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Restoring ecological properties of acidic soils contaminated with elemental sulfur

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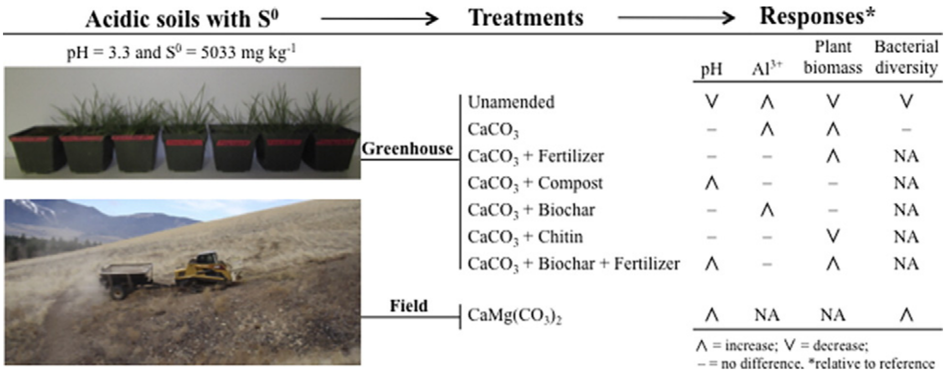
HIGHLIGHTS

- Anthropogenic deposition of elemental sulfur causes extreme soil acidity.
- Polluted soils were amended in pots and in the field with lime and organic matter.
- We monitored soil chemistry, plant growth, and bacterial communities.
- $CaCO_3$ alone partially restored soil chemistry and ecological properties.
- Multiple applications of $CaCO_3$ may be required to prevent future acidification.

GRAPHICAL ABSTRACT



	pH	Al^{3+}	Plant biomass	Bacterial diversity
Unamended	∨	∧	∨	∨
$CaCO_3$	–	∧	∧	–
$CaCO_3$ + Fertilizer	–	–	∧	NA
$CaCO_3$ + Compost	∧	–	–	NA
$CaCO_3$ + Biochar	–	∧	–	NA
$CaCO_3$ + Chitin	–	–	∨	NA
$CaCO_3$ + Biochar + Fertilizer	∧	–	∧	NA
$CaMg(CO_3)_2$	∧	NA	NA	∧

∧ = increase; ∨ = decrease;
– = no difference. *relative to reference

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ABSTRACT

Elemental sulfur (S^0) accumulates in the environment from anthropogenic sources as a byproduct from oil and gas refining and from trap and skeet shooting targets. Bacteria can oxidize S^0 to H_2SO_4, which acidifies soil. We explored whether combinations of soil amendments can be used to remediate acidic soils contaminated with S^0 by restoring soil chemistry, plant growth, and bacterial communities in a greenhouse. Results were compared to a contamination gradient in a field that had been limed with $CaMg(CO_3)_2$ two years prior. Amendments in the greenhouse included $CaCO_3$ by itself, and in combination with fertilizer, compost, biochar, and chitin. Amended soils were incubated for one week and half of all containers were planted with *Poa nevadensis*. We sequenced bacterial DNA from a subset of amended soils and along the field gradient. $CaCO_3$ additions in the greenhouse initially raised the pH of contaminated soil to values found in uncontaminated soils. However, pH decreased over time, which was likely caused by the oxidation of S^0 to H_2SO_4. This was also apparent in the field, where $CaCO_3$ additions raised pH to 4 but not to the desired value of 5 or higher. Plants in the greenhouse failed to grow in the unamended contaminated soil, but $CaCO_3$ alone reduced concentrations of toxic cations and resulted in more plant growth than in the uncontaminated soil. $CaCO_3$ also partially restored the bacterial communities in the greenhouse and in the field by increasing richness and diversity to near values found in uncontaminated soil, suggesting that bacteria can be resilient to prolonged acidic conditions. Organic amendments did not provide a significant benefit to restoration. This study demonstrates that acid neutralization alone can restore abiotic and

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biotic components and productivity of soils contaminated with S^0, but multiple $CaCO_3$ applications may be required to avoid future acidification.

1. Introduction

Acid deposition and generation occurs worldwide predominately from acid rain (Driscoll et al., 2001) and acid mine drainage (Johnson and Hallberg, 2005). The most extreme cases of acidification often occur where reduced sulfur is oxidized (Johnson and Hallberg, 2005; McTee et al., 2016). Approximately 5–10 Mt of reduced sulfur is stockpiled annually as a byproduct of oil and gas refining, much of which is composed of elemental sulfur (S^0) that is stored in blocks (Rappold and Lackner, 2010). Chemolithotrophic and mixotrophic bacteria can oxidize S^0 to H_2SO_4 when H_2O and O_2 are available (Fliermans and Brock, 1972; Lawrence and Germida, 1988; Suzuki et al., 1999). Consequently, effluent water from blocks of S^0 can have pH as low as 0.4, which can contaminate soil and water (Birkham et al., 2010). These blocks likely account for the largest volume of S^0 introduced to the environment, but other vectors exist. Skeuse and Spencer (1999) patented a trap and skeet target composed of approximately 53% $CaCO_3$, 6% modifiers, and 41% S^0. S^0 accumulates where trap and skeet targets fall, which can be at public or private shooting ranges (McTee et al., 2016). Oxidation of S^0 in sulfur-based targets resulted in soil pH below 3 in a previous study (McTee et al., 2016). These cases of extreme acidity from the oxidation of S^0 represent a recent problem and management strategies need to be developed to restore affected areas.

S^0 can be managed by controlling the conditions that allow its oxidation. This would involve manipulating oxygen and water availability, temperature, and the bacterial communities that inhabit particle surfaces (Birkham et al., 2010; Nevell and Wainwright, 1987). The only study to effectively lower oxidation rates used surface additions of NaCl, but NaCl washes away with precipitation (Crescenzi et al., 2006). Management approaches to prevent the conditions that allow S^0 to oxidize in situ are not well studied and would be laborious and costly. Rappold and Lackner (2010) even suggested that H_2S and S^0 could be oxidized to H_2SO_4, neutralized, and disposed of in the ocean. The shortcomings and challenging logistics of these strategies demonstrate the need for alternatives to restore both soil chemistry and biological communities.

Acidic soils strongly affect both plants and bacterial communities (Fierer and Jackson, 2006; Robson, 1989). For example, acidic soils often have high concentrations of Al^{3+} and Fe^{3+} that kill plants (Bowman et al., 2008; De la Fuente et al., 1997), leaving soils bare, and susceptible to erosion (Wong, 2003). The absence of plants and low pH also affect the bacterial communities that are integral in the cycling of nutrients (Lauber et al., 2009; Rousk et al., 2009; Rousk et al., 2010). Bacteria may die or enter dormancy in response to a disturbance (Jones and Lennon, 2010), such as acidification, but their ability to emerge from dormancy in response to restoration of acidic soils needs to be examined.

$CaCO_3$ can rapidly neutralize acidic soils (Robson, 1989; Rappold and Lackner, 2010). But the addition of $CaCO_3$ will not restore nutrients lost from acidification (Bowman et al., 2008; Driscoll et al., 2001; Robson, 1989), so additional soil amendments may be needed. Fertilizer replenishes nutrients and boosts plant yields, which could increase soil organic matter (OM) (Haynes and Naidu, 1998). Organic matter buffers pH in part by increasing concentrations of base cations (Yuan and Xu, 2011), reduces Al^{3+} toxicity to plants (Haynes and Mokolobate, 2001; Seco et al., 2014), and can increase the functional diversity of microbes (Bending et al., 2002). Effective types of OM for restoration include compost, biochar, and chitin. Compost increases plant growth at shooting ranges, partly by reducing the bioavailability of Pb^{2+} and Zn^{2+} (Siebielec and Chaney, 2012). Biochar helps plants establish in contaminated soils because it absorbs and retains toxic substances (Beesley et al., 2011). Chitin, which comprises the exoskeleton of arthropods, has been used to immobilize contaminants and increase pH in acid mine water (Daubert and Brennan, 2007; Robinson-Lora and Brennan, 2010).

It is unknown how to manage acidic soils that receive continual inputs of acid from the oxidation of S^0. It is also unknown how these management strategies might influence soil quality and the plant and bacterial communities that help maintain a healthy ecosystem. Our objective was to determine to what degree various soil amendments could restore soil chemistry, plant growth, and bacterial communities. Soils were amended with $CaCO_3$ by itself, and in combination with fertilizer, compost, biochar, and chitin, which were then incubated in a greenhouse. After one week, we analyzed soil chemistry and planted *Poa nevadensis* in half of the containers. After ten weeks, we analyzed soil chemistry again, measured plant biomass, and characterized the bacterial communities. Results were compared to a contamination gradient in the field that had been limed with $CaMg(CO_3)_2$ two years prior. Three questions were addressed: 1) how do soil amendments change soil chemistry over time, 2) which soil amendments facilitate the greatest plant growth, and 3) do bacterial communities recover when acidic soils are amended? We hypothesized that $CaCO_3$ alone would restore soil chemistry, plant growth, and bacterial diversity because pH is often the most important driver of these properties. We also hypothesized that organic amendments would enhance plant growth by decreasing concentrations of Al^{3+} and stabilizing soil pH over time.

2. Materials and methods

2.1. Soil collection

We collected soil at a former sporting clay range (Bitterroot Sporting Clays) in the Bitterroot Valley, Montana (46° 41′N, 114° 02′W; elevation 970 m). From 1999 to 2006, the range used trap and skeet targets that contained S^0 which caused soil pH to fall below 3 in places (see McTee et al., 2016 for a description of the site). We collected soil (0–15 cm) with a trowel in several areas within five contaminated (termed Contaminated) and five uncontaminated sites (termed Reference hereafter). Contaminated sites were those that had a substantial buildup of S^0 and had soil chemistry (Table 1) representative of what McTee et al. (2016) found in a previous study. Reference soils were taken adjacent to contaminated sites, but outside of where trap and skeet targets fell.

Table 1
Initial soil properties for contaminated and reference soils with detection limits. b.d. represents a mean concentration that was below the detection of the instrument.

Chemical parameter	Contaminated (mg/kg)	Reference (mg/kg)	Detection limit (mg/kg)
pH	3.3	6.3	0.01
S^0	5033	b.d.	500
SO_4^{2-}	1550	46.7	0.1
Al^{3+}	325	1.3	0.1
Fe	284	44.7	0.1
Mn^{2+}	23.9	8.0	0.1
NO_3^-	4.5	7.5	0.1
P	87.3	50.7	0.1
K^+	147	265	0.1
Ca^{2+}	9722	1506	0.1
Mg^{2+}	327	168	0.1
OM	4.3	4.3	0.1[a]

[a] Organic matter (OM) is a percentage of the total mass.