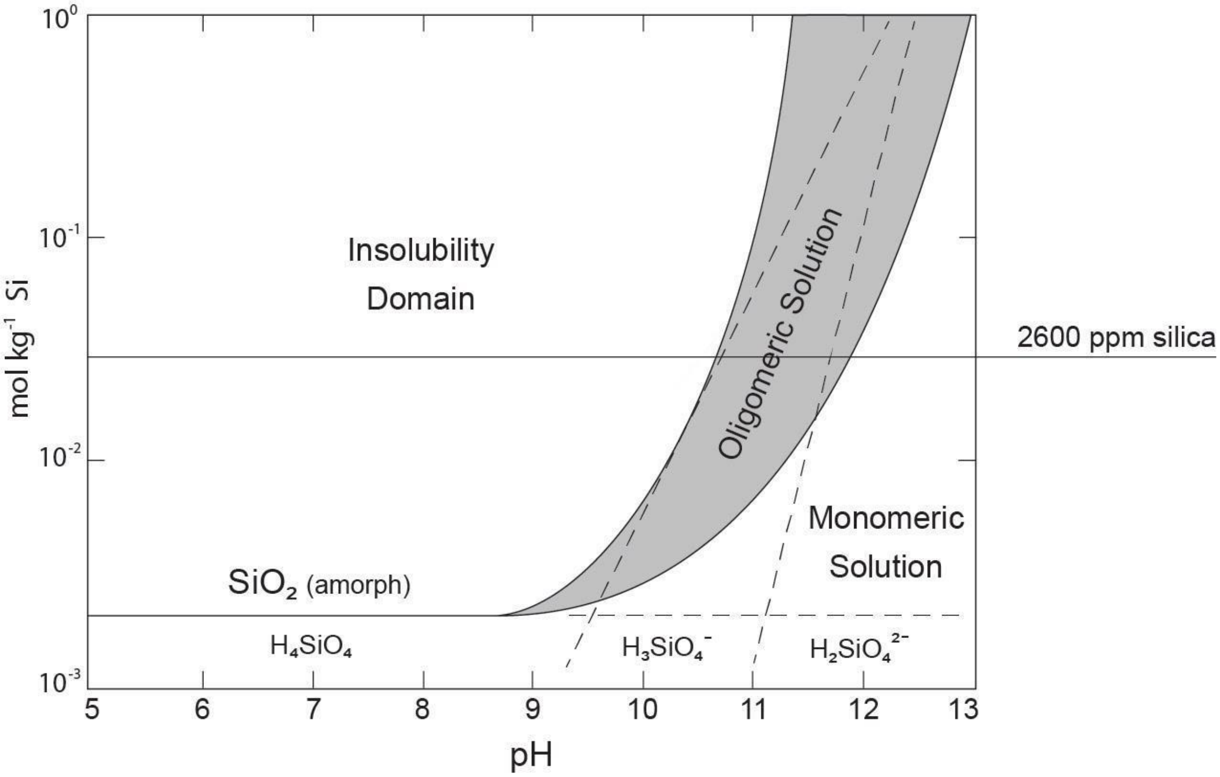

Figure 1: Above pH 9 silicic acid is mostly ionized and solutions contain potassium ions (not shown) and silicate ions (shown). Below pH 8 silicic acid is mostly undissociated and solutions contain soluble silicic acid and insoluble polymers of silicic acid dispersed in small nanoparticles. Drawing adapted from Knight and Kinrade, 2001.

In strongly alkaline solutions near a silica concentration of 100 ppm (1.7 X 10^{-3} moles/kg), the main components are potassium and monosilicate ions (Knight & Kinrade, 2001). Even in these dilute solutions, up to 6% of the silicate may be present as a dimer (Knight & Kinrade, 2001). When these complex solutions are sprayed onto a leaf, the leaf is covered with this ionic matrix. As the solution dries, the leaf is covered with a fine white powder containing potassium ions and various silicate ions. If the spray concentration is near 100 ppm of silica, the powder contains mostly potassium ions and monosilicate ions (Knight & Kinrade, 2001). When water is added, the powder quickly dissolves (PQ, 2006).

Acidic and neutral (pH 7) sprays are also available. If the end-user needs to reduce the pH, the manufacturer recommends pH values for the liquid formulation Sil-Matrix® of either pH 4-5 or pH 7-8 in dilutions between 0.25% to 1% (v/v), 650 to 2600 ppm silica. The manufacturer suggests using either citric or phosphoric acids (Certis, 2017; Certis, 2021). When adjusted and used, sprays at these pH values and concentrations contain silicic acid, polymers of silicic acid, and potassium salts of the acid used to acidify the alkaline formulation (Certis, 2017; Certis, 2021; Laane, 2018; Knight & Kinrade, 2001; Iler, 1979ab).

When an acid is added to an alkaline solution of potassium silicate, silicic acid (H_4SiO_4) is formed. Silicic acid in water at pH 7 has a low solubility of 100-130 ppm (Knight & Kinrade, 2001). Below pH 8, solutions predominantly contain undissociated silicic acid. Above pH 9 silicic acid is dissociated into H+ and $(H_3SiO_4)^{-1}$. At pH greater than 11, the species are 2H+ and $(H_2SiO_4)^{-2}$ (Chien & Huang, 2022).

In solutions below pH 9 with silica concentrations greater than 100-130 ppm, silicic acid starts to polymerize, forming small hydrated particles, in a solution phenomenon called a sol. The insoluble particles at first cannot be seen with the naked eye because "the growing aggregates contain the same concentration of silica and water as the surrounding sol regions" (Iler, 1979b, p. 176). Polymerization is complex and varies with conditions. At pH 4 to pH 5, polymerization is slow, particles are about 2-4 nm (Iler, 1979b, p. 175), and it takes a long time before the sol transitions into a gel of amorphous silica that precipitates from solution. According to Iler (1979b), "dilute solutions remain supersaturated with respect to amorphous silica for appreciable periods" (p. 177). A Certis fact sheet states that the dilute solutions used in commercial sprays at pH 4-5 are stable for four weeks (Certis, 2017).

At pH 6, polymerization is rapid, and the sol quickly transitions to an insoluble silica gel that precipitates (Iler, 1979b). The Certis fact sheet states pH 6 solutions are stable for less than 24 hours (Iler, 1979b; Certis, 2017).

At pH 7 or pH 8, the 5-10 nm polysilicic acid particles are negatively charged, repel each other, do not grow, and remain suspended in the sol (Iler, 1979b). Solutions at pH 7 and pH 8 are generally stable, and amorphous silica does not precipitate (Certis, 2017). These solutions are sprayed on leaves. As the water evaporates, the solution becomes more concentrated, and the sol transitions to a gel of insoluble amorphous silica (Knight & Kinrade, 2001). Dried solutions contain silicic acid, amorphous silica, and the salts of the acids used to neutralize the alkaline formulation (Knight & Kinrade, 2001; Iler, 1979ab, Certis, 2017).

Absorption in plants of aqueous foliar sprays

When potassium silicate is applied as a root drench, silicon is absorbed through plant roots in the form of soluble silicic acid (Laane, 2018; Liang et al., 2006). It is transported passively throughout the plant in the xylem transpiration stream. But some plant species have active transport or active rejection through genetically produced transporter molecules (Liang et al., 2006; Liang et al., 2015). With passive absorption, silicic acid is transported at the same rate as water. With active transport, silicic acid is transported faster than water, with exclusion, water is transported faster than silicic acid (Mitani & Ma, 2005). Plant species are classified as silica accumulators or excluders based on the dry weight concentration of silica found in the aboveground portion of the plant. Accumulators have >1%, intermediate forms 0.5% to 1.0%, and excluders <0.5% (Laane, 2018; Liang et al., 2006). For instance, corn and rice are active accumulators, and tomatoes and fava beans are excluders (Liang et al., 2006).

When soluble silicon is absorbed into the plant, systemic acquired resistance (SAR) is triggered (Agarwal et al., 1999; Fawe et al., 2001), and defensive proteins which serve as plant disease controls are produced (Liang et al., 2015; Dallagnol et al., 2015).

In contrast, aqueous foliar sprays are mostly not absorbed (see Table 1, below), but insoluble silica can accumulate on the surface or just beneath the leaf cuticle (Bowen et al., 1992; Menzies et al., 1992; Rodrigues et al., 2009). There can be limited absorption of silica through foliar sprays depending on the plant species (Rodrigues et al., 2010; Chien & Huang, 2022; Xiao et al., 2022). Because absorption is limited, foliar sprays generally do not produce systemic acquired resistance (Liang et al., 2015; Liang et al., 2005, Rodrigues et al., 2009; Guével et al., 2007; Dallagnol et al., 2015).

Table 1: Comparison of findings across multiple studies on the relative impact of aqueous potassium silicate foliar sprays on silica absorption and pest reduction.

Study	Type of spray (pH)	Concentration	Plant used	Evidence of absorption	Pest impact	Pest type
Liang et al. (2005)	Acidic (5.5)	10 mM (588 ppm silica)	Cucumber	None	Effective	Powdery mildew
Liang et al. (2005)	Acidic (5.5)	20 mM (1176 ppm silica)	Cucumber	None	Effective	Powdery mildew
Guével et al. (2007)	Acidic (5.8-6.0)	1.7 mM silica (100 ppm silica)	Wheat	None	Significant reduction	Powdery mildew
Bowen et al. (1992)	Neutral (7)	17 mM solution (1000 ppm silica)	Grapes	No absorption	70% reduction	Powdery mildew

Study	Type of spray (pH)	Concentration	Plant used	Evidence of absorption	Pest impact	Pest type
Buck et al. (2008)	Acidic (5.5)	0, 2, 4, 8 g/liter Si	Rice	No measured absorption	Up to 50% reduction	*Pyricularia oryzae*
Buck et al. (2008)	Alkaline (10.5)	0, 1, 2, 4, 8, and 16 g/l Si	Rice	No measured absorption	Up to 50% reduction	*Pyricularia oryzae*
Rezende et al. (2009)	Alkaline (10.2)	40 g/liter (about 10680 ppm silica)	Rice	No absorption	No significant effect	*Bipolaris oryzae*
Rodrigues et al. (2009)	Acidic (5.5)	10680-16000 ppm silica	Soy beans	Limited absorption	43% reduction	*Phakopsora pachyrhizi*
Rodrigues et al. (2009)	Alkaline (10.5)	10680-16000 ppm silica	Soy beans	Limited absorption	36% reduction	*Phakopsora pachyrhizi*
Rodrigues et al. (2010)	Acidic (5.5)	16,000 ppm silica	*Phaseolus vulgaris*	Silica concentration increased	30 – 42% reduction	*Pseudocercospora griseola*
Rodrigues et al. (2010)	Alkaline (10.5)	16,000 ppm silica	*Phaseolus vulgaris*	Silica concentration increased	30 – 42% reduction	*Pseudocercospora griseola*
Xiao et al. (2022)	---	75 ppm silica	Strawberries	Some absorption	Effective	Powdery mildew
Chien and Huang (2022)	Neutral (7)	100 ppm silica	Tomatoes	Silica content increased	Effective	*Xanthomonas sp.*
Chien and Huang (2022)	Alkaline (10)	100 ppm silica	Tomatoes	Silica content increased	36% more effective than pH 7	*Xanthomonas sp.*

Overview of related studies
As shown in Table 1, Liang et al. (2005) applied acidic potassium silicate sprays of 10 mM (588 ppm silica) and 20 mM (1176 ppm silica) adjusted to pH 5.5 with phosphoric acid to cucumber leaves for protection against powdery mildew caused by *Podosphaera xanthii*. Sprays were effective, but they found no indications of SAR, and believed the sprays were not absorbed.

Menzies et al. (1992) believed there was limited absorption of acidic sprays in cucumber. Sprays of 1000-2000 ppm silica applied to leaves continued to provide protection after sprays were washed off. Menzies et al., (1992) supplied evidence that disease suppressive effects were not due to the potassium phosphate salts produced when the alkaline potassium silicate was neutralized by phosphoric acid. Potassium phosphate foliar sprays are known to suppress powdery mildew (Reuveni et al., 1995; Deliopoulos, 2010). Menzies et al. (1992) believed that "the coating of potassium silicate crystals that form on the leaf surface after the sprays dry may act as a physical barrier to pathogen penetration of the epidermis" (p. 905).

Guével et al. (2007) applied 1.7 mM silica (100 ppm silica) as the commercial formulation Kasil 6 to protect wheat from powdery mildew caused by *Blumeria graminis*. The pH was adjusted to 5.8-6.0. Silica was absorbed through root application, but "foliar-treated plants accumulated very little Si" (Guével et al., 2007, p. 431). However, "application of foliar sprays caused a significant reduction of powdery mildew" (Guével et al., 2007, p. 432). Guével et al. (2007) believed that any effect of the foliar sprays on disease incidence were due to direct action on the pathogen, not through systemic acquired resistance (SAR).

Bowen et al. (1992) sprayed grape plants with a 17 mM solution (1000 ppm silica) of potassium silicate to treat powdery mildew caused by *Uncinula necator*. The solution was neutralized by adding phosphoric acid before being sprayed and was presumably at pH 7. At this pH, the solution contained about 100 ppm silicic acid, soluble phosphate salts, and most of the rest was insoluble amorphous silica (Knight & Kinrade, 2001). This spray reduced powdery mildew colonies by 67%. The sprays were not absorbed by the grape leaves, but "whitish spots of dried solution were observed on Si sprayed leaves" (Bowen et al., 1992, p. 910). X-ray mapping showed the spots contained silicon. They concluded that "thick potassium silicate deposits that coated a significant portion of the leaf cuticle may have prevented penetration by germinating conidia," (Bowen et al., 1992, p. 911).

Buck et al. (2008) sprayed rice plants with potassium silicate solutions containing 0, 1, 2, 4, 8, and 16 g/liter Si at pH 10.5 and 0, 2, 4, and 8 g/liter Si at pH 5.5. The silica source was a potassium silicate solution containing 26% silica. The solution was diluted to the silica concentrations used in the sprays. Sprays ranged from 0 to about 16,000 ppm silica. As the silica concentrations increased, incidence of rice blast caused by *Pyricularia oryzae* decreased. Incidence was reduced in the best case from 51% to 26%. There was no measurable absorption of silica regardless of pH. However, very small increases in absorption might not have been detected. Effects on rice blast were independent of pH.

Rezende et al. (2009) applied root solutions of calcium silicate and a foliar spray of potassium silicate to rice plants to protect against rice brown spot caused by *Bipolaris oryzae*. The calcium silicate reduced disease incidence from 60% to 40% at 168 hrs after inoculation with *B. oryzae*. Potassium silicate treatments had no significant effect. The tops of leaves were sprayed, and silica was detected only on the top of leaves. Potassium silicate was applied as the formulation Fertisil at pH 10.2 and 40 g/liter (about 10,680 ppm silica). In vitro experiments showed that potassium silicate could not prevent germination of conidia.

Rodrigues et al. (2009) applied foliar potassium silicate sprays (about 10,680-16,000 ppm silica max) to prevent soybean rust caused by *Phakopsora pachyrhizi*. They found there was limited absorption by soybean plant leaves. A layer of silica accumulated just beneath the plant cuticle giving the leaf a silica concentration near 1% dry weight (see below *Comparison of Acidic and Alkaline Sprays*).

Rodrigues et al. (2010) treated beans, *Phaseolus vulgaris*, with potassium silicate sprays for angular leaf spot caused by *Pseudocercospora griseola*. They found that silica concentrations in bean leaves increased by about 57-58% when sprayed by solutions containing 60 g/liter potassium silicate. Solutions contained 26.7% silica or about 16 g silica/liter (16,000 ppm silica). Leaf concentrations with the pH 5.5 spray were 16.1 g/kg silica dry weight and with the pH 10.5 spray, 14.9 g/kg SiO_2 dry weight. There was a 30-42% decrease in disease, and a 30-43% increase in yields with the 60 g/liter (16,000 ppm silica) treatment.

Xiao et al. (2022) applied foliar sprays and root drenches to strawberry plants. Concentration of the sprays and drenches were 75 mg/liter of silica (75 ppm silica). The pH was not specified. Both drenches and sprays increased the silica content of the plants. Direct foliar sprays were the most effective method of protecting the plants against powdery mildew caused by *Podosphaera aphonis*.

Chien and Huang (2022) applied potassium silicate foliar sprays and root drenches to protect tomatoes from bacterial spot caused by *Xanthomonas* sp. Foliar sprays of about 100 ppm silica were more effective than root absorption from growth media. Foliar sprays increased silica content in the plant by 151% compared to growth media application through the root system. Chien and Huang (2022) believed that protection of tomato from bacterial spot caused by *Xanthomonas* sp. was due either to formation of a potassium silicate barrier, a change in osmotic potential of the leaf, or both.

Depending on the plant species, silicate foliar sprays are either not absorbed, or show limited absorption. Limited absorption includes passive accumulation just beneath the leaf cuticle. Tomatoes (Chien & Huang, 2022), beans (Rodrigues et al., 2010), soybeans (Rodrigues et al., 2010), and strawberries (Xiao et al. 2022) show limited absorption.

In plants where foliar sprays of silica have limited absorption, a barrier of silica occurs on the leaf surface or just beneath the leaf cuticle. Where silica is not absorbed, it forms a barrier on the leaf surface. For instance, Rodrigues et al. (2009) found dried solutions of powdery potassium silicate were often observed on the leaf surfaces of soybean plants sprayed with the substance at 40 g/liter potassium silicate (about 10680 ppm silica), and especially with solutions at pH 10.5. A thick layer of silica formed just beneath the leaf cuticle.

Comparison of Acidic and Alkaline Sprays

Whether acidic or alkaline sprays are more effective depends on the plant species and spray concentrations. Acidic sprays at pH 5.5 contain mostly undissociated silicic acid, and alkaline sprays at pH 10 contain mostly ionized silicic acid.

Rodrigues et al. (2009) found acidic sprays were more effective for soybeans. In several experiments, they applied potassium silicate at either pH 5.5 or pH 10 to protect soybeans against soybean rust, *Phakopsora pachyrhizi*. In one experiment, at the highest concentration of the acidic spray, 40 g/liter potassium silicate (about 10680 ppm silica), disease incidence was 70% less than controls. The acidic spray was generally more effective than the alkaline spray in preventing disease. In another experiment, acidic sprays reduced disease incidence by 43% and alkaline sprays reduced disease by 36%. Silica concentration in the leaves were similar with either acidic or alkaline sprays (0.75% greenhouse, 1.1% field). A thick layer of silica formed beneath the leaf cuticle.

Chien and Huang (2022) found alkaline sprays were more effective for tomato. They applied potassium silicate foliar sprays (100 mg Si/liter, 79.4 mg K/liter) at pH 7 and pH 10 to protect tomatoes from bacterial spot caused by *Xanthomonas* sp. The pH 10 spray was more effective than the pH 7 spray, reducing disease severity and the progress of the disease. The pH 10 spray reduced disease severity by about 36% more compared to the pH 7 spray. Foliar sprays were more effective than root absorption from growth media. Foliar sprays increased silica content in the plant by 151% compared to growth media application through the root system. Tomato is an active excluder when silica is applied through the root system; the same mechanism is not present in leaves (Liang et al., 2006)

In contrast to the two previous studies, Buck et al. (2008) found rice protection against rice blast caused by *Pyricularia oryzae* with sprays of potassium silicate was independent of pH.

Mechanism of Leaf Sprays

When soluble silicon is applied through plant roots, it is absorbed only as silicic acid and travels through the xylem to the leaves either passively or through active transport. As it travels through the plant, insoluble silica is deposited in xylem tubes and in leaves. Plants are protected from pathogens by systemic acquired resistance (SAR) and by barriers of silica (Liang et al., 2015; Cherif et al., 1992; Fawe et al., 2001; Epstein, 1999; Mitani & Ma, 2005).

When silica is applied through foliar sprays, there is limited absorption through the leaves. Since there is little absorption, there is no systemic acquired resistance (Liang et al., 2015; Dallagnol et al., 2015; Rodrigues et al., 2009; Guével et al., 2007). Effects are not due to pH or ionic strength. Surface tension of the leaf is not a factor. Both acidic sprays and alkaline sprays can be effective. Effects are due either to a silicate barrier or to dehydration of the pathogen due to the osmotic effects of the applied solutions (Dallagnol et al., 2020; Chien & Huang, 2022; Rodrigues et al., 2009).

Generally, higher concentrations are needed to produce effects with foliar sprays than with hydroponic root drenches. Menzies et al. (1992) applied acidic sprays at pH 5.5 to plant leaves for control of powdery mildew on cucumber, muskmelon and zucchini. Foliar sprays of 17 mM (1000 ppm silica) or 34 mM (2000 ppm silica) were as effective as 1.7 mM (100 ppm silica) applied as nutrient solution through the roots. Though greater concentration was needed to produce the same effect, foliar sprays were effective for a longer time (168 hrs) compared to root application (24 hrs). Acidic sprays were prepared by dissolving potassium silicate in water, and adjusting the pH to 5.5 by adding phosphoric acid. The spray likely contained silicic acid, polymerized silicic acid, and a mixture of potassium phosphate salts.

Dissolution and ground re-application

When it rains, soluble species such as potassium ions, silicate ions, and dried silicic acid on the leaf surface wash off the leaves (PQ, 2006; PQ, 2002). Insoluble amorphous silica is probably dislodged by rain water and falls to the soil. The buffering action of soil finally results in the conversion of potassium silicate sprays to silicic acid and amorphous silica (USDA, 2014).

2. What is its effect on the plant leaf microbial community?

Leaf surfaces are inhospitable places for microbes (Knoll & Schreiber, 1998). Leaves are covered with a thin cuticle composed of the lipid polymer cutin and cuticular waxes. This hydrophobic layer prevents loss of water and nutrients from the leaf interior. This results in reduced water and nutrient availability on the leaf surface; factors that can limit microbial growth on the phylloplane (Knoll & Schreiber, 1998).

Microbial inhabitants of the above-ground surfaces of plants include bacteria, fungi, yeasts, protozoa and even nematodes. But "bacteria are by far the most abundant inhabitants of the phyllosphere" (Lindow & Brandl, 2003, p. 1875). Aerobic gram negative bacteria such as *Pseudomonas* sp. and *Erwinia* sp. predominate. Proteobacteria, Bacteroidetes, and Actinobacteria are common (Moitinho et al., 2020). Solitary bacteria are frequent, but water and nutrients determine colonization patterns. Nutrients and water are more common near stomata, and rough areas where water can accumulate, such as near leaf veins. Small amounts of nutrients such as sugars leach directly through the cuticle (Lindow & Brandl, 2003).

The result is that microbial distribution on a leaf is patchy, and 30-80% of the bacteria on a leaf occur in colonies of mixed species (Lindow & Brandl, 2003). The bacteria work together to prevent desiccation. For example, gram negative bacteria have polysaccharide coverings that prevent water loss. *Pseudomonas* secretes the surfactant tolasin that increases leaf wettability. The bacterial community also secretes a layer of polysaccharides, a slime layer that helps retain water (Lindow & Brandl, 2003).

There are few published studies on the impact of aqueous potassium silicate on the leaf microbial community. There is limited knowledge about the interaction of potassium silicate spray with general leaf microbials, but there are a number of publications that show how potassium silicate interferes with the growth of foliar plant pathogens. Potassium silicate sprays inhibit growth of:

- bacterial spot caused by *Xanthomonas* sp. (Chien & Huang, 2022)
- grape powdery mildew caused by *Uncinula necator* (Bowen et al., 1992)
- powdery mildew of melon, *Podosphaera* sp. (Dallagnol et al., 2020),
- coffee leaf rust, *Hemileia vastatrix* (Carré-Missio et al., 2014)
- Asian soybean rust, *Phakopsora* sp. (Rodrigues et al., 2009)
- powdery mildew of wheat, *Blumeria* sp. (Guével et al., 2007)
- other pathogens (Laane, 2018; Liang et al., 2015; Deliopoulos et al., 2010)

Potassium silicate sprays are generally more effective for fungal pathogens than for bacterial pathogens (Liang et al., 2015; Laane, 2018). Bekker et al. (2009) grew 11 fungal pathogens in growth media amended with alkaline potassium silicate solutions. Over an eight-day period, effects were variable, with *Phytophthora* affected most and *Fusarium* affected least. Growth of all the pathogens was completely inhibited with 40 ml of potassium silicate solution containing 20.7% silica per liter of agar.

Researchers believe that the foliar sprays protect through silicate barriers produced on leaf surfaces and "osmotic effects of the silicate applied" (Liang et al., 2005; Guével et al., 2007). Osmotic effects are basically desiccation of the pathogen.

When sprays of potassium silicate dry on a leaf, the strongly alkaline residue is a fine powder of crystalline potassium silicate. When acidic sprays are used, the residue is silicic acid, amorphous silica, and various salts (Knight & Kinrade, 2001). Amorphous silica is a known desiccant, and crystalline powders can also be desiccants (Ebeling 1971). Due to the properties of potassium silicate, one potential result of using the substance is a change in the microbial leaf community structure. For example, water is critical for microbial growth (Knoll & Schreiber, 1998), and silicate foliar sprays cause microbial desiccation (Liang et al. 2005; Guével et al., 2007). Silicates also preferentially attack fungi and fungal pathogens (Liang et al., 2015; Laane, 2018). It is possible that these factors could cause a relative increase in bacteria that are protected against desiccation, and a reduction in fungal populations that do not have desiccant protection.

The effects of soil silicate applications on soil microbials have been studied, and the general results may be similar for leaf microbials (Zhou et al., 2018). Application of 2 mM sodium silicate as a soil drench in cucumber cultivation increased the abundance of bacteria, but decreased the abundance and diversity of fungi. The silicate treatment increased the populations of beneficial soil microbes and decreased pathogen populations (Zhou et al., 2018).

Soil drenches of 0.2 to 0.4% potassium silicate significantly increased the numbers of soil bacteria and actinomyces, and significantly reduced numbers of fungi (Khalifa et al., 2017). The treatment increased enzyme activity in the soil and induced physiological changes in onions, including resistance to white rot disease caused by the fungus *Sclerotium cepivorum* (Khalifa et al., 2017).

Silicate foliar sprays can also affect soil microbes. Foliar applications of silica nanoparticles to pakchoy, *Brassica chinensis*, changed the metabolic profile of soil microbes (Tian et al., 2020). There were increases in sugars, organic acids and fatty acids, and decreases in amino acids. The soil microbe community structure was not changed, but there were population increases in bacteria and fungi involved in the carbon and nitrogen cycles (Tian et al., 2020).

3. When sprayed under low humidity conditions, can aqueous potassium silicate crystallize in the air and present an inhalation hazard?

This question has two parts: can the substance crystallize in air under low humidity conditions, and can it present an inhalation hazard? In order to address these questions, we will use a representative formulation (Sil-Matrix®), as an example. Label application of the commercial product Sil-Matrix® is not likely to present an inhalation hazard (see discussion below). Air crystallization of alkaline solutions sprayed at maximum label rates is unlikely since spray solutions are dilute, and well below the solubility threshold of silica (see below).

The product label for Sil-Matrix® instructs end-users on how to dilute the formulation to 0.25% and 1%, but not how to acidify the product (Certis, 2021). A supplementary fact sheet suggests that end-users first dilute the product, and then slowly add either citric or phosphoric acid (Certis, 2017). Acidic or neutral solutions of Sil-Matrix® at silica concentrations greater than 100-130 ppm contain hydrated nanoparticles of polymerized silicic acid in stable sols. For transition to an insoluble gel in air, particles would have to aggregate. It is likely that they do not have time to aggregate during the spray process, since aggregation does not occur even over a period of weeks in solution.

The smallest spray droplet is 1500 times the size of the largest suspended nanoparticle (see calculations below). The weight of water in the spray droplets is nearly 400 times that of the silica. A 400-fold loss of water would be needed to produce solidification of silica in air. Solidification of these sprays in air is unlikely (see calculations below).

Sil-Matrix® Sprays

Sil-Matrix® is a commonly used EPA registered potassium silicate product, identified in the 2006 National Organic Program (NOP) petition (PQ, 2006).

According to the petition, "potassium silicate dust and spray mist are considered irritating to the respiratory tract" (PQ, 2006). The 2006 MSDS for the product Sil-Matrix® states, "use a NIOSH-approved dust and mist respirator where spray mist occurs" (PQ, 2006, p. 75). Personal protection included long sleeved shirt, long pants, shoes and socks. Re-entry into treated areas had a 4-hour restriction. Early entry required chemical goggles and chemical resistant gloves (PQ, 2006). The original label and MSDS considered Sil-Matrix® a possible inhalation hazard.

Certis Corporation applied for a new label that was issued by the EPA on October 23, 2019 (USEPA, 2019). The name of the product was Sil-Matrix LC. It contained the same concentrations as the 2006 label, 29% potassium silicate (CAS 1312-76-1) and 71% water. Directions for use include diluting with water to concentrations ranging from 0.25% to 1% (v/v), 650 to 2600 ppm silica. The new label does not require the use of a NIOSH-approved dust and mist respirator (USEPA, 2019). Under "Respiratory Protection," the 2020 SDS states, "None required. Ensure ventilation is adequate" (Certis, 2020, p. 4). But also "mist is irritating to the respiratory tract" (Certis, 2020). The 2021 label requires personal protective equipment that includes "long sleeved shirt and long pants, socks and shoes, chemical resistant gloves, goggles or face shield when handling undiluted concentrate" (Certis, 2021). Respiratory protection is not required, indicating that the EPA did not consider this formulation of Sil-Matrix® to be an inhalation risk.

The maximum application rate of Sil-Matrix is 7.5 lbs ai/acre (Certis, 2021). The label maximum is 3405 g potassium silicate/acre or 0.841 g/m2.

To get the approximate maximum air density of the sprays, consider a box with a vertical dimension of either 5 m or 2 m. If the spray were spread uniformly through these volumes, a box 5 m tall (5 m^3 box) gives 168 mg/m^3, and a box 2 m tall (2 m^3 box) gives 420 mg/m^3. These are densities of 0.168 mg/liter and 0.420 mg/liter. From the SDS for Sil-Matrix, toxic inhalation exposure levels for rats are greater than 2.06 mg/liter (Certis, 2020). Maximum exposures from Sil-Matrix sprays range from 5 to 12 times less than toxic inhalation exposure levels. Based on these calculations, maximum exposures are not likely to present an inhalation hazard.

Likelihood of Air Crystallization

Crystallization in air would be most likely near the silica solubility limit. The silica solubility limit is the maximum concentration of silica present in solution at a given pH and temperature (Alexander et al., 1954). Loss of water from sprays of these saturated solutions could lead to solidification of silica in air. First consider alkaline sprays. The solubility of silica in water at pH 11 is 0.5% by weight according to Alexander et al. (1954), and this amount is about 5000 ppm. Knight and Kinrade (2001) show the solubility limit at pH 11 is about 6000 ppm (0.1 moles/kg or 6 g/kg SiO2). The greatest concentration of Sil-Matrix spray allowed by the label is 1%, and this is about 2600 ppm silica (Certis, 2022). The maximum spray concentration of silica is 1.9 to 2.3 times less than the solubility limit, and crystallization in air is unlikely.

When alkaline solutions of potassium silicate are acidified, undissociated silicic acid is formed. At pH 7, the solubility limit for silicic acid is about 100-130 ppm (Knight & Kinrade, 2001). Excess silicic acid is formed and polymerizes, giving insoluble polysilicic acid. At pH 7, about 95% of the silica in these sprays is composed of polysilicic acid particles, 5-10 nm in diameter (Iler, 1979b, p. 175), suspended as a sol. In acidic spray solutions, particles are even smaller, 2-4 nm (Knight & Kinrade, 2001; Iler, 1979b). Over a period of weeks, these small particles do not aggregate in the liquid sol, and do not have time to aggregate in the spray (Iler, 1979ab; Certis, 2017). Transition from a sol to an insoluble gel during the spray process is unlikely (Certis, 2022).

Another unlikely possibility is solidification in the aerosol spray because aerosol particle size is small relative to the suspended silica nanoparticles. The silica nanoparticles in solution are 2-10 nanometers in size depending on pH.[1] Commercial pest control sprayers applying water-based solutions produce droplets ranging from 15 to 90 microns in diameter (Hoffmann et al., 2007).[2] The largest nanoparticle is about 10 x 10^{-9} meters, and the smallest spray droplet is 15 x 10^{-6} meters. The smallest water droplets are 1500 times the size of the largest nanoparticle. The largest droplets are about 9000 times the size of the largest nanoparticle. The nanoparticles are well hydrated, and solidification in air is unlikely.

Solidification from Water Loss

Could there be enough water loss from the spray droplets to form solid amorphous silica in the air? Calculations based on known factors all indicate that this is unlikely. The volume of the smallest droplet (15 microns) is 38.1 x 10^{-11} liters. The weight of a water droplet this size is 38.1 x 10^{-8} grams.

The most concentrated spray allowed by the Sil-Matrix label is 2600 ppm of silica (Certis, 2021). Straightforward calculations show the weight of silica in a 15 micron droplet with silica concentration 2600 ppm is 99 x 10^{-11} g.

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[1] A nanometer is one-billionth of a meter (10^{-9} meters).

[2] A micron is one-millionth of a meter (10^{-6} meters).

The ratio of the weight of water to silica is 38.1 x 10^{-8} g divided by 99 x 10^{-11} g. This amount is 0.384 x 10^{3}. The weight of water in a droplet is about 384 times the weight of silica. In the most concentrated spray permitted by the label, there would have to be a nearly 400-fold water loss from the spray droplets before solidification in air would occur.

Estimates of evaporation losses from aerosol sprays vary widely. For sprinkler irrigation, 10% to 20% evaporative losses are most common (Edling, 1985; Kohl et al., 1987; Uddin et al., 2010). One publication found 3.7 to 8.6% losses for 300 micron droplets (Lorenzini, 2004; Uddin et al., 2010). Kincaid and Langley (1989) found droplet evaporation losses in sprinkler irrigation are usually less than 2-3% even under conditions of high temperature and low relative humidity (Uddin et al., 2010). In the most extreme case, one study showed that evaporation losses at high temperature and low humidity in Arizona could range from 35-45% (Frost & Schwalen, 1955).

Studies of respiratory aerosols with droplet sizes less than 100 microns show that as relative humidity drops from 50% to 30%, droplet sizes shrink by 10-40% (Bozic & Kandal, 2021, p.11).

Potassium silicate spray droplets, then, would likely shrink no more than 50%, even at higher temperatures and lower humidities. Spray droplets would still be 750 to 4500 times larger than the largest silica nanoparticles, and droplets would have about 200 times more water than silica. Solidification in air is unlikely, and in any event, the maximum silica exposure in these sprays is 5-12 times less than the toxic inhalation threshold. For current label applications of Sil-Matrix, regulators do not require applicators to have respiratory protection.

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