Antimony migration trends from a small arms firing range compared to lead, copper, and zinc

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ABSTRACT

Small arms firing ranges (SAFRs) contain a mixed amount of bullets and bullet fragments accumulated throughout their designed lifetime. Lead-antimony (Pb-Sb) alloy copper (Cu) jacketed bullets are a common modern ammunition used at SAFRs. The impact of bullets with berm material (i.e., soil) generates a heterogeneous distribution of bullets and bullet fragments in the surrounding soil. As bullets and bullet fragments corrode in the berm soil, the migration potential for antimony compared to other metals is quite high. The goal of this study was to evaluate the spatial Sb migration potential from an SAFR as compared to lead, copper, and zinc (Zn) migration from the same SAFR. Berm soil samples were collected along with surface and ground water samples for a preliminary investigation of the Sb migration from an active SAFR. In addition, different aqueous sample preservation techniques were used and evaluated. Soil sample analysis results show the presence of the metals (i.e., Pb, Sb, Cu, and Zn) in the range floor soil samples, indicating the migration of these metals from the berm to the range floor. The groundwater samples indicate that Sb was migrating from the SAFR more readily than the other metals based on the concentration of Sb in the monitoring well farthest from the SAFR berm.

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1. Introduction

Antimony (Sb) is a group 15 element, just below arsenic (As) on the periodic table and above bismuth (Bi), with common oxidation states of +3 (III) and +5 (V) (Norman, 1998). Antimony is considered on the verge of being a metal and is classified as a metalloid. Antimony is commonly used as an alloy in various materials for its beneficial properties including increased strength as a hardening agent in alloys, beneficial additive to plastics manufacture, corrosion resistant coatings, and flame retardant properties (Kiessling, 1934; Pehrson, 1946; Norman, 1998). The United States used over 600 tons of antimony in the production of ammunition in 1990 (Carlin, 1993). Antimony is used in lead (Pb)-Sb alloy bullets as a hardening agent in the United States, typically from 1% to 3% Sb by weight, and in Swiss bullets from 2% to 5% antimony by weight (Alloway, 1995; Defense Ammunition Center, 2005; Scheinost et al., 2006). The typical background concentration of Sb in soils is from 0.2 to 0.5 mg kg^{-1}; a noted exception is the Xikuangshan mining region where Sb is found at concentrations up to 35 mg kg^{-1} (Carlin, 2000; Liu et al., 2010).

The anthropogenic introduction of Sb (and other metals) into the environment can occur at shooting range berms through the act of firing bullets into the berm soil (Heier et al., 2009). Swiss shooting range soil Sb concentrations have been measured up to 13,800 mg kg^{-1} with average background concentrations near 8.6 mg kg^{-1} (Johnson et al., 2005). Another study collected soils from eight small arms firing ranges (SAFRs) and determined that the predominant metals in the range soils were Pb (up to 24,484 mg kg^{-1}) and copper (Cu; up to 2,936 mg kg^{-1}) with lower concentrations of Sb (up to 91 mg kg^{-1}), nickel (Ni; up to 247 mg kg^{-1}), As (up to 28 mg kg^{-1}), and zirconium (Zr; up to 33 mg kg^{-1}) (Brannon et al., 2009). Ultimately, range maintenance and weathering conditions dictate the longevity of the metal in the berm soil (Johnson et al., 2005). Bullet corrosion depends on weathering effects associated with local climate, the physical form (i.e., fragmented or intact bullets), the alloy components of the bullet, and the soil conditions, where the more fragmented bullets can potentially release the components more rapidly into the environment (Ackermann et al., 2009; O'Connor et al., 2009; Larson et al., 2011). Soil analysis using X-ray Diffraction (XRD) and micro-Raman techniques were not a definitive identifier of Sb minerals in the samples analyzed from Swiss small arms range soils, but the use of an electron microprobe (EMP) suggests that Sb was concentrated near iron (Fe)-oxides as confirmed by extended X-ray absorption fine structure (EXAFS) (Ackermann et al., 2009). Depending on the cemented zone, defined as the matrix of weathering products from 2 to 3 μm around

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the bullet, the weight percent of Sb_2O_5 varies; for instance, in iron-depleted cements, the Sb_2O_5 weight percent can be up to 2.08 weight percent (Ackermann et al., 2009). The study by Ackermann et al. (2009) also determined that the secondary minerals present around the bullet (i.e., the bullet crust) as it corrodes include goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and cerussite ($PbCO_3$). Litharge (PbO) and hydrocerussite [$Pb_3(CO_3)_2(OH)_2$] were observed at other Swiss ranges (Ackermann et al., 2009). The implication from the Swiss study is that the Sb as it corrodes should be present in the bullet crust, but the amount may depend on the Fe-oxides present in the soil since Fe-oxides provide a sink for Sb (Ackermann et al., 2009). Antimony has a strong association with hydroxide in the aqueous environment, forming an oxyanion [i.e., predominately $Sb(OH)_3$ and/or $Sb(OH)_6^-$] (Wilson et al., 2010).

In soils, Sb(III) has a strong attraction for humic acids, and they have been shown to bind over 30% of Sb(III) present in soil (Bushmann and Sigg, 2004). Lead-antimony bullets have been shown to promote the oxidation of the Pb in the presence of Sb (i.e., higher reduction potential of Sb) and phosphate amendments added to SAFR soils (Griggs et al., 2011; Larson et al., 2011; Scheinost et al., 2006). Antimony(III) in oxic soils from SAFRs appears to be a small constituent present compared to Sb(0) and Sb(V) (Scheinost et al., 2006). Antimony(III) forms one cation species, $Sb(OH)_2^+$, with a reported pK_a ([$Sb(H_2O)(OH)_2]^+$) ranging from 1.2 to 1.41 while the reported pK_a [$Sb(OH)_3$] ranges from 11.8 to 11.9 (Baes and Mesmer, 1976; Bushmann and Sigg, 2004; Leuz and Johnson, 2005; Wilson et al., 2010), where the distribution of $Sb(OH)_3$ can be present over most environmentally stable pHs.

Antimony(V) has been observed in an oxidation range (E_h) from 360 to −140 mV and a pH 8 (Mitsunobu et al., 2006). In a solution of 0.1 M sodium oxalate at pH 2.2, Sb(III) and Sb(V) can remain stable, in the dark, for up to 5 days (Belize et al., 2001). Under anoxic conditions, the oxidation of Sb(III) to Sb(V) can occur in the presence of natural and synthetic iron (Fe) and manganese (Mn) oxyhydroxides (Belize et al., 2001). Under oxic conditions with an increase in pH, from 3 to 9.9, and the presence of goethite an increased oxidation of Sb(III) to Sb(V) was observed by Leuz et al. (2006). Antimony(V) has been commonly observed as the predominant oxidation state over Sb(III) in environmental samples, where Sb(III) has been observed at very low to non-detectable levels in oxic soil conditions (Leuz et al., 2006). The Sb(V) oxyanion, $Sb(OH)_5$, has a reported pK_a [$Sb(OH)_5$] of 2.72, where the dominant oxyanion form of Sb(V) is $Sb(OH)_6^-$ over most environmentally relevant pH ranges (Wilson et al., 2010; Baes and Mesmer, 1976).

There is the potential that large releases of antimony during heavy rainfall events and subsequent runoff from SAFRs can lead to a greater risk of toxicity threat to organisms living in the vicinity of the SAFR watershed (Strømseng et al., 2009). Elevated levels of Sb, to include Pb and Cu, have been observed in the gills and liver of brown trout (*Salmo trutta L.*) exposed to water runoff from an SAFR located in south east Norway, but the Sb levels were near the analytical detection limit (Heier et al., 2009). Thus, runoff from the berm, especially during large rain events, can increase the metals in the water that ultimately add stress to aquatic organisms (Heier et al., 2009). There is little concern for the bioaccumulation of antimony by aquatic macrophytes, where Sb tends to behave conservatively like lithium (Li) (Wilson and Webster-Brown, 2009).

A leachability study by Johnson et al. (2005) indicated that there was greater than 99% presence of Sb(V) in the leachate solution and little to no Sb(III), with the leachate Sb(V) concentrations up to 5 mg L^{-1}. Natural weathering and corrosion processes will facilitate the migration Pb and Sb from the range soil as potentially particulate and/or soluble forms (Scheinost et al., 2006; Griggs et al., 2011; Larson et al., 2011). An indication of the soluble transport of Sb from SAFRs is its presence as a low molecular mass (LMM) species in the water samples collected near an SAFR (Heier et al., 2009). The migration of Pb is problematic, but since the Pb tends to remain

as a cation, Pb^{2+}, there is a greater likelihood that the Pb^{2+} will become bound to soil particles (Alloway, 1995). Following extensive TCLP and SPLP leaching studies, Laporte-Saumure et al. (2011) determined that the Pb and Sb from the bullet slug have a higher probability to migrate from SAFR soil than will the Cu and Zn from the copper jacket encased the Pb-Sb slug as a direct correlation to the high Pb and Sb concentration in SAFR soils.

Aqueous sample preservation techniques typically preserve metals for laboratory analysis with some exceptions being mercury (Hg) and chromium (i.e., Cr^{6+}). Three techniques commonly used for aqueous metal preservation are (1) for total metals preservation with Nitric Acid (HNO_3) diluted to a pH < 2; (2) for dissolved metals preservation is by filter on site followed by HNO_3 to pH < 2; and (3) for suspended metals samples are filtered on site (USEPA, 2007). Redox reactive metals and metalloids, such as Sb, may be affected by the preservation techniques that are commonly used for most metals (Fillela et al., 2009). There is the potential of abiotic oxidation of Sb(III), similar to arsenic oxidation, during preservation with acid, but the fundamental understanding of this process still needs further investigation (Fillela et al., 2009; Quentel and Filella, 2002). The recommended preservation strategies are filtration, refrigeration or freezing and the addition of an organic acid [i.e., to complex Sb(III) and avoid oxidation] unless conserving the methylated antimony species (Fillela et al., 2009). The preservation of Sb(III) solution with 0.1 M lactic acid or 0.05 M citric acid at elevated temperatures has been shown to not affect the stability of Sb(III) over a 12-month period, but with 0.06 M ascorbic acid, the Sb(III) concentration was affected just after 6 months (Gómez-Ariza et al., 2000).

This study investigated the migration potential of Sb, compared to the Pb, Cu, and Zn, from an active SAFR with the berm located approximately 80 m from the firing line. The Sb migration was investigated through the evaluation of composite soil samples, ground water samples collected at the SAFR and surface water and nearby sediment samples collected from the nearby stream flowing past the SAFR. In addition, three aqueous sample preservation techniques were observed to determine their potential impact on Sb oxidation states.

2. Materials and methods

In the SAFR berm soil, samples were collected from or within a few feet from the bullet pockets where the probabilities of the highest Sb concentrations were expected. Groundwater samples were collected from monitoring wells located below the SAFR range floor and down gradient from the SAFR berm. Stream samples were the most extensive sampling effort in number, with global positioning system (GPS) sample locations notated both up and down gradient from the SAFR of concern in this study. Statistical analysis was performed using SigmaStat 3.5.

2.1. SAFR berm soil samples

Soil samples were collected from an active SAFR that typically fires 5.56 mm Pb-Sb alloy Cu jacketed rounds into the berm. Berm soil samples were collected from or within a few feet from the bullet pockets as possible. Range floor samples were collected just west of the berm at locations where the optimal runoff water flow path was indicated by observed flow patterns. Grab soil samples were placed inside a labeled plastic bag inside a cooler with ice for preservation during shipment. The soil was homogenized in the bag by hand and then a subsample was digested following EPA SW-846 Method 3051A and analyzed on a Perkin-Elmer Optima 4300 Dual View inductively coupled plasma atomic absorption spectrometry (ICP-AES) with a minimum detection level (MDL) for the soils of 5 mg kg^{-1}. For reference, the SAFR soil metal concentrations were compared to a previous background sample collected at the same training area.