

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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Abstract

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 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. The hydroxyapatite in the charcoal also goes into the solution and the iron hydroxide may adsorb some of the products from the charcoal. For large scale experiments or in filter devices we therefore recommend use of a combination of different reactive sorbents.

Keywords: reactive sorbents; heavy metal runoff; iron hydroxide; charcoal; small arms ammunition; antimony.

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 metalloid 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% Fe³⁺.

2.2. Location

The experiment was performed during summer 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: 6751315, 635679). 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 2008-2010 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 1.1-1.3 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 liters. The metal-polluted water had a retention time in the columns of approximately 20 minutes. 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 – 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 of 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 Stumm and Morgan, 1996. 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. To ensure correct quantification of the metals, reference solutions of known metal and anion concentrations were analyzed (TM 23.3, TMDA 61.2, Rain-97 and Battle-02, analytical reference material from Environment Canada, Canada). 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'Augustino & Person omnibus normality test. If necessary, \log_e -transformation was applied to obtain normality.

3. Results and discussion

3.1. Concentrations of Pb, Cu and Sb in the pond

The concentration of heavy metals in the pond was measured twice a day using an ISCO water sampler and showed a mean concentration of $25 \pm 4.8 \mu\text{g/L}$ (mean \pm SD), $2.6 \pm 1.0 \mu\text{g/L}$ and $15 \pm 4.1 \mu\text{g/L}$ of Cu, Sb and Pb respectively. This is similar to what was reported in 2011 (Mariussen et al., 2012). There was a period of substantial precipitation during the experiment in which the concentration of Pb, Cu and Sb in the pond peaked (Fig. 1). In particular, an increase in the concentration of Sb was observed. This element was elevated by a factor of approximately 5 during an event of heavy precipitation.

The increase in the concentration of metal observed after rainfall may be due to several factors, of which the larger transport of water through the upper soil horizons and soil surface is probably the most important (Strømseng et al., 2009). The concentration of Pb and Cu in the pond was negatively correlated with pH (Pearson rank correlation (r_p) Pb = -0.738, $p < 0.01$; r_p Cu -0,798, $p < 0.01$) indicating that a reduction in pH in the water during precipitation may facilitate dissolution of Pb and Cu from the ammunition residues. In Fig. 1S, the concentrations of Zn, Ca, Mg, Fe, Mn and Al are presented, showing an apparent increase in Zn, Al, Ca and Mg concentration and a reduction in Fe concentration after heavy precipitation. Only Al and Zn, however, was significantly correlated with precipitation (r_p Al = 0.411, $p < 0.05$; r_p Zn = 0.503, $p < 0.01$). The concentration of both Al and Fe in the pond was correlated to pH (r_p Al = -0.895, $p < 0.001$; r_p Fe = 0.766, $p < 0.01$).

In addition to the ISCO samples, samples were taken of the inlet water entering the columns. Both non-filtered water and water filtered through $0.45 \mu\text{m}$ filters, which is defined as the soluble fraction, were analyzed. The pH in the water decreased during the experimental period from 5.9 to 5.1, probably due to the heavy precipitation. Apparently this could be reflected in the proportion of Cu and Pb that was associated with particulate matter. There

was a significant increase in particulate bound Cu ($r_p \text{ Cu} = 0.774$, $p < 0.01$) and Pb ($r_p \text{ Pb} = 0.916$, $p < 0.001$) with increasing pH (Fig. 2). In freshwater, Pb and Cu occur as cations at pH $< 6.0 - 7.0$ with high affinity for organic substances, which are primarily acid and anionic phenols (Stumm and Morgan, 1996). The more acidic conditions can probably lead to smaller organic aggregates of which the cationic species are associated (Pédrot et al., 2008).

3.2. Effects of single sorbents

The charcoal and iron hydroxide were tested individually as in our previous study (Mariussen et al., 2012). The charcoal reduced the total concentrations of Cu, Sb and Pb by 85%, 65% and 88% to mean concentrations of 3.8, 0.98 and 1.7 $\mu\text{g/L}$ respectively (Table 1, Fig. 2S). The iron hydroxide reduced the total concentrations of Cu, Sb and Pb by 60%, 85% and 92% to mean concentrations of 10, 0.44 and 1.1 $\mu\text{g/L}$ (Table 1). These results are similar to what was obtained in our previous study (Mariussen et al., 2012). The results of the filtered samples did not differ significantly from the non-filtered samples and are shown in Table 2S. The charcoal had an apparent better performance on Sb in the 2011 experiment (81 % adsorption) than in the 2012 experiment (65 % adsorption). This is probably due to the fact that about twice the amount of water went through the sorbents in the 2012 experiment compared to the 2011 experiment, reflecting its reduced capacity of adsorbing Sb as a function of water load.

The water in the pond contained substantial amounts of organic materials (Table 1, Fig. 3). A biofilm could be observed on the sorbents where the water entered the columns. This biofilm is probably aggregates of humic substances reflecting the peat area in which the pond and creek is located. Both sorbents reduced the TOC content in the water to the same extent (Fig. 3). The concentration of TOC in the outlet water gradually increased during the experimental period (Fig. 3), indicating that organic materials in the water occupy adsorbent sites on the filter and presumably reducing the life time of the sorbent.

The water percolating the columns with charcoal and iron hydroxide was also analyzed for Ca, Mg and phosphate (Table 2, Fig. 3S). Characteristic for the column with charcoal was a time-dependent increase in the Ca and phosphate concentration in the outlet water, whereas the concentration of Mg decreased (Fig. 3S). This is similar to what was observed in our previous work, where there was a considerable leakage of Ca (Mariussen et al., 2012). It is known that hydroxyapatite slowly dissolves in water followed by release of Ca and PO_3^- (Narasaraju and Phebe, 1996; Levinskas and Neuman, 1955). It has been shown that Pb and Cu may be retained by ion exchange with Ca (Fernane et al., 2010; Corami et al., 2008). It has also been shown that phosphate amendment to soil may increase the release of Sb due to anion exchange (Spuller et al., 2007). Whether the dissolution of Ca and phosphate will favor adsorption of the cations such as Pb and Cu, or anions, such as $\text{Sb}(\text{OH})_6^-$, remains to be elucidated.

The water percolating the column with the iron hydroxide was acidic with a pH between 4.0 and 4.2 (Table 1S, Fig. 4). In our earlier study, carried out in 2011, this product made the water alkaline, indicating batch to batch variations of the product (Mariussen et al., 2012). Fig. 3S shows that the outlet water from this sorbent had a much higher release of Ca and Mg in the experiment in 2011. Although mere speculation, this indicates the presence of for example CaOH in the batch, thereby making the sorbent alkaline. However, the performance of the two batches did not differ.

Fig. 3S shows the adsorption efficiency and the total element concentrations in the water as a function of the element concentrations in the pond and precipitation. The adsorption efficiency of Pb was maintained throughout the test period with both sorbents (Pearson rank correlation (r_p) Charcoal = 0.792, $p < 0.05$; r_p Iron hydroxide = 0.560 $p < 0.05$). The adsorption efficiency of Sb and Cu was gradually reduced (r_p Charcoal Cu = -0.664, $p < 0.05$; r_p Charcoal Sb = -0.921 $p < 0.0001$; r_p Iron hydroxide Cu = -0.831, $p < 0.001$; r_p Iron

hydroxide $Sb = -0.784$ $p < 0.01$). Charcoal was significantly better than iron hydroxide at adsorbing Cu (one way ANOVA Bonferroni's post test, $p < 0.0001$), whereas iron hydroxide was significantly better than charcoal at adsorbing Sb (one way ANOVA, Bonferroni's post test, $p < 0.0001$). There was no significant difference in the adsorption of Pb between the two sorbents. A thorough discussion about the adsorption mechanisms of the two sorbents may be found discussed in Mariussen et al., (2012).

3.3. Effects of iron hydroxide and charcoal in combination

Columns were prepared with iron hydroxide on top and charcoal on the bottom and vice versa. In sequence 1, where water percolated the charcoal at the end, the concentrations of Cu, Sb and Pb in the water were reduced 81%, 88% and 92% to mean concentrations of 4.7, 0.33 and 1.4 $\mu\text{g/L}$ respectively (Table 1). In sequence 2, where the water percolated the iron hydroxide at the end, the concentrations of Cu, Sb and Pb in the water were reduced 89%, 90% and 93% to mean concentrations of 2.7, 0.25 and 1.0 $\mu\text{g/L}$ respectively (Table 1). The results of the filtered samples did not differ significantly from the non-filtered samples and are shown in Table 2S. Fig. 5 shows the adsorption efficiency and the total element concentrations in the water as a function of the element concentrations in the pond and precipitation. In both sequences there was a gradual reduction in the adsorption of Cu and Sb during the experiment (r_p sequence 1 Cu = -0.717 , $p < 0.01$; r_p sequence 1 Sb = -0.643 $p < 0.05$; r_p sequence 2 Cu = -0.641 , $p < 0.05$; r_p sequence 2 Sb = -0.788 $p < 0.01$), whereas the adsorption of Pb was maintained throughout the experiment (r_p sequence 1 Pb = 0.224 , $p = 0.46$; r_p sequence 2 Pb = 0.640 $p < 0.05$). Both sequences adsorbed Sb significantly better than charcoal alone (one way ANOVA, Bonferroni's post test, $p < 0.0001$) and both sequences adsorbed Cu significantly better than iron hydroxide alone (one way ANOVA, Bonferroni's post test, $p < 0.0001$). The two sequences did not differ in performance with regards to Pb and

Sb adsorption. Sequence 2 was, however, significantly better than sequence 1 at adsorbing Cu (one way ANOVA, Bonferroni post test, $p < 0.05$). With this mix of sorbents a mean Cu concentration was achieved during the experimental period that was below $3 \mu\text{g/L}$, which is the Norwegian authorities' acceptance criterion of Cu in runoff water.

The better performance of sequence 2 compared to sequence 1 with respect to the sorption of Cu may be attributed to several factors. Sequence 2 appeared to reduce the TOC content in the water more than sequence 1, but the difference was not significant (Table 1, Fig. 3). Cations such as Cu and Pb have a high affinity for organic substances and there is reason to believe that the sorption of organic substances on the filter is an important mechanism in the retention of Cu and Pb from water. One interesting observation was the pH of water after percolating the different sorbents. In sequence 1 in which the water percolated the charcoal at the end, the charcoal had an apparent buffering effect on the acidic water from the iron hydroxide (Fig. 4) and the pH was similar to the water percolating solely charcoal. In sequence 2, where the water percolated the FeOH at the end, the water leaving the column was acidic most of the experimental period, but the level of acidity gradually increased. This was probably due to the buffering effect of the charcoal. The isoelectric point in different hydroxyapatite products ranges between pH 4 and 8 (Kosmulski, 2009; Bengtsson et al., 2009). An acidification of the hydroxyapatite surface by iron hydroxide should not favor binding of positively charged elements and may reduce the Cu and Pb sorption capacity of the charcoal. However, the pH of the outlet water from the charcoal alone and in sequence 1 was not significantly different (Fig. 4), although a feed of H^+ ions from the iron hydroxide would probably have the effect of both increasing the repulsion of cations and increasing the dissolution of hydroxyapatite lattice in the charcoal. The latter was confirmed when analyzing the water percolating the two different columns for Ca, Mg and PO_3^- . Sequence 1 showed an increased leakage of Ca and phosphate from the hydroxyapatite, probably due to the acidic

influence from the iron hydroxide (Table 2, Fig. 3S). By converting the leakage to unit per gram of charcoal, sequence 1 showed an increase in Ca and phosphate leakage by a factor of approximately 3 and 4 respectively compared to leakage from the charcoal alone (Table 2, Fig. 3S). In sequence 2, however, the leakage of phosphate was less than the detection limit. This indicates that the iron hydroxide adsorbed the phosphate dissolved from the charcoal. Increased leakage of Ca during sequence 1 was also observed, but the effect was less pronounced and more difficult to interpret since both the water and the iron hydroxide sorbent contained considerable amounts of Ca. The dissolution of phosphate from the charcoal and the alkalization of the iron hydroxide by the charcoal in sequence 2 probably reduced the adsorption capacity of anionic species such as Sb due to a more negatively charged iron hydroxide surface and increased competition with phosphate for the binding sites. There was no difference, however, in the adsorption of Sb between the two sequences.

4. Concluding remarks

It is a great challenge to develop filter systems with the capability of retaining both cationic and anionic metal species. In this study, charcoal was found to be the most effective means of reducing Pb and Cu efflux, whereas amorphous iron hydroxide was proven to be the most effective in reducing Sb efflux. To increase both the selectivity and efficiency of a filter system, the two sorbents were combined in two different sequences. Columns were prepared with two different sorbents with the iron hydroxide filter on the top and the charcoal filter on the bottom and vice versa. Both sequences improved the adsorption of Cu and Sb compared to samples in which each sorbent was used alone. Cu was adsorbed significantly better by the sequence in which the water percolated the charcoal first and the iron hydroxide last compared to the reversed sequence. This is probably due to a pH effect since the charcoal increased the pH of the iron hydroxide, which in turn was probably followed by an increase in

negatively charged binding sites on the iron hydroxide surface. A large increase in the leakage of phosphate was observed in the sequence in which the water percolated the iron hydroxide first and the charcoal last. Iron hydroxide is acidic and has probably facilitated the dissolution of phosphate from the hydroxyapatite lattice of the charcoal. One question that has been raised is whether reactive sorbents themselves may have deleterious effects on aquatic plants or animals, particularly on sites where sorbents are utilized on a larger scale. The sorbents tested in this study influence the pH of water and may increase the leakage of phosphate and Ca. These are elements that may be harmful to aquatic organisms living downstream from the plant or may potentially increase eutrophication.

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Table 1. Percent sorption of total Cu, Sb, Pb and TOC (mean \pm SD (median)) in the tested sorbents and mean concentrations of elements and TOC in the inlet and outlet water (mean \pm SD (median)).

Sorbent		Cu	Sb	Pb	TOC^a
Charcoal	Ads (%)	85 \pm 6.3 (86)	65 \pm 18 (71)	88 \pm 11 (91)	50 \pm 18 (57)
Outlet water	Conc (μ g/L) ^a	3.8 \pm 1.8 (3.8)	1.0 \pm 0.48 (1.2)	1.73 \pm 1.1 (1.4)	7.5 \pm 3.2 (7.2)
Iron hydroxide	Ads (%)	60 \pm 17 (62)	85 \pm 5.0 (85)	92 \pm 4.3 (93)	47 \pm 14 (46)
Outlet water	Conc (μ g/L)	10 \pm 4.8 (8.5)	0.4 \pm 0.2 (0.5)	1.1 \pm 0.4 (1.0)	7.9 \pm 2.7 (8.4)
Sequence 1	Ads (%)	81 \pm 12 (79)	88 \pm 6.8 (88)	92 \pm 12 (96)	57 \pm 16 (57)
Outlet water	Conc (μ g/L)	4.7 \pm 3.0 (4.1)	0.3 \pm 0.2 (0.3)	1.4 \pm 2.3 (0.7)	6.2 \pm 2.5 (6.3)
Sequence 2	Ads (%)	89 \pm 6.9 (91)	90 \pm 8.6 (94)	93 \pm 4.7 (94)	67 \pm 16 (75)
Outlet water	Conc (μ g/L)	2.7 \pm 1.8 (2.1)	0.3 \pm 0.2 (0.2)	1.0 \pm 0.5 (0.9)	5.0 \pm 2.8 (3.7)
Inlet water	Conc (μ g/L)	25 \pm 5.1 (26)	2.9 \pm 1.3 (2.4)	16 \pm 3.9 (16)	15 \pm 3.0 (15)

^aThe concentration of TOC is in mg/L.

Table 2. Concentrations PO_3^- , Ca and Mg (mg/L) in the inlet and outlet water (mean \pm SD median)). The results are shown as mean \pm SD (median) from the samples collected from one column.

Sorbent	PO_3^-	Ca	Mg	N
Charcoal	3.6 \pm 3.7 (2.4)	7.8 \pm 3.7 (10.0)	3.0 \pm 2.0 (2.1)	13
Iron hydroxide	N.D. ^a	2.1 \pm 1.1 (1.7)	0.75 \pm 0.18 (0.73)	13
Sequence-1	6.8 \pm 2.8 (7.6) ^b	10.7 \pm 1.6 (11.1) ^b	3.6 \pm 3.6 (2.1)	13
Sequence-2	N.D.	7.2 \pm 1.5 (7.5)	4.4 \pm 2.7 (4.0)	13
Inlet water	N.D.	1.7 \pm 0.20 (1.6)	0.31 \pm 0.03 (0.30)	13

^bN.D. Not detected.

^aBy converting the leakage to unit per gram of charcoal, sequence 1 showed an increase in Ca and phosphate leakage by a factor of approximately 3 and 4 respectively compared to charcoal alone.

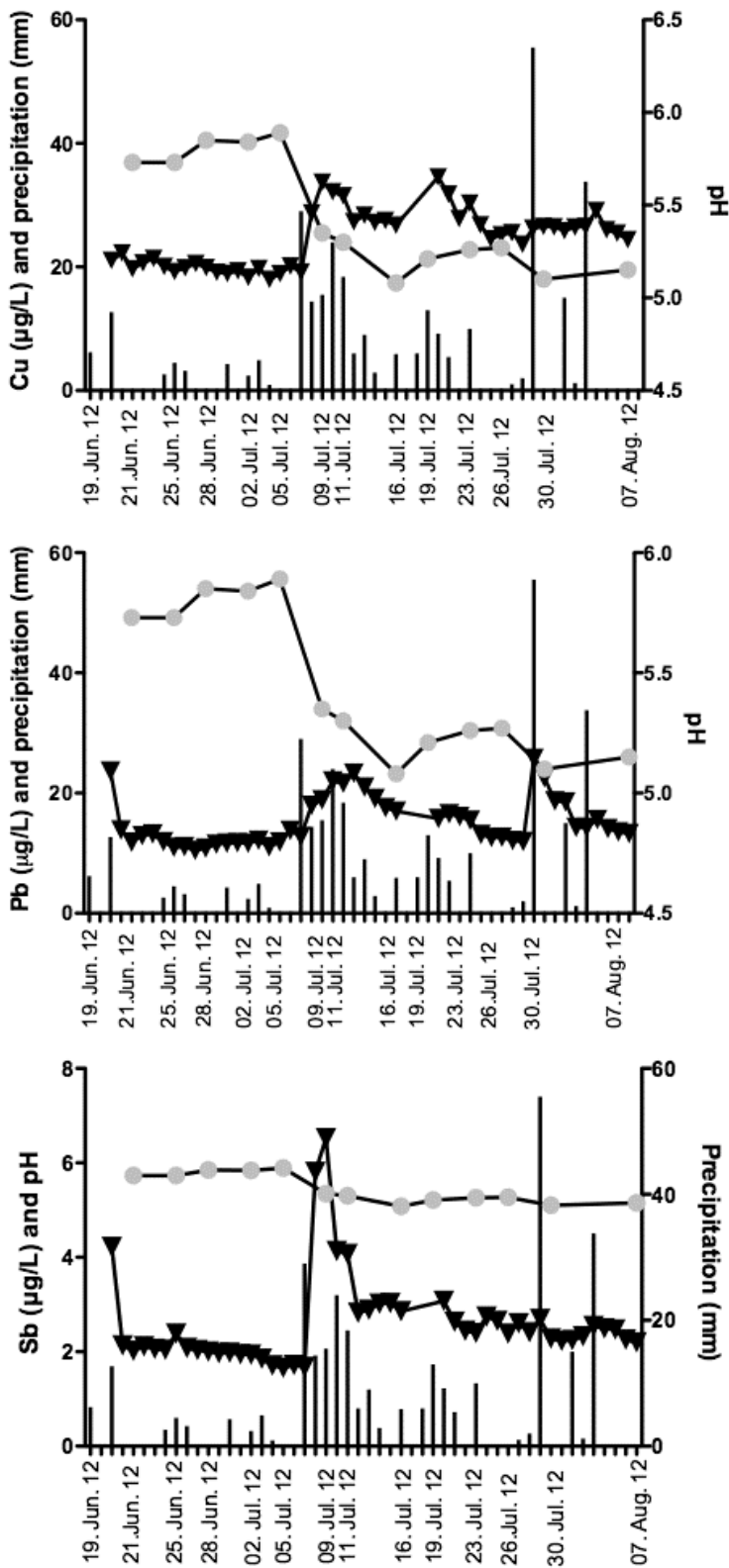


Fig. 1. ▼ ISCO-data for total concentration ($\mu\text{g/L}$) of elements in the pond. ● pH of the inlet water entering the columns. — Precipitation (mm) near Terningmoen shooting range.

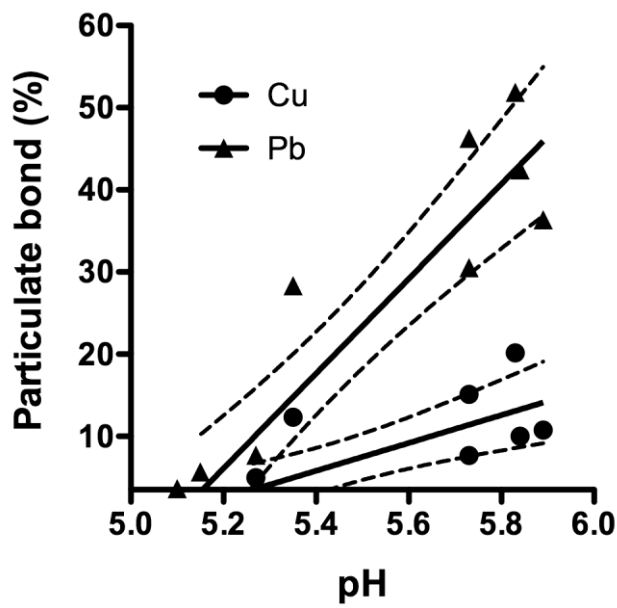


Fig. 2. Linear regression with 95% confidence interval of the portion of particulate bond Cu and Pb as a function of pH in the inlet water entering the columns (regression coefficient, R^2 (Pb) = 0.84, R^2 (Cu) = 0.60).

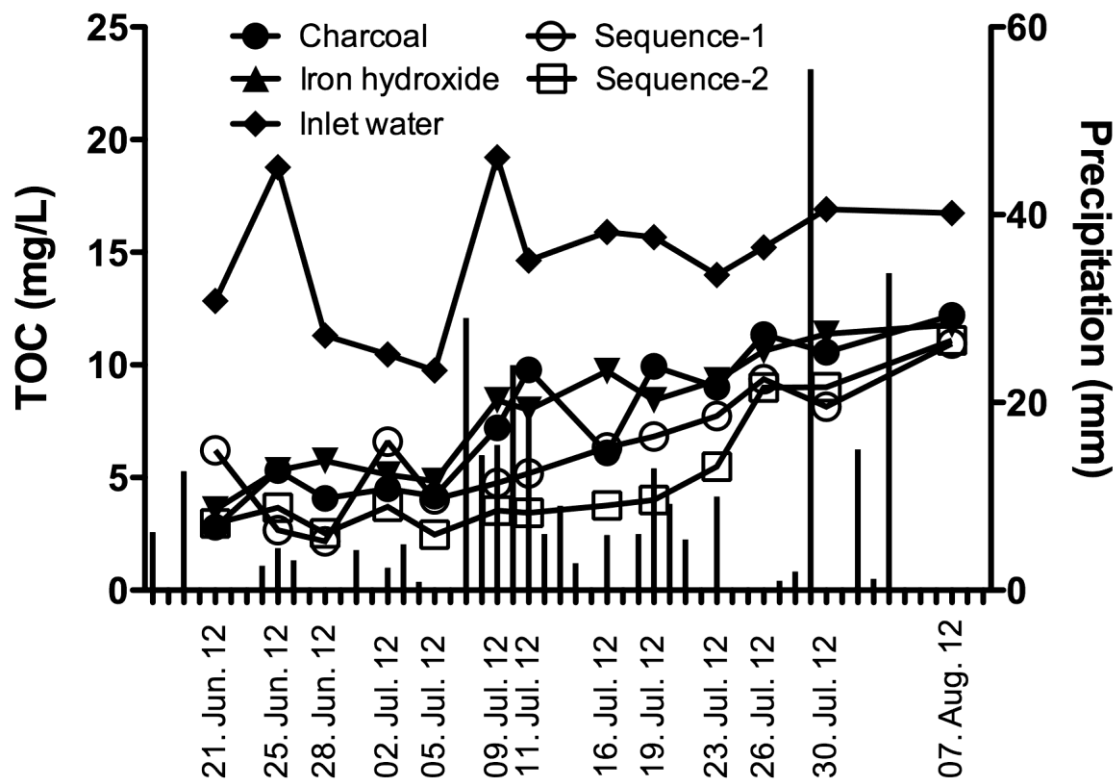


Fig. 3. The concentration of total organic carbon (TOC) in the inlet water and in the water percolating the different filters as a function of time and precipitation. Each point represents the TOC concentration in one sample.

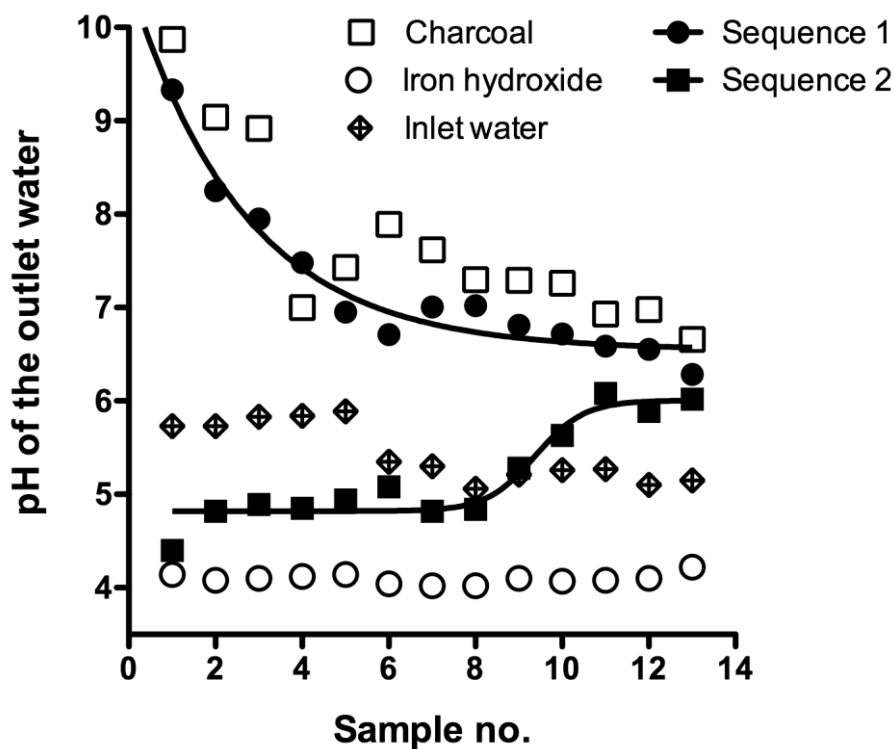


Fig. 4. The measured pH in subsequent samples of the outlet water from the different column materials and from samples taken from the inlet water. Each point from sequence 1 and 2 is the median pH of the triplicate columns. Each of the other points represents the pH in one sample. To better illustrate the trends in the pH, a non-linear regression analysis has been performed on the pH in samples collected from both sequences 1 and 2.

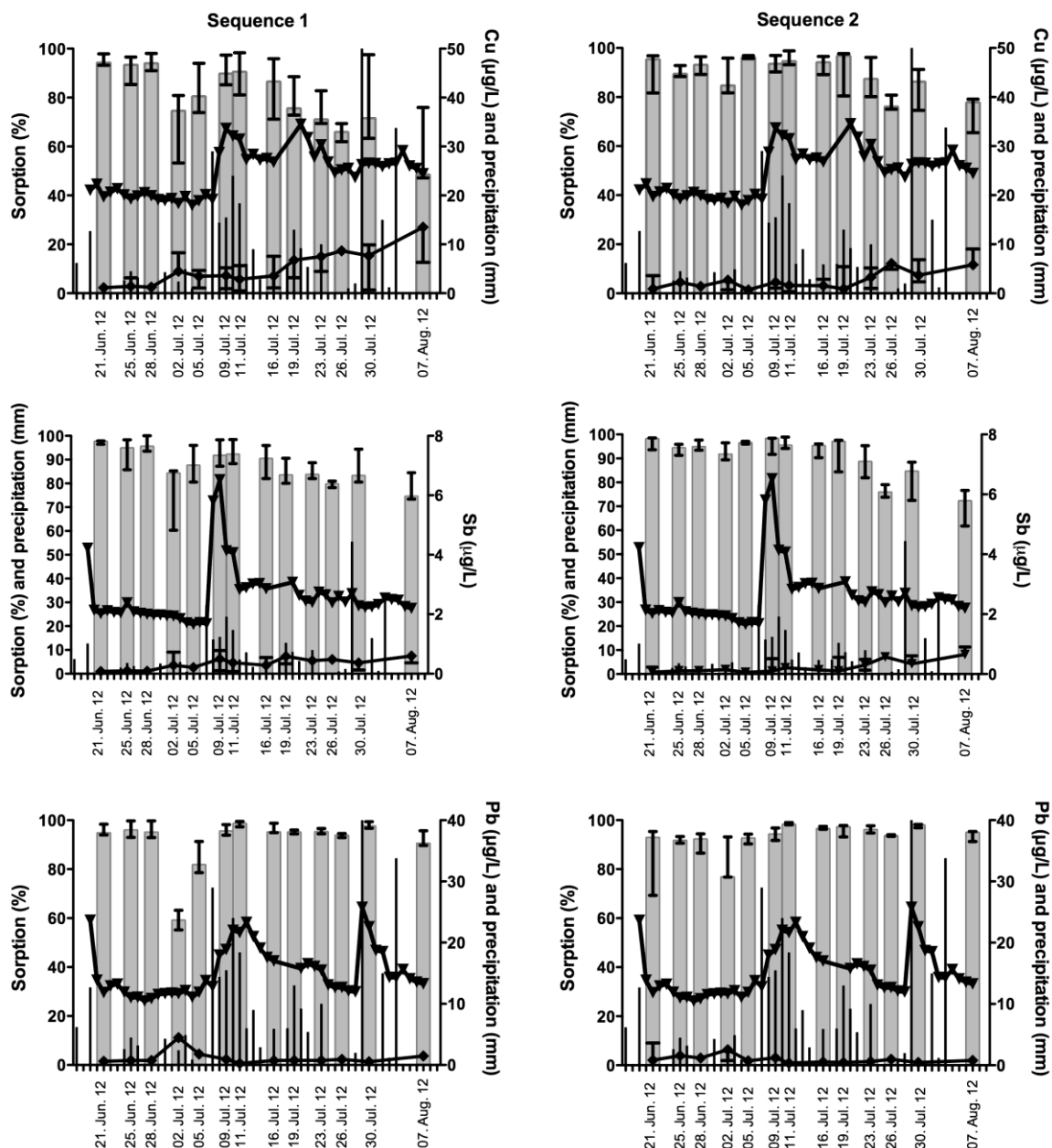


Fig. 5. Sorption of Cu, Sb and Pb (%) as a function a function of the total concentration of elements in the pond with charcoal and iron hydroxide as sorbents in two different combinations. ■ Percent sorption (median ± max and min) ● ISCO data for the total concentration (µg/L) of elements in the pond. ▼ Total concentration of (µg/L, median ± max and min) metals in water that has passed through the column material. — Precipitation (mm) near Terningmoen shooting range.

Supplementary materials

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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Table 1S. Sorbents tested as reactive filters, estimated water load percolating the filters in the study (mean \pm SD of three separate columns), pH of water in the columns at the start and end of the experiments and the liquid solid ration (L/S-ratio).

Sorbent	pH	Water load (L)	L/S-ratio
Charcoal	4.1 – 4.2	26000	1900
Iron hydroxide	9.9 – 6.7	21000	3000
Sequence 1	9.6 – 6.4	21000 \pm 2900	1900 \pm 240
Sequence 2	5.7 – 6.0	19000 \pm 1400	1900 \pm 120

Table 2S. Percent sorption of dissolved Cu, Sb and Pb ((mean \pm SD (median)) in the tested sorbents and mean concentrations of elements in the inlet and outlet water (mean \pm SD (median)).

Sorbent		Cu	Sb	Pb
Charcoal	Ads (%)	86 \pm 6.7 (86)	66 \pm 17 (72)	91 \pm 5.3 (93)
Outlet water	Conc (μ g/L)	3.4 \pm 1.9 (3.7)	0.9 \pm 0.5 (1.2)	0.9 \pm 0.3 (0.9)
Iron hydroxide	Ads (%)	60 \pm 18 (58)	84 \pm 6.4 (84)	93 \pm 3.4 (94)
Outlet water	Conc (μ g/L)	10 \pm 4.8 (8.5)	0.4 \pm 0.2 (0.5)	1.1 \pm 0.4 (1.0)
Sequence 1	Ads (%)	83 \pm 11 (87)	90 \pm 6.3 (92)	94 \pm 3.7 (96)
Outlet water	Conc (μ g/L)	4.0 \pm 2.9 (3.2)	0.3 \pm 0.2 (0.3)	0.6 \pm 0.3 (0.7)
Sequence 2	Ads (%)	89 \pm 7.1 (93)	90 \pm 8.6 (95)	94 \pm 3.7 (95)
Outlet water	Conc (μ g/L)	2.5 \pm 1.9 (1.5)	0.3 \pm 0.2 (0.2)	0.6 \pm 0.2 (0.7)
Inlet water	Conc (μ g/L)	23 \pm 5.5 (26)	2.8 \pm 1.3 (2.4)	13 \pm 5.1 (15)

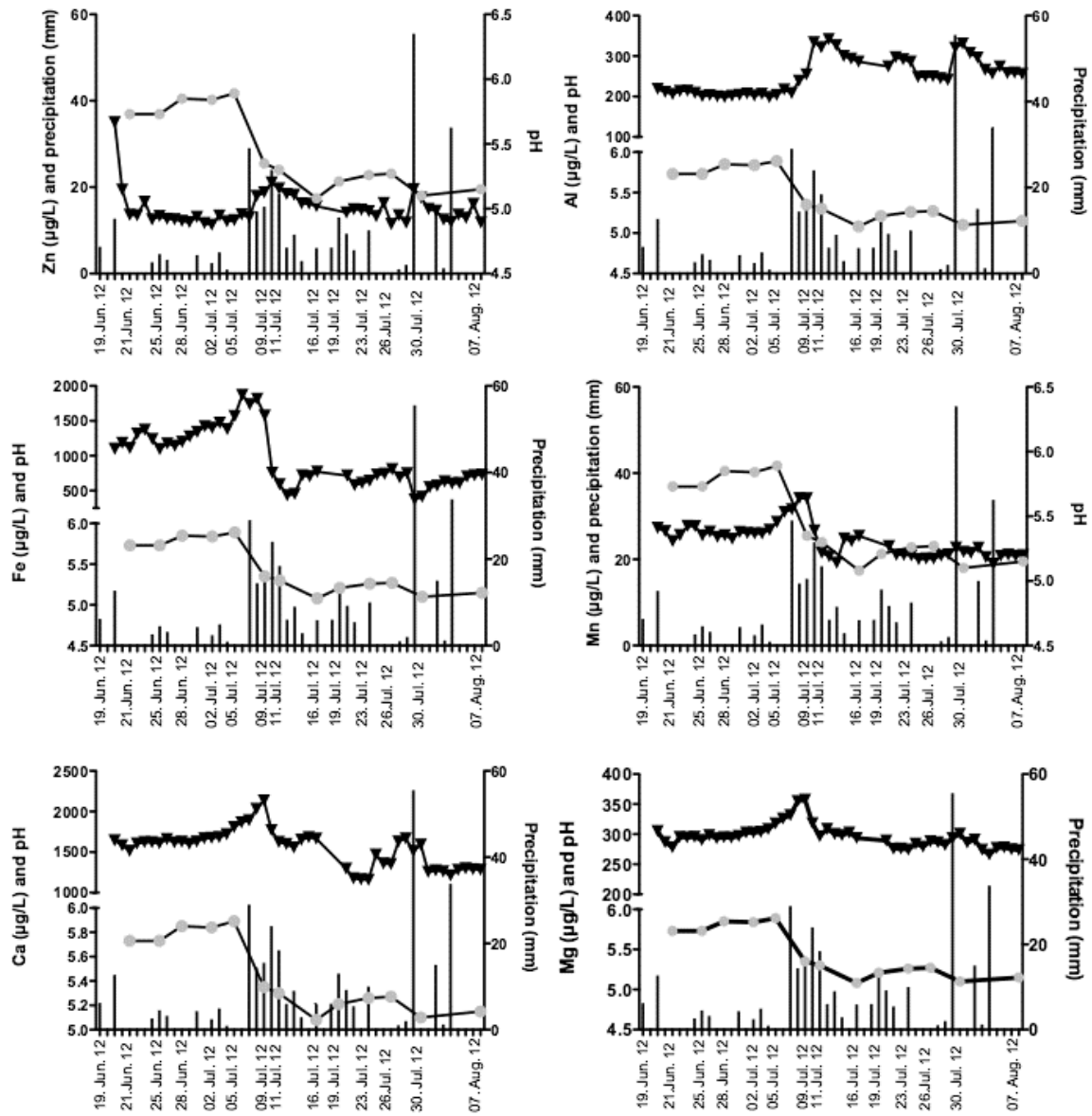


Fig 1S. ▼ ISCO-data for total concentration ($\mu\text{g/L}$) of the elements Zn, Al, Fe, Mn, Ca and Mg in the pond. ● pH of the inlet water entering the columns. — Precipitation (mm) near Terningmoen shooting range.

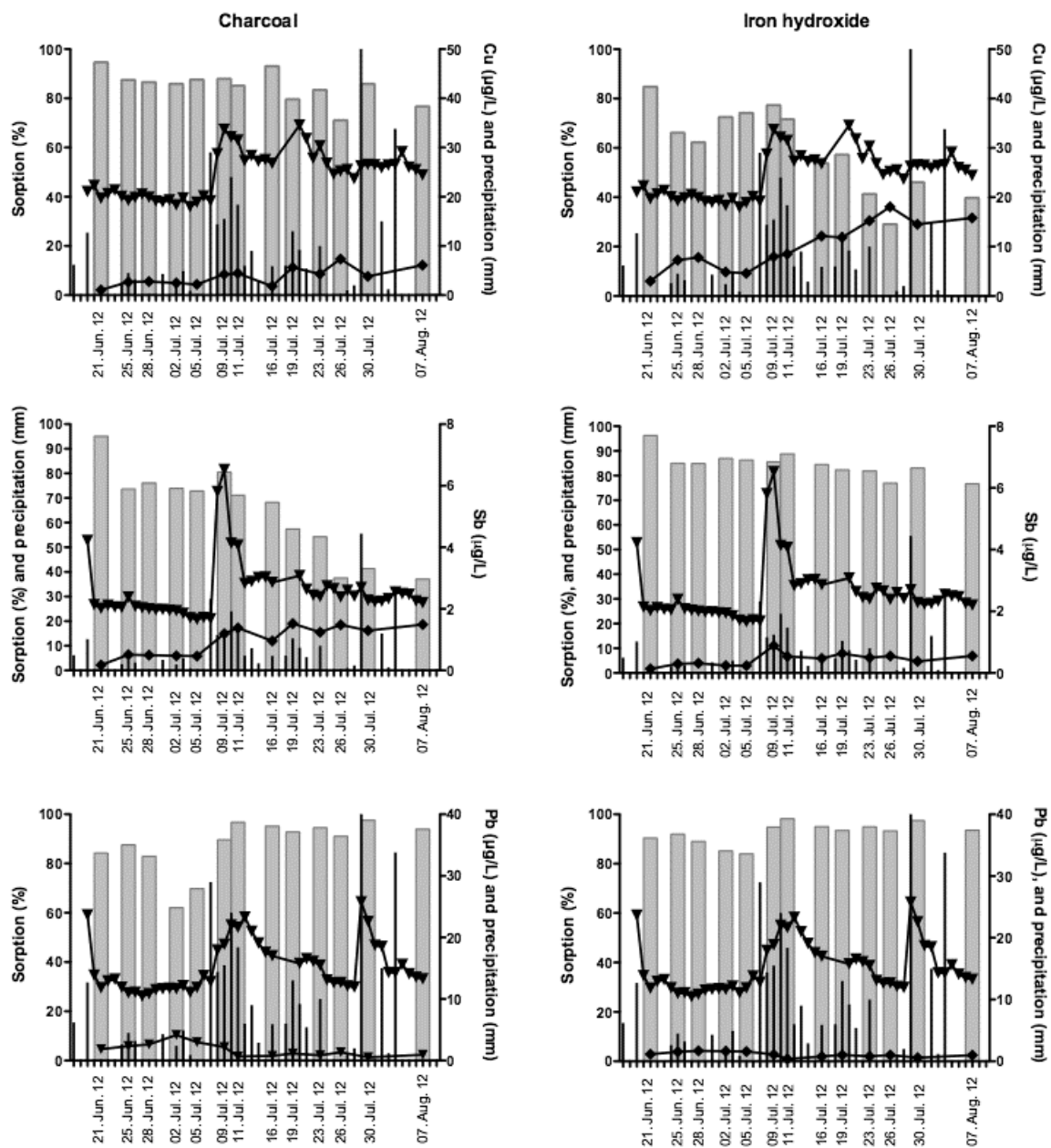


Fig 2S. Sorption of Cu, Sb and Pb (%) as a function of the total concentration of elements in the pond with charcoal and iron hydroxide as sorbents. ■ Percent sorption (median ± max and min) ● ISCO-data for total concentration (µg/L) of elements in the pond. ▼ Total concentration of (µg/L, median ± max and min) metals in the water that pass through the column material. — Precipitation (mm) near Terningmoen shooting range

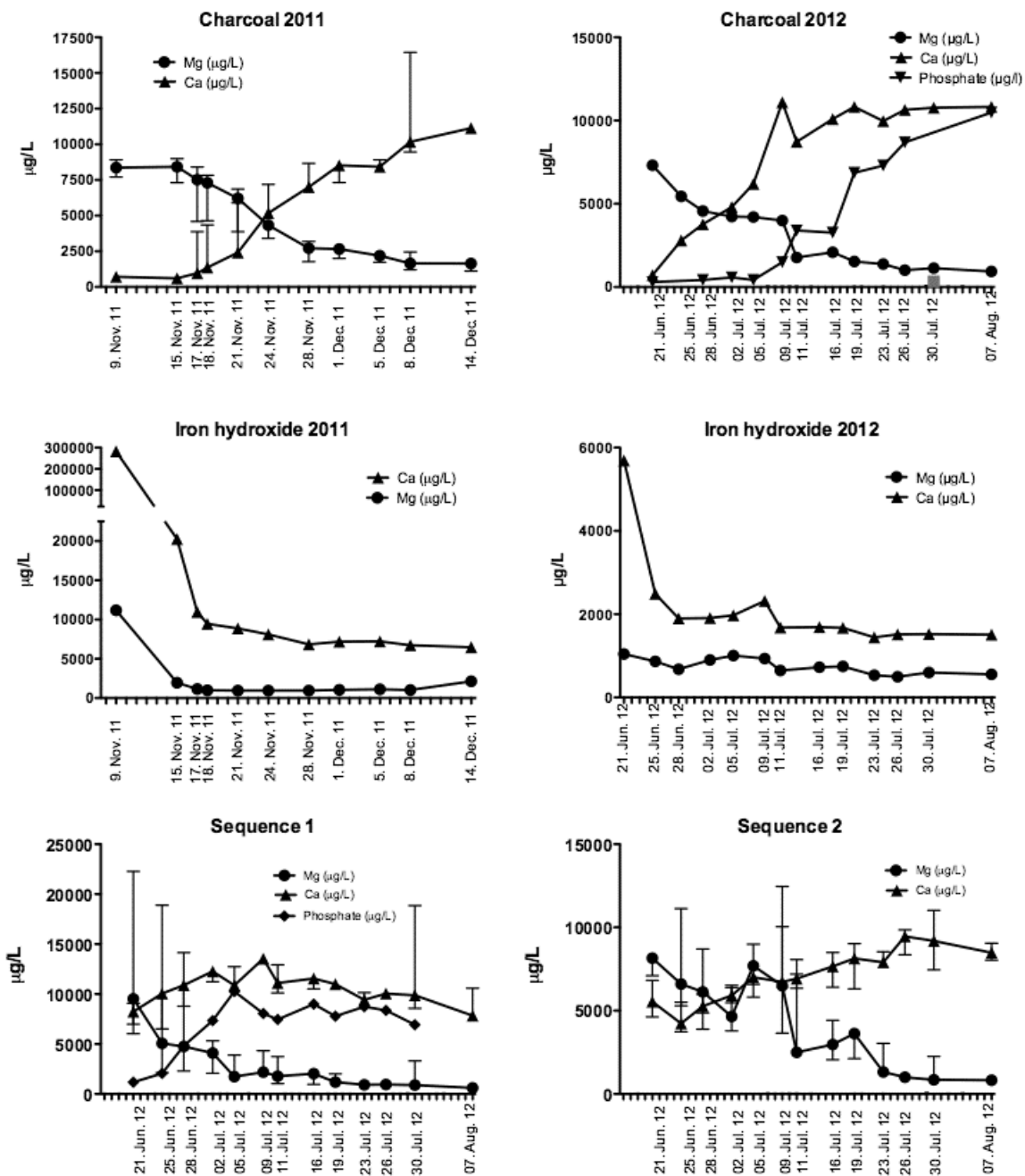


Fig.3S. Concentration of Ca, Mg phosphate in the outlet water of subsequent samples from the column experiment performed with Brimac charcoal, Kemira iron hydroxide in 2011 and 2012, and the two sequences in 2012. The data is either analyses of single samples, or the median with range of triplicate samples.