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Document Cover Sheet
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Document Type:

☐ **National List Petition or Petition Update**

A petition is a request to amend the USDA National Organic Program's National List of Allowed and Prohibited Substances (National List).

Any person may submit a petition to have a substance evaluated by the National Organic Standards Board (7 CFR 205.607(a)).

Guidelines for submitting a petition are available in the NOP Handbook as NOP 3011, National List Petition Guidelines.

Petitions are posted for the public on the NOP website for Petitioned Substances.

☒ **Technical Report**

A technical report is developed in response to a petition to amend the National List. Reports are also developed to assist in the review of substances that are already on the National List.

Technical reports are completed by third-party contractors and are available to the public on the NOP website for Petitioned Substances.

Contractor names and dates completed are available in the report.

Sulfurous Acid

Crops

Focus questions requested by the National Organic Standards Board (NOSB)

To support the sunset review of sulfurous acid used in organic crop production, the National Organic Standards Board (NOSB) requested a response to a single focus question: ***what alternatives to sulfurous acid exist that could be used in organic crop production?*** We have responded to that request below. Additionally, we have provided a basic description of how alkaline soils come about in the first place, and some of their characteristics.

Background:

Soil pH affects plant and microbial growth (Inamuddin et al., 2021). Some crops such as potato, sweet potato, and parsley grow better at a lower pH (5-6), while alfalfa, coconut, and dates prefer more neutral to alkaline pH (6.5-8.0) (McCall, 1980). The optimal pH range is 6.0–6.8 for most crops, although there are many plants that are outliers on either side of this range (Inamuddin et al., 2021). At the optimal pH range, plant nutrients are soluble and available to plants (Inamuddin et al., 2021). The high pH of alkaline soils can reduce the solubility of micronutrients like iron, zinc, boron, and manganese, and can interfere with the uptake of phosphorous (Brautigan et al., 2014; Luo et al., 2021).

The pH also affects the physical properties of soil. The term "hydraulic conductivity" (K_s) represents the ease with which water can pass through or into soil (or rock). Increasing pH decreases the conductivity (K_s) of a given soil (Ali et al., 2019). Increasing pH from 6 to 9 also increases soil degradation processes such as dispersion (breakdown of larger soil particles into smaller ones), leaving soil vulnerable to erosion (Ali et al., 2019). Sodium in particular can expand clay particles, causing them to break apart and, over time, fill pores in the soil structure. The soil then becomes too dense and compacted for plant roots to penetrate and utilize efficiently for nutrients, water, gas exchange, etc. (Franzen & Gerwing, 2006; Nouri et al., 2017). High soil pH can also increase the dissolution of organic matter in the soil, which can lead to higher rates of loss (Tavakkoli et al., 2022), presumably from erosion. For this and other reasons, organic matter is often limited in alkaline soils (Inamuddin et al., 2021; Tavakkoli et al., 2022).

One way to combat the effects of alkalinity on soil and nutrient properties is to increase the amount of organic carbon and bioavailable nutrients—essentially, managing the effects of alkalinity without targeting the alkalinity issue directly. However, as discussed below, increasing organic matter can in some cases also lower soil pH.

A variety of factors determine soil pH, including rainfall, the weathering of different types of rocks, atmospheric pollution, and the use of different types of fertilizers and soil amendments (Inamuddin et al., 2021). One of the fundamental relationships governing soil pH is the balance of rainfall and evaporation. For example, when average rainfall exceeds the annual evapotranspiration, soil pH strongly tends to be acidic (Slessarev et al., 2016). Alkaline soils on the other hand follow the opposite trend. Globally, about one-third of soils are alkaline (Brautigan et al., 2014).

An additional factor involved in agricultural soil pH is irrigation water quality. In practice, all irrigation water contains dissolved ions which can potentially affect the soil environment (Sposito, 2008). Due to scarcity of higher-quality water sources (i.e., higher purity), producers are using marginal or low-quality water containing high levels of sodium and other "base cations" more frequently (Ali et al., 2019). This is especially true in arid and semiarid regions (Ali et al., 2019). Furthermore, in these regions, water tends to be used more efficiently (less is used), due to the need to conserve water (Machado & Serralheiro, 2017). This means that ions that contribute to alkalinity are even less likely to be leached out of the soil (with evapotranspiration exceeding rainfall).

Base cations are of particular interest in relation to the formation of alkaline soils. Base cations include Na+, K+, Ca+ or Mg++, and are able to form carbonates and alkaline hydroxides (bases) which can increase the soil pH (Conklin & Vitha, 2014; Brautigan et al., 2014). Because of this relationship between base cations and pH, saline soils (those with significant amounts of soluble salts), sodic soils (those with a high level of exchangeable sodium), and calcareous soils (soils containing free inorganic calcium, or "lime") will often have an alkaline pH (i.e., greater than 7) (Sibbett, 1995). The manner in which these cations create basic conditions is as follows (Inamuddin et al., 2021):

$$Na_2CO_3 + H_2O \rightarrow 2Na^+ + 2OH^- + H_2CO_3$$

and/or:

$$CaCO_3 + 2H_2O \rightarrow Ca^{2+} + 2OH^- + H_2CO_3$$

Sodium carbonate has a water solubility of 215 g/L at 20° C (TNO Chemistry, 2002). Calcium carbonate is much less soluble, with a water solubility of around 6.8 mg/L at 25° C (Larson et al., 1973). Because of this difference in solubility, sodium carbonate can more easily create alkaline conditions—the molecules break apart according to the equations above. As seen later with gypsum, exchanging calcium for sodium in soils can lower the pH.

Conversely, as soils become more acidic, base cations become soluble and leach from the soil (NRCS, 2011). Soil in humid regions is typically more acidic than in arid regions because rainfall washes off base cations from soil particles, which are replaced by H+ ions within the rainwater (Inamuddin et al., 2021).

Producers using soil with a pH outside of the optimal range for their respective crops sometimes use inputs to make the soil more acidic or alkaline. Calcium carbonate rocks and their derivatives such as calcium hydroxide and calcium oxide are used to "lime" or raise the pH of agricultural land that is too acidic (Crozier & Hardy, 2018). In contrast, the University of Wisconsin-Madison recommends using aluminum sulfate to decrease soil pH prior to planting acid-loving blueberries (Marsden, 2007).[1] With that said, producers do not always need to lower soil pH to a neutral or lower level in order to successfully grow crops (Brautigan et al., 2014). Furthermore, soil pH can be highly variable within any given field. In one study, researchers sampled a number of fields using a grid pattern (Logsdon et al., 2008). They found that in 40% of the fields sampled, variations within the field were 2.0 pH units. Within 18% of the fields sampled, they found differences of over 2.5 pH units.

The behavior of carbonates in soil is important to understand because it affects how difficult it is to change pH at different ranges. Above a pH of around 8, carbonate minerals dissolve slowly, and therefore offer very little capacity to buffer acids used to change pH (Brautigan et al., 2014). When soils have a pH above 8, acidifiers are more effective at reducing pH until around 8. Below this point, carbonate minerals dissolve more quickly, and buffer further pH change. In highly alkaline soils, it may be more cost effective to bring soil pH down to this point (pH 8 or thereabouts), and then address any outstanding growth problems associated with high pH (such as specific nutrient deficiencies) in other ways —such as planting site-appropriate crops, or using foliar or chelated micronutrients (Brautigan et al., 2014).

Sulfurous acid is an acidifying agent for soil and water, neutralizing alkaline materials such as carbonates and bicarbonates (Gong, 2008; NOP, 2014). For a thorough review of sulfurous acid (the substance under review), we recommend reading the 2014 Technical Report. The original petitioner (Gong) of the substance stated that sulfurous acid:

- Is safe to handle, even in concentrated form.
- Is environmentally safe, when used properly.
- Contributes bisulfate ions, which help to keep irrigation systems clean, due to their biocidal properties.
- Is cost effective, relative to its acidifying power.

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[1] Aluminum sulfate is a synthetic substance that is not allowed for use in organic crop production.

The following sections describe the few materials and strategies commonly used to adjust soil pH in organic crop production. All of these materials and strategies have limitations. For example, acids (like those produced from sulfur or organic/pyroligneous acids) can be neutralized by buffers (Brautigan et al., 2014; Qadir et al., 2005). Competitive cationic substances (such as gypsum) lose effectiveness in reducing alkalinity at a certain pH and in certain soil types (as can acids) due to soil chemistry (Franzen & Gerwing, 2006). Organic matter (especially compost) can improve soil so that other strategies are more effective, and organic matter can in some cases be beneficial for lowering pH on its own (Leogrande & Vitti, 2019). Phytoremediation (use of plants to rehabilitate soil) can also help lower levels of alkaline cations, like sodium, which are problematic in some alkaline soils, but this practice requires careful management.

The use of high-quality water (or use practices that improve water quality) so that secondary salinity (salinity developed due to human causes, as opposed to soil parent materials) does not develop in soils and contribute to alkalinity in the first place is another method for managing soil pH. This may not always be practical, however.

In general, lowering pH is a slow process (Vossen, n.d.). Most of the strategies described here to lower pH are dependent on the specific soil chemistry at the given location. Because of this difficult reality, producers most likely need multiple strategies to address alkaline soils. Due to the chemistry of alkaline soils described throughout this report, it is challenging (and expensive) to lower the pH below 8.5–8.0, even in good circumstances. Soils that are naturally high in carbonates may be difficult to maintain at a lower pH, because the parent material for the soil will continue to weather and produce more carbonate, buffering any attempts to change the pH over the long term (Extension Foundation & Cooperative Extension, 2019). For each unit of calcium carbonate in soil, it would take an equal amount of acid to neutralize it. At one percent calcite, a one-acre field, 12 inches deep would contain around 40,000 pounds of carbonate (Cardon, n.d.). Soils in Utah, for example, contain between 15–40% calcium carbonate, making acidification on any scale impractical (Cardon, n.d.). In many cases, other strategies may need to be employed, such as treating micronutrient deficiencies that result from high soil pH and growing tolerant crops.

1. What alternatives to sulfurous acid exist that could be used in organic crop production?

Elemental sulfur and derivatives

While elemental sulfur is used to make sulfurous acid, it is not the same material. It is listed separately as a plant or soil amendment at 7 CFR 205.601(j). Elemental sulfur is a commonly referenced material used for lowering soil pH (Logsdon et al., 2008; Sibbett, 1995; Vossen, n.d.; Extension Foundation & Cooperative Extension, 2019). For example, producers prefer a pH of 6.5–7.0 for growing pecans (Sibbett, 1995). According to older literature, elemental sulfur (allowed at § 205.601(j)(2)) is the most common acidifying amendment used by pecan growers to reduce the pH of alkaline calcareous soils, which often exceed a pH of 8. Over time, the applied sulfur is oxidized to form sulfuric acid, which acidifies the soil. The time necessary for doing this depends on (Sibbett, 1995):

- sulfur particle size (smaller is faster)
- temperature (warmer is faster)
- moisture (wetter is faster, but not to the point of being waterlogged)

Once elemental sulfur is applied, *Thiobacillus* bacteria species begin to metabolize it (Sibbett, 1995). These bacteria metabolize it most quickly at temperatures around 29 °C (84 °F), and only slowly at 21 °C (70 °F). They also do well when soil moisture is at field capacity, but not waterlogged. When sulfur is ground to <0.125 mm and thoroughly mixed into the soil, bacteria can convert it to sulfuric acid within one to two months under ideal conditions. Increasing the coarseness of the sulfur, or decreasing temperature, slows down the conversion and acidification process (Sibbett, 1995).

The amount of sulfur needed to change soil pH is large—on the order of hundreds to thousands of pounds per acre (see Table 1). Furthermore, inorganic calcium (lime) found in many soils can neutralize sulfuric acid, forming gypsum (calcium sulfate, $CaSO_4 \bullet 2H_2O$), carbon dioxide, and water (Sibbett, 1995; Province of Manitoba, n.d.). This means that, in calcareous and other soils containing inorganic calcium, producers must apply larger amounts of elemental sulfur for the same change in soil pH if calcium were not present. In some cases, it may not be reasonable to acidify alkaline soils because of this (Province of Manitoba, n.d.).

Sulfur is relatively inexpensive, though prices are volatile. Between 2014 and 2021, the price has fluctuated dramatically between $24.4 per metric ton in 2020 (low), to $90 per metric ton in 2021, with other years in that range somewhere in between (Fernández, 2022). Sulfur and other acids can be especially useful when soils are not high in sodium (sodic). These types of soils usually can't be effectively treated with other materials like gypsum. Furthermore, gypsum itself can be helpful in some types of soil for lowering pH above 8.4, especially when sufficient water can be used for leaching liberated cations (see the following section for further discussion of gypsum) (Vossen, n.d.).

Table 1: Elemental S (95%) needed to increase acidity of a 0.15–m layer of carbonate-free soil. Adapted from Sibbett, 1995

Desired pH change	Sand	Loam	Clay
	(kg/hectare, equivalent to ~0.892 pounds/acre)		
8.5 to 6.5	2287	2857	3426
8.0 to 6.5	1368	1707	2288
7.5 to 6.5	569	919	1149
7.0 to 6.5	109	164	339

Other sulfur-based acidifying agents are available, but they are synthetic and not compliant with the National Organic Program (NOP) regulations.

- Sulfuric acid. Used in some locales by injecting it in the fall into drip irrigation (Sibbett, 1995).
- Lime-sulfur liquid (calcium polysulfide and calcium thiosulfate). It is produced by reacting calcium hydroxide with elemental sulfur (Sibbett, 1995). Lime sulfur is allowed for some uses in organic crop production (i.e., as a plant disease control and as an insecticide), but not as a soil amendment.

Elemental sulfur is a traditional material used in organic crop production (OMRI, 2022).

Gypsum

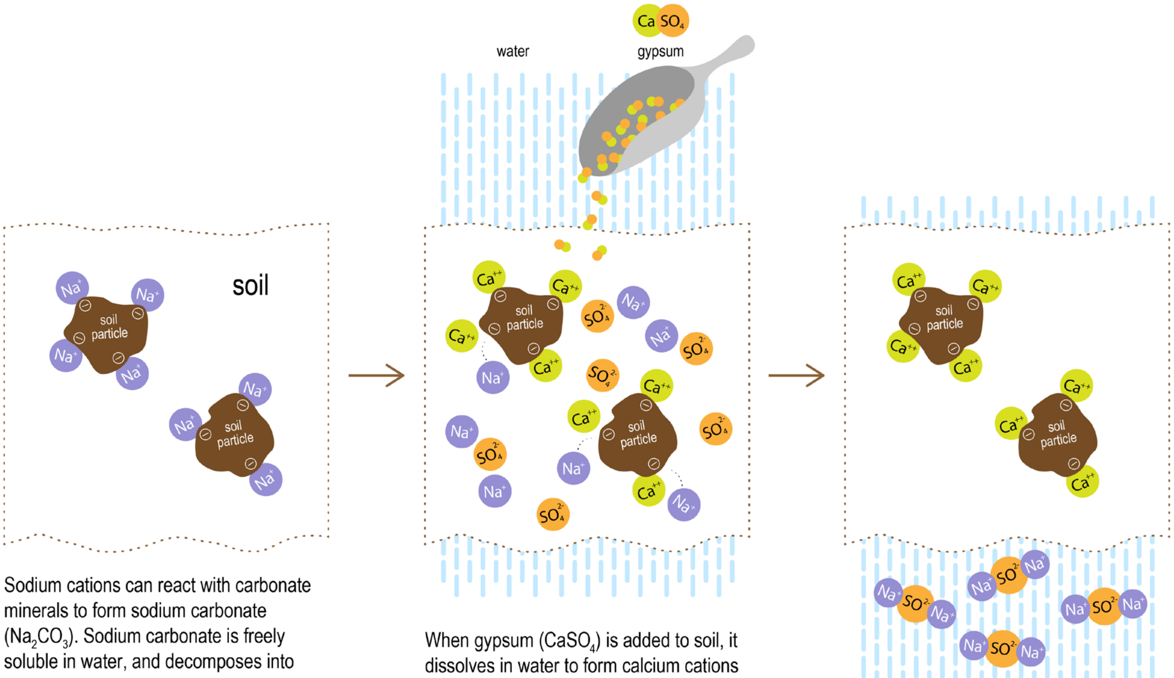
Gypsum (calcium sulfate) is a material that is available in nonsynthetic (mined) and synthetic forms. In sodic (high-sodium) alkaline soils, gypsum can improve soil structure problems, and has some ability to reduce soil pH (Brautigan et al., 2014); however, gypsum is less effective in non-sodic soils (Vossen, n.d.). Even in some non-sodic soils, gypsum can still create small, but statistically significant differences in pH, albeit at large application rates (Tavakkoli et al., 2022). In sodic soils, gypsum not only helps lower pH, but, unlike the use of acids, it also helps exchange calcium for sodium.

Gypsum has complex dynamics with soil. It can be used to raise soil pH that is below 4.5, but according to Franzen & Gerwing (2006), it has limited or no effect between 4.5-8.4. Above 8.4, gypsum again can assist in lowering pH (Franzen & Gerwing, 2006).

Gypsum reacts with exchangeable sodium in the soil, and adds calcium (Brautigan et al., 2014; Vossen, n.d.).

$$\text{Gypsum } (CaSO_4 \bullet H_2O) + \text{sodic soil} \rightarrow \text{calcium soil} + \text{sodium sulfate (leachable in water)}$$

The action of gypsum can be thought of in two steps (see **Figure 1**). The first step "unlocks" sodium from cation exchange sites in the soil, through competition with calcium (Vossen, n.d.). The second step is that freed sodium ions then react with sulfate to form sodium sulfate, which can be removed through leaching if enough water is present. As discussed previously, any free calcium (not bound to cation exchange sites) that combines with carbonate will have lower solubility than sodium carbonate. This means that calcium carbonate will react at a lower rate than sodium carbonate, forming fewer hydroxide ions that raise pH. Because gypsum primarily interacts with sodium, it typically has limited effect in soils with high pH but low sodium content (Vossen, n.d.).



Sodium cations can react with carbonate minerals to form sodium carbonate (Na_2CO_3). Sodium carbonate is freely soluble in water, and decomposes into sodium cations, hydroxide ions, and carbonic acid (H_2CO_3). The hydroxide ions from this reaction can raise soil pH, while carbonic acid can act as a buffer.

When gypsum ($CaSO_4$) is added to soil, it dissolves in water to form calcium cations (Ca^{2+}) and sulfate ions (SO_4^{2-}). Calcium ions displace sodium from soil. Sodium and sulfate are soluble, and can be leached away.

Like sodium, calcium cations can react with carbonate to form calcium carbonate ($CaCO_3$). However, $CaCO_3$ is less soluble in water, and therefore is slower to react to form substances that raise pH.

Figure 1: Reclamation of sodic soil with gypsum.

When the ratio of sodium relative to calcium and magnesium is high (usually measured as ESP, exchangeable sodium percentage, or SAR, sodium absorption ratio), soil particles break apart (disperse), creating dense and erodible soil that is problematic for plant growth (Franzen & Gerwing, 2006). Displacing and removing sodium using gypsum helps to decrease this ratio, allowing calcium and magnesium cations to help bind soil particles together (Franzen & Gerwing, 2006).

According to Tavakkoli et al. (2022), numerous studies have looked at using gypsum and incorporating organic amendments to reclaim alkaline soils. The effectiveness is enhanced when enough water is applied that salts can be leached from the root zone (Tavakkoli et al., 2022). For example, in studies using sodic soil in pots, Brautigan et al. found the following results three months after adding different amounts of gypsum:

- 2 g/kg gypsum; soil pH decrease of 0.9 pH units.
- 5 g/kg gypsum; decrease of 1.4 pH units.
- 10 g/kg gypsum; decrease of 1.7 pH units.

Changes in pH can also be seen in field studies. In one field experiment occurring over two years, researchers added 0, 2.5, and 5 t/ha of gypsum to non-sodic, non-saline alkaline soils (Tavakkoli et al., 2022). The researchers found that the most effective rate of gypsum application was 2.5 t/ha. While the changes in pH are seemingly small (see Table 2, below), these changes were significantly different from controls, and were observed throughout the top 0.30 meters of soil. As discussed above, non-sodic soils do not respond as well to gypsum as sodic soils do. The results represent change from a single application of gypsum, over a two-year time period.

Table 2: Average decrease in pH units as compared with untreated soil, as measured at different soil depths. Data from Tavakkoli et al., 2022

Application rate:	Decrease in pH at 0–0.1 m	0.1–0.2 m	0.2–0.3 m
2.5 t/ha	0.17	0.21	0.15
5 t/ha	0.22	0.27	0.19

Furthermore, relatively small changes in pH can have large impacts on soil properties (notably soil organic carbon). The application of gypsum at 2.5 t/ha and 5 t/ha lowered the amount of organic carbon that was dissolved in the soil (DOC), limiting the amount of carbon that could be lost through leaching (Tavakkoli et al., 2022). Strikingly, Tavakkoli et al. (2022) extrapolated the following for soils in Australia: assuming an average soil organic carbon content of 1% in surface soils, every reduction of 0.1 pH units below a pH of 9.0 could reduce the amount of DOC by 1400 kg/ha. The reduction of pH over a large area could stabilize a large amount of soil.

Gypsum is another traditional material used in organic crop production (OMRI, 2022).

Compost, plant materials, and mixtures of organic materials

The 2014 Technical Report on sulfurous acid notes that applying organic matter can impact sodic/saline soils, by improving soil structure, and critically, enhancing salt leaching (NOP, 2014). One of the issues with many alkaline soils is limited organic matter content, which leads to a lack of water-stable aggregates and a loss of soil porosity (Muscolo et al., 2017; Srivastava et al., 2016; Tavakkoli et al., 2022).

Adding composted organic matter can help reclaim alkaline soils by improving their structural stability and porosity—critical steps for leaching excess cations (Leogrande & Vitti, 2019). Organic matter also increases cation exchange capacity (CEC), allowing soils to absorb and stabilize ions that would otherwise cause alkalinity if free (Leogrande & Vitti, 2019). These functions are synergistic with the use of other soil amendments such as gypsum, where leaching and altering CEC is beneficial for decreasing pH.

As structure, porosity, hydraulic conductivity, and water holding capacity increase, bulk density and erosion decrease (Leogrande & Vitti, 2019). Since composted organic material is fundamentally more biologically stable than fresh organic matter, it tends to offer better effects on soil properties. In one field study, cotton gin compost was more effective than fresh poultry manure at improving bulk density and soil structural stability, when these amendments were applied at rates of 5 and 10 t/ha/year. Researchers noticed that the cotton gin compost had four times more humic acid than the fresh poultry manure. Humic acids can help improve the formation of clay-organic matter complexes (Leogrande & Vitti, 2019).

Organic carbon-based amendments can not only improve the soil problems just mentioned, but also can lead to an increase in the partial pressure of CO_2 within soil, which can help lower soil pH (Srivastava et al., 2016). Decomposition of organic matter leads to the formation of organic acids, which lower soil pH and dissolve carbonates (Leogrande & Vitti, 2019).

In a two-year field soil study, Srivastava et al. (2016) evaluated the efficacy of vermicompost (inoculated with a microbial product), pressmud from sugar processing, and neem seed cake, mixed in a 5:5:1 ratio.[2] The researchers grew wheat in alkaline soil (pH 9.2) where they compared this soil amendment (designated "PF_{OA}") to a conventional 120 N: 60 P: 60 K fertilizer, and to a control where no treatment was used at all. They found that the PF_{OA} treatment reduced the pH to an average of 8.8 compared to the control, while the conventional fertilizer caused no change. However, a 50:50 mix of the conventional fertilizer and the PF_{OA} treatment reduced the average pH further, to 8.5. Total organic carbon (TOC) in

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[2] The application rate published for this material appears to be a mistake—possibly an editing error, changing "mega" to "milli." We contacted the authors for clarification but did not receive a response prior to submitting this report to the NOP.

the soil increased 181% in the 50:50 mix compared with the control, while TOC in the PF_{OA} treatment increased by 103% after 2 years. There were other beneficial changes with the PF_{OA} treatment, including a large increase in soil enzyme activity (representing the rate of nutrient cycling), substantial increases in chlorophyll, carotenoids, and various growth and nutrient components in wheat plants (Srivastava et al., 2016).

In potted soil experiments, Brautigan et al. (2014) tested the effects the following materials had on lowering the pH of sodic soils: glucose, molasses, lucerne green manure, horse manure, horse manure and worms (*Eisenia fetida*, 100 worms per kg soil), and humus. They used these amendments at 2% of the soil weight.

Table 3: Effect of organic amendments on soil pH (in pots) over a 10-to-16-week period. Data compiled from Brautigan et al., 2014.

Treatment	Effect on pH
Glucose	No effect on soil pH initially. The pH decreased by 0.9 units between weeks 4-8. After 8-16 weeks, pH returned to pre-amendment levels.
Molasses	Shortly after application, soil pH decreased by 0.5 units. After four weeks, soil pH decreased by 0.7 units, as compared with pre-amendment levels. After 16 weeks, soils returned to pre-amendment pH levels.
Horse manure	No significant effect on soil pH.
Horse manure and worms	Soil pH steadily decreased by 1.2 pH units over the course of this 10-week study.
Green manure	No significant effect on soil pH.
Humus	Soil pH increased slightly (0.2 units) over the first eight weeks, then remained at that level.

In the worm study, the same quantity of worms would be difficult to replicate in field conditions. Furthermore, worm mortality was high (Brautigan et al., 2014). By the end of the study, the density of worms decreased from 100 per pot to 57. The researchers believed that the worms were contributing to the breakdown of manure and the production of acids. They also believed that the decomposition of the worm bodies likely contributed to the decrease in soil pH.

Adding organic matter may increase populations of acid-secreting microorganisms (Brautigan et al., 2014). The authors attributed the loss of effectiveness of glucose and molasses shown in Table 3 (above) to depletion of the microbial food sources. After acid production ceases, pH levels likely increased again because of the semi-fixed pool of carbonates in the soil reacting with water and slowly re-establishing equilibrium. It is also possible that other substances (fatty acids) produced by microorganisms subsequently degraded and consumed hydrogen ions (Brautigan et al., 2014). As a caveat to the Brautigan et al. pot experiments, these results may not always translate well to field studies because of the large differences in soil volumes (more on this topic is discussed within the section, *Plant-induced soil change*).

Like elemental sulfur and gypsum, compost and plant-based soil amendments are traditional materials used in organic crop production (OMRI, 2022).

Plant-induced soil change (phytoremediation)

In a review, Qadir et al. (2005) note that the goal of phytoremediation of sodic and saline-sodic soils is to increase the dissolution rate of low solubility calcium substances such as calcite ($CaCO_3$). These components from dissolved calcium substances can then replace sodium at cation exchange sites within soil, freeing sodium and providing the possibility for it to be leached away. Phytoremediation shares similarities with the use of gypsum in that is uses calcium to compete with sodium in the soil, so that the sodium can be removed through leaching (Qadir et al., 2005).

As shown in **Figure 2** (below), plants drive the competition of calcium with sodium by increasing the partial pressure of CO_2 (P_{CO2}) in the soil via respiration in roots, and in some cases by enhancing proton release (H^+) by plants such as legumes (Qadir et al., 2005). Some plants release more H^+ when they are supplied with ammonium (NH_4^+), and release more alkaline materials when supplied with nitrate (NO_3^-). This process results in a few potential dissolution reactions (see **Figure 1**). In non-calcareous soils, the increases in CO_2 and H^+ lead to a decrease in pH. In calcareous soils, the dissolution of calcite creates carbonate, which buffers H^+ ions (so no net change in pH), but the carbonate does leave calcium available to displace sodium at cation exchange sites (Qadir et al., 2005).

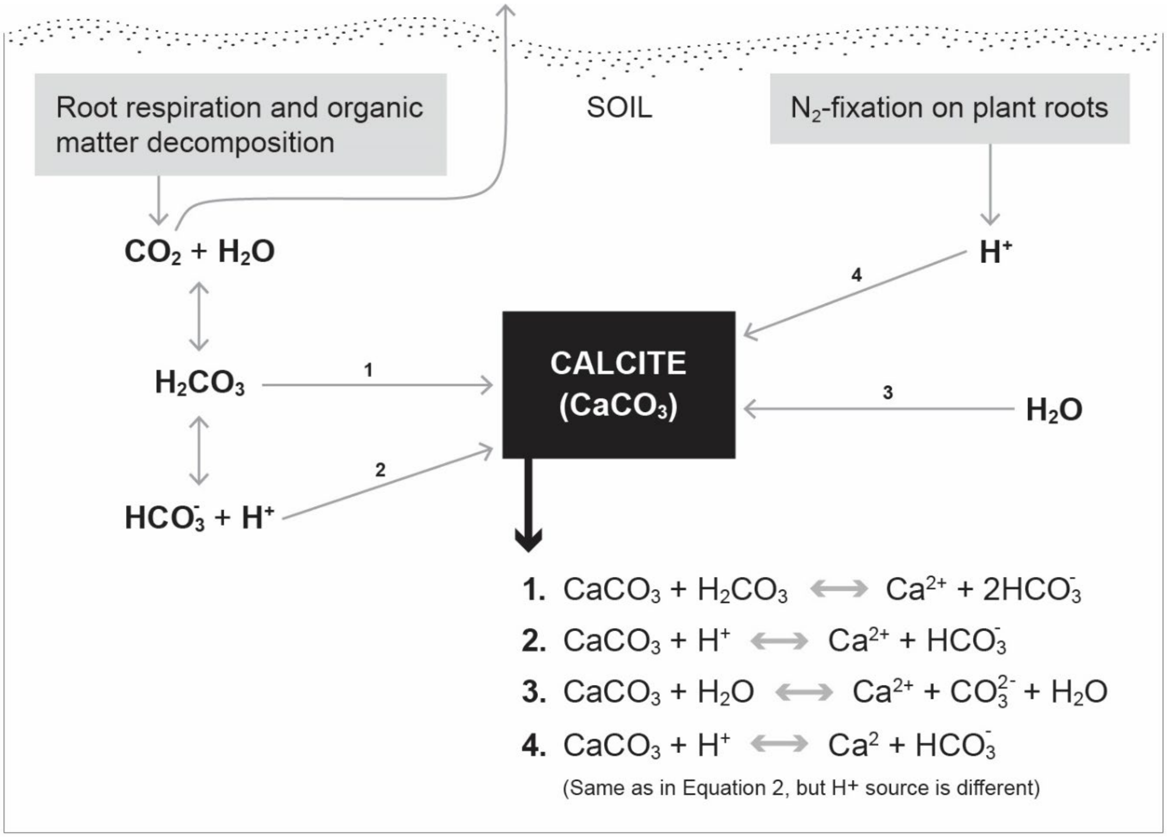

Figure 2: Model of how plant roots contribute to the dissolution of calcium carbonate in soils. Adapted from Qadir et al., 2005.

While phytoremediation may seem to be pH-neutral in some instances, ultimately decreasing the proportion of sodium in alkaline soil can improve characteristics such as hydraulic conductivity (Leogrande & Vitti, 2019). This can lead to improved drainage, which may make other strategies such as use of acids, gypsum, and leaching more effective. Decreasing the ratio of sodium to other cations can also help plants to be more successful at a given pH (Qadir et al., 2005).

Plants vary greatly in their ability to increase P_{CO2}. For example, a sorghum-sudangrass hybrid produced up to 14 kPa P_{CO2}, while cotton produces <3.6 kPa (see Table 4).

Table 4: Mean values of net Na+ removal in different treatments as a function of PCO2 in a lysimeter experiment. Modified from Qadir et al., 2005 and Robbins, 1986.

Treatment	P_{CO2} (kPa)	Net Na^+ removal (mol) per lysimeter column (starting with 7.5 mol)
Control	0.9–4.3	1.0 ± 0.1
Gypsum (5 kg/m)	0.9–2.4	3.3 ± 0.3
Manure	3.1–6.0	1.6 ± 0.2
Cotton	3.0–3.6	1.4 ± 0.1
Alfalfa	4.8–7.2	2.6 ± 0.2
Sorghum-sudangrass hybrid	5.8–14.1	4.0 ± 0.3

Table 5: Comparison of gypsum and phytoremediation for the amelioration of sodic and saline-sodic soils. Adapted from Qadir et al., 2005. Results measured as exchangeable sodium percentage (ESP). ESP is a measure of the proportion of a soil's cation exchange capacity that is occupied by sodium ions (decreasing ESP should improve alkaline soils).

Treatment and crop	Initial ESP	Final ESP	Soil texture
Gypsum at 14 t/ha + rice–wheat	94.0	32.0	Sandy loam
Leptochloa fusca[3] (1 year) + rice–wheat	94.0	44.0	Sandy loam
Gypsum at 15.6 t/ha (no crop)	103.0	14.5	Sandy clay loam
Leptochloa fusca grown for 1 year	103.0	24.9	Sandy clay loam
Gypsum at 13 t/ha (no crop)	76.1	23.6	Sandy clay loam
Leptochloa fusca grown for 15 months	66.4	42.0	Sandy clay loam
Gypsum at 25 t/ha (no crop)	49.0	30.0	Loam
Sesbania–wheat–sesbania (1 year)	49.0	28.0	Loam
Gypsum at 14 t/ha + rice	95.0	45.0	Unknown
Leptochloa fusca grown for 1 year	95.0	60.0	Unknown

The plants that are best suited to rehabilitating soils are those that can withstand saline/sodic soils and produce large amounts of biomass. Plants can store sodium in aerial plant parts, which can then be harvested and removed as well (Qadir et al., 2005). Some examples of promising phytoremediation plants include *Pennisetum giganteum* (giant juncao), sorghum/sudangrass hybrids, *Diplachne fusca* (sprangletop), and *Salicornia* spp. (sometimes called *Halocnemum;* pickleweed or glasswort) (Ahmadi et al., 2022; Hayat et al., 2020; Qadir et al., 2005). Qadir et al. (2005) note that phytoremediation can equal chemical approaches in some instances (see Table 4 and Table 5), especially soils with coarse to medium texture. However, phytoremediation is less efficient (or unsuccessful) as compared with chemicals when (Qadir et al., 2005):

- crops that are not resistant to ambient soil salinity/sodicity, such as rice and wheat, are used in the rotation.
- the phytoremediation period is too short, such as only one season.
- insufficient water is used to leach any sodium released by phytoremediation.

Plant roots are capable of releasing hydrogen ions into soil, which also lowers soil pH (Brautigan et al., 2014). When researchers grew lucerne, faba (fava) beans, field peas, and vetch in pots with highly alkaline soil (pH 8.7-9.6), the average pH of the soil decreased by 0.5 pH units. Within the area directly adjacent to roots (the rhizosphere), the decrease in average pH was 1.1 units. Not all plants were equal:

- faba beans decreased bulk soil 0.7 pH units.
- lucerne decreased bulk soil 0.6 pH units.
- vetch and field pea decreased bulk soil pH by around 0.4 pH units.

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[3] *Leptochloa fusca* is also known as *Diplachne fusca*, or sprangletop (Calflora, 2022).

However, the researchers found that this effect was transient. Twelve weeks after removing the plants, the pH of the soil in the pots had returned to pre-modified levels (Brautigan et al., 2014). One possible explanation for this is that previously insoluble soil carbonates dissolved over time, returning the pH to previous levels. Also, as we show later, pot experiments do not translate well to field soil, probably due to the volume and depth of soil in fields. The effective distance that plants can acidify soil is typically 2-3 mm from the root surface (Kuzyakov & Razavi, 2019). Brautigan et al. did not explore the role of plants in solubilizing calcium either. In calcareous soils, for example, pH is buffered by the dissolution of calcite (Qadir et al., 2005). This can subsequently allow for leaching, but the researchers would have needed to specifically perform additional investigations to study this effect.

In contrast to the Brautigan et al. potted plant study, Tavakkoli et al. (2022) were unable to reproduce a bulk soil pH change in field soil using legumes. Tavakkoli et al. used a non-sodic soil, whereas Brautigan et al. (2014) used a sodic soil. However, Brautigan et al. (2014) measured not only bulk soil pH, but also the pH directly in the area around plant roots (rhizosphere), where they found changes in pH about twice that of the bulk soil in pots. Tavakkoli et al. only measured bulk field soil pH and noted that their method would not catch localized changes near the plant roots. The Tavakkoli et al. and Brautigan et al. experiments show that when soil volume is limited (such as in pots), plants appear to be able to create enough acid to see changes in bulk soil; however, this does not occur in the much larger volumes of field soil. Like Brautigan et al., Tavakkoli et al. did not explore the role of plants solubilizing calcium, and potentially displacing sodium from cation exchange sites within the soil.

Another way in which plants can be used to help improve soil pH is by decreasing soil-water evaporation (Kumar et al., 2022). Earlier, we discussed how the occurrence of alkaline soils correlates strongly with the effects of rainfall and evaporation. Using cover crops (as well as mulches) can decrease evaporation when combined with strategies that aim to limit soil disruption—such as minimum tillage and direct seed drilling (Kumar et al., 2022).

Chelated micronutrients

One of the issues with soil pH above 7 is the availability of some nutrients, especially zinc and iron (Sibbett, 1995). For example, the solubility of zinc in water (which relates to mobility/bioavailability) decreases 100-fold with each whole number increase in pH. One strategy that growers use to grow crops at elevated levels of soil pH is to apply micronutrients in chelated form. Another way is to use foliar sprays (chelated or not). The application of plant available micronutrients does not fix the root cause (alkaline soil) (Sibbett, 1995).

Souri and Hatamian (2019) note that amino acid-chelated nutrients are effective in helping plants meet nutrient requirements in alkaline and calcareous soils. Chelation creates stable, chemical bonds that protect metal micronutrients from reactions that might otherwise cause them to oxidize, precipitate, or become immobilized (Lehman, 1963; Liu et al., 2012). Unlike some other chelation agents, amino acid-based chelates can stimulate root cells to take up the nutrients faster, and translocate them within the plant more quickly (Souri & Hatamian, 2019).

Not all micronutrient chelate treatments are effective in combatting the effects of high pH soil. For example, researchers looked at iron deficiency chlorosis in soybeans due to alkaline soils in Alabama (Gamble et al., 2014). While foliar and in-furrow applications of iron chelated with EDDHA (ethylenediamine-N,N′-bis(2-hydroxyphenylacetic acid)) increased plant yield, treatments of iron citrate and iron sulfate did not.

Many chelated micronutrients are allowed in organic production (OMRI, 2022).

Salicylic acid and silicic acid

Several studies noted that salicylic and silicic acid are substances that could be used for alleviating symptoms of either alkaline or salt stress (often involving alkaline conditions) (Khan et al., 2019; Kumar et al., 2022; Machado & Serralheiro, 2017). Salicylic and silicic acids do not lower soil pH, but may help plants tolerate alkaline soils (Khan et al., 2019). Aside from affecting nutrient solubility, alkaline soils can produce damaging reactive oxygen species (ROS) like hydrogen peroxide, superoxide, and hydroxyl radicals. Plants defend themselves from damage produced by ROS with a variety of antioxidant enzymes. Salicylic acid and silicic acid can stimulate the production of these enzymes (Khan et al., 2019).

In studies using potted tomatoes, Khan et al. found that salicylic acid and silicic acid counteracted negative growth effects caused by alkaline conditions (pH 9), as compared with controls (pH 6). In beneficial ways, these substances stimulated enzyme activity in the plants, increased potassium ion (K^+) intake, and modulated the production of other plant hormones, such as abscisic acid. In their experiments Khan et al. (2019) found that:

- Without treatment, plants at higher pH exhibited smaller roots and shoots.
- Treated plants (salicylic acid, silicic acid, and both) at pH 9 had longer root lengths than treated and untreated plants at pH 6.
- Treated plants had longer and larger diameter stems at pH 9 than untreated plants at pH 6.

Even though these materials are usually manufactured synthetically, both salicylic acid and silicic acid occur naturally (Davies, 2010; Law & Exley, 2011). Salicylic acid for example has long been known to exist in willow bark, but now is recognized to be an important plant hormone involved in plant responses to pathogens (Davies, 2010). Plants like horsetail (*Equisetum sp.*) are "biosilicifiers," which harvest silicic acid from the soil and deposit it within cells as amorphous hydrated silica (Law & Exley, 2011).

Some nonsynthetic products containing horsetail extracts are exist which are allowed for organic use; however most (but not all) of these products are listed as pesticides (OMRI, 2022). Manufacturers can use microorganisms to produce nonsynthetic salicylic acid, and some products exist that contain willow bark (OMRI, 2022).

Other

Numerous home and garden websites advocate using substances like vinegar (dilute acetic acid) to lower soil pH for growing blueberries. However, no published scientific literature could be found investigating this for crop use.

Spent coffee grounds are similarly recommended, but again we found little published scientific research evaluating their effectiveness. One study noted that using spent coffee grounds at rates of 1 and 2.5% of soil weight did not cause any change in pH after 40 days (Cervera-Mata et al., 2021). The authors also found that spent coffee grounds and derivative products inhibited lettuce growth.

Numerous studies exist that investigate pyroligneous acid (PA, wood vinegar) (Lashari et al., 2013; Maliang et al., 2020; Togoro, 2014), and experimentally, this material can lower soil pH. For example, Togoro (2014) used eucalyptus-based PA at 1%, 2%, 4%, and 8% concentrations on an oxisol soil in column experiments. The initial soil pH was 5.5. At 1% and 2%, no differences could be found throughout the soil column. However, at 4% and 8%, statistical differences occurred, with the 4% PA solution lowering soil pH by 0.7 units in the top 0-10 cm of the column. At 8% PA, the top 0-10 cm of the soil column were reduced by 0.9 pH units, and the next 10-20 cm decreased around 0.4 pH units. However, the amount of PA required in a field application to achieve this result would be very large. Furthermore, as PA functions as an acid solution (Togoro, 2014), it could lose effectiveness in the presence of buffering agents such as calcium or sodium carbonates (common in alkaline soils).

Combination of strategies

Ultimately, effective reduction of soil pH likely requires a range of approaches. For example, Kumar et al. (2022) in their review of 101 studies on topics including drip irrigation, fertigation system, saline-sodic soils, and salinization note that to restore saline-sodic soils (typically above pH 8.5), gypsum can be used to release calcium and displace sodium. However, irrigation should also be applied at a rate high enough to leach the sodium. Organic amendments including biochar, straw, green plant residues and microorganisms should also be used to improve soil organic carbon, along with crop rotation and minimum tillage (Kumar et al., 2022).

In another example of a multi-material approach, researchers found that adding crop wastes (orange or olive oil pomace, 5%) to a mixture of elemental sulfur (85%) and bentonite clay (10%; a mined substance) improved germination, plant height, and fruit size in potted red onion, red bean, and cayenne pepper plants (Muscolo et al., 2017). Three months after applying the sulfur-bentonite-orange crop waste mix (0.88 mg/liter of soil), the pH of the soil was 1.6 pH units lower than the control, which had no fertilizer applied (6.8 vs 8.4). Compared to the sulfur (90%)-bentonite (10%) mix, the sulfur-bentonite-orange crop waste mix was 0.8 pH units lower (Muscolo et al., 2017). The study showed that adding acidic organic matter (orange or olive pomace) was useful in lowering pH and improving crop performance. The researchers noted that adding agricultural wastes stimulated the growth of sulfur-oxidizing bacteria (Muscolo et al., 2017). As previously mentioned, sulfur-oxidizing bacteria convert elemental sulfur to sulfuric acid, and elemental sulfur is an allowed synthetic soil amendment at § 205.601(j).

Report Authorship

The following individuals were involved in research, data collection, writing, editing, and/or final approval of this report:

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