



Purification of Acid Sulfate Soil Runoff Water Using Biochar: a Meso-Scale Laboratory Experiment

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Abstract Acid sulfate soils worldwide pose a risk to water bodies due to acidic, metal-rich runoff. Efficient water protection methods to reduce this diffuse load in forestry sites do not exist currently. Biochar is a promising adsorbent due to its high porosity and ion exchange capacity but has not been studied for water protection for forestry in acid sulfate soils. Our objective was to study the metal adsorption capacity of biochar for acid sulfate soil runoff water, where several metals are competing for the adsorption. We also assessed whether the use of wood ash in biochar reactors can improve adsorption. Furthermore, we studied if desorption occurs when the metal concentrations in

the water decrease. In a meso-scale laboratory experiment, hundreds of liters of runoff water from acid sulfate soils were circulated through biochar and biochar-ash filled reactors. We extracted water samples from the inlet and outlet of the reactors and determined the metal concentrations (Al, Fe, Co, Ni, Cu, Zn, and Cd). These were used to construct adsorption kinetics models. We studied desorption by diluting the water and measuring the concentration changes. Biochar increased the solution pH and adsorbed multiple metals simultaneously. The adsorption capacity and rate were higher in biochar-ash reactors than in the biochar reactors. Biochar-ash reactors adsorbed 70–99% of six of the seven metals. However, Al was released from ash. We observed no significant desorption after the dilutions. Therefore, biochar could be considered as a potential water protection tool in forests located on acid sulfate soils.

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1 Introduction

Acid sulfate soils around the world pose a risk to water bodies due to their acidic, metal-rich runoff. Acid sulfate soils have formed mainly due to sea level changes thousands of years ago (Nordmyr et al., 2008; Sutela et al., 2012), and they are found in Latin America, Australia, South-East Asia, Africa, and

Europe (Roos & Åström, 2005; Fältmarsch & Vuori, 2007). They typically contain sulfide-rich sediment layers, buried in anoxic conditions below the water table (Nordmyr et al., 2008; Sutela et al., 2012). The largest areas of acid sulfate soils in Europe are located on the south and west coasts of Finland (1600–3000 km², Fältmarsch & Vuori, 2007), where coastal lowlands are often drained for agriculture and forestry purposes. Lowering of the water table through drainage results in oxidation of metal sulfides, which increases metal solubility and export to the surrounding water bodies (Roos & Åström, 2005; Fältmarsch & Vuori, 2007; Saarinen et al., 2013). This leads to acidification and metal pollution. Forest clear-cutting, ditching, and runoff peaks during the spring snowmelt can enhance the leaching and create short-term pulses with extremely high acidity and metal contents.

In Finland, the metal export and acidity from acid sulfate soils have severely damaged water bodies on the western coast during the last decades (Sutela et al., 2012). Generally, a pH of 5.5 is used as a threshold, below which most aquatic organisms cannot survive (Hovinen et al., 2012). Acid sulfate soil can have a pH of around 2.5–4.5 (Fältmarsch & Vuori, 2007). The metals also have adverse effects of their own. For example, aluminum (Al) disturbs fish breathing and osmoregulation, cadmium (Cd) is a carcinogen, and iron (Fe) coagulates on fish gills and eggs causing physical stress, as well as releasing protons and thus further accelerating acidification (Fältmarsch & Vuori, 2007; Gensemer et al., 2018). These metals are commonly leached from acid sulfate soils (Roos & Åström, 2005; Fältmarsch & Vuori, 2007). In Finland, the metal export from acid sulfate soils is many fold higher compared to that from industry (Roos & Åström, 2005; Sutela et al., 2012). It causes deterioration of water quality, which occasionally leads to extensive deaths of fish populations (Roos & Åström, 2005; Fältmarsch & Vuori, 2007; Sutela et al., 2012). Thus, there is a clear need for water protection methods to decrease acidity and metal export into the water courses.

Effective water purification methods for metal pollution exist for point sources, such as industrial and municipal wastewaters. These include, for example, chemical precipitation, ion exchange, membrane technologies, and electrolysis (Wong et al., 2020). However, these methods are not directly applicable to the purification of diffuse loads typical to forestry. This load originates from large areas simultaneously, the volume of runoff

is high, and the metal concentrations vary considerably throughout the year. Biochar filtration is a potential additional tool in water protection due to its efficient adsorption properties, but it has not yet been studied as a metal adsorbent in forestry.

Biochar has recently been applied for purification of agricultural and urban runoff water (Garcia-Chevesich et al., 2020; Mohan et al., 2014). It features good adsorption capabilities because of its high porosity and large specific surface area (Duwieujuh et al., 2020; Saarela et al., 2020; Zhao et al., 2019). Compared to activated carbon, biochar is cheaper and easier to produce, without needing any chemicals as some activated carbon types do (Li et al., 2017; Thompson et al., 2016). The adsorption capacity of biochar depends on the source material, pyrolysis temperature, and particle size (Chen et al., 2011; Park et al., 2016; Saarela et al., 2020; Zhao et al., 2019). Laboratory studies have shown that biochar can effectively adsorb various metals such as Cd (Li et al., 2017), Cu, and Zn (Chen et al., 2011; Wong et al., 2020). Furthermore, adsorption depends on the concentrations of metals in the solution, their competing adsorption, and the solution pH (Chen et al., 2011; Duwieujuh et al., 2020). This simultaneous adsorption of multiple metals with competition and varying concentrations is our key interest in this study. Meso- or large-scale studies of multimetal adsorption on biochar are scarce, and little work has been done to study how different concentrations affect the possible desorption of metals from biochar back to the water.

In a small-scale laboratory experiment, spruce biochar and ash as a pH-increasing additive have shown promising results in adsorbing multiple metals at the same time (Kinnunen et al., 2021). Therefore, we chose these materials to assess upscaling of the experiment in meso-scale column reactors. The theory behind the pH-increasing additives is that increasing the solution pH can transform the metals into their free ionic forms, where they can better interact with and be adsorbed into the negatively charged biochar surface (Chen et al., 2011; Jiang et al., 2016). We also introduce dilutions with tap water to study the possible desorption of metals from the biochar back into the water with lower metal concentrations. The aim of this study was to evaluate a reactor-type biochar filtration in removing metals (Al, Fe, Cd, Co, Ni, Cu, Zn) and neutralizing acidity from runoff water collected

from drained peatland forests located on acid sulfate soil. Our specific research objectives were:

1. To study the effectiveness of a meso-scale biochar reactor to adsorb Al, Fe, Cd, Co, Ni, Cu, and Zn and to neutralize water acidity, in a setting that resembles field conditions.
2. To determine how ash addition to the reactors changes the adsorption of metals.

We hypothesize that biochar can effectively adsorb several metals from acid sulfate soil runoff water and that ash improves the adsorption capacity.

2 Materials and Methods

2.1 Water Collection

Water was collected from the main ditch of the Kii-makorpi study area located in Alaveteli, Kruunupy (63° 43' N, 23° 24' E) in western Finland (Supplementary 1). The size of the study area was 100 ha, and it was drained for forestry in the late 1960s.

Continuous water quality data is available online (<https://ehp-data.com/>, at monitoring stations KKY Kokkola1, -2 and -control). The forest stand was dominated by Scots pine (*Pinus sylvestris* L.) with a mixture of downy birch (*Betula pubescens* Ehrh.). A total of 1000 L of water was pumped into a plastic storage tank on May 10, 2022, and transported to the laboratory in Kuopio. The experiment started on May 11th. The water was divided into two 500-L tanks, one of which was used in biochar-only reactors and the other was used in biochar-ash reactors.

2.2 Biochar Reactor and the Experiment

The water was used in a biochar reactor experiment testing the removal of Al, Fe, Co, Ni, Cu, Zn and Cd, as well as neutralization of acidity from runoff water in a meso-scale laboratory setting as described in Lafdani et al. (2020). Three PVC plastic columns (inner diameter 15 cm, length 150 cm) acting as replicates were filled without compressing with 25 L of biochar each (Fig. 1). The reactor column volume was 0.0265 m³, and the dry bulk density of biochar was 200 kg m⁻³, which is equivalent to 5.3 kg of biochar.

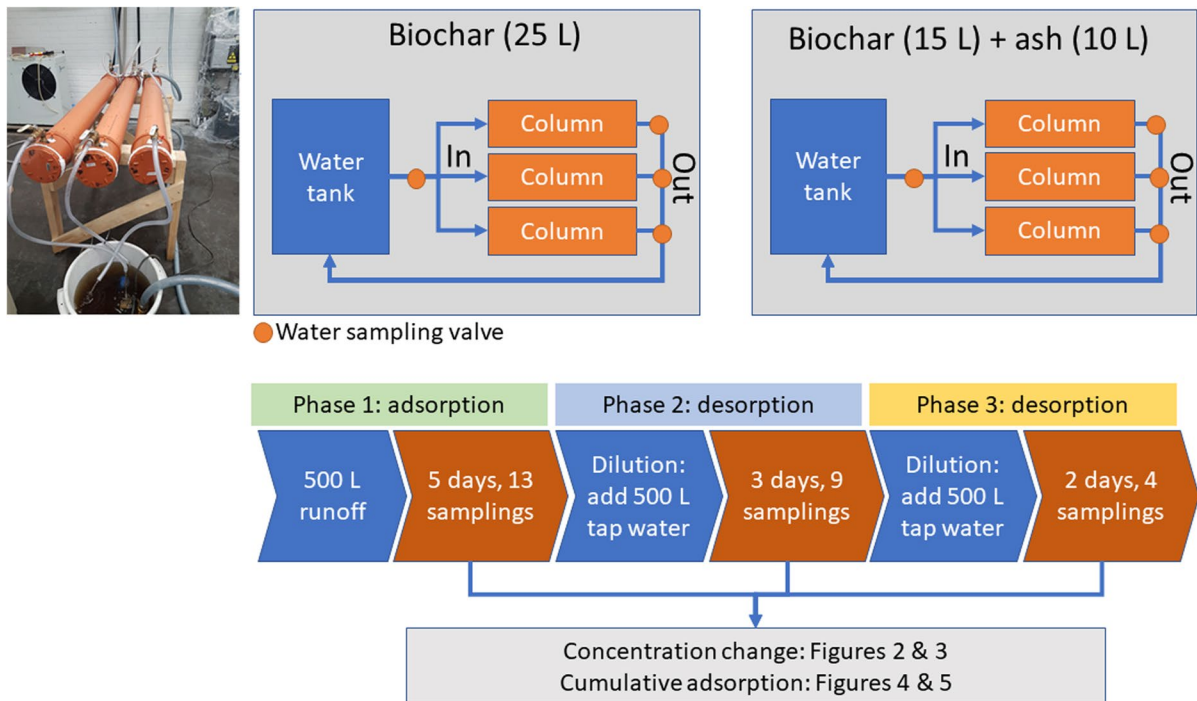


Fig. 1 Biochar reactors and experimental setup

Valves at the inlet supplying all three columns with water and at the outlets were used to adjust the flow rates, as well as to collect water samples through plastic hoses (Fig. 1). A submersive pump was used to circulate water back from the outlet into the storage tank, located 3 m above the reactor setup.

The biochar was produced from Norway spruce (*Picea abies*, Karst) wood chips by Carbofex Ltd. (Tampere, Finland) under continuous pressurized slow pyrolysis conditions at 600 °C (Table 1). The factory carbonizes 400–500 kg of wood chips per hour (residence time is 5–10 min) and produces 100–140 kg of EBC-certified biochar. The process yields 25–30% biochar, 12% pyrolysis oil, and 20% pyrolysis gas. The biochar was sieved to have a particle size of less than 8 mm. We also used commercial ash from the same provider as in the study by Kinunen et al. (2021) (T.U.H.K.A—Oulun Energia).

The water was continuously circulated through the reactor. Water sampling was done from the inlet hose before the reactor, as well as from each of the three outlets. In the first phase of the experiment, we studied the adsorption, and undiluted runoff water was circulated through the reactor. The water sampling was done 4 times during the first day, 3 times during the second day, and 2 times per day during the following

3 days. In the second and third phases, we studied the possible desorption of metals from the reactors. In the second phase, the water in the tank was diluted by adding 500 L of tap water (pH 8, electric conductivity (EC) 217 $\mu\text{S cm}^{-1}$). Thereafter, the water sampling was continued for three days with a similar interval than during the first phase. In the third phase, the water was diluted once more by removing half of the water and adding 500 L of tap water. For 2 days, the sampling interval was again 4 times during the first day and 3 times during the second day.

A similar experiment as described above was conducted with the biochar-ash reactors (Fig. 1). The columns contained 50% of biochar and 50% of ash by mass (15 L biochar, 10 L ash by volume).

The water samples were taken by collecting 1 L of the water in a glass container and immediately taking the samples from that with 20-mL plastic syringes (BD Plastipak, BD Ab, Stockholm, Sweden) and 0.45- μm hydrophilic syringe filters (Minisart, Sartorius, Göttingen, Germany). The filtered samples were kept at +4 °C until analysis. The flow was adjusted using the valves to 0.5–1 L min^{-1} which corresponds to a flow velocity range of 0.001–0.002 m s^{-1} and results in a residence time of 12–23 min inside the reactor. This was chosen to represent low water flow velocities that are common in ditch drains of forested peatlands (Haahti et al., 2014). The experimental setup is explained in Fig. 1.

Metal concentrations in water samples were measured with an ICP-MS analyzer (PerkinElmer NexION 350D, PerkinElmer, Waltham, Massachusetts), with detection limits down to ppb—ppt scale. With the 0.45- μm filtering applied, these only included metals dissolved into the solution. pH and EC were analyzed with WTW pH 340i and WTW pH/cond 340i, respectively (WTW GmbH, Weilheim, Germany), and NH_4^+ and NO_3^- concentrations were measured spectrophotometrically.

2.3 Calculations and Statistical Analysis

Linear mixed effects (LME) models were used to study whether the concentrations of metals decreased or increased relative to the first inlet measurement or the first measurement after the dilutions for both reactors (Eq. 1). This was used as the first step to detect which metals were adsorbed or desorbed and how the different dilutions affected that. A following LME model was fitted to the data

Table 1 Biochar properties

Feedstock	Norway spruce wood chips
Pyrolysis temperature	600 °C
pH (1:2.5 v:v biochar/water solution)	9.25 (0.01)
Electric conductivity ($\mu\text{S cm}^{-1}$) (1:2.5 v:v biochar/water solution)	221 (15)
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	320
Dry matter content (%) (105 °C, 48 h)	72.69 (2.74)
C content (%)	79.07 (0.83)
N content (%)	1.19 (0.09)
C:N ratio	66.93 (5.51)
H/C ratio (molar)	0.1
O/C ratio (molar)	0.016
Cd (mg kg^{-1})	0.2
Co (mg kg^{-1})	1
Ni (mg kg^{-1})	1
Zn (mg kg^{-1})	1
Fe (mg kg^{-1})	100

The values are means \pm standard deviation

$$c_{im} = \beta_{oi} + \beta_{im} + \varepsilon_{im} \quad (1)$$

where c_{im} is the concentration of metal i at the last measurement in phase m (phase 1, 2,3). β_{oi} is the concentration of metal i in the first inlet value of the phase, β_{im} is the change in the metal i concentration for phase m , and ε_{im} is the residual term, with an expected value of zero.

The concentration changes were used to calculate cumulative adsorptions on the biochar during the experiment using Eq. 2:

$$Q_{ti} = \frac{(C_{iniim} - C_{outit})xV}{m_{biochar}} \quad (2)$$

where Q_{ti} is the cumulative adsorption of metal i on biochar (mg g^{-1} biochar), C_{iniim} is the inlet concentration of metal i at the first measurement of phase m (phase 1, 2, 3, mg L^{-1}), C_{outit} is the outlet concentration of metal i at time t , V is the volume of water circulating through the reactor, and $m_{biochar}$ is the dry mass of the biochar in the reactor.

A pseudo-first-order kinetic model was used to study the adsorption isotherms: cumulative adsorptions and adsorption rates (Eq. 3):

$$Q_i = Q_{max}(1 - e^{-k_{ad}xt}) \quad (3)$$

where Q_i is the cumulative adsorption of metal i (mg g^{-1} biochar) at time t (h), Q_{max} is adsorption capacity (mg g^{-1}), and k_{ad} is the adsorption rate ($\text{g mg}^{-1} \text{h}^{-1}$) of metal i . First, a simple base model applying shared Q_{max} and k_{ad} for each treatment was constructed. Afterwards, we tested varying Q_{max} and k_{ad} between treatments, one at a time. Residual normality was tested for this process. The best performing model was selected, using Akaike Information Criterion (AIC) and Bayesian Information Criterion (BIC), as well as log likelihood values and significance of the individual parameter values. Modeling was performed with the lme and nlme packages of R (Pinheiro et al., 2021).

3 Results

3.1 Concentration Changes in Water

Two-week tests with two dilutions were used to monitor the metal concentrations in the water

circulating through the biochar and biochar-ash reactors (Fig. 1). Using the inlet and outlet concentration values measured at each time point, we could calculate the cumulative adsorption through the test phases, as well as the adsorption isotherms. A decrease in metal concentration in the water was interpreted as adsorption on the reactor.

The concentration changes varied between metals and phases. Al, Fe, Co, Ni, and Cd were adsorbed to biochar reactors, whereas Cu and Zn concentrations increased indicating a release from the adsorbates (Fig. 2). Cd concentration fluctuated heavily, possibly due to being at a very low level from the beginning. The dilutions did not change these trends, but seemingly slowed down the concentration changes in water (Fig. 2). Biochar with ash showed improved adsorption compared to biochar only: Fe, Co, Ni, Cu, Zn, and Cd concentrations decreased in water, with only Al showing increasing concentrations. The concentration decreases using biochar-ash reactors were generally larger and faster than in biochar reactors (Fig. 3). Dilutions mainly kept these trends, but there were more short-term fluctuations where the outlet values are sometimes even higher than the inlet ones. This happened, e.g., for Fe, Cu, Zn, and Cd, after the second dilution (Fig. 3).

Ash addition overall improved the adsorption for all metals except Al. Cu and Zn desorbed with the biochar reactor, but had strong, around 89–99% adsorptions with the biochar-ash reactor (Table 2). Fe, Co, Cd, and Ni were also adsorbed stronger with ash, although Ni concentrations fell under the detection limit thus resulting in near 100% reduction in concentration. Dilutions decreased adsorption in most cases with and without ash; for example, 96% of Fe was adsorbed before dilutions but only 7% after the second dilution (phase 3). Excluding the Ni below the detection limit, adsorption was never as strong after dilutions as it was before them.

The decrease was calculated from the first inlet and last outlet values in each phase. Bolded values indicate an increase in metal concentration in water. Ni in biochar-ash reactor fell below the detection limit.

3.2 Adsorption kinetics

The concentration changes were used to calculate the adsorption of metals into biochar, with the base

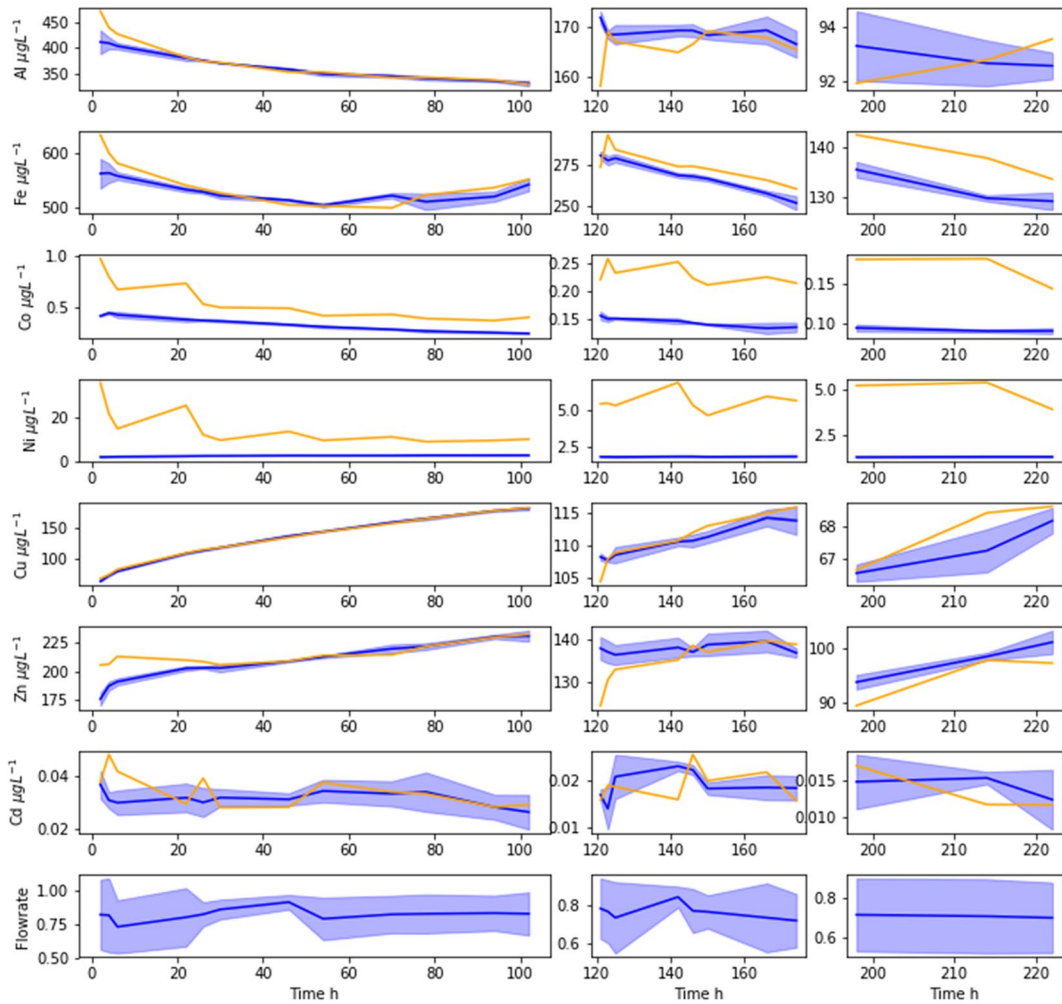


Fig. 2 Metal concentrations in water and the water flow rate in the biochar reactors. Orange line is the inlet concentration, and the blue line and the blue shaded area describe the mean and standard deviation of outlet concentrations of the 3 biochar-

ash reactors, respectively. Each row is split at the time points where the test phase changed (left to right phase 1, 2, and 3). Downward trends indicate a decrease of a metal concentration in water, which can be attributed to adsorption into the reactor

assumption that any decrease is due to adsorption (Figs. 4 and 5). Adsorption capacity (Q_{max}) and rate (k_{ad}) are calculated using Eq. 3.

Q_{max} and k_{ad} were calculated for metals that were adsorbed from water. Table 3 contains data for biochar reactor (Al, Fe, Co), and Table 4 presents biochar-ash reactor (Fe, Co, Ni, Cu, Zn, Cd). Q_{max} was highest for Fe, likely due to its high initial concentration. However, Fe had the lowest k_{ad} , which was highest for Co in the biochar reactor and Cd in the biochar-ash reactor. Ash addition improved Q_{max} for Fe significantly, while also

introducing or improving adsorption for Ni, Cu, Zn, and Cd.

3.3 pH, EC, and Nutrients

Both pH and EC changed during the experiment (Fig. 6). With biochar reactor, pH increased rapidly to around 7.3–7.5, where it remained until the dilutions. After the dilution, the pH increased to around 7.5–7.6, but at the same time, much more fluctuation was introduced into the pH values, likely due to the dilutions. With biochar-ash reactor, there was a

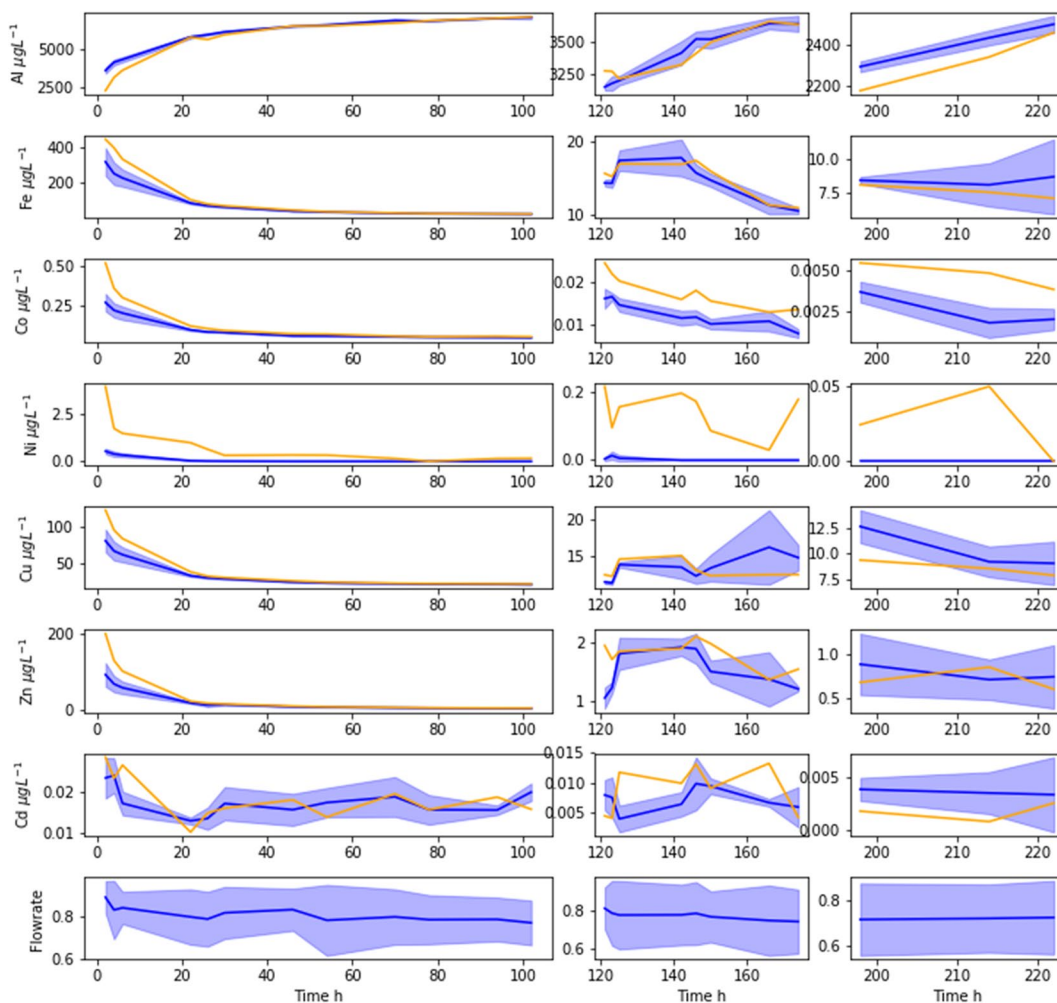


Fig. 3 Metal concentrations in water and the water flow rate in the biochar-ash reactors. Orange line is the inlet concentration, and the blue line and the blue shaded area describe the mean and standard deviation of outlet concentrations of the 3 bio-

char reactors, respectively. Each row is split at the time points where the test phase changed (left to right phase 1, 2, and 3). Downward trends indicate a decrease of a metal concentration in water, which can be attributed to adsorption into the reactor

Table 2 The changes in metal concentrations in water (%)

	Al	Fe	Co	Ni	Cu	Zn	Cd
Biochar reactor							
Phase 1	-41.32	-27.68	-88.95	-96.31	216.45	-0.08	-49.07
Phase 2	-32.35	-8.06	-53.21	-80.55	10.48	15.14	15.2
Phase 3	7.47	-6.67	-57.06	-81.51	9.69	31.74	1.58
Biochar-ash reactor							
Phase 1	1059.94	-96.12	-95.53	≥99.7	-89.34	-99.17	-70.88
Phase 2	21.7	-31.33	-70.85	≥99.7	23.88	-37.97	3.87
Phase 3	17.78	-6.74	-70.97	≥99.7	-12.73	-4.88	-0.6

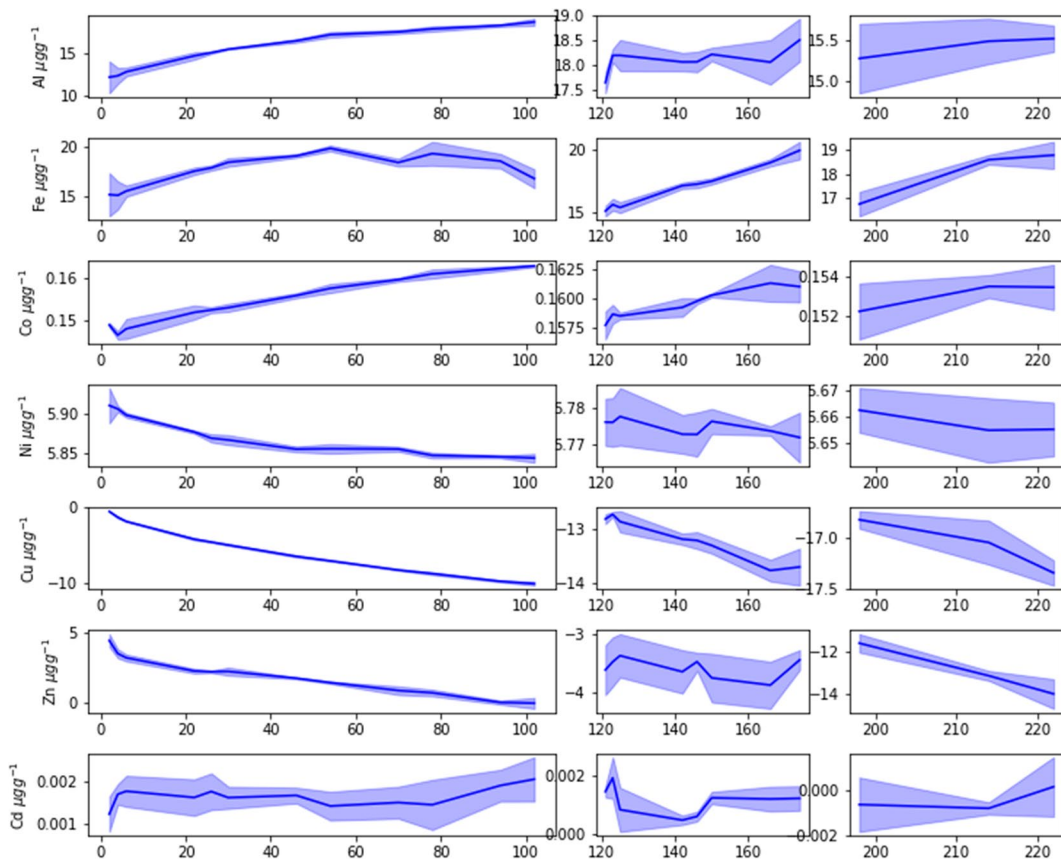


Fig. 4 Metal adsorption from water to the biochar reactors. Each row is split at the time points where the test phase changed (left to right phase 1, 2, and 3). Upward-facing lines

indicate the accumulation of the metal into biochar via adsorption. Shaded areas indicate the standard deviation between the three outlets at each time point

similar increment towards stable pH, but this time, the pH value increased to a much higher level of around 11.5. Dilutions again introduced fluctuations, but this time pH was so high that they decreased the pH only momentarily, and the pH started to climb back to over 11 soon after the dilutions.

EC also changed somewhat between the treatments: For biochar reactor, there was a fast increase in EC right at the start of the experiment, followed by stabilization, and then a steady increase until the first dilution. After the dilution, there was a similar fast increase to a stable level, but no steady increase. Biochar-ash reactor resulted in over 10 times higher EC values to the water, with fast increase until the stabilization. Dilution again further stabilized the EC values, but this time, it decreased the EC.

NH_4^+ and NO_3^- values were low (below 0.2 mg L^{-1}) throughout the experiment, barely rising above the Milli-Q water reference samples in most cases. No significant differences were found. Therefore, the nutrient data mainly tells us that the overall concentrations of NH_4^+ and NO_3^- were low and there were no significant releases of NH_4^+ and NO_3^- during the experiment.

4 Discussion

4.1 Adsorption and Desorption

This was, according to our knowledge, the first meso-scale laboratory experiment to study the recovery of multiple metals and neutralization of acidity from acid sulfate soil runoff water using biochar and

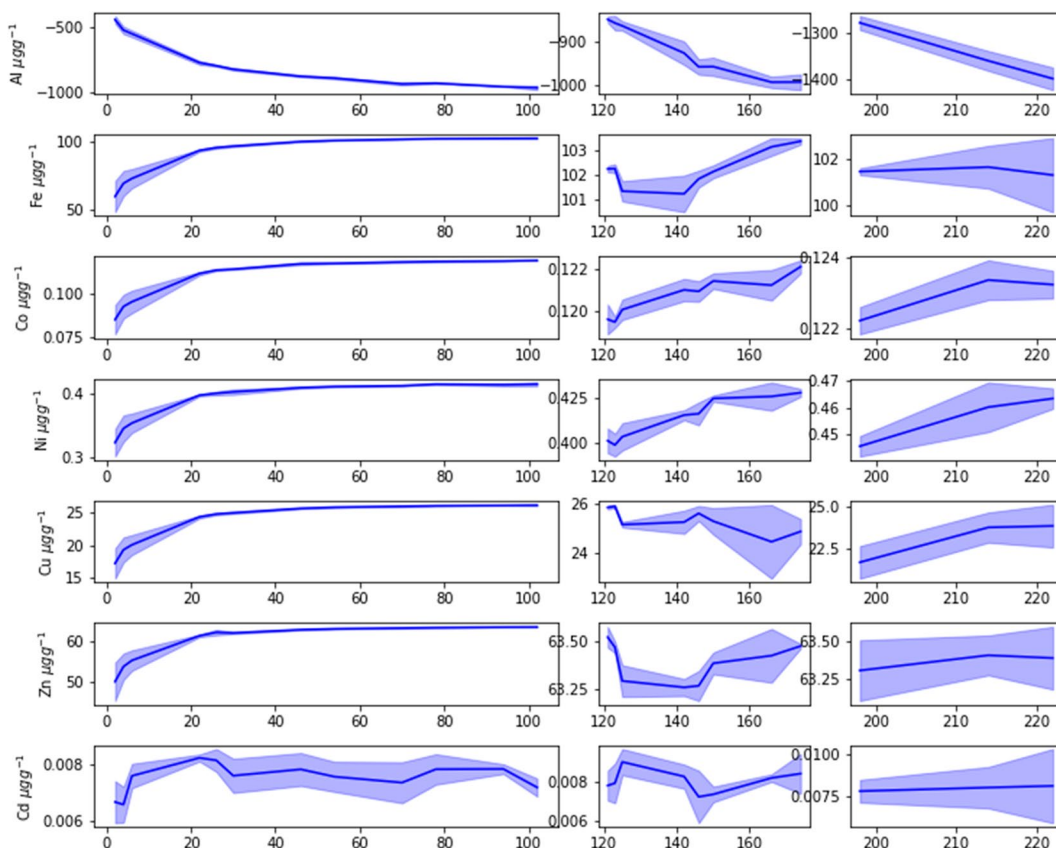


Fig. 5 Metal adsorption from water to biochar-ash reactors. Each row is split at the time points where the test phase changed (left to right phase 1, 2, and 3). Upward-facing lines

indicate the accumulation of the metal into biochar via adsorption. Shaded areas indicate the standard deviation between the three outlets at each time point

Table 3 Adsorption rate (k_{ad}) and adsorption capacity (Q_{max}) for selected metals in biochar reactor (Eq. 3)

	Value	SE	<i>p</i> value		Value	SE	<i>p</i> value
Al				Co			
k_{ad}	0.44	0.04	<0.001	k_{ad}	1.52	0.155	<0.001
Q_{max} phase 1	16.6	0.245	<0.001	Q_{max} phase 1	0.155	0.0006	<0.001
Q_{max} phase 2	1.48	0.36	<0.001	Q_{max} phase 2	0.004	0.001	<0.001
Q_{max} phase 3	-1.19	0.49	0.018	Q_{max} phase 3	-0.0025	0.001	0.077
Fe							
k_{ad}	0.72	0.099	<0.001				
Q_{max} phase 1	18.03	0.277	<0.001				
Q_{max} phase 2	-0.89	0.415	0.034				
Q_{max} phase 3	0.005	0.576	0.99				

The Q_{max} phase 1 value for each metal is an absolute value, and the Q_{max} phase 2 and Q_{max} phase 3 values are the differences from it

biochar-ash column reactors. The chemical composition of forest runoff water differs markedly from urban, industrial, or agricultural runoff water, and the previous results from these environments are not

directly applicable for forest areas (Ambaye et al., 2021; Bilal et al., 2013; Oliveira et al., 2017; Reddy et al., 2014). The other key novelty in this experiment was that after the adsorption phase, the reactors were

Table 4 Adsorption rate (k_{ad}) and adsorption capacity (Q_{max}) for selected metals in biochar-ash-reactor (Eq. 3)

	Value	SE	<i>p</i> value		Value	SE	<i>p</i> value
Fe				Cu			
k_{ad}	0.32	0.018	<0.001	k_{ad}	0.42	0.027	<0.001
Q_{max} phase 1	98.7	0.98	<0.001	Q_{max} phase 1	25.3	0.25	<0.001
Q_{max} phase 2	3.45	1.44	0.019	Q_{max} phase 2	-0.013	0.37	0.97
Q_{max} phase 3	2.76	1.97	0.16	Q_{max} phase 3	-2.16	0.52	<0.001
Co				Zn			
k_{ad}	0.51	0.03	<0.001	k_{ad}	0.72	0.04	<0.001
Q_{max} phase 1	0.11	0.001	<0.001	Q_{max} phase 1	61.7	0.38	<0.001
Q_{max} phase 2	0.006	0.001	<0.001	Q_{max} phase 2	1.62	0.57	0.006
Q_{max} phase 3	0.008	0.001	<0.001	Q_{max} phase 3	1.59	0.8	0.05
Ni				Cd			
k_{ad}	0.68	0.04	<0.001	k_{ad}	0.89	0.18	<0.001
Q_{max} phase 1	0.4	0.003	<0.001	Q_{max} phase 1	0.007	0.0001	<0.001
Q_{max} phase 2	0.01	0.005	0.009	Q_{max} phase 2	0.0003	0.0002	0.13
Q_{max} phase 3	0.05	0.006	<0.001	Q_{max} phase 3	0.0003	0.0003	0.26

The Q_{max} phase 1 value for each metal is an absolute value, and the Q_{max} phase 2 and Q_{max} phase 3 values are the differences from it

exposed to diluted water to study possible desorption.

can vary considerably in different seasons (Hovinen

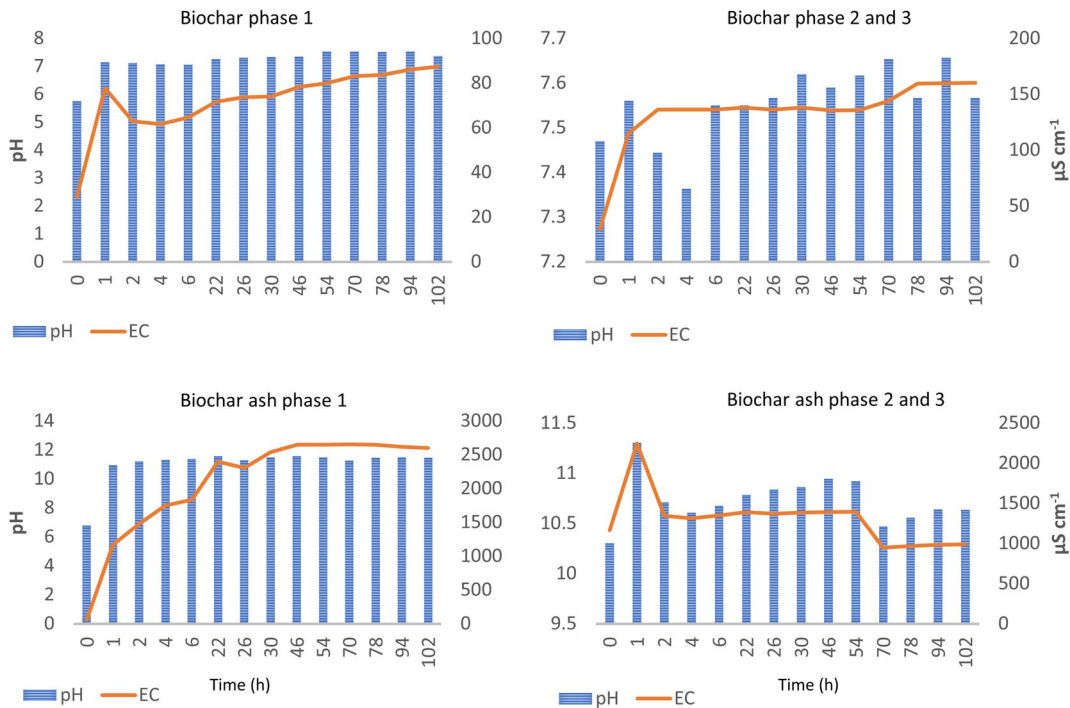


Fig. 6 pH and EC values in the inlet (time point 0) and outlets (other time points) of the biochar reactor across the experiment. Blue columns represent pH at each time point, and the orange line follows the development of EC

This provides useful information about the applicability of biochar reactors because metal concentrations

et al., 2012; Saarinen et al., 2013). The results showed that both reactors rapidly adsorbed multiple metals.

When metals were adsorbed, no significant desorption took place when the reactor was exposed to water with lower concentration of metals. Fe and Co were always adsorbed, whereas Al, Cu, Ni, Zn, and Cd adsorption varied between the reactors and dilutions. Biochar-ash reactor had generally higher adsorption than the biochar reactor for all metals, except for Al.

The initial metal concentrations in the studied runoff water were generally higher than in a preceding small-scale laboratory experiment (Kinnunen et al., 2021), but still rather typical for Finnish acid sulfate soils (Hovinen et al., 2012; Saarinen et al., 2013). However, initial Ni and Zn concentrations were close to the highest values found in Finnish acid sulfate soils by Hovinen et al. (2012). In acid sulfate soils, the highest metal concentration peaks usually take place during the spring snowmelt, and our sampling was done roughly 2 weeks after the snowmelt. The water had an initial pH value of 4.5, which is on the higher side for acid sulfate soils (Fältmarsch & Vuori, 2007), yet still below the threshold value of 5.5.

We used spruce biochar and wood ash as adsorbents in the reactors, because these materials showed the best performance in the study by Kinnunen et al. (2021). The adsorption of Al, Fe, Co, and Ni to biochar reactors lined up with those in Kinnunen et al. (2021). Biochar-ash reactors adsorbed metals better than biochar reactors. The only exception was Al, which was adsorbed to biochar reactors but was released from the biochar-ash reactors. Adsorption isotherms (Tables 3 and 4) showed lower Q_{max} for Fe in biochar reactor (16.6 against 32.8 for spruce biochar in Kinnunen et al., 2021). However, it had higher Q_{max} for Al (16.62 against 6.78) and Co (0.155 against 0.046). There also was steady adsorption of Al, Fe, and Co into the biochar throughout the entire 220-h test period, even after the dilutions. This could indicate that there might have been further adsorption of these three metals with more time and that our calculated Q_{max} values may not represent their true maximum. The concentrations of Ni decreased rapidly below the detection limit (Fig. 2), which indicates effective and fast adsorption of Ni with biochar.

The biochar-ash reactor showed a high adsorption rate during the first 20 h, after which the rate slowed down (Fig. 5). This suggests that the adsorption of metals is dependent on their concentration in the solution (Saarela et al., 2020). The Q_{max} for Fe in biochar reactors was $16.6 \mu\text{g g}^{-1}$, and for biochar-ash

reactors, it was $98.7 \mu\text{g g}^{-1}$. This is a significant increase, but slightly less than observed by Kinnunen et al. (2021). This could be explained by the slightly lower initial Fe concentration in this study ($750 \mu\text{g L}^{-1}$) compared to the laboratory study by Kinnunen et al. (2021) ($1050 \mu\text{g L}^{-1}$). The fact that our initial Ni and Zn concentrations and their adsorption capacities were higher in this study compared to Kinnunen et al. (2021) indicates the effect of the concentrations on the adsorption as well.

We used ash as a pH-increasing additive. Water pH increased above the critical 5.5 threshold for aquatic life with both reactor types. An increase in water pH generally transforms the metals into their free ion forms where their affinity for the biochar surface becomes higher (Chen et al., 2011; Jiang et al., 2016). Increasing the pH also results in negative surface charges for the biochar (Guilhen et al., 2022). This introduces electrostatic interactions between the positively charged metal ions and the negatively charged biochar surface, enabling or improving adsorption mechanisms such as electrostatic attraction, complexation, ion exchange, and precipitation (Duwiejuah et al., 2020; Cheng et al., 2021; Ambaye et al., 2021). Considering the speed of the adsorption with and without ash, the generally slower adsorption with biochar only could be due to limited adsorption space: Metals could be competing for the limited physical adsorption space and substituting weaker competitors such as Zn (Park et al., 2016), for which we see increasing concentrations in water. However, when ash is added, Zn is adsorbed from water rapidly and retained, along with all other studied metals except Al. This seems to indicate that metals no longer must compete for the adsorption sites since their concentrations in water decreased by around 89–99% before dilutions. This is likely due to the introduction of the electrostatic interactions that create new adsorption sites. The exceptions to this are Cd and Al. Cd adsorption was lower than that of the other metals, but still substantial at 70% decrease in water before dilutions. The low initial concentration of Cd could explain this. Al, however, behaved differently compared to all the other metals. It is known that there are specific optimal pH ranges for each metal, and exceeding these ranges can weaken the adsorption capacity (Chen et al., 2011; Duwiejuah et al., 2020). Chen et al. (2011) proposed that decreasing adsorption at

higher pH is due to the formation of hydroxide complexes. However, our pH values with the biochar-ash reactor were generally higher than the optimal ranges proposed in laboratory studies (Chen et al., 2011; Kołodyńska et al., 2012). Despite this, our biochar-ash reactor showed fast adsorption and removed up to over 90% of the metals from water. Figure 6 shows that the pH increased up to over 10 only after around 20 h. Therefore, it is possible that this decrease in adsorption was also affected by the pH reaching too high levels and transforming the metals into their hydroxyl forms. Although many of these hydroxyls are negatively charged and thus poorly adsorbed, there are also some forms that are positively charged at pH 10–11, and thus could be readily adsorbed. These include, for example, $\text{Cu}(\text{OH})^+$, ZnOH^+ , and $\text{Cd}(\text{OH})^+$ as well as Cd^{2+} itself (Cairns et al., 2022). These could explain the adsorption still happening after the dilutions when pH was above 10 from the start. Therefore, the decrease of metal adsorption after 20 h with biochar-ash reactors was likely due to the combination of the pH increase and the metal concentration decrease.

Biochar-ash columns showed a substantial increase in Al concentrations in water. The Al concentrations increased after the first inlet measurement, indicating that the Al originates from the ash. This potential release, and either lack or weakness of its adsorption, could be due to how Al behaves in high pH. As shown by Pitre et al. (2014), Al is soluble under low and high pH conditions and relatively insoluble in between. The key feature is its tendency to occur as negative hydroxyl ions in high pH, above pH 8 or 9. Since the biochar surface in this high pH is also dominated by negative charges (Dwiejuah et al., 2020; Guilhen et al., 2022), the adsorption of these Al ions would likely be poor. Our biochar reactor without ash always had a pH below 8 (Fig. 6), therefore likely avoiding the formation of these negative Al ions. In these lower pH values, surface sorption, pore filling, and precipitation could be the mechanisms that lead to the adsorption of Al into our biochar reactor.

A review article by Jha et al. (2023) reports adsorption efficiencies for different metals with biochar. Cd adsorption efficiency was 75–87%. Our respective value was slightly lower (50–70%) which can partly be explained by our lower initial Cd concentration. Similarly, Chen et al. (2011) and Jiang et al. (2016) had adsorption capacities for Cu and

Zn at the range of mg g^{-1} (1.47–12.52 mg g^{-1} for Cu and 1.00–11.00 mg g^{-1} for Zn), while our values were 0.025 mg g^{-1} for Cu and 0.062 mg g^{-1} for Zn. Comparisons to other biochar adsorption studies are demanding because the studies contain a wide array of laboratory experiments, single metal adsorption tests, variable metal concentrations, and biochar feedstocks. Our experiment featured high water volumes, competing adsorption and relatively low initial concentrations and pH values, all of which can decrease the adsorption of individual metals.

Biochar has not been assessed as a ditch-scale solution for acid sulfate soil drainage in Finland before. Therefore, we must seek comparisons with alternative water protection methods employed, both for acid sulfate soils and other metal-rich runoff waters. Constructed wetlands offer a passive system with no chemicals or industrial installations needed, but regardless take a lot of space, and the area can be contaminated by the metals (Palmer et al., 2015). Constructed wetlands can be inefficient in adsorbing metals, or they can even release sulfate (SO_4^{2-}), Fe, and P (Palmer et al., 2015; Wu et al., 2013). Biochar filters do not require large areas as they can be installed into the ditches. Our results indicate that most metals can be effectively retained into biochar with a low risk of metal desorption under changing concentrations. Palmer et al. (2015) presents data of multiple metal adsorption from mining effluents using constructed wetlands and found that they removed 52–92% of Fe and 81–90% of Ni. Saeed et al. (2021) found that constructed wetlands reduced Zn concentrations by 20–97% and Ni concentrations by 55–75%. We found 28–96% Fe removal, 96–99% Ni removal, and 0–99% Zn removal.

4.2 Reactor Evaluation

The biochar reactor has several advantages for field use, such as fast adsorption process, an increase in adsorption capacity with increasing metal concentrations in water, and low desorption in conditions when the metal concentrations decrease. It also requires relatively small space to function. Therefore, the biochar reactor could help to cut the high metal concentration peaks that are the most harmful to aquatic ecosystems (Sutela et al., 2012). Fast adsorption, in turn, suggests that biochar reactors can also adsorb metals with short water residence times. This is particularly important

during the snowmelt when both metal concentrations and runoff are typically high. Locating a biochar reactor in ditches where the metal concentrations are high enhances the adsorption capacity and, therefore, the efficiency of the water purification. Consequently, this would decrease the required amount of biochar and the related costs. It is also essential to locate the reactors in such ditches where the area of the above catchment is rather small. This is because the reactor can become saturated as well as cause flooding under high flow conditions. Therefore, it is vital to identify the locations in the landscape where the risk of metal export is highest. These hotspots can be identified using hydrological or ecosystem models (e.g., Laurén et al., 2021 NutSpaFHy, Laurén et al., 2021) together with soil maps showing the location of the acid sulfate deposits. Hydrological and ecosystem models can predict water table depth and the thickness of the layer where the acid sulfate deposits can be oxidized. These models can account for the role of forest management, drainage, soil characteristics, and weather conditions, and therefore, they can be used to search for the most suitable locations for the reactors.

Reactor use must be carefully planned beforehand considering the logistics and other technical and economic viewpoints. Practical implementation requires the use of a forest forwarder in biochar and other material transportation and a hydraulic crane for installation and removal of the reactors. In practice, the reactors can be heavy-duty mesh bags that can be moved using the hydraulic crane. Using machinery in the transportation, installation and de-installation are vital because the biochar mesh bags become excessively heavy when wet.

Environmental threshold values exist for some, but not all the metals we monitored in this study (Hovinen et al., 2012). For Ni, it is $21 \mu\text{g L}^{-1}$ (Hovinen et al., 2012), and both our biochar and biochar-ash reactors were able to lower the concentrations in water below this value. For Cd in Finland, the threshold is $0.08 \mu\text{g L}^{-1}$ (Finnish Parliament, 2015), but our concentrations were below this value from the beginning of the experiment. Threshold values for Zn also exist, $7.2 \mu\text{g L}^{-1}$ on coast and $7.5 \mu\text{g L}^{-1}$ at rivers (Hovinen et al., 2012). These were met with biochar-ash reactors. Our Al concentration decrease was 41% with biochar. Fe concentration was reduced by over 95% with biochar-ash (concentration decreased to $29 \mu\text{g}$

L^{-1}). We can conclude that the tested reactors can reduce concentration of multiple metals below environmental threshold values.

5 Conclusions

Our results indicate that biochar reactors can effectively adsorb metals and increase water pH. In most cases, the adsorption was enhanced when ash was added as a mixture to the reactor. Fast adsorption indicates that the reactor can retain metals also with short water residence times, and the desorption of metals is negligible. Thus, biochar reactors can be useful in cutting high metal outflow peaks. Further work would be needed to investigate different pH-increasing additives. Field-scale experiments are needed to investigate how long the reactors can be maintained in water protection before they become saturated.

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Data Availability The data will be provided as supplementary material if the manuscript is accepted for the journal.

Code Availability N/A.

Declarations

Conflict of Interest The authors declare no competing interests.

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