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Use of sorbents for purification of lead, copper and antimony in runoff water from small arms shooting ranges

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HIGHLIGHTS

- ► Amorphous iron hydroxide and charcoal showed good sorption for Pb, Cu and Sb.
- ► Zerovalent iron mixed into olivine sand showed good sorption for Pb, Cu and Sb.
- ► The selectivity of filter devices for the purification of contaminated drainage water may be increased by combining different sorbents.

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ABSTRACT

Different sorbents were tested in situ for their ability to reduce the concentration of Cu, Sb and Pb in drainage water from a shooting range. The sorbents tested were: Brimac® charcoal, olivine mixed with elemental iron powder, magnetite and Kemira® iron hydroxide. The mean sorption of Cu, Sb and Pb was 84%, 66%, 85% with Brimac® charcoal and 58%, 78% and 69% with Kemira® iron hydroxide. Good sorption of Cu and Pb was achieved using olivine with 5% elemental Fe powder, which resulted in a sorption of 81% and 87%, respectively. The Fe-olivine filters were less efficient in reducing the concentration of Sb, but increasing the Fe content improved Sb sorption. In periods with high concentrations of Pb, Cu and Sb in the creek, such as during precipitation, the sorbent efficacy improved. This might be due to changes in the physico-chemical form of the metals, or to a higher fraction of elements being physically retained in the form of particles or colloids.

1. Introduction

Small arms shooting ranges are major deposits of metal residues that originate from the ammunition. In Finland it has been estimated that the mean annual accumulation of lead (Pb) is approximately 500 kg per range, both military and civilian [1]. In the United States there are more than 3000 active military small arms shooting ranges, and it is estimated that approximately 70,000 t are added to the berms annually [2]. Although a more environment-friendly steel ammunition has replaced the use of Pb ammunition in small arms in Norway, a mean annual deposition of approximately 111 t of Pb, 68 t of copper (Cu) and 13 t of antimony (Sb) has been estimated Norwegian military small arms shooting ranges for the years 2004–2008 [3]. The small arms ammunitions most frequently used by the Norwegian Armed Forces previously contained approximately 60% Pb, 29% Cu, 8% Sb and 3% Zinc (Zn) [4]. The deposition of ammunition residues in shooting ranges may pose a threat to the surrounding environment and fauna. For example, domestic animals or wildlife may drink from contaminated streams or lakes, or they may graze on contaminated pasture in the shooting range area [5–7]. Considerable amounts of Pb can accumulate in vegetation growing within impacted areas [8]. The discharge of ammunition residues from berms into stream waters may also lead to aquatic organisms being exposed to contaminants.

Today, efforts are being made to reduce the leaking of metals from berms. Historically, however, Norwegian shooting ranges have not been protected from weather, and they have been constructed without consideration of the discharge of contaminated water percolating through the berms. Several Norwegian shooting ranges are also located in marsh areas with a high potential for contaminants spreading to aquifers. Depending on the soil chemistry, several shooting ranges give rise to a significant run-off of heavy metals [9,10]. In order to reduce the spread of contaminants from the ranges, one may establish systems that intercept the pollution, such as reactive barriers, soil amendments and sediment traps. Filter devices may reduce the spread of contaminants and clean contaminated water. Such filters may be suitable at shooting areas where the contaminated water cannot be fed into public sewage system, but where excess contaminated water can be isolated and directed into special outlet drains. Since contaminated water from

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shooting ranges contains a range of elements with different properties, such as Pb, Cu, Sb and Zn, a major challenge is to find filter sorbents that are effective against all of them. Sorbents may reduce the concentration of elements in water by different mechanisms, such as adsorption, ion exchange and redox reactions. In addition, the filter units should have an acceptable hydraulic conductivity. In situ, organic matter, both dissolved and particulate matter, may influence the capability of the sorbents to retain metals. Especially cations tend to associate with acidic functional groups in organic matter rather than being dissolved as free ions [e.g. 11]. In this work, different reactive sorbents were column-tested in a field laboratory at a small arms shooting range in order to test their ability to retain Pb, Cu and Sb. The sorbents tested were Brimac® thermally activated charcoal, olivine sand mixed with elemental iron powder, magnetite, and Kemira® iron hydroxide. Each sorbent was tested for at least a month with water from a drainage creek that was moderately contaminated by metals received from four shooting ranges with fixed targets. Some of the results of the study were recently presented in a technical report written in Norwegian for the Norwegian armed Forces [12].

2. Materials and methods

2.1. Location

Experiments were performed during summer and autumn in the years 2008–2011. A field laboratory was placed near a small creek named Larsmyrbekken at the Steinsjøen small arms shooting range located in the southeastern part of Norway (UTM 32, Euref 89, coordinates: 6712823, 614780). The creek has an estimated mean discharge of 4.4 L/s and covers a drainage area of approximately 0.37 km^2 [10]. The area has been used as a shooting range for at least 50 years and is described in detail in earlier studies [10,11,13]. Briefly, according to [11], the creek water has a relatively low pH during the summer ranging from 5.5 to 6.6, a conductivity ranging from 3.0 to 4.7 mS/m, and a high DOC (dissolved organic carbon) of approximately 9 mg/L reflecting the peat area in which it is located. A surveillance program by Norwegian defence estate agency the last decade have showed a TOC (total organic carbon) level in the creek ranging from 4.7 to 12.5 mg/L (unpublished results). In this study, the median pH of the water was 6.2. The water has a low ionic strength with respect to for example calcium (Ca) level, ranging from 2.8 to 5.5 mg/L. This is within normal values for Norwegian freshwaters [14], and similar to our findings summer and autumn 2009, showing median Ca and magnesium (Mg) concentrations of 3.7 mg/L and 0.54 mg/L respectively ($n = 78$). The creek receives metal pollution from three shooting ranges.

Three of the sorbents were also tested with another water quality at Terningmoen small arms shooting range, located in the southeastern part of Norway (UTM 32, Euref 89, coordinates: 6751315, 635679). The water was taken from a pond with an estimated mean discharge of 2 L/s and covers a drainage area of approximately 0.25 km^2. The area has been used as a shooting range for several decades and is described in detail in earlier studies [15]. According to [15], analyses of 60 samples from 2008 to 2010 showed that the water in the pond had a conductivity ranging from 1.5 to 2.5 mS/m and a median TOC of 12.7 mg/L reflecting the peat area in which it is located. In our study, the median pH of the water was 5.6, with a range of 5.4–5.8. The water had a low ionic strength with respect to Ca and Mg level, ranging from 1.3–1.1 mg/L to 0.22–0.26 mg/L ($n = 20$).

2.2. Setup of the column experiments

With a hydraulic water pump (Tsurumi pump 50PU24S) placed in the creek, water was pumped into the field laboratory into nine columns in an upflow system filled with reactive sorbents. The columns were made of PVC that measured 23.5 cm in diameter, 30 cm in height and had a volume of 13 L. The water had a residence time in the columns of approximately 20 min and each sorbent was tested for at least 30 days. The water flow was regulated by constant flow valves for liquids (Flowmatic RW-8). The water flow through the columns was set to approximately 300 mL/min corresponding to a filter velocity of 10 m/d. In three of the columns pH electrodes were submerged into the column materials. In addition, the field laboratory was equipped with a surveillance unit (ABB SM 2000) which registered the pH level and temperature of the inlet water. An automatic water sampler (ISCO 6700) with a water height sensor (ISCO 730 bubbler flow module) was placed near the creek for daily sampling of water. The total concentrations of Pb, Cu and Sb in the study areas were measured twice a day following sampling by the ISCO water sampler during the experiments. The field laboratory was also equipped with a rain gauge coupled to the ISCO water sampler.

2.3. Reactive sorbents

Six sorbents were tested: (A) Brimac® charcoal; olivine mixed with (B) 2.5% elemental iron powder, (C) 5% elemental iron powder, (D) 5% granular elemental iron in which the iron was oxidized into the olivine beforehand; (E) magnetite, and; (F) 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%) [16]. According to the producer the product has a density of 550–700 kg/m^3, and a surface area of approximately 80–120 m^2/g. Olivine (Vanguard 250–500 μm particle size, North Cape Mineral), which is a Mg/Fe-mineral ($(Mg, Fe)_2SiO_4$), was used as a filling material for the reactive components. Olivine was mixed with 2.5% and 5% (weight basis) elemental iron powder (≥99% with particle size < 150 μm, Fluka catalog no. 12310). In one filter, 5% granulated iron (300–1000 μm, Cast Iron Grit FG300/1000 iPutec, Germany) was oxidized into the olivine beforehand by mixing salt water (approximately 12l of 2.5% sea salt) with olivine and Fe^0 in a cement mixer for 24 h. The mix was occasionally blended manually by hand to avoid lumps and encrustation. The mix of olivine and Fe^0 had an approximate density of 1.6 kg/L. Magnetite, which is an iron mineral (Fe(II, III) oxide, Fe_3O_4) was purchased from Minelco A/S (Sweden) in two different particle size and mixed. The mix consisted of 37% (weight basis) Minelco MagnaChem WT-2.2 with particle sizes of 20–150 μm (74% < 125 μm, 90% > 20 μm) and density of 2.6 kg/L, and 63% (weight basis) Minelco Magnetitt 0.6, with particle sizes of 0.1–1 mm (82% < 1 mm, 90% > 0.125 mm) density of 1.7 kg/L. The iron hydroxide used in the tests was granulated iron hydroxide (Kemira® CFH12) from Kemira A/S (Finland) and was a gift from Dr. Roger Roseth (Bioforsk, Norway). According to the producer the product has 39–48% Fe^{3+} and a density of 1.1–1.3 kg/L.

2.4. Sample preparation and analysis

Between each sampling the water flow through the columns declined, probably due to particles clogging the filter. It could be observed a biofilm where the water entered the columns, which probably are aggregates of humic substances reflecting the peat area in which the pond and creek are located. Therefore, before each sampling, water flow through the columns was measured to adjust for the reduction in flow. After sampling the water flow was readjusted to approximately 300 mL/min. The reduction in flow through the columns between each sampling was assumed to be linear. The total water load is therefore a crude estimate. Each column received approximately between 9000 and 17,000 L of water with final liquid to solid ratios between 400 and 1350