



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



W. Andy Martin^{a,b,*}, Linda S. Lee^b, Paul Schwab^{c,b}

^a U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS, 39180, USA

^b Department of Agronomy, Purdue University, West Lafayette, IN 47907, USA

^c Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77724, USA

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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

* Corresponding author at: U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS, 39180, USA. Tel.: +001 601 634 3710; fax: +001 601 634 3518.

E-mail address: Andy.Martin@usace.army.mil (W.A. Martin).

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 ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), and cerussite (PbCO_3). Litharge (PbO) and hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] 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 $\text{Sb}(\text{OH})_3$ and/or $\text{Sb}(\text{OH})_6^-$] (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, $\text{Sb}(\text{OH})_2^+$, with a reported pK_a [$[\text{Sb}(\text{H}_2\text{O})(\text{OH})_2]^+$] ranging from 1.2 to 1.41 while the reported pK_a [$\text{Sb}(\text{OH})_3$] 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 $\text{Sb}(\text{OH})_3$ 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, $\text{Sb}(\text{OH})_5^-$, has a reported pK_a [$\text{Sb}(\text{OH})_5^-$] of 2.72, where the dominant oxyanion form of Sb(V) is $\text{Sb}(\text{OH})_6^-$ 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.

2.2. Water sample characteristics

Aqueous sample pH, dissolved oxygen (DO; %), temperature ($^{\circ}\text{C}$), and conductivity (ms m^{-1}), which is a measure of the ability of the water sample to pass a current, turbidity (Nephelometric Turbidity Units - NTU), and oxygen reduction potential (ORP; mV), were measured during sample collection using a portable meter. The samples were placed in wide mouth Nalgene® sample bottles, double bagged, and shipped in a cooler with ice.

2.3. Surface water and sediment samples

The surface water (SW) samples and corresponding sediment samples were collected along the creek running from the range to the settling pond located approximately 1,400 m west of the SAFR (Fig. 1). A sample was collected about 50 m upstream from the SAFR, SW1, and SW2. A surface water sample from an adjoining creek, SW6, was collected about 600 m from the SAFR; this sample was considered a background sample. An additional off-site background sample was collected at the head of one of the adjoining creeks, labeled as SW15. This is a background surface water sample collected off-site that flows into the creek that passes by the south end of the SAFR. In summary, surface water samples were collected from areas up gradient and down gradient from the SAFR.

Three water sample preservation techniques were used per sample location: (1) samples were collected with no preservation and later lab filtered (LF) through a $0.45\text{-}\mu\text{m}$ filter, (2) samples were field filtered (FF) through a $0.45\text{-}\mu\text{m}$ filter, and (3) samples were FF through a $0.45\text{-}\mu\text{m}$ filter and then acid preserved with HNO_3 (FF/ HNO_3) to a $\text{pH} < 2.0$. The aqueous samples were analyzed following EPA SW-846 Method 6010B on a Perkin-Elmer Optima 4300 Dual View ICP-AES with an MDL for the water samples of 0.002 mg L^{-1} and a corresponding laboratory reporting limit of 0.01 mg L^{-1} .

Sediment samples were collected and then placed inside a labeled plastic bag in a cooler with ice for preservation during shipment. The sediment samples were homogenized by hand in the bag, dried, and then digested following EPA SW-846 Method 3051A and analyzed

on a Perkin-Elmer Optima 4300 Dual View ICP-AES with a minimum detection level (MDL) for the soils of 5 mg kg^{-1} .

2.4. Monitoring well samples

Monitoring well (MW), or ground water, samples were collected from wells located at the SAFR where the soil samples were collected (Fig. 1). Three water sample preservation techniques were used per sample location: (1) samples were collected with no preservation and later lab filtered (LF) through a $0.45\text{-}\mu\text{m}$ filter, (2) samples were field filtered (FF) through a $0.45\text{-}\mu\text{m}$ filter, and (3) samples were FF through a $0.45\text{-}\mu\text{m}$ filter and then acid preserved with HNO_3 (FF/ HNO_3) to a $\text{pH} < 2.0$. The aqueous samples were analyzed following EPA SW-846 Method 6010B on a Perkin-Elmer Optima 4300 Dual View ICP-AES with an MDL for the water samples of 0.002 mg L^{-1} and a corresponding laboratory reporting limit of 0.01 mg L^{-1} .

2.5. Surface and monitoring well sample preparation

Once samples were received from the field, they were kept in the dark at $4\text{ }^{\circ}\text{C}$ until ready for processing and analysis. Ammonium pyrrolidine dithiocarbamate (APDC, $\text{C}_5\text{H}_9\text{NS}_2 \cdot \text{NH}_3$) with a purity of approximately 99% was purchased from Sigma-Aldrich and used in aqueous samples to separate the Sb(III) from the Sb(V). A 1% APDC solution was prepared daily by adding 0.2 g APDC and bringing it to volume in a 20-mL volumetric flask using ultra-pure water with a resistivity greater than or equal to $18.2\text{ }\Omega\text{-cm}$ at $25\text{ }^{\circ}\text{C}$, similar to the procedure used by Yu et al. (2002). The APDC was added to the sample, shaken for 30 s, and allowed to sit for 30 min to complex to the Sb(III). Then the analyte was passed through a solid phase extraction (SPE) separation step using a cyanopropyl (CN) SPE cartridge, and the elutriate was collected for analysis. The analyte passing through the SPE cartridge would be Sb(V) and the Sb(III) remained on the SPE cartridge. Antimony(III) was determined via difference of the total dissolved Sb analyzed and the Sb(V), determined as per Yu et al. (2002).

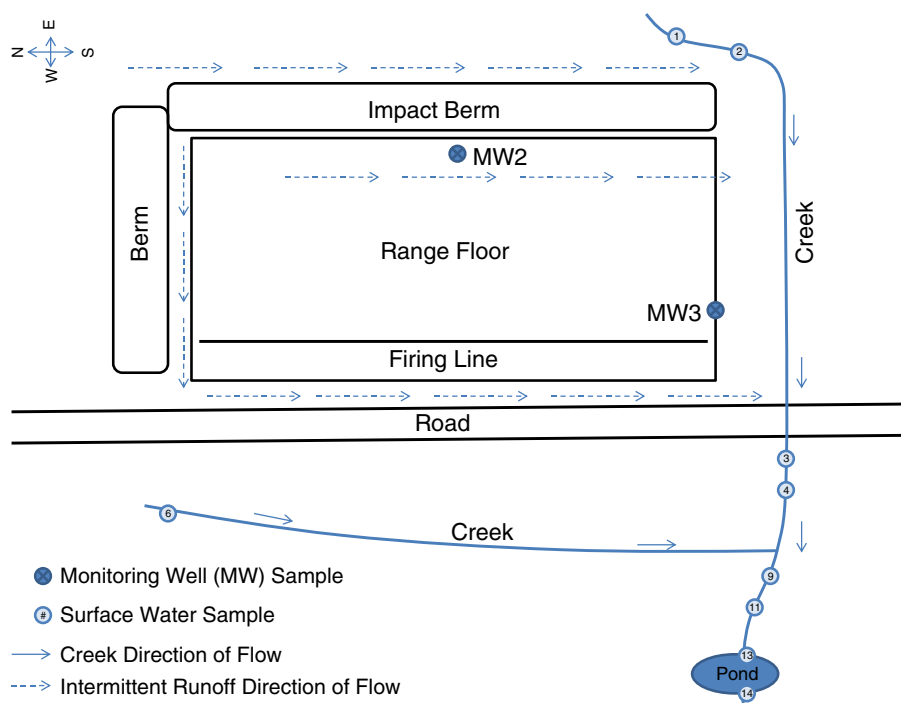


Fig. 1. Schematic (not to scale) of the range with monitoring well and surface water sample locations noted.

3. Results

Sample collection focused on the trends associated with the migration of Sb from the SAFR relative to other common metals (i.e., Pb, Cu, and Zn) that are typically found at an SAFR. Sampling efforts did not focus on detailed individual berm, stream, and ground-water characterization; but focused on developing a comprehensive understanding of the Sb migration potential from the SAFR.

3.1. SAFR berm soil samples

The soil samples collected from the berm had average Pb and Sb concentrations of 14,444 and 164 mg kg⁻¹, respectively, with the highest reported concentration of 21,807 and 198 mg kg⁻¹, respectively (Table 1). A previous SAFR berm soil sample was used for comparison purposes (Table 1) to demonstrate the relative concentration Pb, Sb, Cu, and Zn in samples collected from an SAFR. The range floor (Fig. 1) had an average Pb and Sb concentration of 4,667 and 8.5 mg kg⁻¹, respectively (Table 1), much lower than the berm itself, as was expected, but the Sb concentration was still 17 times higher than background of 0.5 mg kg⁻¹ (Carlin, 2000). A concentration qualifier, U-value, was used for samples that had a reading less than the MDL of 5 mg kg⁻¹, as noted in Table 1.

There was an average of 1.06% Sb in the berm soil by weight compared to the Pb present. The value is statistically within range of the typical bullet Sb percentage (1–3%) based on the common Pb-Sb bullet slug. The range floor (Fig. 1) had concentrations above background concentrations (Table 1) for Pb, Sb, Cu, and Zn, indicating that there is migration of the metals to the range floor. The average percent of Sb in the range floor soil, compared to the percent Sb in the typical bullet, were statistically different. The percent Sb in the range floor was at least an order of magnitude less than what was seen in the berm. The difference between the berm and range floor Pb and Sb concentrations is considered statistically different, with $p < 0.05$, but not for the Cu and Zn concentrations. In addition, the average wt% of Sb to Pb in the berm floor samples is approximately 0.22% Sb. The berm soil, at 1.06%, is more representative of what would be expected since the bullet Sb percent is between 1% and 3%, but the percent Sb on the range floor was much less than would be expected if the Pb and Sb migrated from the berm at the same rate, potentially indicating a greater loss of Sb through additional transport mechanism.

3.2. Water sample characteristics

The SW and MW water samples were analyzed for metals (i.e., Pb, Sb, Cu, and Zn) that are typically associated with bullets and bullet

fragments as well as the aqueous temperature, pH, DO, conductivity, turbidity, and ORP (Table 2). The water temperatures ranged from 6.8 °C to 19.2 °C. The typical pH of the soil in this region has been reported with a range from 4.0 to 8.0 (USDA, 2012; Martin et al., 2012). The water samples were acidic with a pH range from 3.65 to 6.27, which was expected from the acidic soil. The dissolved oxygen ranged from 13.68% to 19.99% in the samples. The conductivity ranged from 3 to 8 ms m⁻¹. The turbidity of the water samples ranged from 1.73 to 33.20 NTU and the ORP ranged from 99 to 298 mV.

3.3. Surface water and sediment samples

The Sb concentration detected in the background samples, SW6 and SW15, were non-detectable (Table 3). The sample preservation methods LF and FF were not statistically different for Pb, Sb, Cu, and Zn, but the LF and FF samples were statistically different when individually compared to the FF/HNO₃ samples.

In general, for the Sb in the surface water samples, there was a significant difference between the background sample (SW15) and SW1, SW2, SW3, SW4, and SW9. There was no significant difference for Pb in all of the surface water samples collected. For Cu and Zn, the metal concentration varied depending on the sample location. For instance, metal concentrations in SW3 and SW4, located approximately 350 m from the SAFR, were significantly different from all of the other surface water samples collected, except for SW9. The concentration of Zn in SW3 and SW4 was significantly different from all of the surface water samples collected.

The surface water samples, SW1 and SW2, collected behind the SAFR berm were not significantly different for Pb, Sb, Cu, and Zn as would be expected since they were collected near each other. Similarly, the surface water samples, SW3 and SW4, collected along the creek around 350 m west of the SAFR are not significantly different for Pb, Sb, Cu, and Zn. The surface water sample, SW6, was collected from a creek that flows into the creek adjacent to the SAFR, and this sample was non-detectable for Sb, but there were measurable concentrations (<10 µg L⁻¹) detected for Pb, Cu, and Zn. The SW6 and SW15, considered to be background samples, were not significantly different from each other for Pb, Sb, Cu, or Zn. The two sample points, SW9 and SW10, located approximately 750 m downstream or west of the SAFR, were not significantly different from each other for Pb, Sb, and Cu; but they were significantly different for Zn. The samples collected from the settling pond, SW13 and SW14, approximately 1,400 m west of the SAFR, were not significantly different from each other for Pb, Sb, Cu, and Zn. The samples collected behind or east of the SAFR Berm, SW1 and SW2, and the samples located about 750 m west or downstream from the SAFR

Table 1
Average Pb, Sb, Cu, and Zn concentrations (mg kg⁻¹) in berm soil and range floor soil samples.

| Location | Sample ID | Pb (mg kg ⁻¹) | | Sb (mg kg ⁻¹) | | Cu (mg kg ⁻¹) | | Zn (mg kg ⁻¹) | |
|------------------------------|------------|---------------------------|--------|---------------------------|-----|---------------------------|-----|---------------------------|----|
| | | Average | SD | Average | SD | Average | SD | Average | SD |
| Background | Near Tower | 4 ^a | <1 | <1 ^a | 1 | 1 ^a | <1 | 43 | <1 |
| Previous sample ^b | Previous | 5,930 | 1,032 | 144 | 21 | 260 | 81 | 42 | 5 |
| Berm | SS1 | 19,920 | 10,207 | 352 | 357 | 1,514 | 193 | 150 | 18 |
| | SS2 | 17,107 | 3,802 | 180 | 79 | 590 | 49 | 47 | 4 |
| | SS3 | 10,447 | 2,022 | 137 | 18 | 1,210 | 274 | 131 | 30 |
| | SS4 | 7,607 | 1,579 | 56 | 29 | 510 | 282 | 48 | 27 |
| | SS5 | 9,778 | 1,601 | 62 | 16 | 641 | 204 | 58 | 20 |
| | SS6 | 21,807 | 8,522 | 198 | 107 | 1,453 | 179 | 126 | 14 |
| Floor ^c | SS7 | 6,062 | 58 | 13 | 5 | 578 | 22 | 48 | 2 |
| | SS8 | 2,225 | 123 | 3 ^a | 0 | 227 | 7 | 25 | 1 |
| | SS9 | 5,871 | 411 | 8 | 3 | 557 | 27 | 52 | 2 |
| | SS10 | 12,360 | 577 | 16 | 4 | 1,233 | 73 | 102 | 7 |
| | SS11 | 360 | 9 | 1 ^a | 0 | 38 | 1 | 5 | 0 |
| | SS12 | 3,126 | 196 | 10 | 3 | 225 | 36 | 24 | 1 |

^aU—concentration qualifier for positive reading less than the MDL. ^bPrevious samples collected from an SAFR at the same location in a different study but used as a relative point of reference in this study. ^cFloor = range floor, between the firing point and the berm. SS = soil sample

Table 2
Water sample parameters taken during sample collection.

| Sample ID | Temperature (°C) | pH | DO (%) | Conductivity (ms m ⁻¹) | Turbidity (NTU) | ORP or E _H (mV) | pE ^a + pH |
|-----------|------------------|------|--------|------------------------------------|-----------------|----------------------------|----------------------|
| SW1 | 12.0 | 6.27 | 19.99 | 3 | 4.70 | 138 | 8.7 |
| SW2 | 12.7 | 5.04 | 19.99 | 3 | 1.73 | 135 | 7.4 |
| SW3 | 10.8 | 4.58 | 19.99 | 4 | 6.76 | 231 | 8.7 |
| SW4 | 11.9 | 4.80 | 19.99 | 4 | 5.19 | 229 | 8.8 |
| SW6 | 14.8 | 5.06 | 19.99 | 5 | 13.70 | 163 | 7.9 |
| SW9 | 11.7 | 5.10 | 19.99 | 4 | 7.54 | 199 | 8.6 |
| SW11 | 13.1 | 5.35 | 19.99 | 3 | 2.84 | 186 | 8.6 |
| SW13 | 19.2 | 5.18 | 13.68 | 3 | 3.52 | 142 | 7.6 |
| SW14 | 15.9 | 5.58 | 18.99 | 4 | 6.94 | 99 | 7.3 |
| SW15 | 13.6 | 5.78 | 19.99 | 6 | 22.20 | 135 | 8.2 |
| MW2 | 8.5 | 3.65 | 18.81 | 6 | 33.20 | 298 | 9.0 |
| MW3 | 6.8 | 5.03 | 19.99 | 8 | 24.00 | 110 | 7.0 |

^apE adjusted for water temperature. SW = surface water; MW = monitoring well.

Berm, SW9 and SW11, were not statistically different from each other except for Sb. The data indicate that the Sb migrated from the SAFR to a distance of at least 750 m from the berm in the surface water.

The sample preservation method used for the surface water samples was not significantly different between the three Sb sample preservation techniques studied (LF, FF, and FF/HNO₃). There was not a significant difference for the Pb, Cu, and Zn in samples that were lab and field filtered, but there was a significant difference between the LF and FF samples and the FF/HNO₃.

Using the Pearson correlation, it was determined that in the surface water samples there is a positive correlation between Sb concentration and the sample pH and a negative correlation between the Sb concentration and the sample conductivity. Sediment samples contained low concentrations of metals relative to the SAFR soil (Table 4), with Sb having the least detectable concentrations of the four metals observed in this study. The sediment samples had a

Table 3
Surface water metal concentrations for all three sample preservation techniques.

| Sample ID | | Concentration (µg L ⁻¹) | | | |
|-----------|---------------------|-------------------------------------|-----------------|-----------------|------|
| | | Pb | Sb | Cu | Zn |
| SW1 | LF | 2 | 6 | n.d. | n.d. |
| | FF | n.d. | 5 | n.d. | n.d. |
| | FF/HNO ₃ | 7 | 7 | n.d. | n.d. |
| SW2 | LF | n.d. | 5 | n.d. | n.d. |
| | FF | n.d. | 3 | n.d. | n.d. |
| | FF/HNO ₃ | 8 | 3 | 2 | n.d. |
| SW3 | LF | 17 | <1 ^a | 12 | 12 |
| | FF | 39 | 1 ^a | 16 | 12 |
| | FF/HNO ₃ | 138 | 1 ^a | 27 | 14 |
| SW4 | LF | 18 | n.d. | 10 | 14 |
| | FF | 39 | 1 ^a | 17 | 14 |
| | FF/HNO ₃ | 191 | n.d. | 29 | 14 |
| SW6 | LF | <1 ^a | n.d. | <1 ^a | 2 |
| | FF | n.d. | n.d. | n.d. | 3 |
| | FF/HNO ₃ | 5 | n.d. | 4 | 7 |
| SW9 | LF | 26 | 6 | 8 | 7 |
| | FF | 28 | 3 | 8 | 7 |
| | FF/HNO ₃ | 138 | 2 | 18 | 9 |
| SW11 | LF | n.d. | 3 | n.d. | n.d. |
| | FF | n.d. | n.d. | n.d. | n.d. |
| | FF/HNO ₃ | 12 | n.d. | 4 | 3 |
| SW13 | LF | n.d. | 3 | n.d. | n.d. |
| | FF | n.d. | n.d. | n.d. | n.d. |
| | FF/HNO ₃ | 1 ^a | n.d. | n.d. | n.d. |
| SW14 | LF | n.d. | n.d. | n.d. | n.d. |
| | FF | n.d. | n.d. | n.d. | n.d. |
| | FF/HNO ₃ | n.d. | n.d. | n.d. | n.d. |
| SW15 | LF | n.d. | n.d. | n.d. | n.d. |
| | FF | n.d. | n.d. | n.d. | n.d. |
| | FF/HNO ₃ | 12 | n.d. | 5 | 8 |

^aU—concentration qualifier for reading less than the MDL. n.d. = non-detectable.

negative correlation between the Sb concentration and surface water turbidity (Table 4).

3.4. Monitoring well samples

Monitoring well (MW) samples were collected from two wells located at the SAFR. Monitoring well 2, MW2, was located about two meters in front of the SAFR berm on the range floor, with the ground water at a depth of several meters below ground surface (bgs). Monitoring well 3, MW3, was located about 97 m from the SAFR berm at the edge of the SAFR range floor, with the ground water depth at approximately 4 m (bgs). The Sb(III) concentration in MW2 is much less than the Sb(III) concentration in MW3 for all three sample preservation techniques, but this observation is based on only two samples collected (Fig. 2). There is a trend associated with the distance from the berm, where the Sb concentrations are higher in the samples collected furthest from the berm, and there is a difference when you compare the sample preservation techniques individually. The monitoring well data presented suggest that there was more Sb(III) at the well farthest from the berm, demonstrating a potential groundwater Sb migration trend and the use of additional monitoring wells and a temporal monitoring approach may provide more defined trends.

MW3 FF and FF/HNO₃ formed a black precipitate with the addition of 1% APDC solution, prior to the SPE procedure. The samples from MW2 had significantly more dissolved metals in the sample compared to samples from MW3. Interestingly, there is much more Sb(III) in the MW3 samples with a pH of 5.03 and a lower ORP at 110 mV compared to MW2 with a pH of 3.65 and an ORP at 298 mV regardless of the preservation technique, also indicating the potential migration of Sb compared to Pb, Cu, and Zn.

4. Discussion

The SAFR berm and berm floor soil metal concentrations ranged from non-detectable to percent levels for the metals (Pb, Sb, Cu, and Zn) that were investigated. The Sb concentrations in the berm and berm floor were orders of magnitude higher when compared to background concentrations of 0.5 mg kg⁻¹ with average of 164 and 8.5 mg kg⁻¹, respectively. The elevated anthropogenic concentration is from the migration of corroded bullets and bullet fragments exposed to environmental conditions.

Surface water samples collected in a creek adjacent to the SAFR had varying concentrations of Sb depending on the distance from the range. Typically, the samples collected nearest to the SAFR had higher Sb concentrations than the samples collected further from the SAFR. There was evidence that Sb was migrating from the SAFR in surface water flow, but there was little evidence of Sb in the sediment samples collected at the same location as the surface water samples. There was an observed positive correlation between the sample pH and the Sb in

Table 4
Surface water and corresponding sediment sample metal concentrations.

| Sample ID | Surface water samples (FF/HNO ₃) (mg L ⁻¹) | | | | Sediment samples (mg kg ⁻¹) | | | |
|-----------|--|------|------|----------------|---|----------------|-----------------|-----------------|
| | Pb | Cu | Zn | Sb | Pb | Cu | Zn | Sb |
| 1 | 7 | n.d. | n.d. | 7 | 67 | 15 | 1 ^a | <1 ^a |
| 2 | 8 | 2 | n.d. | 3 | 39 | 4 ^a | <1 ^a | <1 ^a |
| 3 | 138 | 27 | 14 | 1 ^a | 29 | 4 ^a | 8 | n.d. |
| 4 | 191 | 29 | 14 | n.d. | 141 | 22 | 6 | <1 ^a |
| 6 | 5 | 4 | 7 | n.d. | 26 | 4 ^a | 2 ^a | n.d. |
| 9 | 138 | 18 | 9 | 2 | 72 | 12 | 2 ^a | <1 ^a |
| 11 | 12 | 4 | 3 | n.d. | 13 | 6 | <1 ^a | n.d. |
| 13 | 1 ^a | n.d. | n.d. | n.d. | 17 | 4 ^a | 13 | n.d. |
| 14 | n.d. | n.d. | n.d. | n.d. | 45 | 13 | 26 | <1 ^a |
| 15 | 12 | 5 | 8 | n.d. | 32 | 7 | 21 | n.d. |

^aU—concentration qualifier for reading less than the MDL. n.d. = non-detectable.

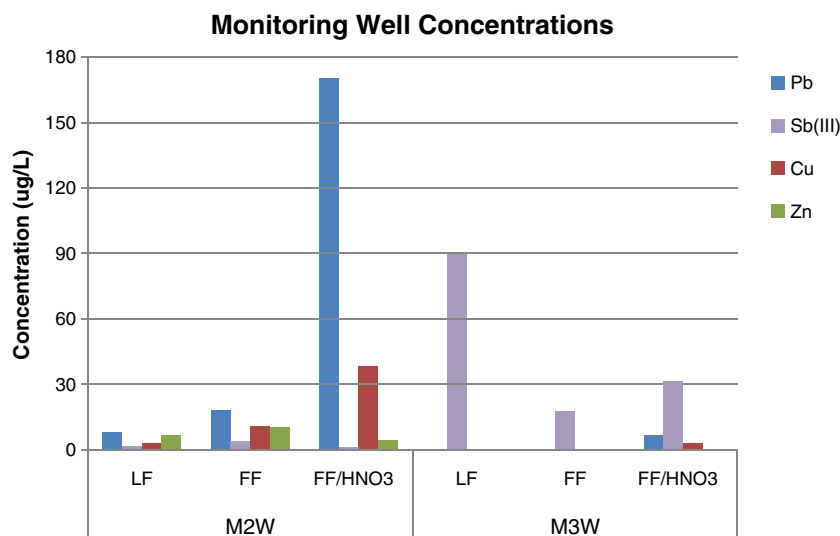


Fig. 2. Monitoring well metal concentrations for MW2 and MW3 with different preservation techniques.

the surface water, and there was a negative correlation between the sample conductivity and the Sb in the surface water sample. In addition, there is a slight negative correlation between the surface water turbidity and the Sb in the sediment sample concentrations.

The soluble Sb is typically found in the Sb(III) and Sb(V) oxidation state depending on site conditions and surface or groundwater transport route. Antimony in the monitoring wells varied; MW2 had much smaller Sb concentration, at non-detectable or below MDL, and MW3 had Sb concentration ranging from 17 to 90 $\mu\text{g L}^{-1}$ with these concentrations depending on the sample preservation method used. The vertical elevation drop for the groundwater based on previous sample efforts is roughly one meter from MW2 to MW3 with a horizontal distance of approximately 97 m. Through some sound parameter estimates and basic understanding of the soil conditions, the ground water flow characteristics in this area can be estimated assuming a conservative hydraulic conductivity, K , of $10^{-4} \text{ cm s}^{-1}$ for the silty sand soil type that are commonly found in this area (USDA, 2012). Also making the assumption of a confined aquifer with a thickness of 30 m and a width of 5 km and an average porosity, $n = 0.2$, the estimated groundwater flow rate of $160 \text{ m}^3 \text{ day}^{-1}$ with a Darcy velocity of $0.0011 \text{ m day}^{-1}$, means that there will be a slow migration of the Sb in the ground water as compared to the surface flow rate and this could be a reason why there is a higher Sb concentration at MW3 than at MW2.

The potential migration of metals (e.g., Pb, Sb, Cu, and Zn) from the SAFR was observed in the soil, surface water, and groundwater samples that were collected. The relative migration of Pb, Cu, and Zn was less than the Sb migration when compared to the overall concentration of metal in the berm, especially in the groundwater samples collected. The bullet and bullet corrosion processes will enhance the migration of Sb over time and understanding the migration trends and the migration potential are important to reducing the environmental impacts of such metalloids. There is the potential migration of Sb in the form of an anion or as a colloidal particle. Additional research is needed to determine the environmental interactions of Sb, its oxidation state under varied environmental conditions, samples preservation effects on Sb oxidation states, and the Sb migration potential from SAFRs based on new research parameters.

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References

- Ackermann S, Gieré R, Newville M, Majzlan J. Antimony sinks in the weathering crust of bullets from Swiss shooting ranges. *Sci Total Environ* 2009;407:1669–82.
- Alloway BJ. *Heavy Metals in Soils*. 2nd ed. New York, NY: Blackie Academic and Professional Publication; 1995.
- Baes CFJ, Mesmer RE. *The Hydrolysis of Cations*. New York, NY: John Wiley & Sons; 1976:370–5.
- Belize N, Chen YW, Wang Z. Oxidation of antimony (III) by amorphous iron and manganese oxyhydroxides. *Chem Geol* 2001;174:379–87.
- Brannon DI, Drexler JW, Fent GM, Casteel SW, Hunter PJ, Brattin WJ, et al. Evaluation of small arms range soils for metal contamination and lead bioavailability. *Environ Sci Technol* 2009;43:9071–6.
- Bushmann J, Sigg L. Antimony (III) binding to humic substances: influence of pH and type of humic acid. *Environ Sci Technol* 2004;38:4535–41.
- Carlin JFJ. Bureau of Mines, Minerals Yearbook 1993 U.S.B.o.Mines, 1; 1993:117–25.
- Carlin J.F.J. Antimony Recycling in the United States in 2000, U.S. Geological Services, U.S. Department of the Interior.
- Defense Ammunition Center. MIDAS Detailed Structure for CTG 5.56MM Ball M855, NSN 1305014673008, 1305014673033, 1305014673026, and 1305011555455. Department of Defense; 2005.
- Fillela M, Philippo S, Belzile N, Chen Y, Quentelm F. Natural attenuation processes applying to antimonu: a study in the abandoned antimony mine in Goesdorf, Luxembourg. *Sci Total Environ* 2009;407:6205–16.
- Gómez-Ariza EMJL, Morales E, Sánchez-Rodes D, Giráldez I. Stability of chemical species in environmental matrices. *Trends Anal Chem* 2000;19:200–9.
- Griggs CS, Martin WA, Larson SL, O'Connor G, Fabian G, Zynda G, et al. The effect of phosphate application on the mobility of antimony in firing range soils. *Sci Total Environ* 2011;409:2397–403.
- Heier LS, Lien IB, Strømseng AE, Ljønes M, Rosseland BO, Tollefsen K-E, et al. Speciation of lead, copper, zinc and antimony in water draining a shooting range—time dependant metal accumulation and biomarker responses in brown trout (*Salmo trutta* L.). *Sci Total Environ* 2009;407:4047–55.
- Johnson CA, Moench H, Wersin P, Kugler P, Wenger C. Solubility of antimony and other elements in samples taken from shooting ranges. *J Environ Qual* 2005;34:248–54.
- Kiessling OE. *Minerals Yearbook 1934*. United States Government Printing Office; 1934.
- Laporte-Saumure M, Martel R, Mercier G. Characterization and metal availability of copper, lead, antimony and zinc contamination at four Canadian small arms firing ranges. *Environ Technol* 2011;32:767–81.
- Larson SL, Martin WA, Griggs CS, Thompson M, Nestler CC. Comparison of lead dissolution from antique and modern ammunition. *Environ Forensics* 2011;12:149–55.
- Leuz A-K, Johnson CA. Oxidation of Sb(III) to Sb(V) by O_2 and H_2O_2 in aqueous solutions. *Geochim Cosmochim Acta* 2005;69:1165–72.
- Leuz A-K, Mönch H, Johnson CA. Sorption of Sb(III) and Sb(V) to goethite: influence on Sb(III) oxidation and mobilization. *Environ Sci Technol* 2006;40:7277–82.
- Liu F, Le XC, McKnight-Whitford A, Xia Y, Wu F, Elswick E, et al. Antimony speciation and contamination of waters in the Xikuangshan antimony mining and smelting area, China. *Environ Geochem Health* 2010;32:401–13.

- Martin WA, Larson SL, Nestler CC, Fabian G, O'Connor G, Felt DR. Hydrated lime for metals immobilization and explosives transformation: treatability study. *J Hazard Mater* 2012;215–216:280–6.
- Mitsunobu S, Harada T, Takashi Y. Comparison of antimony behavior with that of arsenic under various soil redox conditions. *Environ Sci Technol* 2006;40:7270–6.
- Norman NC. *Chemistry of Arsenic, Antimony, and Bismuth*. Bristol, UK: Blackie Academic & Professional; 1998.
- O'Connor G, Martin WA, Larson SL, Weiss C, Malone P. Distribution of tungsten on soil particles following firing of tungsten ammunition into various soil types. *Land Contam Reclam* 2009;17:67–73.
- Pehrson EW. *Minerals yearbook 1944*. United States Government Printing Office; 1946.
- Quentel F, Filella M. Determination of inorganic antimony species in seawater by differential pulse anodic stripping voltammetry: stability of the trivalent state. *Anal Chim Acta* 2002;452:237–44.
- Scheinost AC, Rossberg A, Vantelon D, Xifra I, Kretzshmar R, Leiz A-K, et al. Quantitative antimony speciation in shooting-range soils by EXAFS spectroscopy. *Geochim Acta* 2006;70:3299–312.
- Strømseng AE, Ljøernes M, Bakka L, Mariussen E. Episodic discharge of lead, copper and antimony from a Norwegian small arm shooting range. *J Environ Monit* 2009;11:1259–67.
- USDA. United States Department of Agriculture (USDA), Natural Resources Conservation Service (NRCS), Web Soil Survey completed on September 25, 2012. <http://websoilsurvey.nrcs.usda.gov/app/HomePage.htm>.
- USEPA. United States Environmental Protection Agency. Office of Solid Waste Management. [Chapter 3, USEPA SW-846] Washington, DC: USEPA; 2007.
- Wilson N, Webster-Brown J. The fate of antimony in a major lowland river system, the Waikato River, New Zealand. *Appl Geochem* 2009;24:2283–92.
- Wilson SC, Lockwood PV, Ashley PM, Tighe M. The chemistry and behaviour of antimony in the soil environment with comparison to arsenic: a critical review. *Environ Pollut* 2010;158:1169–81.
- Yu C, Qiantao C, Gua Z-X, Yang Z, Khoo SB. Antimony speciation by inductively coupled plasma mass spectrometry using solid phase extraction cartridges. *Analyst* 2002;127:1380–5.