

# Mobilization of Bound Arsenic and Antimony from Peat used for the Treatment of Mining-Affected Waters

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## Abstract

Mining-affected waters need to be purified for their safe discharge into water bodies. In Finland, peatlands are frequently used in the polishing phase of water treatment. Changes to inflow water quality to the treatment peatlands can trigger release of previously bound contaminants from the peat. A laboratory column experiment was designed to simulate leaching of arsenic and antimony from peat by transition from highly contaminated wastewater to less contaminated water. Inflow water composition change led to leaching and redistribution of bound arsenic and antimony in the peat column. Peak of bound arsenic/antimony shifted towards the outlet during the leaching phase.

**Keywords:** Mining-affected Water, Peatlands, Arsenic, Antimony, Mobilization

## Introduction

Peatlands used for passive treatment of mining-affected waters are common in Finland. As a final treatment step, they are employed to remove various contaminants such as sulphate, nitrogen, phosphorous, metals, and metalloids before the water is discharged into the environment. It has been demonstrated that even in a cold climate, they can provide effective removal of many contaminants (Khan *et al.*, 2020; Kujala *et al.*, 2019) as the adsorption and retention capacity of peat for many of the contaminants commonly found in mining-affected waters is well established (Brown *et al.*, 2000; Liu *et al.*, 2008). In recent years, attention has been diverted to risks associated with using natural peatlands for mining-affected water treatment in the long-term. Over the course of their service life, contaminants removed in treatment peatlands can accumulate in very high concentration in the peatland media and can subsequently leach out under favourable conditions (Khan *et al.*, 2019; Palmer *et al.*, 2015). Such leaching events can happen as a result of changes in biogeochemistry of the peatlands brought about by changes in inflow water composition. Inflow water composition can change due to mine closure or as a result of dilution during snowmelt season and

storm events. Arsenic and antimony are two of the most common contaminants in mining affected waters, which co-occur in mines extracting sulphide ores e.g., pyrite (Arai *et al.*, 2010). Both metalloids have very similar chemical properties despite having some characteristic differences and are efficiently removed in treatment peatlands (Palmer *et al.*, 2015). However, there is a possibility of their mobilization as they are mostly removed by adsorption on peat (Besold *et al.*, 2018; 2019) and precipitation with sulfide (Gammon & Frandsen, 2001). Arsenic and antimony are hazardous for human health, and their elevated concentration in the environment can have detrimental effects for the ecosystem (Abernathy *et al.*, 1999; Cooper & Harrison, 2009; Dovick *et al.*, 2016).

In this study, we simulated the effect of changes in inflow mining-affected water composition on outflow water quality in treatment peatlands by employing flow-through peat columns. The objective was to ascertain whether a substantial decline in arsenic and antimony concentration in the inflow can lead to leaching from peat columns loaded with these contaminants. Thus, this study provides a unique opportunity to see changes in contaminant concentration in peat and water simultaneously while peat

undergoes leaching, hence providing a rare insight into contaminant redistribution characteristics of peatlands heavily polluted with mining-affected water.

## Methods

### Site description and sampling

Peat for the column experiment was obtained from a treatment peatland polishing pre-treated mine process water at a gold mine in Northern Finland. The mean annual temperature at the site is  $-0.5\text{ }^{\circ}\text{C}$  and mean annual precipitation 500-600 mm. The site is typically snow covered from October to May. The peatland has been in operation since 2010 and receives  $3100\text{ m}^3\text{ d}^{-1}$  water. A more detailed description of the sampling site can be found in Khan *et al.* (2020). The peat was collected outside the main flow area of the process wastewater to minimize background concentrations of arsenic and antimony. Peat was sampled from the upper 20 cm in autumn 2019 and stored at  $4\text{ }^{\circ}\text{C}$  prior to column construction. Arsenic and antimony concentrations in the peat were  $43.5\text{ mg kg}_{\text{DW}}^{-1}$  and  $7.8\text{ mg kg}_{\text{DW}}^{-1}$ , respectively.

### Column construction and experimental set-up

The experiment consisted of eight flow through columns: four to study loading and leaching of arsenic and antimony each (Figure 1). Each column comprised a 30 cm long and 5.2 cm diameter plastic column. A perforated plastic disc was used on both sides for even flow distribution across the entire cross section. In addition, a 2.5 cm layer of inert quartz sand (particle size 2-3 mm) was provided on both ends of the column between peat and the circular plastic disc. The columns were filled with peat. Three porewater samplers (Rhizon samplers, Rhizosphere Research Products B.V.) were installed in each column at 7.5 cm, 15 cm, and 22.5 cm from the bottom. Rhizon samplers have a pore size of  $0.15\text{ }\mu\text{m}$  and are a convenient way to collect porewater in a non-destructive way for determination of dissolved constituents. Columns were incubated at  $5\text{ }^{\circ}\text{C}$  throughout the experiment which corresponds to the average *in situ* temperature measured in

10 cm depth. Inflow at the bottom of each column was provided at an average rate of  $5\text{ mL d}^{-1}$  using a peristaltic pump (MINIPULS 3, Gilson Inc.). Columns were loaded with artificial mining-affected water containing high concentrations of arsenic (four columns) or antimony (four columns) for 35 days. The artificial mining-affected water contained  $6\text{ mg L}^{-1}$  arsenic or antimony (supplied as arsenate or antimonate, respectively),  $6\text{ g L}^{-1}$  sodium sulfate,  $25\text{ mg L}^{-1}$  ammonium chloride and  $60\text{ mg L}^{-1}$  sodium nitrate. The pH was adjusted to 7. After 20 days of loading, the arsenic and antimony concentrations were lowered to  $2\text{ mg L}^{-1}$  and one column loaded with antimony containing water was sacrificed. After 35 days, one column per set was sacrificed and the inflow water changed to low arsenic/antimony water ( $0.2\text{ mg L}^{-1}$  arsenic/antimony,  $2\text{ g L}^{-1}$  sodium sulfate,  $25\text{ mg L}^{-1}$  ammonium chloride,  $60\text{ mg L}^{-1}$  sodium nitrate, pH 7) to induce leaching. The remaining columns were sacrificed after 8 days (arsenic, antimony), 16 days (arsenic) and 40 days (arsenic, antimony) under leaching conditions.

### Determination of arsenic and antimony concentrations in inflow water, outflow water and peat

Arsenic and antimony concentrations in column inflow and outflow water were determined using colorimetric assays in 96-well plates based on Dhar *et al.* (2004) and Tighe *et al.* (2018). Briefly, for determination of arsenic concentrations, arsenic in samples and standards was oxidized with potassium iodate to arsenate which was subsequently

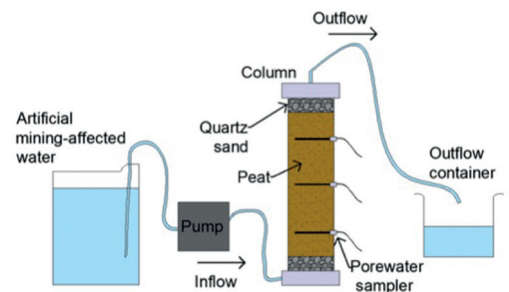


Figure 1 Schematic diagram of the flow-through column experiment.

reacted with a colour reagent containing ascorbic acid, ammonium molybdate, antimony potassium tartrate and sulfuric acid to form arseno-molybdate complexes with absorbance at 880 nm. Phosphate forms phosphor-molybdate complexes when reacting with the colour reagent which likewise absorb at 880 nm, and any phosphate contained in the samples will thus increase the total absorbance. To correct for potential colour formation due to phosphate, in a second set of reactions all arsenic was reduced to arsenite (which does not form arseno-molybdate complexes) with a reducing agent containing sodium metabisulfite, sodium thiosulfate and sulfuric acid prior to the addition of the colour reagent. Arsenic concentrations were calculated from the corrected absorbance using calibration curves in a concentration range from 0 to 10,000  $\mu\text{g arsenic L}^{-1}$ .

For determination of antimony concentration, antimony in the samples was acidified with sulfuric acid and reacted with potassium iodide reagent (20 g  $\text{L}^{-1}$  ascorbic acid, 112 g  $\text{L}^{-1}$  potassium iodide) to form potassium iodoantimonite complexes with absorbance at 425 nm. Concentrations were calculated using calibration curves in a concentration range from 0 to 10,000  $\mu\text{g antimony L}^{-1}$ .

Sacrificed peat columns were divided into 3 to 4 cm thick segments. Arsenic, antimony, iron, and manganese concentrations in peat

were determined by a certified laboratory (Eurofins oy) using ICP-MS after aqua regia microwave digestion.

## Results

The peat flow-through columns were loaded with artificial process and mine dewatering water containing high concentrations of arsenic and antimony, respectively, for approximately 1 month. During the late loading phase, the columns removed both arsenic and antimony with removal efficiencies ranging from 50-85% (arsenic) and 65-95% (antimony) (Fig. 2). There were two sampling timepoint during loading stage where leaching of antimony was observed (day -15). It may be attributed to a sampling error or the inherent heterogeneity of peat. When the inflow was changed to water with lower arsenic/antimony concentration, leaching was induced (Fig. 2). Arsenic concentrations in the outflow increased rapidly and reached a maximum 6 to 16 days after the onset of leaching conditions (Fig. 2A). After that, arsenic concentrations in the column outflow slowly declined again, but were higher than inflow concentrations until day 40 when the last of the columns was sacrificed.

Antimony concentrations in the outflow likewise increased after the onset of leaching (Fig. 2B). However, unlike with arsenic, no peak in outflow concentration was observed but concentrations increased slowly until day 40. Contrary to the results seen here, it has

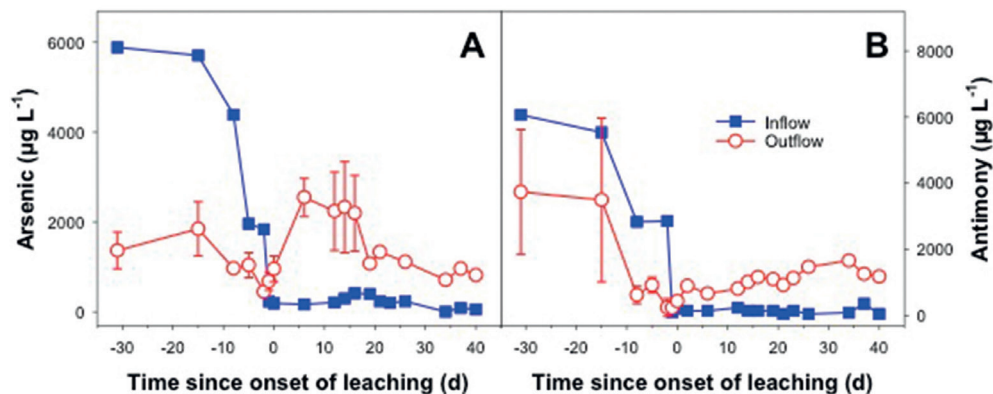


Figure 2 Concentrations of arsenic and antimony in inflow and outflow waters of columns used to test arsenic leaching (A) and antimony leaching (B). Mean values and standard deviations of four columns (until 2 days before onset of leaching), three columns (until 6 days since the onset of leaching), two columns (until 16 days since the onset of leaching) and one column (until 40 days since the onset of leaching) are displayed.

been demonstrated previously that antimony is more readily leached than arsenic from peat (Khan *et al.*, 2019). However, since higher amounts of arsenic were removed than antimony in this experiment (Fig. 3), a higher concentration gradient between peat and water was created for arsenic. This gradient may have led to the observed peak in arsenic leaching. After this initial peak in leaching passed, arsenic and antimony both behaved very similarly as the concentration gradient became more comparable. Both contaminants are removed in peatlands through very similar mechanisms e.g., binding to natural organic matter (Besold *et al.*, 2018; 2019).

Columns were sacrificed during the loading phase (antimony only), at the end of the loading phase and at different timepoints during the leaching phase. At the end of the loading phase, highest concentrations of both arsenic and antimony were observed in the first 10 cm from the column inflow (Fig. 3). In the column loaded with arsenic, peak concentrations were close to  $600 \text{ mg kg}_{\text{DW}}^{-1}$  and there was a sharp drop in concentration towards the end of the column, with concentrations near the outflow of less than  $50 \text{ mg kg}_{\text{DW}}^{-1}$  (Fig. 3A). In the column loaded with antimony, peak concentrations were substantially lower, amounting to only  $150 \text{ mg kg}_{\text{DW}}^{-1}$  (Fig. 3B). Concentrations were likewise lower near the end of the column, but overall, the distribution of antimony was

more even than the distribution of arsenic. In contrast to this a column sacrificed in an earlier stage of loading showed overall lower antimony concentrations and very low concentrations near the end of the column (Fig. 3B), indicating that the capacity for antimony retention in peat might be lower than for arsenic retention, leading to more antimony bound farther away from the inlet in the later loading phase after retention capacity near the inlet was exhausted. The peak concentration of antimony in peat observed in this experiment is in line with the long-term measurements made in the mining-affected treatment peatland in Kittilä where concentration in peat stabilized around  $150\text{--}200 \text{ mg kg}_{\text{DW}}^{-1}$  after 5 years of loading (Khan *et al.*, 2020). In addition, a decline in antimony peat concentration was observed in one of the peatlands after inflow water quality improved due to additional water treatment. Results of this study show that it is more likely that the full-scale peatland is still undergoing redistribution/homogenization of contaminants and substantial leaching to the outflow may be expected in the future.

After eight days under leaching conditions, arsenic was distributed more evenly in the column: While concentrations directly at the inflow were still high ( $310 \text{ mg kg}_{\text{DW}}^{-1}$ ), the highest concentration of  $340 \text{ mg kg}_{\text{DW}}^{-1}$  was observed 14 cm from column inflow (Fig. 3A). Concentrations close to the outflow were substantially higher than after loading. After

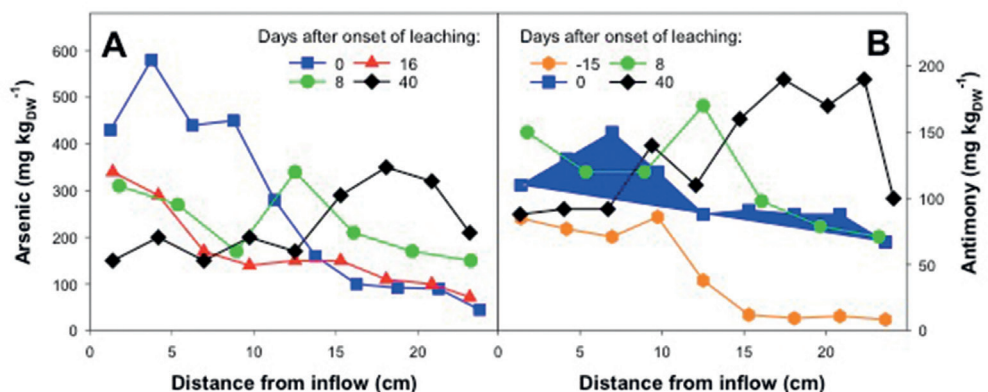


Figure 3 Effect of artificial mining water with low arsenic/antimony concentrations on the distribution of arsenic and antimony along peat columns. Inflow water was changed from water with high arsenic/antimony concentrations to water with low arsenic/antimony concentrations at day 0. Since columns were destroyed for measurement of concentrations in peat, only unicate measurements were available for each timepoint.

40 days under leaching conditions, arsenic concentrations near the inflow had decreased to approximately  $150 \text{ mg kg}_{\text{DW}}^{-1}$ , and a concentration peak was observed close to the column outflow (Fig. 3A).

Peak antimony concentrations likewise moved closer to the column outflow with increasing time under leaching conditions (Fig. 3B). Based on this progression, it can be concluded with a fair amount of confidence that the entire amount of accumulated arsenic and antimony will have eventually leached out to the outflow with longer exposure. However, experiments with longer leaching phase should be carried out to say this with certainty.

## Conclusion

A flow-through column experiment was run to study leaching of arsenic and antimony from mining-affected water treatment peatlands. Peat columns were first loaded with high concentration artificial mining-affected water and then low concentration water was passed to induce leaching. The results showed that both arsenic and antimony were efficiently retained in the column during the loading phase with removal efficiencies reaching around 90% although arsenic retention capacity of peat was observed to be substantially higher than antimony retention capacity. Reducing inflow arsenic and antimony concentrations led to leaching of the retained arsenic and antimony with outflow concentrations constantly higher than the inflow concentrations till the end of the experiment. Measurement of concentrations in peat revealed that peak concentration of both arsenic and antimony moved farther away from the inlet as leaching phase progressed. This study raises serious questions about the long-term use of natural peatlands for mining-affected water treatment and the fate of metals and metalloids in peatlands currently under use.

## References

- Abernathy, C. O., Liu, Y. P., Longfellow, D., Aposhian, H. V., Beck, B., Fowler, B., Goyer, R., Menzer, R., Rossman, T., Thompson, C., Waalkes, M. (1999). Arsenic: health effects, mechanisms of actions, and research issues. *Environmental Health Perspectives*, 107(7), 593–597. <https://doi.org/10.1289/ehp.99107593>
- Arai, Y. (2010). Arsenic and Antimony. In P. S. Hooda (Ed.), *Trace elements in soil* (pp. 383–407). Blackwell Publishing Ltd.
- Besold, J., Eberle, A., Noël, V., Kujala, K., Kumar, N., Scheinost, A. C., Pacheco, J.L., Fendorf, S., Planer-Friedrich, B. (2019). Antimonite Binding to Natural Organic Matter: Spectroscopic Evidence from a Mine Water Impacted Peatland. *Environmental Science & Technology*, 53(18):10792–10802. <https://doi.org/10.1021/acs.est.9b03924>
- Besold, J., Biswas, A., Suess, E., Scheinost, A. C., Rossberg, A., Mikutta, C., Kretzschmar, R., Gustafsson, J.P., Planer-Friedrich, B. (2018). Monothioarsenate Transformation Kinetics Determining Arsenic Sequestration by Sulfhydryl Groups of Peat. *Environmental Science & Technology*, 52(13):7317–7326. <https://doi.org/10.1021/acs.est.8b01542>
- Brown, P. A., Gill, S. A., & Allen, S. J. (2000). Metal removal from wastewater using peat. *Water Research*, 34(16):3907–3916. [https://doi.org/10.1016/S0043-1354\(00\)00152-4](https://doi.org/10.1016/S0043-1354(00)00152-4)
- Cooper, R. G., & Harrison, A. P. (2009). The exposure to and health effects of antimony. *Indian Journal of Occupational and Environmental Medicine*, 13(1):3–10. <https://doi.org/10.4103/0019-5278.50716>
- Dhar, RK, Zheng, Y, Rubenstone J, van Geen, A (2004) A rapid colorimetric method for measuring arsenic concentrations in groundwater. *Anal Chim Acta* 526:203-209. <https://doi.org/10.1016/j.aca.2004.09.045>
- Dovick, M. A., Kulp, T. R., Arkle, R. S., & Pilliod, D. S. (2016). Bioaccumulation trends of arsenic and antimony in a freshwater ecosystem affected by mine drainage. *Environmental Chemistry*, 13(1):149–159. <https://doi.org/10.1071/EN15046>
- Gammons, C. H., & Frandsen, A. K. (2001). Fate and transport of metals in H<sub>2</sub>S-rich waters at a treatment wetland. *Geochemical Transactions*, 2(1). <https://doi.org/10.1186/1467-4866-2-1>
- Khan, U. A., Kujala, K., Planer-Friedrich, B., Räisänen, M. L., & Ronkanen, A.-K. (2020). Long-term data reveals the importance of hydraulic load and inflow water quality for Sb removal in boreal treatment peatlands. *Ecological Engineering*, 148, 105785. <https://doi.org/10.1016/J.ECOLENG.2020.105785>
- Kujala, K., Karlsson, T., Nieminen, S., & Ronkanen, A.-K. (2019). Design parameters for nitrogen removal by constructed wetlands treating mine

- waters and municipal wastewater under Nordic conditions. *Science of The Total Environment*, 662, 559–570. <https://doi.org/10.1016/j.scitotenv.2019.01.124>
- Liu, Z. rong, Zhou, L. min, Wei, P., Zeng, K., Wen, C. xi, & Lan, H. hua. (2008). Competitive adsorption of heavy metal ions on peat. *Journal of China University of Mining and Technology*, 18(2):255–260. [https://doi.org/10.1016/S1006-1266\(08\)60054-1](https://doi.org/10.1016/S1006-1266(08)60054-1)
- Palmer, K., Ronkanen, A.-K., & Kløve, B. (2015). Efficient removal of arsenic, antimony and nickel from mine wastewaters in Northern treatment peatlands and potential risks in their long-term use. *Ecological Engineering*, 75(0), 350–364. <https://doi.org/10.1016/j.ecoleng.2014.11.045>
- Tighe, M, Edwards, MM, Cluley, G, Lisle, L, Wilson, SC (2018) Colorimetrically determining total antimony in contaminated waters and screening for antimony speciation. *J Hydrol* 563:84-91. <https://doi.org/10.1016/j.jhydrol.2018.05.056>