



Extreme soil acidity from biodegradable trap and skeet targets increases severity of pollution at shooting ranges



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HIGHLIGHTS

- We investigated the environmental influence of biodegradable trap and skeet targets.
- Biodegradable trap and skeet targets contain 53% CaCO₃, 41% S⁰, and 6% modifiers.
- The oxidation of S⁰ released H₂SO₄ into the soil and pH values were below 3.
- Acidic soils killed plants and created conditions that may leach Pb from shot pellets.

GRAPHICAL ABSTRACT



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ABSTRACT

Lead pollution at shooting ranges overshadows the potential for contamination issues from trap and skeet targets. We studied the environmental influence of targets sold as biodegradable by determining the components of the targets and sampling soils at a former sporting clay range. Targets comprised approximately 53% CaCO₃, 41% S⁰, and 6% modifiers, and on a molar basis, there was 2.3 times more S⁰ than CaCO₃. We observed a positive correlation between target cover and SO₄²⁻ (ρ = 0.82, P < 0.001), which indicated the oxidation of S⁰ to H₂SO₄. Sulfate was negatively correlated with pH (ρ = -0.93, P < 0.001) because insufficient CaCO₃ existed in the targets to neutralize all the acid produced from S⁰ oxidation. Plant cover decreased with decreasing soil pH (ρ = 0.62, P = 0.006). For sites that had pH values below 3, 24 tons of lime per 1000 tons of soil would be required to raise soil pH to 6.5. Lime-facilitated pH increases would be transitory because S⁰ would continue to oxidize to H₂SO₄ until the S⁰ is depleted. This study demonstrates that biodegradable trap and skeet targets can acidify soil, which has implications for increasing the mobility of Pb from shotgun pellets.

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1. Introduction

Research about shooting ranges has focused almost exclusively on the fate and toxicity of Pb derived from spent ammunition (Bannon et al., 2009; Cao et al., 2003; Laporte-Saumure et al., 2011; Lewis et al., 2001; Sanderson et al., 2012; Selonen et al., 2012). Few of these studies

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evaluate secondary contamination from trap and skeet targets. Traditionally, trap and skeet targets comprised CaCO_3 bound with coal tar pitch (Baer et al., 1995). These targets were found to be poisonous to animals upon ingestion (Davis and Libke, 1968; Graham et al., 1940). This finding prompted the replacement of coal tar pitch with petroleum pitch, the latter of which contains carcinogenic polycyclic aromatic hydrocarbons (PAHs) (Baer et al., 1995). Baer et al., 1995 showed that the bioavailability of PAHs in targets is low unless the targets are consumed. Many studies that investigate contamination at shooting ranges rule out trap targets as a contamination source based on Baer et al. (1995) findings, although the composition of some of the targets have changed.

To provide an alternative to petroleum pitch targets, new ingredient combinations were explored. Ingredients were limited to those that produced targets sturdy enough to maintain structural integrity during transport and varying environmental conditions, but also break when struck with shotgun pellets (Spencer and Skeuse, 2002). At least five patents replaced petroleum pitch with elemental sulfur (S^0) and some used CaCO_3 , white sand, and/or fly ash as filler (Ludwig and Dale, 1974; Paulson, 1975; Spencer and Skeuse, 2002). Modifiers were often added to decrease flammability, increase fluidity and molding properties during manufacturing, as well as increase brittleness; these modifiers include: lignin sulfonate, bentonite clay, maleic acid, aluminum silicate, and styrene monomer. Most of the targets produced adhering to the patented processes yielded products either too difficult to manufacture or too fragile for use (Spencer and Skeuse, 2002).

Skeuse and Spencer (1999) patented several ingredient combinations that overcame the shortcomings of previous patents; they improved upon the patent over three years (Spencer and Skeuse, 2002). The new patent claimed that the product was substantially pitch free, had a high LD_{50} toxicity level, and had high frangibility. They patented an ingredient combination composed of 50% CaCO_3 as filler, 41% S^0 as binder and the following modifiers: 4% polyvinyl chloride (PVC), 3% aluminum silicate, 2% lignin sulfonate, and 0.12% carbon black. Targets manufactured with these ingredients became available in 1998 and are distributed internationally. The targets are marketed to biodegrade to 5% of their original weight within two years of use, depending on precipitation. Shooters and range managers who seek to reduce waste and the environmental problems associated with petroleum pitch targets may purchase biodegradable targets. Inventors patented targets that contain S^0 to provide an alternative to petroleum pitch targets, but no studies evaluate the environmental fate of trap and skeet targets that contain S^0 .

To investigate the environmental influences of trap and skeet targets that contain S^0 , we studied a sporting clay range (Bitterroot Sporting Clays) in Florence, MT. Recreational shooting and league and tournament competitions between 1996 and 2006 brought 30–120 shooters per week to a 23-station course that covered 18 ha in a floodplain and hillsides adjacent to the Bitterroot River. In 1999, the range began shooting targets that contained S^0 . Areas denuded of vegetation, ranging in size from 5 to 1500 m^2 , persisted over 5 years after the range closed where target debris accumulated. This prompted us to assess the potential for targets to influence soil properties and plant cover. To do this, we analyzed the chemistry of the targets and determined relative abundances of the chemical components. We also sampled the site to see how soil chemistry and pH related to target and plant cover.

2. Materials and methods

2.1. Sampling

The study site is located in the Bitterroot Valley, Montana ($46^\circ 41' \text{N}$, $114^\circ 02' \text{W}$; elevation 970 m). We collected soil outside contaminated areas, air-dried the soil, and analyzed soil chemistry (Ward Laboratories, Kearney, NE) to determine the background site chemistry (Table 1). The concentration of S^0 was determined using ion chromatography based on the methods described by McGuire and Hamers (2000) (SGS Canada,

Lakefield, ON). We stratified the sampling design so that areas with visible trap target buildup were sampled at higher density than uncontaminated areas (Fig. 1). Soil samples were taken with a soil auger (7.6-cm diameter) to a 16.5-cm depth throughout the sporting clay range at 46 points. Each soil sample was air-dried in a 3.8-liter plastic bag. At each point, plant and target cover was visually estimated within a 25-cm \times 50-cm quadrat frame centered on soil collection sites. Because data were collected in late October, many forbs were either undetected or senesced, so they did not contribute to the plant cover variable as much as if they had been measured in the summer growing months. For that reason, our vegetation cover measures best-represented perennial and winter annual grasses.

2.2. Chemical analysis

Plant material was removed from the sampled soil and the soil was homogenized. Soil (30–50 g) was weighed and dried in an oven (105°C) overnight to determine soil moisture, and 270–310 g was weighed to make saturation pastes to measure electrical conductivity. Pastes were left overnight and extracts were filtered under vacuum pressure with a 500 mL Buchner funnel and a Barnant Model no. 400–3910 pressure pump (Carter and Gregorich, 2008). Four of the 46 pastes did not yield a measurable amount of extract. Electrical conductivity of the extracts was measured using an Orion Star and Star Plus Meter (Thermo Scientific, Beverly, Massachusetts, USA).

Soil pH was measured on water extracts of soils. Air-dried and sieved soil (10 g; $<2 \text{ mm}$) was added to a tube and 20 mL distilled water was then added. Samples were stirred initially, again after 30 min, and then let stand for 1 h (Carter and Gregorich, 2008). pH was measured using an Orion Star and Star Plus Meter (Thermo Scientific, Beverly, Massachusetts, USA).

Twenty samples were chosen for chemical analysis. We chose samples that spanned the pH gradient observed from the original 46 samples. Calcium and SO_4^{2-} were extracted with a saturated paste extract and analyzed using an Inductively Coupled Argon Plasma (ICP) Emission Spectrometer (Analytical Laboratory, University of California Davis); because of the low solubility of S^0 (Boulegue, 1978), we assumed that no S^0 was present in the saturated paste extract. Lime requirement is an analysis that can be used to determine the amount of CaCO_3 , or other liming material, that must be used to raise the soil pH to a desired level. Lime requirement was determined for twelve sub-samples that spanned the pH gradient observed in the field, using the SMP buffer lime requirement method with a desired pH of 6.5 (MSE Analytical Laboratory, Butte, MT 59701) (Shoemaker et al., 1961). Not all sub-samples were paired to sub-samples taken for chemical analysis due to lack of soil.

Table 1

Chemical properties of uncontaminated soils from the study site (mean \pm s.e., $n = 3$). b.d. represents a mean concentration that was below the detection limit of the instrument.

Chemical parameter	Concentration (mg/kg)	Detection limit (mg/kg)
pH	6.3 ± 0.1	0.01
S^0	b.d.	500
SO_4^{2-}	46.7 ± 16.7	0.1
Al^{3+}	1.3 ± 0.7	0.1
Fe	44.7 ± 8.3	0.1
Mn^{2+}	8.0 ± 0.5	0.1
NO_3^-	7.5 ± 1.7	0.1
P	50.7 ± 3.8	0.1
K^+	265.3 ± 4.7	0.1
Ca^{2+}	1506.3 ± 21.7	1.0
Mg^{2+}	168.3 ± 2.1	0.1
OM	4.3 ± 0.1^a	0.1 ^a

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

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