Selective adsorption of lead, copper and antimony in runoff water from a small arms shooting range with a combination of charcoal and iron hydroxide

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A B S T R A C T

Metals and metalloids from ammunition residues at small arms shooting ranges leach into the soil and surrounding watercourses and may pose a threat to exposed wildlife and humans. To reduce the potential impact of heavy metal on the environment a field study was performed with different sorbents in order to reduce the metal concentration in polluted water from a shooting range. Two sorbents were tested *in situ* for their ability to reduce the concentration of Cu, Sb and Pb: Brimac® charcoal and Kemira® iron hydroxide. The mean sorption of Cu, Sb and Pb was 85%, 65%, and 88% respectively when using the charcoal and 60%, 85% and 92% respectively with the iron hydroxide. Even better sorption of the elements was achieved when the two sorbents were combined in order to increase their selectivity. The best results were achieved in the filter in which the water percolated the charcoal first and the iron hydroxide last, with a mean sorption of Cu, Sb and Pb of 89%, 90% and 93% respectively. This preparation gave a significant better sorption of Cu compared to the filter in which the water percolated the iron hydroxide first and the charcoal last. The different effect between the two filters may be due to pH, since charcoal has alkaline properties and iron hydroxide has acidic properties. For large scale experiments or in filter devices we therefore recommend use of a combination of different reactive sorbents.

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1. Introduction

Each year a considerable amount of metal residue emanating from the use of ammunition is deposited on small arms shooting ranges. It has been estimated that there was a mean annual deposition of approximately 111, 68 and 13 metric tons of lead (Pb), copper (Cu) and antimony (Sb) respectively on Norwegian military small arms shooting ranges for the years 2004–2008 (Reistad et al., 2010). In Norway there are more than 500 ranges for small arms and several of the ranges have been active for decades. In the United States there are more than 3000 active small arms shooting ranges under the auspices of the U.S defense authorities and it has been estimated that approximately 70 000 metric tons of Pb are added to the berms annually (Larson et al., 2005). Small arms ammunition contains primarily Pb, Cu, Fe, Zn and Sb. Sb is used as a hardening alloy in the lead bullets. The content of Sb varies, depending on the manufacturer and production lot. The lead bullets most frequently used by the Norwegian Armed Forces contain

approximately 60% Pb, 29% Cu, 8% Sb and 3% Zink (Zn) (Voie and Strømseng, 2000), whereas Canadian forces use lead bullets containing approximately 93% Pb, 4.5% Cu, 1.9% Sb and 0.5% Zn (Laporte-Saumure et al., 2011).

The deposition of ammunition residues in shooting ranges may pose a threat to the environment. Domestic animals and birds are reported to be particularly vulnerable to lead poisoning (Lewis et al., 2001; De Francisco et al., 2003; Braun et al., 1997). Aquatic organisms such as fish are particularly sensitive to Cu exposure (Lydersen et al., 2002). Several training areas for small arms in Norway and other countries have a significant run-off of heavy metals into nearby aquifers (e.g. Sorvari et al., 2006; Strømseng et al., 2009; Heier et al., 2009; Martin et al., 2013). To reduce the spread of contaminants from the ranges, systems may be established that intercept the pollution in the form of reactive barriers, soil amendments, sediment traps or by use of reactive sorbents. One method of reducing the spread of contamination and cleaning contaminated water is to direct the water into filter devices with reactive sorbents. This approach may be suitable at shooting areas where excess water, percolating berms, or runoff water from a contaminated area can be isolated and directed into special outlet

drains or where the drained water cannot be fed into public sewage systems. The sorbents in the filter devices may reduce the concentration of elements in the water through different mechanisms such as adsorption, ion exchange and redox reactions. In addition, the filter units should have an acceptable hydraulic conductivity.

Recently our laboratory tested different sorbents *in situ* to reduce element concentrations in run-off water from a Norwegian shooting range (Mariussen et al., 2012). We found that iron hydroxide and charcoal could be effective in reducing both the cationic heavy metals Pb and Cu, in addition to the anionic metal-loid Sb. The charcoal had the best effect on Cu and the iron hydroxide had the best effect on Sb. It is a challenge to develop sorbents that can adsorb both anionic and cationic substances. A combination of different sorbents may therefore increase the selectivity and improve the performance of a filter device. The aim of the study was to combine two different sorbents, a bone char and an iron hydroxide, in sequences to test whether improved performance of the filter could be achieved. The performance of the sequences was compared with the performance of the sorbents alone. The main finding was that a filter with increased selectivity could be achieved and that the effect is dependent on the order in which the sorbents are introduced into the column. The main results of the study were recently presented in a technical report written in Norwegian for the Norwegian Armed Forces (Mariussen and Strømseng, 2013).

2. Materials and methods

2.1. Materials

Two different sorbents were tested: Brimac® charcoal and Kemira® iron hydroxide. Brimac® thermally activated charcoal (Brimac Carbon Services Ltd, Scotland) is a commercially available product containing carbon (9–11 %), hydroxyapatite (70–76 %) and calcium carbonate (7–9 %). The Kemira® iron hydroxide is a granulated iron hydroxide from Kemira A/S (Finland) with more than 39% Fe^{3+}.

2.2. Location

The experiment was performed during the summer of 2012. A field laboratory was placed near a small pond at Terningmoen shooting range located in the southeastern part of Norway (UTM 32, Euref 89, coordinates: 6 751 315, 635 679). The water samples were taken from a pond with an estimated mean discharge of 2 L/s. The pond covers a drainage area of approximately 0.25 km². The area has been used as a shooting range for several decades (Roseth et al., 2011). According to Roseth et al. (2011), analyses of 60 samples from 2008 to 2010 showed that the water in the pond had a conductivity ranging from 1.5–2.5 mS/m and a median total organic carbon (TOC) content of 12.7 mg/L reflecting the peat area in which it is located. In our study, the median pH of the water was 5.3, with a range of 5.1–5.9. Analysis of 13 samples showed a TOC content of 14.7 mg/L. The water had a low ionic strength with respect to Ca and Mg level, ranging from 1.1 to 1.3 mg/L and 0.22–0.26 mg/L ($n = 20$) respectively. Statistics of daily precipitation near Terningmoen shooting range (the town of Elverum) during the experimental period were accessed from Norwegian Meteorological Institute's website (www.eklima.no).

2.3. Setup of the column experiments

With a hydraulic water pump (Tsurumi pump 50PU24S) placed in the pond, water was pumped into columns filled with reactive sorbents. The columns were made of PVC measuring 23.5 cm in diameter, 30 cm in height and with a volume of 13 L. The metal-polluted water had a retention time in the columns of approximately 20 min. The water was introduced into the column in an up-flow system and the experiment lasted for a period of 50 days. The water flow was regulated by constant flow valves for liquids (Flowmatic RW-8) with an adjustable flow rate ranging from 0.3 to 3.0 L/min. The water flow through the columns was set to approximately 300–400 ml/min. Between each sampling (approximately every third day), the water flow through the columns declined. This was probably due to particles clogging the filter. Therefore, before each sampling, the water flow through the columns was measured to adjust for the reduction in flow. After sampling the water flow was readjusted. The reduction in flow through the columns between each sampling was assumed to be linear. The total water load is therefore a crude estimate. An automatic water sampler (ISCO 6700) was placed near the pond for daily sampling of water. Table 1S shows the pH range and the estimated total water load percolating the different sorbents, and the liquid to solid ratio.

2.4. Sample preparation and analysis

Samples from the columns were taken twice a week. An aliquot of water was filtered through a 0.45 μm filter (Whatman) *in situ* with a syringe pump (NE-1000, 10 ml/min). Both filtered and non-filtered water was then conserved with ultra-pure nitric acid (0.6% final concentration) before chemical analysis. The metal concentrations monitored in a 0.45 μm filtrate corresponds to elements dissolved as free ions and colloidal bound elements as described in Gustafsson and Geschwend, 1997. The water samples from the ISCO sampler were not subjected to filtration, but conserved with nitric acid before element analysis.

2.5. Analysis

Water samples were analyzed for Cu, Sb, Pb, Mg, Ca, Fe, Mn and Al on an ICP-MS (Thermo X-series II), and for phosphate on a Thermo Scientific Dionex ion chromatography system (IC). The samples were added internal standard and quantified with the use of a four-point standard curve. To ensure correct quantification of the metals, reference solutions of known metal concentration were analyzed (TM 23.3, TMDA 61.2, Rain-97 and Battle-02, analytical reference materials from Environment Canada, Canada). The samples for IC analysis were quantified by an external four-point standard curve. A deviation of 5% from the given concentration in the reference solution was accepted. Blanks were regularly analyzed to control for background contamination.

Organic carbon (Total organic carbon analyzer from Shimadzu TOC corporation) was measured in unfiltered conserved samples and reflected the content of total organic carbon in the sample. The analyses were performed by Norwegian University of Life Sciences (UMB).

2.6. Statistics

Statistics (descriptive statistics, one-way ANOVA, Student *t*-test), non-linear (Hill-function) and linear regression analysis and mathematical calculations were computed in GraphPad Prism 5 or Excel 2007. Normal distribution in the variables was assessed using the D'Augostino & Person omnibus normality test. If necessary, $\log_e$-transformation was applied to obtain normality.