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Arsenic, antimony, and nickel leaching from northern peatlands treating mining influenced water in cold climate

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Abstract

Increased metal mining in the Arctic region has caused elevated loads of arsenic (As), antimony (Sb), nickel (Ni), and sulfate (SO_4^{2-}) to recipient surface or groundwater systems. The need for cost-effective active and passive mine water treatment methods has also increased. Natural peatlands are commonly used as a final step for treatment of mining influenced water. However, their permanent retention of harmful substances is affected

by influent concentrations and environmental conditions. The effects of dilution, pH, temperature, oxygen availability, and contaminant accumulation on retention and leaching of As, Sb, Ni, and sulfate from mine process water and drainage water obtained from treatment peatlands in Finnish Lapland were studied in batch sorption experiments, and discussed in context of field data and environmental impacts. The results, while demonstrating effectiveness of peat to remove the target contaminants from mine water, revealed the risk of leaching of As, Sb, and SO_4^{2-} from treatment peatlands when diluted mine water was introduced. Sb was more readily leached compared to As while leaching of both was supported by higher pH of 9. No straightforward effect of temperature and oxygen availability in controlling removal and leaching was evident from the results. The results also showed that contaminant accumulation in treatment peatlands after long-term use can lead to decreased removal and escalated leaching of contaminants, with the effect being more pronounced for As and Ni.

Keywords: *Mine water, peat, wetlands, leaching, removal, metals, metalloids, sulfate*

1. Introduction

Mining operations typically result in enormous quantities of process waters (e.g. from beneficiation) and acid or alkaline mine drainage waters (e.g. from mine dewatering and seepage from tailings and waste rock piles). These waters usually contain high concentrations of contaminants, including metals, metalloids and salts, which can have devastating impact on the nearby groundwater and surface water bodies and their respective users and ecosystems (Johnson and Hallberg, 2005; Kaupilla et al., 2011; Nordstrom and Alpers, 1999). While it is a global issue, the impacts can become particularly amplified in high-latitude regions because of their pristine environment, cold climate, and the fact that pollutants tend to persist longer under these conditions (Macdonald et al., 2000). Special attention is needed to minimize these impacts because the Arctic region is home to some of the largest extracted and explored metal mineral reserves in the world (Boyd et al., 2016).

Process and drainage waters from mines extracting sulfide ores (e.g. pyrite and galena) may contain arsenic (As) and antimony (Sb) as the principal environmental contaminants,

especially since pollution from these two elements often co-occur (De Gregori et al., 2003; Rieuwerts et al., 2014; Toujaguez et al., 2013; Wu et al., 2011). Sources of metal and metalloid pollution in the environment are however not limited to mining. Elevated concentrations of As have been reported in soil near coal combustion based thermal power plants (Jurkovič et al., 2011) and in groundwater sources all over the world (Bhattacharya et al., 2007). Similarly, high concentrations of Sb in soils are linked to anthropogenic activities such as smelting industry (Ainsworth et al., 1990). Severe health effects of As, Sb (Abernathy et al., 1999; Cooper and Harrison, 2009; U.S. Environmental Protection Agency, 2013a) and another important constituent of sulfide ores such as nickel (Ni) (Borba et al., 2006; U.S. Environmental Protection Agency, 2013b) are well known. Moreover, As and Sb are linked to eco-toxicity in aquatic and soil ecosystems (Borgmann et al., 2005).

Active treatment methods such as oxidation, dosing with alkali, accelerated sedimentation (ODAS), ion exchange and sorption, sulfate reduction and bio-desalination are essentially used in the mining industry (Hengen et al., 2014; Stuhlberger et al., 2007; Younger et al., 2002). These methods are reliable, operationally flexible, can treat high pollution loads, and generally do not require very large areas. On the down side, they are energy- and resource-intensive and require continuous monitoring, as well as frequent maintenance. Moreover, operational costs of active treatment become even more financially unappealing to mining companies once the mine has ceased to produce economic revenues (Gazea et al., 1996) especially in the Arctic region where amount of produced mine waters are typically high. For these reasons, passive treatment has received much attention in recent years.

Constructed wetlands are the most popular passive treatment method used for mine water treatment (PIRAMID Consortium, 2003). They imitate many processes of active treatment in a naturally sustained environment powered by ambient solar energy. These processes

include equalization, settling, filtration, sorption, chemical precipitation, microbial decomposition and biological oxidation, among others (Crites et al., 2006; Palmer et al., 2015; Sheoran and Sheoran, 2006; Sundaravadivel and Vigneswaran, 2001; Vymazal, 2010). After mine closure, passive methods can be especially attractive for the treatment of mine drainage water, since they keep working with an almost negligible requirement for maintenance and supervision. Peatlands, a type of natural wetland, cover around 3% of the global land area and are most prevalent in high-latitude regions and in the tropics (Turetsky et al., 2014). Peatlands have been used as a treatment step in the mining industry for years (Palmer et al., 2015).

The ability of peat soil to remove metals and metalloids from contaminated water is well established (Allen et al., 1994; Bunzl et al., 1976; Gosset et al., 1986). The removal processes include ion exchange, surface adsorption, chemisorption, complexation and adsorption-complexation (Brown et al., 2000). These processes are controlled by environmental conditions such as pH, temperature, and dissolved oxygen. The pH and cation concentrations in natural peatlands depend on the peatland type; ombrotrophic bogs are, in general, characterized by lower pH and cation concentrations ($\text{pH} < 4$, $\text{Ca} < 1 \text{ mgL}^{-1}$) than minerotrophic fens ($\text{pH} > 4$, $\text{Ca} > 2 \text{ mg L}^{-1}$) (Glaser et al., 1990; Griffiths and Sebestyen, 2016). In general, metal removal has been found to be the most effective in the pH range 3.5 to 6.5, while metals start to leach at lower pH (Brown et al., 2000; Coupal and Lalancette, 1976; Randall et al., 1974; Sen Gupta et al., 2009; Tipping et al., 2003). The role of temperature, however, remains unclear, as both negative and positive correlations between peat metal adsorption capacity and temperature have been reported (Ansone et al., 2012; Champagne et al., 2008; Lalvani et al., 1997; Viraraghavan and Dronamraju, 1993). At the same time, low dissolved oxygen has been linked to better removal of metals, such as cadmium (Cd), manganese (Mn), zinc (Zn), aluminum (Al), Ni, copper (Cu), and iron (Fe),

from mine water in peat based biofilter columns (Champagne et al., 2008), while competition with other aqueous species (metals, cations and anions) has been shown to negatively affect adsorption of certain metals (Brown et al., 2000; Palmer et al., 2015; Wilson et al., 2010). Dissolved oxygen concentration affects the redox conditions and speciation of metals and metalloids influencing their removal/retention. In addition to this, sulfates, after reduction to sulfides in anoxic environments, effectively contribute to metal removal from water by metal sulfide precipitation that is a major metal removal mechanism in wetlands treating mine waters (Reddy and DeLaune, 2008).

Environmental conditions in treatment peatlands can be quite variable, affecting their treatment efficiency (Karjalainen et al., 2016). The oxygen availability in peatlands varies with peat depth (Heikkinen et al., 2018; Megonigal et al., 1993) and is also affected by groundwater level (Patrick et al., 1985) and temperature. Furthermore, snow and ice cover that accumulate over the long winter in the treatment peatland, restrict diffusion of oxygen from the atmosphere into the peat and pore water in Arctic region (Kadlec and Reddy, 2001). However, there is a lack of knowledge about how these factors can be linked to the removal/leaching processes in field conditions.

In addition to reduced treatment efficiency, the risk of contaminant leaching from treatment peatlands can increase when contaminants have accumulated to high concentrations in the peat after many years of operation (Palmer et al., 2015; Ronkanen and Kløve, 2009). These bound contaminants can detach from peat and become mobile due to changes in pH and redox conditions (Coupal and Lalancette, 1976; Frohne et al., 2011; Gambrell, 1994; Rothwell et al., 2010) brought about by a large influx of water, e.g. during snowmelt season and storm events. In waters rich in anions (e.g. sulfates, phosphates), the anions can exchange with adsorbed metals, thus affecting their retention (Stuckman et al., 2011).

Furthermore, metals and metalloids removed by formation of insoluble metal sulfides under anoxic conditions can leach out under oxidizing conditions, when sulfides are oxidized to sulfates (Reddy and DeLaune, 2008). Leaching also poses a long-term risk, and the risks for leaching of contaminants are still poorly understood.

This study is based on the hypotheses that drop in influent water concentration and accumulation of contaminants in northern peatlands used for treatment of mining influenced water both lead to a decline in removal efficiency and an increase in the risk of contaminant leaching. In order to clarify this, fresh and unmodified peat from two treatment peatlands were sampled for batch adsorption/desorption experiments. Most studies to date have used treated and/or modified peat (Leiviskä et al., 2018; Sen Gupta et al., 2009) and studies using unmodified and untreated peat are scarce. Unlike constructed wetlands, natural peatlands are uncontrolled passive treatment systems. Thus, probable environmental impacts related to use of natural peatlands in mine water treatment include the degradation of peatlands by contaminants accumulation and risk of pollutant leaching to recipient waters in long term. These can be a setback to the efforts towards sustainable mining. More explicitly, the following aspects have been explored in detail in this study:

- i) The effectiveness of unmodified peat from peat-based treatment wetlands to remove contaminants from mining influenced water
- ii) The effect of pH, temperature, and dissolved oxygen availability as critical parameters on removal and leaching of contaminants from northern peatlands treating mining influenced water.
- iii) The decline in effectiveness of peat-based treatment wetlands to remove contaminants from mining influenced water after long-term use.

The results, although focused on mining influenced water, are applicable in the broader context to pristine and constructed wetlands loaded with metals, metalloids and sulfates from both natural and anthropogenic sources.

2. Materials and Methods

2.1. Site description

The study site comprised two mining influenced water treatment peatlands, one receiving pre-treated process water (TP A) and the other receiving pre-treated drainage water (TP B) from a gold mine in Finnish Lapland (67°54'N; 25°22'E) (Figure 1a). The region is classified as Dfc (snow climate characterized by moist, cold winters) in the Köppen climate classification system (Autio and Heikkinen, 2002; Köppen, 1936). There is permanent snow cover from October to May, and summer temperatures lie in the range 4-20°C (Finnish Meteorological Institute, 2017). For this study, constituents of interest in the process water and drainage water from the mine are As, Sb, Ni, and sulfate (SO_4^{2-}). Since the water received by both peatlands is pre-treated, the inflow concentrations of many parameters are well below the concentrations usually found in mining influenced water, e.g. mean concentrations of suspended solids in inflow water are 5.83 mgL^{-1} and 4.44 mgL^{-1} for TP A and TP B, respectively. The pH in the peatlands varies between 6.0 and 7.5 (mean \pm SD: 6.87 \pm 0.59) as monitored with pH loggers from 2013 to 2015, and the combined concentration of major cations (K, Mg, Ca and Na) in soil samples lies in the range of 8-42 g kg^{-1} indicating high cation exchange capacity (CEC) that is in line with those reported for moss peat in northern latitude regions (Rippy and Nelson, 2007). Hydraulic conductivities in the peatlands, measured in 2015 through a falling head piezometer test, were quite high even in deeper peat layers. Average hydraulic conductivity at 80 cm depth was 0.0182 $\text{cm s}^{-1} \pm 0.0179$ compared to 0.032 $\text{cm s}^{-1} \pm 0.027$ near the surface.

2.2. Peat and mine water sampling

Peat samples were taken as soil cores with a Russian peat corer on three different occasions: In June 2013 and August 2014, single samples were taken from three locations in TP A and four locations from TP B, respectively. In March 2016, three replicate peat samples (within an area of 1 m²) were taken from two locations in each peatland. The samples used in the majority of the experiments were from sampling points located quite close to the wetland inlets: 77 m from the inlet for TP A (total length 1200 m) and 194 m from the inlet for TP B (total length 550 m). Sampled peat soil was separated according to depth prior to storage. The samples were stored in airtight LDPE bags at 4±1°C. The samples collected in 2013 and 2014 contained less water than the samples collected in 2016 and were used in batch experiments without any further processing. The peat samples taken in 2016 were dewatered through centrifugation at 4500 rpm (4754 RCF) for 2 hours. Centrifugation resulted in phase separation, with accumulation of relatively drier peat at the bottom and pore-water at the top, which was removed using a pipette.

Mine drainage water, from open pits and underground mining, and process water samples were collected for the batch experiments from their respective basins. These basins contain pre-treated process water and neutralized mine drainage water before these are released into their respective treatment peatlands. Process water sampling was carried out in June 2014, while drainage water samples were collected in August 2014. For the later phase of the experiments, water samples from both basins were collected again in March 2016. All water samples were stored at 4±1°C in an HDPE container, and their elemental chemical composition was analyzed prior to the batch tests.

2.3. Sorption and desorption experiments

Batch sorption (removal)/desorption (leaching) experiments were performed with peat soil from the treatment peatlands. Mine process or drainage water was used as the liquid phase, both undiluted and diluted to various degrees with MilliQ water (1:10, 1:100, 1:500 and 1:1000). Peat soil from the peatland receiving process water (TP A) was subjected to process water, while peat soil from the treatment peatland receiving drainage water (TP B) was subjected to drainage water. The experiments were conducted under oxic and anoxic conditions using peat samples from different locations and depths (10 cm and 70 cm from peat surface) while temperature (1°C, 10°C and 25°C) and pH (pH 6 and pH 9) were varied in the experiments. Furthermore, batch experiments were performed with samples taken at two different points in time about 2-3 years apart, in order to study long-term changes in treatment behavior and accumulation of contaminants in the treatment peatlands. A schematic overview of the study set-up is given in Figure 1b.

The incubations were carried out in accordance with the procedure laid down by Roy et al. (1992). A soil-solution ratio of 1:60 (2.5 g of soil in 147.5 mL of solution) was used, as it has been found to be appropriate by other authors (Koivula et al., 2009; Palmer et al., 2015) for sorption experiments involving metals and peat. Batches were incubated for 24 hours on a rotary overhead shaker rotating at 30 rpm. This incubation period was selected to provide sufficient time for the sorption/desorption reaction to reach equilibrium. After incubation, the peat was allowed to settle from solution, and the supernatant was removed using a syringe and filtered through a 0.45 µm polyethersulfone membrane syringe filter. The filtrate was analyzed for equilibrium concentrations of As, Sb, Ni, Fe, Al and SO_4^{2-} . Redox potential and pH of the solution were also measured post incubation.

Oxic incubations were carried out with ambient air in the headspace, while anoxic incubations were carried out in crimp-sealed glass serum bottles that were made anoxic by

replacing the ambient air in the headspace and dissolved oxygen by purging with dinitrogen gas (for about 20 minutes) until the remaining dissolved O₂ concentration was less than 0.1 mgL⁻¹. Dissolved O₂ concentration in oxic incubations was higher than 9 mgL⁻¹.

The dilution ratios used were selected to represent the range of concentrations expected to be encountered in the treatment peatlands. The selection was based on analysis of water quality data for the receiving water body upstream of the TP A and TP B outlets (which were taken as examples for the lowest possible concentration ranges) and the water quality data of process and drainage water (which were taken as examples for the highest possible concentration ranges; Supplemental Table S1). The data on the receiving water body were taken from a database maintained by the Finnish Environmental Institute (Hertta-database).

2.4. Analytical procedure

Peat and pore water were analyzed separately for their chemical characteristics. For concentrations in peat, analyte extracted from peat through HNO₃/HCl extraction (EPA3051A) was analyzed. Chemical analyses were carried out at an accredited laboratory (AHMA ympäristö Oy) using ICP-MS (for As, Sb, Ni, Fe and Al; SFS-EN ISO 17294-2:2005) and ion exchange chromatography (for SO₄²⁻; SFS-EN ISO 10304-1:2009). Peat and pore water characteristics are summarized in Supplemental Table S2 and Supplemental Table S3, respectively, while Supplemental Table S4 presents concentrations of various contaminants in the process and drainage water samples.

Dry mass of the peat samples was calculated from the moisture content of the dewatered peat samples (ASTM D 2974) by oven drying at 86°C (O'Kelly, 2005). In addition to the moisture content, ash content and organic content of the peat samples were also measured (Supplemental Table S2), following the same standard specifications.

2.5. Calculations and statistical analysis

The amounts of contaminants removed from, or leached to, the liquid phase were calculated as:

$$C_{removed} = C_i - C_{eq}$$

where $C_{removed}$ is amount of contaminant removed from the solution (mgL^{-1}), C_i is initial concentration of contaminant in the solution (mgL^{-1}) and C_{eq} is equilibrium concentration of contaminant in the solution (mgL^{-1}).

In this study, the use of the term adsorption is not restricted to the strict definition of the physical phenomena of adsorption. Rather, it describes removal of an entity from the liquid phase, regardless of the mechanism and process leading to removal. Therefore, the term adsorption is used interchangeably with the term removal throughout the text. Similarly, the term desorption is used interchangeably with the term leaching.

In order to enable comparison of results from two sampling sets taken in two different years, and eliminate initial peat concentration differences between these, the distribution coefficient (K_d) defined by Kaplan et al. (1995) was employed:

$$K_d = A_{removed}/C_{eq}$$

Where K_d is the distribution coefficient (Lg^{-1}) and $A_{removed}$ is the amount of contaminant removed per unit dry mass of adsorbent (mgg^{-1}).

Statistical analysis was carried out using R version 3.3.1. Normality of data distribution was checked using Shapiro-Wilk test. Since the data was found to be not normally distributed, therefore the non-parametric Man-Whitney U test was used for comparing samples with the significance level set at $p \leq 0.05$.

The range of concentrations used in the batch experiments was selected based on the range observed in the mining influenced waters and recipient water bodies in the region that allowed for applying results obtained in laboratory condition to the field environment. Therefore, linear isotherms were applied and plotted where useful to highlight certain patterns in adsorption/desorption behavior.

In order to identify the variables with a significant impact on adsorption and leaching values and to reduce the multivariate data into simplified graphics, ordination was performed on the adsorption/desorption dataset using the vegan package in R (Oksanen et al., 2017). Principal component analysis (PCA) was employed as the ordination method and the data was standardized between range 0-1. The vectors of variables which significantly correlated with the ordination were fitted on the ordination.

3. Results

3.1. Removal and leaching of contaminants

The quantities of contaminants removed from the mining influenced water by the peat and the amount leached from the peat to the mining influenced water covered a broad range and varied with dilution ratio, temperature, pH, sampling depth, and location of the peat sampling point. The quantities also changed with the year of sampling and dissolved oxygen availability during incubation. A summary of contaminant removal and leaching is provided in Supplemental Table S5. Average removal was $4.6 \mu\text{gL}^{-1}$ for As, $9.7 \mu\text{gL}^{-1}$ for Sb, $20 \mu\text{gL}^{-1}$ for Ni and 148mgL^{-1} for SO_4^{2-} . Similarly, average leached quantities were $14.23 \mu\text{gL}^{-1}$ for As, $22.5 \mu\text{gL}^{-1}$ for Sb, $1.97 \mu\text{gL}^{-1}$ for Ni, and 99.6mgL^{-1} for SO_4^{2-} .

3.2. Effect of dilution on removal and leaching of contaminants

Dilution of the tested water had a major effect on removal/leaching pattern in the peat. As the dilution ratio increased, and consequently the initial contaminant concentration in the solution decreased, the behavior of the peat changed from removal to leaching. This trend was observed in almost all experiments and can be clearly seen in the case of As for the process water under oxic conditions (Figure 2), and in the case of Ni for the drainage water under anoxic conditions (Supplemental Figure S1). Thus, this indicates that the contaminants are not sorbed permanently, but more likely chemically or physically bound and therefore easily leachable if chemical balance changes. Linear isotherms plotted with data from all three sampling years (both depths, oxic and anoxic, 10°C) also yielded trend lines representing a shift from adsorption to leaching as the equilibrium concentration decreased. Linear isotherms were determined separately for contaminant removal (Figure 3a) and leaching (Figure 3b).

3.3. Effect of temperature and pH on removal and leaching of contaminants

In most of the experiments, pH in the alkaline range resulted in higher As leaching and reduced removal compared with the slightly acidic pH of 6 (Supplemental Figure S2a). Similar behavior was generally observed for Sb under oxic conditions.

Under anoxic conditions, Sb removal seemed to be more efficient at pH 9 than at pH 6, as there was higher removal with dilution ratio 1:1 (Supplemental Figure S3a) or less leaching with higher dilution ratios (Figure S4a). There were some deviations, mostly for drainage water involving replicate 3 (Supplemental Figure S5a). For Ni and SO_4^{2-} , removal was likewise stronger at pH 9 and leaching was more pronounced at pH 6 anoxic but also under oxic conditions.

In comparison with pH, the effect of temperature was somewhat more complicated. For oxic incubations conducted with peat sampled in 2013, As removal was highest at 1°C

(Supplemental Figure S2b), followed by 25°C or 10°C depending on the degree of dilution (at higher dilutions 10°C was more effective for As removal than 25°C). In anoxic incubations conducted with peat sampled in 2016, the behavior also varied from one dilution to the other; removal of As was only observed for the undiluted process water at 10°C, whereas leaching from the diluted samples was most pronounced at 25°C.

On the other hand, process and drainage water behaved differently in terms of Sb removal. The removal was generally higher at the mid temperature (10°C) for process water (Supplemental Figure S3b), and at the highest temperature tested (25°C) for drainage water (Supplemental Figure S6b), in all oxic and anoxic incubations. Leaching of Sb was greatest at the highest temperature tested (Supplemental Figure S4b and Supplemental Figure S5b). Nickel showed leaching only to the highest dilution (1:1000), while the effect of temperature on removal and leaching seemed to vary without any clear pattern. The results, as a whole, indicated that temperature is not a major controller of removal and leaching processes, at least in the range of 1-25 °C.

3.4. Contaminant accumulation in peatlands after long-term use

Long-term use of treatment peatlands can be expected to result in high accumulation of contaminants in the peat, leading to a decline in treatment efficiency and an increased risk of leaching. A comparison of distribution coefficients from different sampling years (2013-2016) was carried out (Figure 4). In general, less removal and more leaching of As was observed with samples (water and peat) collected in 2016 than with samples taken in 2013/2014 (Figure 4a). The difference was significant for process water ($p=1.69 \cdot 10^{-8}$) but not for drainage water ($p=0.53$). For Sb (Figure 4b), on the other hand, no significant difference in removal and leaching behavior was detected between the sampling years for process water peatland (TP A, $p=0.19$), while even higher removal and lower leaching were

observed for the more recent water samples taking from the peatland treating drainage water (TP B, $p=0.024$). Difference in distribution coefficients for Ni removal/leaching between the two sampling years was significant for process water peatland ($p=0.04$), but not for drainage water peatland ($p=0.06$) (Figure 4c). The load of each contaminant to both treatment peatlands (TP A and TP B) between the two sampling time points (June 2013 to March 2016 and August 2014 to March 2016, respectively) were estimated using inflow rates and water quality data. Based on this, TP A received around 20200 tons of SO_4^{2-} , 323 kg of As, 148 kg of Sb and 91 kg of Ni, while SO_4^{2-} and As loads to TP B were much smaller being only 4.5 tons of SO_4^{2-} and 105 kg of As. However Sb and Ni loads to TP B were clearly higher (911 kg of Sb and 270 kg of Ni) compared to TP A. These differences in pollutant loads partly explain observed differences in removal/leaching behavior of the treatment peatlands.

3.5. Effect of oxygen availability on removal and leaching

No significant difference in removal and leaching behavior was observed between oxic and anoxic incubations, indicating that the risk of contaminants leaching from deeper peat layers is likely not enhanced by the anoxic conditions. However, there were isolated cases where the results of removal/leaching behavior of incubations conducted under oxic conditions differed substantially from those conducted anoxic conditions, e.g. in the case of Sb removal from undiluted process water at 25°C or As removal and leaching from undiluted process water at all temperatures (Figure 5). However, no clear and across the board correlation between oxic/anoxic environment and removal/leaching was observed (Supplemental Figure S7).

4. Discussion

Wetlands are used to decrease environmental impacts of mining influenced waters worldwide and treatment peatlands are more common in Finland and Ireland. However, some potential risks are associated generally with those treatment wetlands: Limits in the removal and storage capacity as well as leaching of initially stored contaminants can be substantial threats to the environment. The present study demonstrated in batch incubations, that peat from treatment peatlands is capable of removing contaminants from mining influenced waters, even though removal efficiencies are variable. The variability observed in the results is partly caused by the spatial heterogeneity of natural peatlands (Arsenault et al., 2018; Beckwith et al., 2003; Waddington and Roulet, 2000) that has already been linked to differences in removal capacity of peat (Bonnett and Cousins, 1987; Ringqvist et al., 2002). However, this study is first attempt to figure out the role of environmental factors in As, Sb, and Ni removal capacity of natural peat collected from peatlands treating mine waters.

4.1. Effect of dilution on contaminant removal from mining influenced waters

During the life cycle of a mine, various events can cause differences in the composition of the treatment peatland inflow waters in the Arctic region. Changes in the ore extraction and beneficiation processes or changes in active water purification processes at the mine typically influence ratios of different contaminants in mine waters, while events like spring snowmelt, heavy rainfalls or mine closure will influence the concentrations of contaminants by diluting the inflow waters at the treatment peatland. It is to be expected that each of these scenarios affect the removal efficiency of treatment peatlands since washout of metals from flood plain soil sediments polluted with domestic and industrial effluents has been reported during storm seasons (Chaudhary et al., 2016). However, for treatment wetlands, dilution with unpolluted water has been suggested to improve pollutant — particularly metal —

attenuation (Höglund et al., 2004), and has to date not been discussed as a trigger of contaminant mobilization.

The results of the batch incubations with peat from TP A and TP B showed that dilution of mining influenced waters resulted in decreased contaminant removal, and, as dilution ratios increased, increased contaminant leaching (Figure 2 and Supplemental Table S5). The effect of dilution infers that the concentration gradient between water and peat determines whether removal or leaching is more likely to occur. The dominant influence of dilution can be clearly seen by fitting the vectors of parameters with a significant correlation onto the ordination of multivariate data from the experiments (Figure 6). As evident from the results, Sb started to leach at lower dilutions while As was still being removed. Furthermore, the largest leached quantity of Sb ($512.4 \mu\text{gL}^{-1}$) was almost double that of As ($288.9 \mu\text{gL}^{-1}$). This disparity between As and Sb may be explained by the results of the study by Palmer et al. (2015) involving batch incubations with peat. They reported that at low concentrations, slight increase in Sb concentration resulted in substantial gains in its adsorption unlike As. In line with the results of this study, it suggests higher sensitivity of Sb removal to changes in concentration in the liquid phase. In comparison with As and Sb, peat was found to be more effective in Ni removal and retention even at higher dilution, with greater quantities removed and significantly lower leaching across all dilution ranges tested. Ni is indeed known for its strong binding to peat even in conditions where other metals start to leach, e.g. low pH environments (Gosset et al., 1986) which was confirmed also in this study.

A comparison of the contaminant concentrations in mine influenced water after various levels of dilution and the base concentrations in the recipient water body provided the practical rationale for the selected dilution range (Supplemental Table S1). After mine closure, waters somewhat similar to those measured in the recipient water body can be

expected to represent inflow water to the treatment peatlands, thus the dilutions scenarios simulated in the experiments of this study give important hints on what has to be considered in the future. In addition, concentrations of the recipient water body can also be seen as an indicator of concentrations in snowmelt and rainfall runoff reaching the treatment peatlands in boreal region. Closely monitoring concentrations in the peatland influent and bypassing peatlands when concentrations become too low can, to some extent, be one measure for control of leaching. For such a measure, special attention should be paid to Sb concentrations in inflow when making the decision about temporarily bypassing the peatlands as it seemed to be most sensitive for leaching.

4.2. Effect of oxygen on contaminant removal from mining influenced waters

Wetlands soils are temporarily or permanently waterlogged, and anoxic, reducing conditions often prevail in deeper peat layers. Under reducing conditions, the speciation of contaminants like As and Sb can change, and SO_4^{2-} can be reduced to sulfide by sulfide reducing bacteria (Fortin et al., 2000; Muyzer and Stams, 2008; Wilson et al., 2010). Sulfate, reduced to sulfide, leads to the precipitation of metals and metalloids as sulfides and to adsorption of metals on iron sulfides such as FeS and FeS_2 (Huerta-Diaz et al., 1998). All these processes are thought to influence the removal of contaminants from mining influenced waters through treatment wetlands. However, results from batch incubations with peat soil conducted under oxic and anoxic conditions indicated that there was no clear difference in the removal and/or leaching of As, Sb, and Ni at different oxygen conditions. For SO_4^{2-} , lower leaching was observed under anoxic conditions ($93.0 \pm 91.7 \text{ mgL}^{-1}$) than under oxic conditions ($101.7 \pm 101.7 \text{ mgL}^{-1}$), which may be due to enhanced sulfate reduction and subsequent sulfide precipitation under anoxic conditions.

Anoxic conditions can both promote As release from soil by reduction of As sorbed iron hydroxides through microbial sulfidogenesis, and stabilize As through co-precipitation with Fe sulfides (Kocar et al., 2010; O'Day et al., 2004). Arsenic sulfide precipitation is also hindered by high concentrations of pore-water sulfide due to abundance of soluble thioarsenate species (Burton et al., 2011). Recently, peat has been shown to immobilize As through direct binding of As on organic sulphur species under anoxic conditions (Hoffmann et al., 2012; Langner et al., 2011). A combination of one or more of these mechanisms—under different situations due to heterogeneity of peatlands—may be responsible for no clear effect of oxic and anoxic conditions on As removal/leaching in the experiments with 24-hour retention time. To clarify this, experiments with longer retention time are needed.

Oxygen availability, nevertheless, influenced how pH affected Sb removal/leaching. Under anoxic conditions, Sb removal was better at pH 9 than at pH 6 while the opposite was true under oxic conditions. Both high pH and anoxic conditions cause a drop in redox potential (Calmano et al., 1993). Maurer et al. (2010) documented changes in humic substances with redox conditions and attributed higher pH and reducing conditions to an increase in binding sites with high proton affinity in humic acid. This could mean stronger removal under these conditions for entities which are removed by proton exchange or through formation of H-bridges, e.g. Sb(III) (Buschmann and Sigg, 2004). However, Sb (III) in peatlands is often found as anions for which proton exchange may be ruled out as the removal mechanism.

Antimony and As are often thought to have similar geochemical behavior as they belong to the same group in periodic table, however there are differences in their redox properties (Arai, 2010; Mitsunobu et al., 2006; Wilson et al., 2010). This could explain why in this study, anoxic conditions affected the influence of pH on Sb, but not on As removal. For example, antimonate is less readily reduced than arsenate under reducing conditions

(Mitsunobu et al., 2006). In contrast to the thermodynamic predictions, whether antimonite and/or antimonate are present in water is not always dictated by the presence of oxygen. Antimonite has been detected in many oxygenated natural waters while oxidized Sb species have been found under anoxic conditions (Filella et al., 2002). Arsenic, on the other hand, is predominantly found as uncharged H_3AsO_3 under reducing conditions for the pH range (6-9) involved in the experiments (Smedley and Kinniburgh, 2002).

Nickel speciation is even less redox sensitive than both As or Sb speciation under conditions normally found in nature (Weiner, 2008), and no clear effect of oxygen availability on Ni removal and leaching was observed in this study. However, Ni removal might be indirectly influenced by oxygen availability, as insoluble Ni-sulfides might form under anoxic conditions. Similarly, As and Sb can also precipitate as sulfides under anoxic conditions.

4.3. Effect of pH on contaminant removal from mining influenced waters

Generally, biological and chemical processes in treatment wetlands are affected by pH (Kadlec and Knight, 1996). In peatlands treating mining-influenced water, pH affects both the characteristics of peat—due to presence of acidic species in peat organic matter— and the speciation and behavior of contaminants such as As, Sb, and Ni (de Oliveira et al., 2015; Herath et al., 2017; Xue et al., 2001). As expected, a pronounced effect of pH on the removal and leaching of As, Sb, and Ni was observed in the experiments. Higher leaching and reduced removal of As and Sb were observed when pH was in the alkaline range which is in agreement with other studies (Ansone-Bertina and Klavins, 2016; Buschmann and Sigg, 2004; de Oliveira et al., 2015; Thanabalasingam and Pickering, 1986). This can be attributed to the effects of high pH on humic acids, such as enhanced deprotonation and loss of binding sites due to humic acid dissolution (de Oliveira et al., 2015; Thanabalasingam and Pickering, 1986). The species of As found in aqueous solutions at pH 6 are different than the ones

found at pH 9 that contributed to the differences in removal/leaching of As between the two tested pH. Under oxidizing conditions, more protonated H_2AsO_4^- is the dominant species at pH 6 while less protonated HAsO_4^{2-} is prevalent at pH 9 (Smedley and Kinniburgh, 2002; Ungureanu et al., 2015). Similarly, arsenite is uncharged at low pH (H_3AsO_3 at pH 5-8) while negatively charged (H_2AsO_3^-) at pH closer to 9 (Kang et al., 2000). Stronger repulsion between deprotonated organic functional groups in peat and the more negatively charged As species may be the reason for less removal at pH 9 (Besold et al., 2018). On the other hand, the difference in removal/leaching of Sb at different pH may be less attributable to differences in Sb speciation due to pH alone. Sb (III) and Sb (V) are most commonly present as H_3SbO_3 and $\text{Sb}(\text{OH})_6^-$, respectively. Both of these species are found across the tested pH range and can be present under both oxidizing and reducing conditions (Filella et al., 2002; Kang et al., 2000; Ungureanu et al., 2015). In order to avoid excessive leaching of Sb and As from the near surface layers of peat where concentrations of accumulated contaminants are usually the highest (Supplemental Table S2), influent pH below or near neutral should be targeted during pre-treatment of wastewaters before peatland treatment.

Unlike As and Sb, Ni adsorption increased with increasing pH that is consistent with findings by Ho et al. (1995). Higher mobility of Ni at pH 6 is obvious from the Ni speciation for natural waters under different pH conditions (Brookins, 1988). Ni is mostly present as Ni^{2+} free ion below pH 8 under oxidizing conditions. Although Ni leaching was higher at pH 6, the amounts were still negligible compared with those of As and Sb.

4.4. Effect of temperature on contaminant removal from mining influenced waters

In Northern latitudes, wetlands are exposed to rather cold temperatures and are affected by snow and ice in the winter. Temperature is known to affect many biotic and abiotic reactions in treatment wetlands (Kadlec and Knight, 1996), and many reactions are considerably

slowed down at near-zero temperatures. Microbial processes involving oxidation, reduction, methylation, and demethylation reactions are especially important in cycling, speciation and mobility of As and Sb (Li et al., 2016; Oremland and Stolz, 2003). Temperature has also been shown to affect the diversity of microbial communities (Edwards et al., 1999; Méndez-García et al., 2015; Volant et al., 2014) which may be responsible for different biotic reactions. However, the processes are complex and the incubation period in the experiments may have been too short to develop any meaningful changes in microbial communities. The results of the present study indicate that temperature is not the major factor controlling contaminant removal in treatment peatland as the most effective removal did not consistently occur at one specific temperature (Supplemental Figures S2 and S4). The tested temperature range is representative for temperatures encountered in situ in spring to fall, i.e., in the time when the peatlands are unfrozen and not covered by snow. Metal removal processes related to microbial sulfate reduction may not be affected by temperature variations as sulfate reducing bacteria have been shown to maintain their effectiveness at low temperatures and their performance depends more on the sulfate concentration than on temperature (Fortin et al., 2000; Sagemann et al., 1998). This coincide also in this study as Sb removal for the process water with a high sulfate concentration (Supplemental Table S4) was higher than it for the drainage water (Figure 7).

The effect of temperature on As removal was not clear as it was high at both high and low temperatures tested in aerobic condition. The relatively higher As removal at the lowest temperature can be attributed to stronger sorptive forces at colder temperatures (Viraraghavan and Dronamraju, 1993) whereas at the highest temperature tested, observed efficient As removal can be linked to increased affinity of metal ions at warmer temperatures (Ansone et al., 2012).

Ni adsorption on peat moss has been shown to increase with temperature (Bulgariu et al., 2010) however no such effect was clear from the current experiments. The difference between findings may be due to a number of factors such as the solution chemistry (containing only Ni), concentrations used (exponentially higher than this study) and the treatment of peat (dried, grounded and sieved) used in the other study. In this study, natural fresh peat was used highlighting natural condition in treatment peatlands and enhancing applicability of the results.

4.5. Implications for long-term use of treatment peatlands

Wetland treatment is a common passive water treatment method for closed mines. In Finland, wetlands are often required as a final water treatment step in the environmental permit of operating mines. Closed mine sites use wetland treatment for decreasing environmental impacts of their waters even a long time after mining operations have ceased. On the other hand, mining companies might discontinue the use of their treatment wetland, e.g. after building additional active treatment units, by discharging the water directly into the receiving water body or after mine closure. The risks related to abandoning the treatment wetlands (e.g. peatlands) are not well known. As the results of the present study showed, an increased risk of leaching followed increased dilution of the mining influenced water. In addition, since use of peatlands for wastewater treatment leads to contaminant accumulation and build-up over time, the service life of peatlands may not be indefinite and a higher contaminant build-up may pose a higher risk of contaminant leaching at any particular point in their service life or afterwards.

The accumulation of metals in peatlands under investigation was found to be dependent on their duration in use and loading rates. A comparison of peat samples from TP A and TP B (Supplemental Table S2) shows that TP B has much higher accumulation of pollutants—

except SO_4^{2-} —due to its longer service period; TP B is in use since 2006 compared to 2010 for TP A. Additionally, TP B receives significantly higher inflows on average resulting in higher Sb and Ni loads, compared with TP A. Conversely, the As and SO_4^{2-} loads to TP A are much higher because of higher concentration of these entities in the process water, although flows are lower on average. In addition to these figures, TP A has a much larger total area (44 ha, compared with 17 ha for TP B), although how much of the area in both peatlands is active for treatment is debatable and variable from season to season (Palmer et al., 2015).

Lesser removal and higher leaching of As by TP A in more recent samples (Figure 4a) may be symptomatic of the decreasing As-retaining capacity of peatlands due to As accumulation. On the other hand, recent peat samples from TP B showed higher removal and lower leaching of Sb, which may be connected to higher leaching of sulfate from these samples (Figure 7). A comparison of distribution coefficients—between older and newer samples—indicated that Sb removal and leaching was negatively linked to sulfate removal and leaching. However, the effect was not always present in one-to-one comparisons of Sb and SO_4^{2-} removal/leaching in the same samples.

A noteworthy finding was that although the Ni content in peat samples was comparable to, or higher than, the corresponding As and Sb concentrations, there was still very limited leaching of Ni, indicating strong retention of Ni by peat, which is less sensitive to changes in pH and redox conditions, in agreement with the literature (Gosset et al., 1986; Weiner, 2008). Thus, treatment peatlands could be a functional passive treatment method for Ni removal from wastewater as compared to other contaminants e.g. As and Sb as their removal mechanism seem too complicated to predict the associated risks.

Peatlands comprise a complex combination of biogeochemical processes and in order to reasonably predict the sustainable service life of treatment peatlands under different loads and conditions, long term monitoring of conditions and influent and effluent contaminant concentrations would be required from a number of sites. Sustainable service life may be defined as the point up to which peatlands may be used for wastewater treatment without posing a significant risk to the environment. At the end of the service life, these treatment peatlands would need to be managed (e.g. treated and restored) to prevent contaminant leaching.

5. Conclusions

Even though the use of wetlands for treatment of mining-influenced waters is common, comprehensive knowledge on the possible risks associated with their use is still scarce. The present study assessed contaminant removal and leaching in batch incubations with unmodified, natural peat. The collective data indicate that (i) unmodified peat has a good capacity to remove As, Sb, Ni, and SO_4^{2-} from mining-influenced waters, (ii) long-term use of wetlands decreases the capacity for As and Ni removal (iii) dilution of mining-influenced waters leads to contaminant leaching, and finally, (iv) environmental parameters like temperature and oxygen availability play only a minor role in contaminant removal or leaching. Based on these results use of treatment wetlands and especially the abandoning of treatment wetlands after many years of use should be carefully considered, as wetlands can turn from a contaminant sink to a contaminant source when influent water quality and quantity changes drastically. Overall, the study showed that leaching risk of Ni is lower than that of As and Sb, indicating that the wetland treatment is a more suitable passive treatment system for Ni containing waters as compared to waters containing As and Sb. The results from this study can be applied also to natural wetlands across the world loaded with As, Sb,

and Ni from various sources since there may also be risk of contaminant leaching to the environment.

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7. Competing interests statement

The authors declare that there have been no competing interests that might have influenced the performance and presentation of the work described in this manuscript.

8. 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. *Environ. Health Perspect.* 107, 593–597. https://doi.org/sc271_5_1835
- Ainsworth, N., Cooke, J.A., Johnson, M.S., 1990. Distribution of antimony in contaminated grassland: 1— vegetation and soils. *Environ. Pollut.* 65, 65–77. [https://doi.org/https://doi.org/10.1016/0269-7491\(90\)90165-9](https://doi.org/https://doi.org/10.1016/0269-7491(90)90165-9)
- Allen, S.J., Murray, M., Brown, P., Flynn, O., 1994. Peat as an Adsorbent for Dyestuffs and Metals in Wastewater. *Resour. Conserv. Recycl.* 11, 25.
- Ansone-Bertina, L., Klavins, M., 2016. Sorption of V and VI group metalloids (As, Sb, Te) on modified peat sorbents. *Open Chem.* 14, 46–59.

- Ansone, L., Eglite, L., Klavins, M., 2012. Removal of Arsenic Compounds with Peat, Peat-Based and Synthetic Sorbents. *Ecol. Chem. Eng. S* 19, 513–531. <https://doi.org/10.2478/v10216-011-0037-4>
- Arai, Y., 2010. Arsenic and Antimony, in: Hooda, P.S. (Ed.), *Trace Elements in Soil*. pp. 383–407.
- Autio, J., Heikkinen, O., 2002. The climate of northern Finland. *Fenn. - Int. J. Geogr.* 180, 61–66.
- 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. *Environ. Sci. Technol.* 52, 7317–7326. <https://doi.org/10.1021/acs.est.8b01542>
- Bhattacharya, P., Welch, A.H., Stollenwerk, K.G., McLaughlin, M.J., Bundschuh, J., Panaullah, G., 2007. Arsenic in the environment: Biology and Chemistry. *Sci. Total Environ.* 379, 109–120. <https://doi.org/https://doi.org/10.1016/j.scitotenv.2007.02.037>
- Borba, C.E., Guirardello, R., Silva, E.A., Veit, M.T., Tavares, C.R.G., 2006. Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: Experimental and theoretical breakthrough curves. *Biochem. Eng. J.* 30, 184–191.
- Borgmann, U., Couillard, Y., Doyle, P., Dixon, D.G., 2005. Toxicity of sixty- three metals and metalloids to *Hyaella azteca* at two levels of water hardness. *Environ. Toxicol. Chem.* 24, 641–652.
- Boyd, R., Bjerkgård, T., Nordahl, B., Schiellerup, H., 2016. *Mineral resources in the Arctic: An introduction*.
- Brookins, D.G., 1988. *Eh-pH Diagrams for Geochemistry*, illustrate. ed. Springer-Verlag, Berlin.

- Brown, P.A., Gill, S.A., Allen, S.J., 2000. Metal removal from wastewater using peat. *Water Res.* 34, 3907–3916. [https://doi.org/10.1016/S0043-1354\(00\)00152-4](https://doi.org/10.1016/S0043-1354(00)00152-4)
- Bulgariu, L., Bulgariu, D., Macoveanu, M., 2010. Kinetics and equilibrium study of Nickel(ii) removal using peat moss. *Environ. Eng. Manag. J.* 9, 667–674.
- Bunzl, K., Schmidt, W., Sansoni, B., 1976. Kinetics of ion exchange in soil organic matter. IV. Adsorption and desorption of Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Ca^{2+} by peat. *J. Soil Sci.* 27, 32–41.
- Burton, E.D., Johnston, S.G., Bush, R.T., 2011. Microbial sulfidogenesis in ferrihydrite-rich environments: Effects on iron mineralogy and arsenic mobility. *Geochim. Cosmochim. Acta* 75, 3072–3087. [https://doi.org/https://doi.org/10.1016/j.gca.2011.03.001](https://doi.org/10.1016/j.gca.2011.03.001)
- Buschmann, J., Sigg, L., 2004. Antimony (III) binding to humic substances: influence of pH and type of humic acid. *Environ. Sci. Technol.* 38, 4535–4541.
- Calmano, W., Hong, J., Förstner, U., 1993. Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. *Water Sci. Technol.* 28, 223–235.
- Champagne, P., Van Geel, P., Parker, W., 2008. Impact of temperature and loading on the mitigation of AMD in peat biofilter columns. *Mine Water Environ.* 27, 225–240.
- Chaudhary, S., Banerjee, D.K., Kumar, N., Yadav, S., 2016. Assessment of bioavailable metals in the sediments of Yamuna flood plain using two different single extraction procedures. *Sustain. Environ. Res.* 26, 28–32. [https://doi.org/https://doi.org/10.1016/j.serj.2015.09.004](https://doi.org/10.1016/j.serj.2015.09.004)
- Cooper, R.G., Harrison, A.P., 2009. The exposure to and health effects of antimony. *Indian J. Occup. Environ. Med.* 13, 3–10. <https://doi.org/10.4103/0019-5278.50716> [doi]
- Coupal, B., Lalancette, J.-M., 1976. The treatment of waste waters with peat moss. *Water Res.*

- 10, 1071–1076. [https://doi.org/10.1016/0043-1354\(76\)90038-5](https://doi.org/10.1016/0043-1354(76)90038-5)
- Crites, R.W., Middlebrooks, J., Reed, S.C., 2006. Natural Wastewater Treatment Systems. CRC Press, Boca Raton, FL.
- De Gregori, I., Fuentes, E., Rojas, M., Pinochet, H., Potin-Gautier, M., 2003. Monitoring of copper, arsenic and antimony levels in agricultural soils impacted and non-impacted by mining activities, from three regions in Chile. *J. Environ. Monit.* 5, 287–295.
- de Oliveira, L.K., Melo, C.A., Goveia, D., Lobo, F.A., Armienta Hernández, M.A., Fraceto, L.F., Rosa, A.H., 2015. Adsorption/desorption of arsenic by tropical peat: influence of organic matter, iron and aluminium. *Environ. Technol.* 36, 149–159.
- Edwards, K.J., Gihring, T.M., Banfield, J.F., 1999. Seasonal Variations in Microbial Populations and Environmental Conditions in an Extreme Acid Mine Drainage Environment. *Appl. Environ. Microbiol.* 65, 3627 LP-3632.
- Filella, M., Belzile, N., Chen, Y.-W., 2002. Antimony in the environment: a review focused on natural waters: I. Occurrence. *Earth-Science Rev.* 57, 125–176. [https://doi.org/10.1016/S0012-8252\(01\)00070-8](https://doi.org/10.1016/S0012-8252(01)00070-8)
- Finnish Meteorological Institute, 2017. Climate-Normal Period. URL <http://en.ilmatieteenlaitos.fi/normal-period>
- Fortin, D., Goulet, R., Roy, M., 2000. Seasonal Cycling of Fe and S in a Constructed Wetland: The Role of Sulfate-Reducing Bacteria. *Geomicrobiol. J.* 17, 221–235. <https://doi.org/10.1080/01490450050121189>
- Frohne, T., Rinklebe, J., Diaz-Bone, R.A., Du Laing, G., 2011. Controlled variation of redox conditions in a floodplain soil: impact on metal mobilization and biomethylation of arsenic and antimony. *Geoderma* 160, 414–424.

- Gambrell, R.P., 1994. Trace and toxic metals in wetlands—a review. *J. Environ. Qual.* 23, 883–891.
- Gazea, B., Adam, K., Kontopoulos, A., 1996. A review of passive systems for the treatment of acid mine drainage. *Miner. Eng.* 9, 23–42. [https://doi.org/10.1016/0892-6875\(95\)00129-8](https://doi.org/10.1016/0892-6875(95)00129-8)
- Glaser, P.H., Janssens, J.A., Siegel, D.I., 1990. The Response of Vegetation to Chemical and Hydrological Gradients in the Lost River Peatland, Northern Minnesota. *J. Ecol.* 78, 1021–1048.
- Gosset, T., Trancart, J.-L., Thevenot, D.R., 1986. Batch Metal Removal by Peat - Kinetics and Thermodynamics. *Water Res.* 1, 21–26.
- Griffiths, N.A., Sebestyen, S.D., 2016. Dynamic Vertical Profiles of Peat Porewater Chemistry in a Northern Peatland. *Wetlands* 36, 1119–1130. <https://doi.org/10.1007/s13157-016-0829-5>
- Heikkinen, K., Karppinen, A., Karjalainen, S.M., Postila, H., Hadzic, M., Tolkkinen, M., Marttila, H., Ihme, R., Kløve, B., 2018. Long-term purification efficiency and factors affecting performance in peatland-based treatment wetlands: An analysis of 28 peat extraction sites in Finland. *Ecol. Eng.* 117, 153–164. <https://doi.org/10.1016/j.ecoleng.2018.04.006>
- Hengen, T.J., Squillace, M.K., O’Sullivan, A.D., Stone, J.J., 2014. Life cycle assessment analysis of active and passive acid mine drainage treatment technologies. *Resour. Conserv. Recycl.* 86, 160–167. <https://doi.org/10.1016/j.resconrec.2014.01.003>
- Herath, I., Vithanage, M., Bundschuh, J., 2017. Antimony as a global dilemma: Geochemistry, mobility, fate and transport. *Environ. Pollut.* 223, 545–559. <https://doi.org/10.1016/j.envpol.2017.01.057>

- Ho, Y.S., John Wase, D.A., Forster, C.F., 1995. Batch nickel removal from aqueous solution by sphagnum moss peat. *Water Res.* 29, 1327–1332. [https://doi.org/10.1016/0043-1354\(94\)00236-Z](https://doi.org/10.1016/0043-1354(94)00236-Z)
- Hoffmann, M., Mikutta, C., Kretzschmar, R., 2012. Bisulfide Reaction with Natural Organic Matter Enhances Arsenite Sorption: Insights from X-ray Absorption Spectroscopy. *Environ. Sci. Technol.* 46, 11788–11797. <https://doi.org/10.1021/es302590x>
- Höglund, L.O., Herbert, R., Lövgren, L., Öhlander, B., Neretniks, I., Moreno, L., Malmström, M., Elander, P., Lindvall, M., Lindström, B., 2004. MiMi-Performance assessment: Main report. MiMi print, LuLeå, Sweden.
- Huerta-Diaz, M.A., Tessier, A., Carignan, R., 1998. Geochemistry of trace metals associated with reduced sulfur in freshwater sediments. *Appl. Geochemistry* 13, 213–233. [https://doi.org/10.1016/S0883-2927\(97\)00060-7](https://doi.org/10.1016/S0883-2927(97)00060-7)
- Johnson, D.B., Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. *Sci. Total Environ.* 338, 3–14. <https://doi.org/10.1016/j.scitotenv.2004.09.002>
- Jurkovič, L., Hiller, E., Veselská, V., Pet'ková, K., 2011. Arsenic Concentrations in Soils Impacted by Dam Failure of Coal-Ash Pond in Zemianske Kostolany, Slovakia. *Bull. Environ. Contam. Toxicol.* 86, 433–437. <https://doi.org/10.1007/s00128-011-0222-2>
- Kadlec, R.H., Knight, R.L., 1996. *Treatment Wetlands*. CRC Press, Boca Raton, FL.
- Kadlec, R.H., Reddy, K.R., 2001. Temperature effects in treatment wetlands. *Water Environ. Res.* 73, 543–557.
- Kang, M., Kawasaki, M., Tamada, S., Kamei, T., Magara, Y., 2000. Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes. *Desalination* 131, 293–298. [https://doi.org/10.1016/S0011-9164\(00\)90027-4](https://doi.org/10.1016/S0011-9164(00)90027-4)

- Kaplan, D.I., Serne, R.J., Piepho, M.G., 1995. Geochemical factors affecting radionuclide transport through near and far fields at a low level waste disposal site - Available sorption constants and recommendations for future studies. Pacific Northwest Laboratory, Richland, Washington.
- Karjalainen, S.M., Heikkinen, K., Ihme, R., Kløve, B., 2016. Long-term purification efficiency of a wetland constructed to treat runoff from peat extraction. *J. Environ. Sci. Heal. Part A* 51, 393–402. <https://doi.org/10.1080/10934529.2015.1120519>
- Kaupilla, P., Räisänen M., L., Myllyoja, S., 2011. Best Environmental Practices in Metal Ore Mining. Finnish Environment Institute, Helsinki.
- Kocar, B.D., Borch, T., Fendorf, S., 2010. Arsenic repartitioning during biogenic sulfidization and transformation of ferrihydrite. *Geochim. Cosmochim. Acta* 74, 980–994. <https://doi.org/10.1016/j.gca.2009.10.023>
- Koivula, M.P., Kujala, K., Rönkkömäki, H., Mäkelä, M., 2009. Sorption of Pb(II), Cr(III), Cu(II), As(III) to peat, and utilization of the sorption properties in industrial waste landfill hydraulic barrier layers. *J. Hazard. Mater.* 164, 345–352. <https://doi.org/10.1016/j.jhazmat.2008.08.008>
- Köppen, W., 1936. Das geographische System der Klimate, in: Köppen, W., Geiger, R. (Eds.), *Handbuch Der Klimatogie 1C*. Verlag von Gebrüder Bornträger, Berlin, pp. 1–44.
- Lalvani, S.B., Wiltowski, T.S., Murphy, D., Lalvani, L.S., 1997. Metal Removal from Process Water by Lignin. *Environ. Technol.* 18, 1163–1168. <https://doi.org/10.1080/09593331808616636>
- Langner, P., Mikutta, C., Kretzschmar, R., 2011. Arsenic sequestration by organic sulphur in peat. *Nat. Geosci.* 5, 66.

- Leiviskä, T., Khalid, M.K., Gogoi, H., Tanskanen, J., 2018. Enhancing peat metal sorption and settling characteristics. *Ecotoxicol. Environ. Saf.* 148, 346–351. <https://doi.org/10.1016/j.ecoenv.2017.10.053>
- Li, J., Wang, Q., Oremland, R.S., Kulp, T.R., Rensing, C., Wang, G., 2016. Microbial Antimony Biogeochemistry: Enzymes, Regulation, and Related Metabolic Pathways. *Appl. Environ. Microbiol.* 82, 5482 LP-5495.
- Macdonald, R.W., Barrie, T.F., Bidleman, T.F., Gregor, D.J., Gregor, D.J., Semkin, R.G., Strachan, W.M.J., Li, Y.F., Wania, F., Alae, M., Alexeeva, L.B., Backus, S.M., Bailey, R., Bowers, J.M., Gobeil, C., Halsall, C.J., Harner, T., Hoff, J.T., Jantunen, L.M.M., Lockhart, W.L., Mackay, D., Muir, D.C.G., Pudykiewicz, J., Reimer, K.J., Smith, J.N., Stern, G.A., Schroeder, W.H., Wagemann, R., Yunker, M.B., 2000. Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. *Sci. Total Environ.* 254, 93–234.
- Maurer, F., Christl, I., Kretzschmar, R., 2010. Reduction and reoxidation of humic acid: influence on spectroscopic properties and proton binding. *Environ. Sci. Technol.* 44, 5787–5792.
- Megonigal, J.P., Patrick, W.H., Faulkner, S.P., 1993. Wetland identification in seasonally flooded forest soils: soil morphology and redox dynamics. *Soil Sci. Soc. Am. J.* 57, 140–149.
- Méndez-García, C., Peláez, A.I., Mesa, V., Sánchez, J., Golyshina, O. V, Ferrer, M., 2015. Microbial diversity and metabolic networks in acid mine drainage habitats. *Front. Microbiol.*
- Mitsunobu, S., Harada, T., Takahashi, Y., 2006. Comparison of antimony behavior with that of

- arsenic under various soil redox conditions. *Environ. Sci. Technol.* 40, 7270–7276.
- Muyzer, G., Stams, A.J.M., 2008. The ecology and biotechnology of sulphate-reducing bacteria. *Nat. Rev. Microbiol.* 6, 441.
- Nordstrom, D.K., Alpers, C.N., 1999. Geochemistry of acid mine waters. *Environ. geochemistry Miner. Depos.* 6, 133–160.
- O'Day, P.A., Vlassopoulos, D., Root, R., Rivera, N., 2004. The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *Proc. Natl. Acad. Sci. U. S. A.* 101, 13703 LP-13708.
- O'Kelly, B.C., 2005. New method to determine the true water content of organic soils. *Geotech. Test. J.* 28, 365–369.
- Oksanen, J., Blanchet, F.G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., Minchin, P.R., O'Hara, R.B., Simpson, G.L., Solymos, P., Stevens, M.H.H., Szoecs, E., Wagner, H., 2017. *vegan: Community Ecology Package*. R package version 2.4-2.
- Oremland, R.S., Stolz, J.F., 2003. The Ecology of Arsenic. *Science*. 300, 939-944.
- 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. *Ecol. Eng.* 75, 350–364. <https://doi.org/10.1016/j.ecoleng.2014.11.045>
- Patrick, W.H., Mikkelsen, D.S., Wells, B.R., 1985. Plant nutrient behavior in flooded soil. *Fertil. Technol. use* 197–228.
- PIRAMID Consortium, 2003. Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters. University of Newcastle Upon Tyne, Newcastle Upon Tyne UK.
- Randall, J.M., Garrett, V., Bermann, R.L., Waiss Jr, A.C., 1974. Use of bark to remove heavy

- metal ions from waste solutions. *For. Prod. J.* 24, 80–84.
- Reddy, K.R., DeLaune, R.D., 2008. *Biogeochemistry Of Wetlands: Science and Applications*. CRC Press, Boca Raton.
- Rieuwerts, J.S., Mighanetara, K., Braungardt, C.B., Rollinson, G.K., Pirrie, D., Azizi, F., 2014. Geochemistry and mineralogy of arsenic in mine wastes and stream sediments in a historic metal mining area in the UK. *Sci. Total Environ.* 472, 226–234. <https://doi.org/10.1016/j.scitotenv.2013.11.029>
- Rippy, J.F.M., Nelson, P. V, 2007. Cation exchange capacity and base saturation variation among Alberta, Canada, moss peats. *HortScience* 42, 349–352.
- Ronkanen, A.-K., Kløve, B., 2009. Long-term phosphorus and nitrogen removal processes and preferential flow paths in Northern constructed peatlands. *Ecol. Eng.* 35, 843–855. <https://doi.org/10.1016/j.ecoleng.2008.12.007>
- Rothwell, J.J., Taylor, K.G., Chenery, S.R.N., Cundy, A.B., Evans, M.G., Allott, T.E.H., 2010. Storage and behavior of As, Sb, Pb, and Cu in ombrotrophic peat bogs under contrasting water table conditions. *Environ. Sci. Technol.* 44, 8497–8502.
- Roy, W.R., Krapac, I.G., Chou, S.F.J., Griffin, R.A., 1992. *Batch-type Procedures for Estimating Soil Adsorption of Chemicals*. United States Environmental Protection Agency.
- Sagemann, J., Jørgensen, B.B., Greeff, O., 1998. Temperature dependence and rates of sulfate reduction in cold sediments of svalbard, arctic ocean. *Geomicrobiol. J.* 15, 85–100. <https://doi.org/10.1080/01490459809378067>
- Sen Gupta, B., Curran, M., Hasan, S., Ghosh, T.K., 2009. Adsorption characteristics of Cu and Ni on Irish peat moss. *J. Environ. Manage.* 90, 954–960. <https://doi.org/10.1016/j.jenvman.2008.02.012>

- Sheoran, A.S., Sheoran, V., 2006. Heavy metal removal mechanism of acid mine drainage in wetlands: A critical review. *Miner. Eng.* 19, 105–116. <http://dx.doi.org/10.1016/j.mineng.2005.08.006>
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochemistry* 17, 517–568. [https://doi.org/10.1016/S0883-2927\(02\)00018-5](https://doi.org/10.1016/S0883-2927(02)00018-5)
- Stuckman, M.Y., Lenhart, J.J., Walker, H.W., 2011. Abiotic properties of landfill leachate controlling arsenic release from drinking water adsorbents. *Water Res.* 45, 4782–4792. <https://doi.org/10.1016/j.watres.2011.06.024>
- Stuhlberger, C., Peck, A.P., Tremblay, A.G., Dave, N., 2007. Innovative Techniques and Technologies for Contaminated Mine Waters Assessment, Management and Remediation; Technical Workshop Report. Environment and Security Initiative, Geneva.
- Sundaravadivel, M., Vigneswaran, S., 2001. Constructed wetlands for wastewater treatment. *Crit. Rev. Environ. Sci. Technol.* 31, 351–409.
- Thanabalasingam, P., Pickering, W.F., 1986. Arsenic sorption by humic acids. *Environ. Pollut. Ser. B, Chem. Phys.* 12, 233–246.
- Tipping, E., Smith, E.J., Lawlor, A.J., Hughes, S., Stevens, P.A., 2003. Predicting the release of metals from ombrotrophic peat due to drought-induced acidification. *Environ. Pollut.* 123, 239–253. [https://doi.org/10.1016/S0269-7491\(02\)00375-5](https://doi.org/10.1016/S0269-7491(02)00375-5)
- Toujaguez, R., Ono, F.B., Martins, V., Cabrera, P.P., Blanco, A. V, Bundschuh, J., Guilherme, L.R.G., 2013. Arsenic bioaccessibility in gold mine tailings of Delita, Cuba. *J. Hazard. Mater.* 262, 1004–1013. <https://doi.org/10.1016/j.jhazmat.2013.01.045>
- Turetsky, M.R., Benscoter, B., Page, S., Rein, G., van der Werf, G.R., Watts, A., 2014. Global

- vulnerability of peatlands to fire and carbon loss. *Nat. Geosci.* 8, 11.
- U.S. Environmental Protection Agency, 2013a. Antimony Compounds-Hazard Summary. URL <https://www.epa.gov/sites/production/files/2016-09/documents/antimony-compounds.pdf>
- U.S. Environmental Protection Agency, 2013b. Nickel Compounds-Hazard summary. URL <https://www.epa.gov/sites/production/files/2016-09/documents/nickle-compounds.pdf>
- Ungureanu, G., Santos, S., Boaventura, R., Botelho, C., 2015. Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption. *J. Environ. Manage.* 151, 326–342. <https://doi.org/10.1016/J.JENVMAN.2014.12.051>
- Viraraghavan, T., Dronamraju, M.M., 1993. Removal of copper, nickel and zinc from wastewater by adsorption using peat. *J. Environ. Sci. Heal. .Part A Environ. Sci. Eng. Toxicol.* 28, 1261–1276. <https://doi.org/10.1080/10934529309375941>
- Volant, A., Bruneel, O., Desoeuvre, A., Héry, M., Casiot, C., Bru, N., Delpoux, S., Fahy, A., Javerliat, F., Bouchez, O., Duran, R., Bertin, P.N., Elbaz-Poulichet, F., Lauga, B., 2014. Diversity and spatiotemporal dynamics of bacterial communities: physicochemical and other drivers along an acid mine drainage. *FEMS Microbiol. Ecol.* 90, 247–263.
- Vymazal, J., 2010. Constructed wetlands for wastewater treatment: five decades of experience. *Environ. Sci. Technol.* 45, 61–69.
- Weiner, E.R., 2008. *Applications of Environmental Aquatic Chemistry: A Practical Guide*, Second Edition, 2nd ed. CRC Press, Boca Raton.
- Wilson, S.C., Lockwood, P. V, Ashley, P.M., Tighe, M., 2010. The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: a critical review. *Environ. Pollut.* 158, 1169–1181.

- Wu, F., Fu, Z., Liu, B., Mo, C., Chen, B., Corns, W., Liao, H., 2011. Health risk associated with dietary co-exposure to high levels of antimony and arsenic in the world's largest antimony mine area. *Sci. Total Environ.* 409, 3344–3351. <https://doi.org/10.1016/j.scitotenv.2011.05.033>
- Xue, H. Bin, Jansen, S., Prasch, A., Sigg, L., 2001. Nickel Speciation and Complexation Kinetics in Freshwater by Ligand Exchange and DPCSV. *Environ. Sci. Technol.* 35, 539–546. <https://doi.org/10.1021/es0014638>
- Younger, P.L., Banwart, S.A., Hedin, R.S., 2002. *Mine Water: Hydrology, Pollution, Remediation*. Kluwer Academic Publishers, Dordrecht. https://doi.org/10.1007/978-94-010-0610-1_3

Figure 1. a) Location and layout of the study site. b) Schematic overview of the study set-up. The oxic incubations were initially carried out in the period 2013-2014 and were repeated with fresh peat samples in 2016. Anoxic incubations were only conducted with samples taken in 2016.

Figure 2. Arsenic (As) removal (+) and leaching (-) from undiluted and diluted (four levels of dilution) process water in peat incubations under oxic conditions at 10°C. Three replicate peat samples from TP A were tested. The experiment was conducted with peat and pore water samples obtained in 2016.

Figure 3. Linear isotherms of a) Ni removal and b) Ni leaching from undiluted and diluted process and drainage water applied to peat from the respective treatment peatlands. The isotherms are sorted by sampling year and water type, and include data from both oxic (2013, 2014 and 2016) and anoxic experiments (only 2016) carried out on peat samples from various depths at 10°C.

Figure 4. Comparison of distribution coefficients from different sampling years (2013-2016) for (a) As, (b) Sb and (c) Ni calculated from the adsorption (+) and desorption (-) batch experiments under oxic conditions. Data include experiments with both process water and drainage water and peat samples from both treatment peatlands.

Figure 5. Comparison of removal (+) and leaching (-) of (a, b) As, (c, d) Sb and (e, f) Ni from peat to undiluted process water at three different temperatures under oxic (a, c, e) and anoxic (b, d, f) conditions. Three replicate peat samples collected in 2016 were tested.

Figure 6. Ordination of multivariate data from removal/leaching batch experiments using principal component analysis (PCA). Arrows show the scale and direction of correlation vectors for parameters with the highest correlation. Data from all process and drainage water experiments are included, but samples with missing values for any of the parameters have been omitted in entirety.

Figure 7. Comparison of Distribution coefficients of As, Sb, Ni and SO_4^{2-} removal/leaching between older and newer samples for all experiments under oxic conditions. The y-axis scale is restricted to magnify the center of the plot.

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Highlights:

1. Retention of As, Sb, and Ni in peat from natural treatment wetlands was studied
2. Contaminant accumulation in natural wetlands make them vulnerable to leaching.
3. Dilution of mining influenced water leads to leaching of As, Sb, and Ni.
4. Long-term use of wetlands decreases As and Ni removal/retention capacity.
5. Use of wetlands for treatment of wastewater should be carefully considered.

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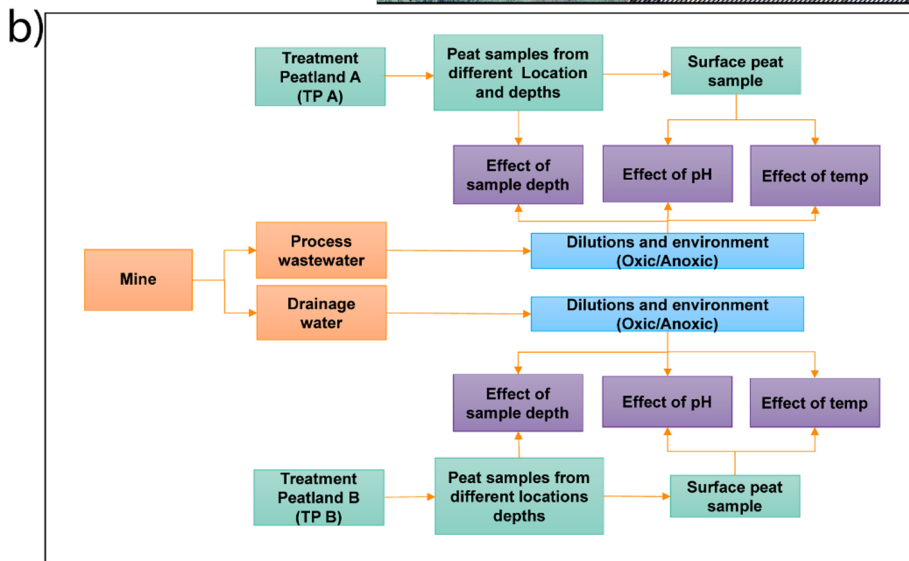
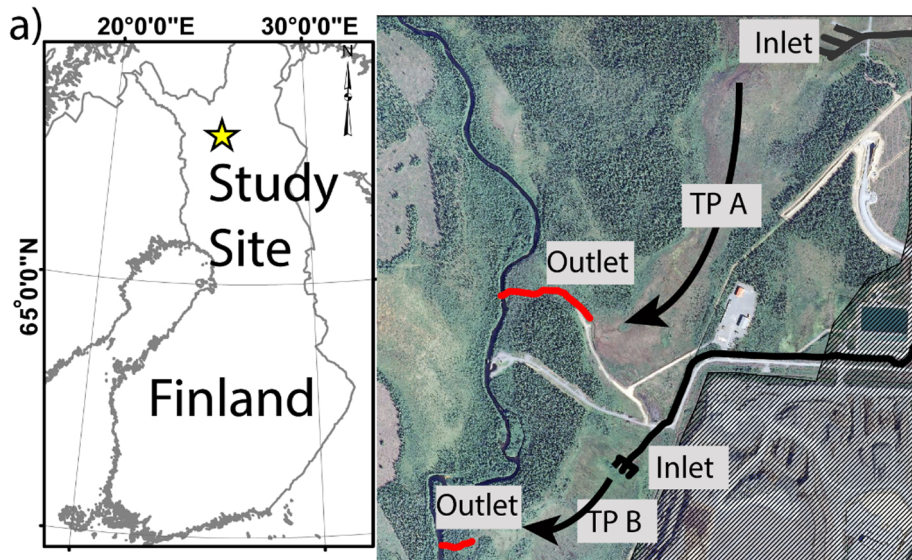


Figure 1

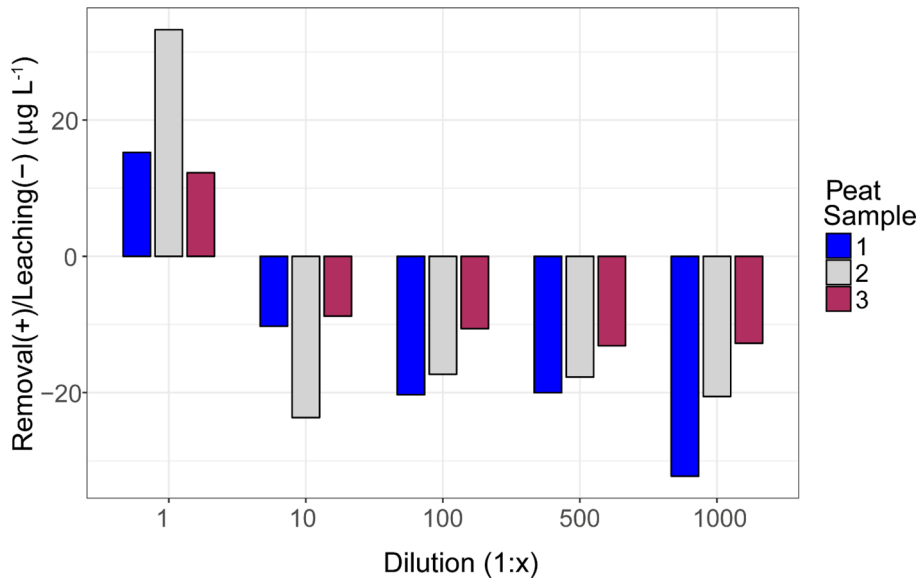


Figure 2

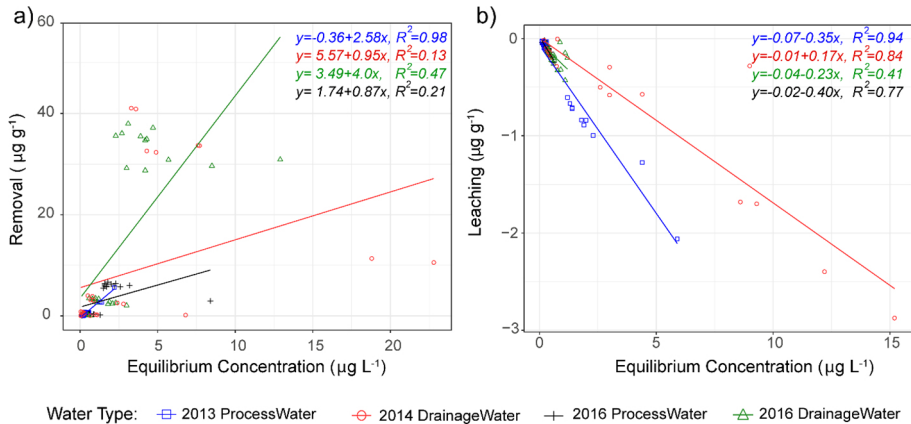


Figure 3

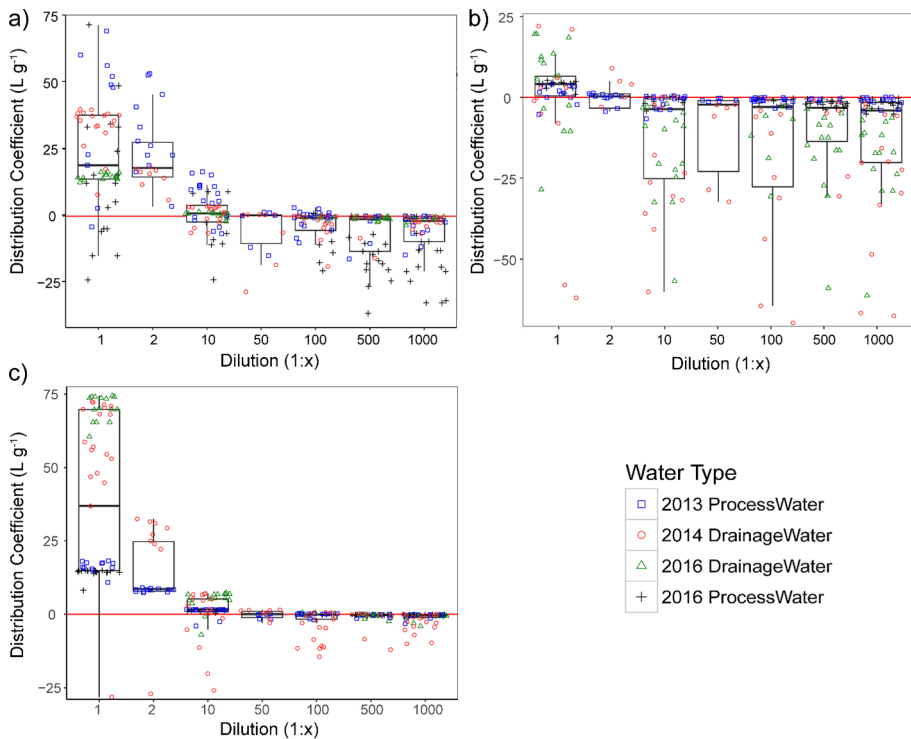


Figure 4

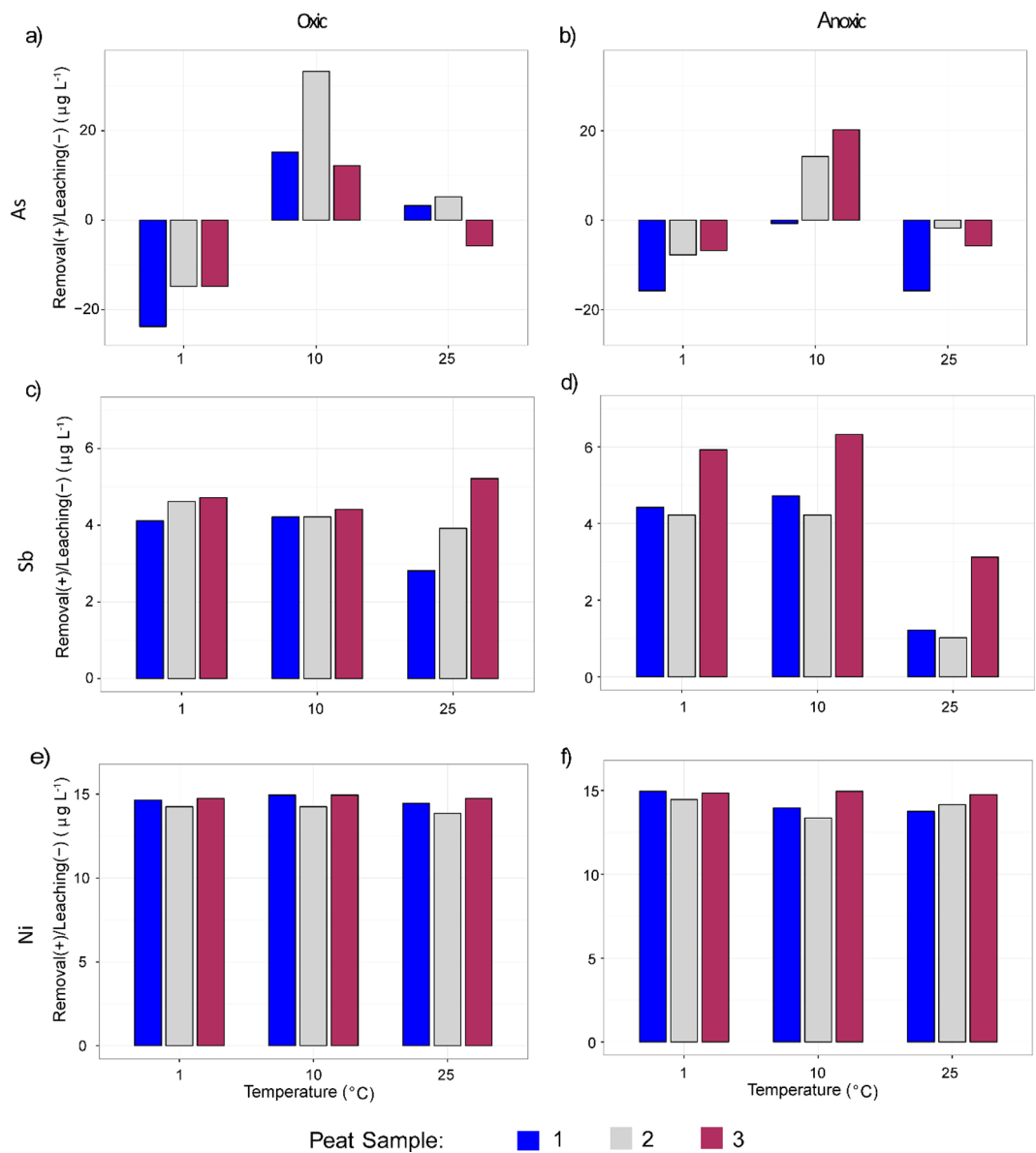


Figure 5

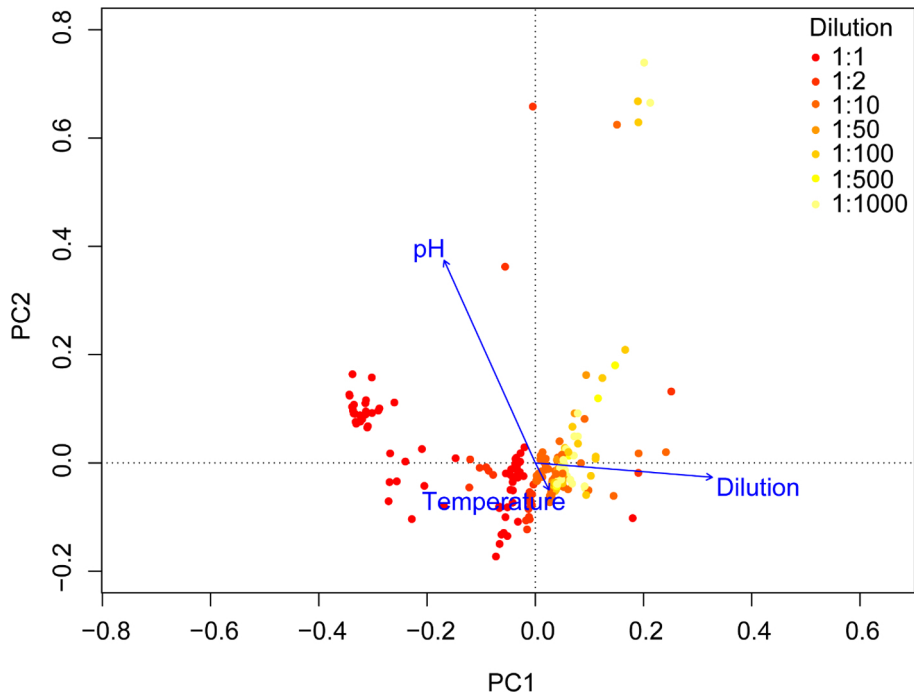


Figure 6

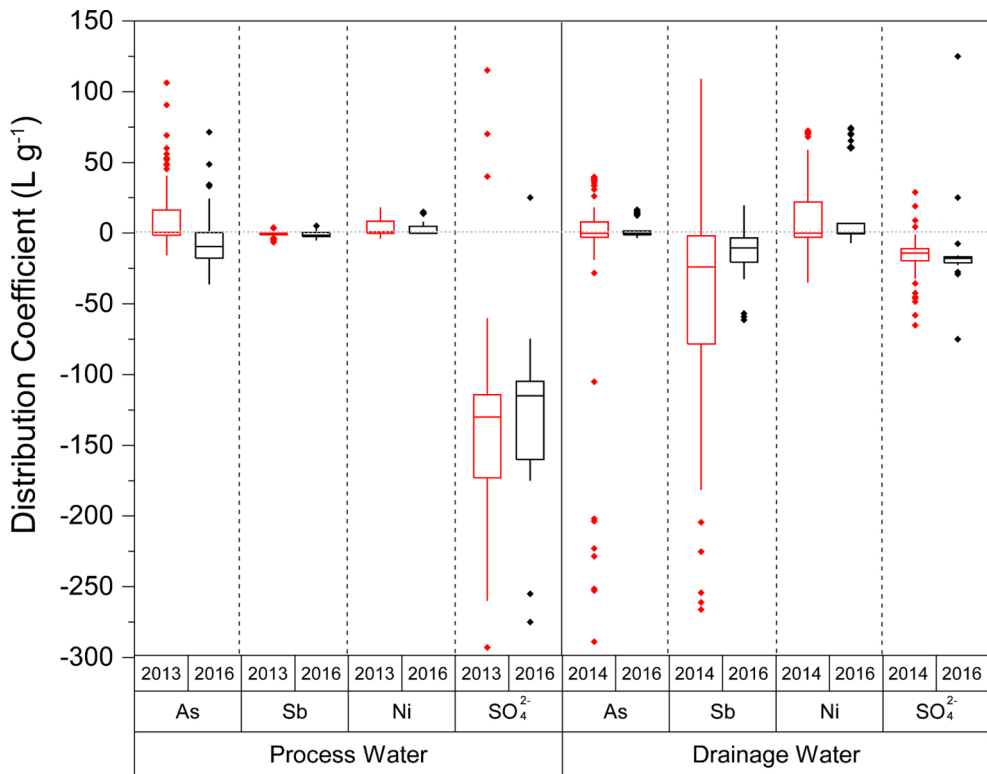


Figure 7