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Can biochar and designer biochar be used to remediate per- and polyfluorinated alkyl substances (PFAS) and lead and antimony contaminated soils?

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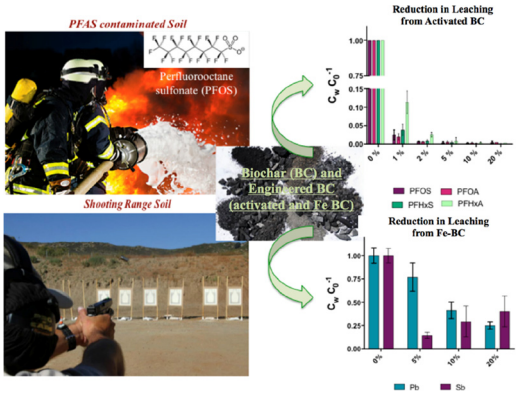
HIGHLIGHTS

- Designer biochars were used to remediate industrially contaminated soils.
- Activated biochar reduced PFAS leachate concentrations more than unactivated biochar.
- Activated biochar was most effective in low TOC soil.
- Iron enriched biochar reduced Pb and Sb leaching more than unactivated biochar.
- Iron enriched biochar was most effective in low TOC soil.

GRAPHICAL ABSTRACT



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ABSTRACT

Designer biochars can be used to remediate organic and inorganic contaminant polluted soils. Here, a waste timber biochar (BC), a coconut shell activated biochar (aBC) and a wood shrub iron enriched designer biochar (Fe-BC) were investigated. Per- and polyfluorinated alkyl substances (PFAS) contaminated soils with different total organic carbon (TOC) contents (1.6 and 34.2%) were amended with six doses of BC and aBC. Two shooting range soils (TOC 5.2 and 10.2%) contaminated with heavy metals (mainly Pb and Sb) were amended with four doses of BC and Fe-BC. An amendment of 20% BC reduced the PFOS leachate concentration by 86% for the low TOC soil but was not effective for the high TOC soil. An amendment of 1% aBC reduced PFOS leachate concentrations by over >96% for both soils. For the low TOC shooting range soil, a 20% amendment of BC reduced Pb and Sb leaching by 61% and 12%, respectively. An amendment of 20% Fe-BC to soil with low TOC reduced Pb and Sb leaching by 99% and 40%, respectively. The need for "designer" biochars using processes such as iron enrichment or activation should be considered depending on the TOC of the soil, the type of contaminants and remediation goals.

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1. Introduction

The contamination of soil with metals and organic pollutants, alone or as a mixture, represents a worldwide environmental issue (Zhang et al., 2013) owing to threats to groundwater quality, ecosystem and human health and food safety (Heier et al., 2009; Carlsson et al., 2017). Per- and polyfluorinated alkyl substances (PFAS) are hydrophobic, fluorine alkylated, saturated carbon chain compounds with a hydrophilic sulfonate or carboxylate head attached at a terminal end (Tittlemier et al., 2007; Armitage et al., 2009). PFAS are mobile in the environment and have even been found in remote areas such as the Arctic and Antarctic (Carlsson et al., 2017; Skaar et al., 2018). The use of PFOS and PFOA, the most commonly used and detected PFAS, is strictly regulated (Carlsson et al., 2017) and they are included in the in the EU Water Framework Directive (http://ec.europa.eu/environment/water/water-framework/index_en.html, n.d.) as well as PFOS being listed in Annex IV of the Stockholm Convention (Carlsson et al., 2017).

Shooting range soils often contain high levels of lead (Pb) and antimony (Sb) that arise from the weathering of spent bullets (Mariussen et al., 2012; Okkenhaug et al., 2018; Hockmann et al., 2018). The highest Pb and Sb concentrations are usually found near bullet traps (Okkenhaug et al., 2016), however, due to weathering of spent bullets and metal mobility, the pollution can become highly diffuse and persist for hundreds of years (Okkenhaug et al., 2018; Okkenhaug et al., 2016; Strømseng et al., 2009; Clausen et al., 2011). The excavation of contaminated soils, which is often carried out in order to remediate such sites, places pressure on environmental resources. Within the EU and Norway such soils must be stabilized before they can be disposed of at landfill and effective and suitable methods to do this must be found (European Union Council, 1999).

The high environmental relevance of soils contaminated with PFAS and/or heavy metals, the toxicity of these contaminants, as well as stringent regulations, necessitates the development of cost-effective remediation strategies. Carbonaceous material (CM) sorbent amendment is a promising strategy (Xu et al., 2016) in which a strongly sorbing CM is added to a contaminated soil, leading to a repartitioning of the contaminants from the soil to the sorbent itself, thus reducing their availability for plant and biota uptake or further environmental transport (Ghosh et al., 2011). Activated carbon (AC) is one of the most commonly used sorbents for soils contaminated with organic compounds due to its high surface area, large binding capacity and thus high removal effectiveness (Ghosh et al., 2011; Hale et al., 2017). For Pb and Sb contaminated soils, iron oxyhydroxides are very effective as they complex both cations and anions, thus immobilizing Pb and Sb[11]. Recently, biochar amendment has gained widespread attention as a more sustainable, climate-friendly and cost-effective alternative sorbent amendment material, especially when the biochar is made from organic waste materials (Ahmad et al., 2014; Silvani et al., 2017). In addition to remediation, using biochar also has several additional environmental advantages. Biochar aids in combating climate change as the material itself contains significant amounts of carbon that is stable for thousands of years, providing an opportunity for carbon storage (Lorenz and Lal, 2014). As a result, activated biochar has been shown to be favourable with respect to its environmental impact when compared to the use of coal based AC (Sparrevik et al., 2011).

Norway generates large amounts of organic waste including waste timber (shredded wood panels, furniture, spent pellets – 660,000 t y^{-1}), garden waste (150,000 t y^{-1}), forestry residues (3,700,000 t y^{-1}), food/biological waste (340,000 t y^{-1}) and sewage sludge (200,000 t y^{-1}) (http://www.miljodirektoratet.no/no/Publikasjoner/2016/September-2016/Tiltaksplan-for-arbeidet-med-per–og-polyfluorerte-stoffer-i-perioden-2016-2018/, n.d.). These waste fractions currently have a negative economical and societal value, but a value chain can be created if they are turned into a resource (biochar) and used for example, in sorbent remediation. By doing so, the additional benefits of the use of biochar (sequestration of CO_2 from the atmosphere, a reduction in soil NO_2 and CH_4 emissions (Jeffery et al., 2017) as well as reduced pollutant leaching) are also felt. Furthermore, using these materials to produce biochar has a commercial benefit in line with the circular economy as a sustainable method is used to produce a resource (Stahel, 2016).

In the present study, two PFAS contaminated industrial soils and two metal contaminated shooting range soils (both with variable total organic carbon contents), all received at a Norwegian landfill, were stabilized using one unaltered and two biochars with optimized properties. By applying a wide range of sorbent dosages (0 to 20%), sorption isotherms were constructed and the concentration dependence of sorbent performance was determined. The hypotheses of the work were that; i) the amendment of these biochars would reduce the leaching of PFAS and heavy metals from the soils and ii) the designer biochars would be more effective than the unaltered biochar. This study is one of the first to investigate the remediation of real world soils (PFAS and metals contaminated) using a waste material converted to a valuable resource. The present work is in accordance with Sustainable Development Goal 12, "Responsible Consumption and Production" (Haines et al., 2017), covering both the sustainable management and efficient use of natural resources, as well as the goal of substantial reduction of waste generation through prevention, reduction, recycling and reuse (waste timber is recycled into a resource for contaminant management and climate change mitigation).

2. Materials and methods

2.1. Soils

Two PFAS contaminated soils with different TOC contents, 1.6% and 34.2% (termed low and high TOC PFAS soil, respectively) were tested. The TOC of the soil was measured at a commercial laboratory (ALS Norway) using an accredited method on a single sample. The TOC of PFAS contaminated soils can vary considerably and a comparison with literature TOC values can be found in the supporting information (SI). PFAS soils were sampled at a former firefighter training facility at Rygge airport (59.3732 N, 10.7935 E) on the 1st of July 2017. Five subsamples were mixed from the upper organic horizon for the high TOC sample, while the low TOC sample was collected from the eluvial and illuvial mineral horizons below in the podzol. These soils were sent to a Norwegian waste handling facility which is where they were obtained from for this work. In addition, two metal and metalloid contaminated shooting range soils with different TOC contents, 5.2% and 10.2% (termed low and high TOC metal soils, respectively) were tested. As for the PFAS contaminated soils, the TOC of such soils can vary considerably and a comparison with the literature is given in the SI. Soil from the Tittelsnes military shooting range in Norway (59.7231 N, 5.5156 E) were sampled on the 1st of July 2017 in combination with site excavation and remediation. The soil was sent to the Norwegian waste handling facility and was obtained from the site for this work. Five subsamples were mixed from sandy masses from a backstop berm for the low TOC soil and five subsamples were taken from a peatland adjacent to the backstop berm for the high TOC soil. The soils were sampled using multiple grabs, mixed and stored in propylene bags 4 °C prior to use in the experiments. PFAS soils were dried at 60 °C and sieved to a

size <1 mm while shooting range soils were dried at room temperature, sieved to <2 mm and manually homogenized.

2.2. Sorbent materials

Biochar (BC) was produced from three representative samples of shredded timber waste that was also received by the Norwegian waste handling facility. The waste is a mixture of demolition timber, container leases and pallets from industry and furniture and construction wood from private persons. These materials are a mixture of hardboard, softboard and wood, with some remains of paint and polish and only traces of plastic. A full chemical screening for contaminants (PFAS and metals) revealed that the BC made from this waste timber did not contain any significant levels of the contaminants discussed in the main paper (PFOS, PFOA, PFHxS, PFHxA, Pb and Sb), see the SI (Table S1). However, in some case the concentrations of contaminants (PFBA, Mg, K, Cr) were higher in the BC and Fe-BC than in the soils to be amended. This is a confounding issue and makes data interpretation for these chemicals challenging as it is difficult to discern sorption to the amendment materials from desorption from them. The results for these chemicals must be considered with caution. The BC was produced via pyrolysis at 500–650 °C using the flame curtain kiln technology (Schmidt et al., 2014). This method of biochar production has been extensively tested and is a cost effective method that pyrolyzes biomass layer by layer (Cornelissen et al., 2016). The BC had a surface area (SA) of 133.6 $m^2\ g^{-1}$ (pores >1.5 nm determined N_2 sorptometry and BET theory) and a micropore SA of 525.9 $m^2\ g^{-1}$ (pores 0.4–1.5 nm determined using CO_2 sorptometry and DFT theory). Elemental analysis was carried out using an Energy Dispersive X-Ray Analysis (EDX) INCA Energy 350 and showed 89.18%, 10.54% and 0.28% of C, O and other elements (mainly Na, Mg, Ca, K). Concentrations of these other elements can be found in Table S1 in the SI. BC was dried overnight (100 °C), ground and sieved (<2 mm) and stored at room temperature in the dark before use.

Activated biochar (aBC), obtained from Jacobi Carbons (Kalmar, Sweden) was manufactured from coconut shell waste. The activation process resulted in a SA of 978.4 $m^2\ g^{-1}$ (pores 0.4–1.5 nm determined using CO_2 sorptometry and DFT theory) and aBC was used as the received powder (average particle size 20 μm, 85% smaller than 45 μm). Elemental analysis showed 94.2%, 5.4% and 0.5% C, O and other elements (mainly Na, Al, Si, Ca, K), respectively and additional information about this sorbent can be found in a previous publication (Amstaetter et al., 2012a). aBC was amended to PFAS contaminated soil, as activation most often results in an increase in SA and a decrease in surface functional groups and sorption of PFAS to biochar is driven by SA (Zareitalabad et al., 2013).

For the remediation of the metal contaminated shooting range soil, both BC (described above) and an iron enriched biochar (Fe-BC) were tested. Fe-BC was produced using the flame curtain kiln method (at a temperature of approximately 600 °C), from the globally ubiquitous shrub *Eupatorium adenophorum* that is invasive in many countries. Details related to the method used can be found elsewhere (Cornelissen et al., 2016; Pandit et al., 2018). The biochar was enriched with Fe by adding powdered iron oxide-hydroxide (FeOOH) (around 2 kg of FeOOH to 20 kg biomass) between the layers of fresh feedstock prior to the pyrolysis of each layer (Okkenhaug et al., 2013). The resulting material had a CO_2 SA (pores between 0.4 and 1.5 nm) of 287.7 $m^2\ g^{-1}$ and a N_2 SA (pores >1.5 nm) of 59.8 $m^2\ g^{-1}$. The designer Fe-BC was tested for the shooting range soil as the addition of Fe is known to increase the sorption capacity of amendment materials added to metal contaminated soils (Okkenhaug et al., 2013). Carbon, oxygen and iron contents were 79%, 9.9% and 6.4%, respectively and the remaining 4.7% was mostly Mg, Al, Si, P, S, K, Ca and Cl. SEM analyses and other characterisation information can be found in the SI (Fig. S1a–c). Fe-BC was dried overnight (100 °C), ground and sieved (<2 mm) and stored at room temperature in the dark before use.

2.3. Sorption tests

2.3.1. PFAS soil

Leaching of PFAS from the soils (low and high TOC) both with and without sorbent amendment was carried out according to method EN 12457-2 as detailed by Hale et al. (Hale et al., 2017) and Kupryianchyk et al. (Kupryianchyk et al., 2016) with slight modifications. Briefly, 40 g dry weight (d.w.) of PFAS contaminated soils (with and without amendment) were weighed into 0.5 L polyethylene bottles and filled with 0.4 L Millipore water (L/S = 10). Soil amendment was carried out by adding 0%, 1%, 2%, 5%, 10% and 20% d.w. BC and aBC to both soils. The use of 1–5% (w/w) of sorbent material is considered reasonable for soil amendment based on logistics and cost (Kupryianchyk et al., 2016). This study investigated higher doses as a proof of principle and because the cost of biochar is very low making it a viable economic solution. The slurry (soil with or without biochar in water) was shaken (100 rpm on a horizontal shaking table at 25 °C) for 14 days and further information can be found in the SI. Based on a previous study (Kupryianchyk et al., 2016), 14 days has been shown to be sufficient to reach equilibrium and in cases where biochar is added, sorption is even faster. PFAS in soil were analysed following method DIN 38414-14 which is based on a methanol or acetonitrile ultrasonic extraction followed by a SPE clean up and quantified using liquid chromatography coupled with mass spectrometry (LC/MS-MS). PFAS in the leachate were analysed using method DIN 38407-42 based on the same set up but tailored to the water matrix. Further information can be found in the SI (Tables S2 and S3).

2.3.2. Shooting range soil

Metal and metalloid leaching from shooting range soils with and without biochar amendment was determined using a similar batch method as for PFAS contaminated soil. The batch tests were carried out as reported by Okkenhaug et al. (Okkenhaug et al., 2013) with slight modifications and additional information can be found in the SI. Briefly, 20 g of both high and low TOC soil (d.w.) was weighed into 0.25 L polyethylene bottles that were filled with 0.2 L Millipore water (L/S = 10). Isotherms were obtained by adding 0% (control), 5%, 10% and 20% of the BC and Fe-BC to the soils (d.w.). Biological activity was not controlled in the PFAS or metal batches based on the known persistence and resistance to biological degradation of the chemicals studied (Lindstrom et al., 2011; Giller et al., 1998).

2.3.3. Data processing

The reduction of contaminant leaching from the PFAS and shooting range soils was calculated as the ratio between the water concentration in the leachate at equilibrium (C_w) (ng L^{-1} for PFAS and μg L^{-1} for metals) and the water concentration in the control batch leachate at equilibrium (C_0) (ng L^{-1} for PFAS and μg L^{-1} for metals). The soil-water or biochar-water distribution ratios (K_D) (L kg^{-1}) were determined as described in the SI.

The Freundlich isotherm was used to model sorption onto biochars for both PFAS and metals (Kupryianchyk et al., 2016; Chen et al., 2011; Hale et al., 2011) and the Freundlich adsorption constant (K_F), expressed in (μg kg^{-1}) (μg L^{-1})$^{-n}$, was determined as describe in the SI. Sorption isotherms could only be constructed for PFAS due to the lack of a clear trend in the sorbed concentration as a function of amendment dose for the metals.

2.4. Sample analysis

2.4.1. PFAS soil

All the PFAS analyses were carried out following method DIN 38407-F42 with quantification using LC/MS-MS; details can be found in Hale et al. (2017) and in the SI (Tables S2 and S3). Dissolved organic carbon (DOC) and pH were determined in all leachate samples using TOC-5000 (Shimadzu, Japan) and inoLab pH Level 2 (WTW), respectively as

described previously (Okkenhaug et al., 2018). TOC analysis of soils and biochars was carried out by element analysis after combustion at 1050C in a Shimadzu element analyser using standard procedures (ISO-10694). The concentration of PFAS was determined in the leachate water following sorption tests and in both soils prior to starting the tests. Results for perfluorooctanoic sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorohexanoic sulfonate (PFHxS) and perfluorohexanoic acid (PFHxA) which are the sulfonate and carboxylic form with eight and six carbons, respectively are shown in the main paper while the other PFAS are shown in the SI.

2.4.2. Shooting range soil

The concentration of metals (Na, Mg, Al, K, Ca, Ti, V, Cr, Fe, Ni, Zn, Cu, Sb and Pb) in the leachate and in the shooting range soils was determined following a previous method (Okkenhaug et al., 2018). Accordingly, hydrofluoric acid was used to determine total concentration of Sb in soil samples, while nitric acid was used for other metals. Results for Pb and Sb are shown in the main paper as they are among the most commonly occurring metals in shooting range soils (Okkenhaug et al., 2018; Okkenhaug et al., 2016; Okkenhaug et al., 2013), and because they represent cationic (Pb^{2+}) and anionic (antimonite, $Sb(OH)_6^-$) metal/metalloid species. Results for all other metals can be found in the SI. Fluoride, chloride nitrate and sulfate were assessed in the leachate and in the soils using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 8900 QQQ ICP-MS).

2.5. Statistical analysis and data treatment

One-way ANOVA was carried out using GraphPad Prism 7 (©2017 GraphPad Software, Inc.) to determine whether there was a statically significant effect of biochar amendment and biochar dose. The chemical equilibrium model, Visual MINTEQ (ver. 3.0), was used to model the speciation of metals in the leachate and details can be found in Okkenhaug et al. (Okkenhaug et al., 2018) and in the SI. As described by Gustafsson (Gustafsson, 2012), the program allows the user to model the speciation of elements in soil and water. The database thermo.vdb provided with the software was used for the calculations. For modelling complexation with DOC, the NICA-Donnan model included in Visual MINTEQ was used with parameters for fulvic acid (Milne et al., 2003). Modelling was carried out for the control and, as an example, for the 5% BC and 5% Fe-BC amendments in order to assess metal speciation for both biochar types at the same dose and for both high and low TOC content soils. The modelling was carried out for just one dose since speciation was assumed not to be affected by dose. During the modelling the redox potential E_H was set at 400 mV.

3. Results and discussion

3.1. Soil physico-chemical properties and PFAS leaching from unamended soils

PFOS and PFHxS were the most abundant PFAS detected in the low and high TOC soils. The PFOS and PFOA concentrations in the soils were 3400 and 27 μg kg^{-1} respectively in the low TOC soil, and 1000 and 6.4 μg kg^{-1} respectively in the high TOC soil. Concentrations of PFHxS and PFHxA were 200 and 44 μg kg^{-1} and 110 and 8.2 μg kg^{-1} in the low and high TOC soils, respectively. The concentration of the other PFAS is listed in Table S1 and a comparison with literature studies is also given. PFOS and PFOA concentrations in the leachate water were approximately 230,000 and 2400 ng L^{-1} respectively in the low TOC soil and 12,300 and 200 ng L^{-1} respectively, in the high TOC soil, with somewhat lower concentrations of PFHxS and PFHxA. All PFAS leachate concentrations can be found in Table S4 in the SI. The concentrations of PFAS found in this study are similar to those of the only previous study that carried out batch leaching tests on industrially contaminated soil (Hale et al., 2017).

3.2. Soil-water distribution ratios (K_D) for unamended PFAS soils

Measured PFOS K_D values were 4.7 and 52.1 L kg^{-1} respectively for the low and high TOC soils, being in the same region as previously reported literature values between 0.1 and 120 L kg^{-1} for unamended sands, sediments, clay and sludge (Zareitalabad et al., 2013). K_D values were highest for the high TOC soil, in agreement with a previous study, and indicating that organic carbon is a soil (or sediment) physico-chemical parameter that affects sorption of PFAS (Higgins and Luthy, 2006). Zareitalabad et al. (Zareitalabad et al., 2013) reported a correlation between PFAS sorption and organic carbon content, clay content, oxide content and specific surface area for several different soils and sediments. All K_D values can be found in Table S5 in the SI and further discussion can be found in SI. In addition, K_{OC} values were calculated for PFOS and PFOA and a comparison with literature values can be found in Table S6 in the SI. K_{OC} values determined here are slightly different from literature values likely related to the difference between the soils and experimental set ups used and further information related to this can be found in the SI.

3.3. Remediation efficacy for PFAS contaminated soils

Fig. 1a–d shows the pH in the leachate water and the ratio between the water concentration of PFOS, PFHxS, PFOA and PFHxA in the leachate at equilibrium and the water concentration in the control batch leachate at equilibrium (i.e. $C_w\ C_0^{-1}$) after BC and aBC amendment for both soils. Amending 20% BC to the low TOC soil led to reductions in leachate concentrations of 86%, 72%, 70% and 31% for PFOS, PFHxS, PFOA and PFHxA, respectively (Fig. 1a). A statistically significant effect of BC amendment compared to the control without BC, and a statistically significant effect of BC dose was observed ($p < 0.05$). For the same soil, the amendment of the activated aBC reduced the PFOS, PFHxS, PFOA, PFHxA leachate concentrations to a greater extent for all doses when compared to the BC. Following the amendment of 1% aBC, a reduction of >99.7% for PFOS, PFHxS, PFOA and PFHxA was seen (Fig. 1b). The 20% amendment of aBC led to an almost complete removal of PFOS, PFHxS, PFOA and PFHxA from the leachate water (>99.9%). Statistically significant differences were seen following the amendment of aBC and for the different aBC doses ($p < 0.05$). The DOC content in the corresponding leachates is shown in Fig. S2a–d. The concentration of all the other PFAS is reported in Fig. S3–6 in the SI. In contrast to the low TOC soil, for the high TOC soil, the amendment of BC (Fig. 1c) did not lead to any significant ($p < 0.05$) reduction of PFOS, PFHxS, PFOA or PFHxA leachate concentrations at any amendment dose. However, for the aBC, there were significant reductions compared to the control, and significant differences between the amendment doses ($p < 0.05$). The amendment of 1% aBC resulted in a reduction of between 89 and 96% for PFOS, PFHxS, PFOA and PFHxA (Fig. 1d). Increasing the amendment dose to 2% resulted in reductions of ≥99% for PFOS, PFHxS and PFOA. The relationship between PFAS sorption and chain length for BC and aBC was investigated, however a correlation was not observed as can be seen in the SI. The results show that both materials perform well when considering the remediation of PFAS contaminated soils. While it is clear that the aBC performs better than the unactivated biochar, and that this is most likely due to the activation process, a direct comparison between the materials should be made with caution as (i) the biochars do not have the same particle size distribution and (ii) they are not make from the same feedstock and any data on the effectiveness of the designed biochars prior to processing is available. Particle size can affect sorption as a greater degree of smaller pores (often accompanying smaller particles) provide increased surface area for sorption. However such pores are also prone to clogging with other soil constituents and thus sorption is reduced (Amstaetter et al., 2012b).

The efficacy of BC and aBC can also be affected by soil TOC as has previously been reported for AC (Kupryianchyk et al., 2016; Werner et al., 2005). Guo et al. (Guo et al., 2019) have shown organic carbon is the

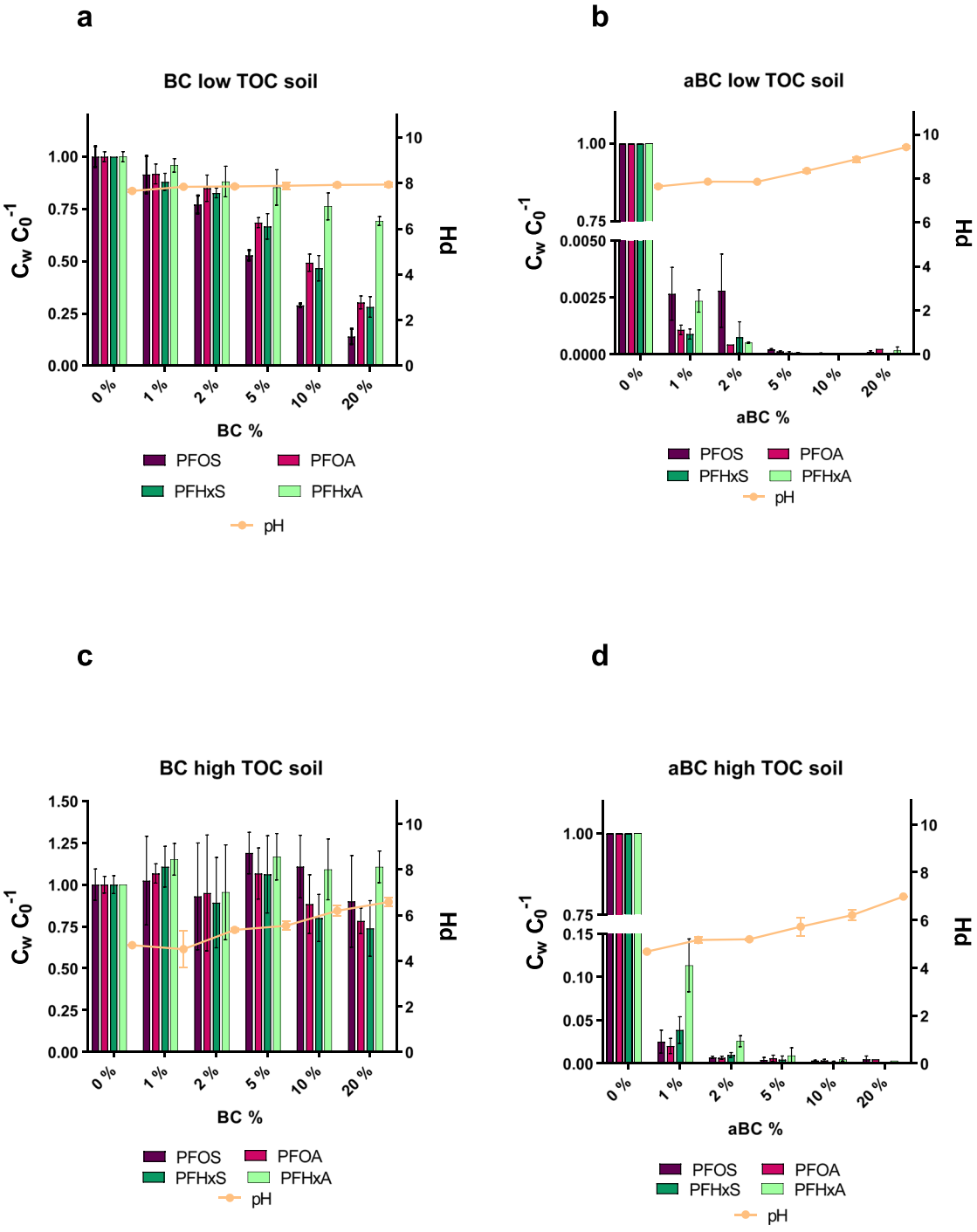

Fig. 1. a–d. Trend of $C_w C_0^{-1}$ (i.e., the relative concentration in the presence of the sorbent) for PFOS, PFOA, PFHxS and PFHxA along with pH after a) BC low TOC soil, b) aBC amendment low TOC soil, c) BC high TOC soil and d) aBC amendment in the high TOC soil. Where C_w is the PFAS concentration in the leachate at equilibrium after the amendment and C_0 is the PFAS concentration in the leachate before amendment. [Standard deviations are calculated based on 3 replicates].

key parameter affecting the sorption of PFOS to sediment. The low TOC soil inherently contains less material with a sorption capacity for PFAS and adding the sorbents to this soil introduces a greater relative amount of strong sorption sites and thus leads to a larger increase in sorption in the soil-sorbent system (Kupryianchyk et al., 2016; Werner et al., 2005). In addition to this, the higher effectiveness of sorbent amendment observed in the low TOC soil is likely due to a lack of competition for PFAS sorption sites between the soil TOC itself and the BC or aBC, and a lower degree of sorbent pore blockage by natural organic matter released from the low TOC soil. The DOC concentration in the low TOC soil was 11.4 mg L^{-1}, and for the high TOC soil was 146 mg L^{-1}, supporting this hypothesis and agreeing with previous studies for other hydrophobic organic compounds (Pignatello et al., 2006; Cornelissen and Gustafsson, 2006; Koelmans et al., 2009; Brändli et al., 2009).

The positive effect of biochar amendment is in line with results from a previous study (Kupryianchyk et al., 2016) in which PFAS contaminated soils with TOC contents between 0.2 and 34% were amended with 4% of two biochars (mixed wood and paper mill waste) and a fine powdered coal based AC. Amendment efficacy was dependent on the type of biochar and soil. For PFOS, PFHxS, PFOA and PFHxA, reductions in leaching ranged between 25 and 60%, 5 and 30%, 15 and 40%

and 10 and 55%, respectively. Following the amendment of AC, an almost complete removal of PFAS from leachate was observed. Similarly, Hale et al. (Hale et al., 2017), reported a decrease of between 94% and 99% PFOS from the leachate of aqueous film forming foam (AFFF) contaminated soils (TOC between 0.17 and 1.2%) following the amendment of coal based AC. To the best of our knowledge, the present study is the first to demonstrate that the performance of a biomass based and sustainable biochar is comparable to that of coal based non-sustainable AC for the remediation of PFAS contaminated soils.

The amendment of BC to the high TOC soil, and of aBC to both soils, led to a slight increase in the pH of the leachate (Fig. 1a–d, respectively from 4.7 to 6.9) similar to earlier studies of soils with different organic contaminants (Hale et al., 2017; Brändli et al., 2009). A correlation between pH and PFAS removal was not observed (Fig. S7); nor was a correlation between DOC content in the leachate and PFAS removal (Fig. S7) confirming the findings of Hale et al.[17] (DOC of 0.68–5.83 mg L^{-1} compared to 13–117 mg L^{-1} range in this study).

3.4. PFAS sorption isotherms

PFOS and PFOA isotherm parameters Log K_F [(μg kg^{-1}) (μg L^{-1})$^{-n}$] and n values are given in Table 1, while values for all other PFAS are provided in the SI. For PFOS, the log K_F values for BC and aBC were 3.38 and 5.49 respectively in the low TOC soil respectively and were 3 to 5 orders of magnitude larger than the log K_D of the unamended soil which was 0.67. In the high TOC soil, the log K_F for the aBC was 5.00, 2000 times higher than the K_D of the soil (52 L kg^{-1}), but also 0.49 log units lower than the log K_F for the aBC in the low TOC soil. These results support the fact that DOC released by the high TOC soil may have attenuated the sorption strength of the aBC. Trends were similar for PFOA, with log K_F values for BC and aBC being factors 100 and 200,000, respectively, higher than K_D for the low TOC soil. In the high TOC soil with aBC amendment, the log K_F for PFOA was 4.74, a factor of 20,000 higher than the K_D of the soil (3 L kg^{-1}). Thus, the sorption strength of the aBC exceeded that of the BC by a factor of around 150 for PFOS and a factor of 2000 for PFOA (low TOC soil). This can in part be explained by the higher SA of the aBC (978.4 m^2 g^{-1}) than of the BC (525.9 m^2 g^{-1}) and the smaller particle size of the aBC (powder) than the BC (<2 mm) which also likely increases the effectiveness of the sorption processes.

For all isotherms, the n values ranged between 0.54 and 0.93, indicating non-linear sorption with K_D decreasing with PFAS concentration. Highly variable n values between 0.18 and 0.90 have previously been reported for other sorbents (Kupryianchyk et al., 2016; Ochoa-Herrera and Sierra-Alvarez, 2008; Yu et al., 2009; Hansen et al., 2010). The Freundlich isotherm fitted the data well and r^2 ranged between 0.73 and 0.98 for both PFOS and PFOA, confirming the suitability of this model (Kupryianchyk et al., 2016; Yu et al., 2009; Hansen et al., 2010). In a concentration range similar to the findings in this study (although for experiments without soil), Hansen et al. (Hansen et al., 2010), reported log K_F [(μg kg^{-1}) (μg L^{-1})$^{-n}$] values for granular AC of 5.86 and 4.45 respectively for PFOS and PFOA amended to a PFAS contaminated well water (Table 1). Kupryianchyk et al. (Kupryianchyk et al., 2016) reported log K_F [(μg kg^{-1}) (μg L^{-1})$^{-n}$] values of 4.61, 4.41 and >5.6 for sorption to mixed wood biochar, paper mill waste biochar and AC respectively for PFOS and 3.02, 3.01 and >5.6 for PFOA (Table 1).

3.5. Soil physico-chemical properties and metal leaching from unamended soils

Concentrations of Pb and Sb dominated the metal contamination profile and were 4300 and 100 mg kg^{-1} respectively for the low TOC soil and 6600 and 210 mg kg^{-1} respectively for the high TOC soil. Concentrations of other metals (in Table S1 in the SI) and a comparison with literature values can be found in the SI. Pb and Sb concentrations in the leachate from the water extractions were approximately 307 and 180 μg L^{-1} respectively in the low TOC soil and 243 and 303 μg L^{-1} respectively in the high TOC soil. These values exceed the leaching benchmarks that must be fulfilled if waste is to be disposed of as "ordinary" at Norwegian landfills (150 μg L^{-1} for Pb and 100 μg L^{-1} for Sb) (European Union Counci, 1999). Concentration of all other metals in the leachate water can be found in Table S4 in the SI. The percentage of metals leached from the soils ranged from 0 to 9% for both soils. Previous studies (Okkenhaug et al., 2018; Okkenhaug et al., 2016; Okkenhaug et al., 2013) have reported highly variable leachate concentrations, most likely due to variable soil physicochemical properties that influence Pb and Sb sorption. Further discussion and comparison with literature values can be found in the SI.

3.6. Soil-water distribution ratios (K_D) for unamended shooting range soils

K_D for Pb and Sb were 17,661 and 316 L kg^{-1} for the low TOC shooting range soil, and 21,748 and 1156 L kg^{-1} for the high TOC soil. Okkenhaug et al. (Okkenhaug et al., 2018) also observed less strong sorption of Sb than Pb and ascribed this to the different sorption mechanisms for the metals. Pb is most often sorbed to soil organic matter (SOM), clay minerals and oxides/hydroxides (Clausen et al., 2011; Filella et al., 2002), whereas Sb most often occurs as negatively charged $Sb(OH)_6^-$ and shows limited sorption to SOM and clay minerals at neutral pH[50] (pH low TOC soil = 8.2, pH soil high TOC = 7.6). The absolute K_D values determined in this study were lower (factor of 2–5) than those reported by Okkenhaug et al. (Okkenhaug et al., 2018) This may be due to the different soils that were used as Okkenhaug et al. (Okkenhaug et al., 2018) used a peat soil with a TOC of 45–50%, which may have affected the mobility of Pb and Sb.

Table 1
log K_F [(μg kg^{-1}) (μg L^{-1})$^{-n}$] for PFOS and PFOA sorption onto the biochar materials used in this study as well as a comparison with values reported in the literature. All values are measured in the presence of soil (see text).

Carbonaceous geosorbents	Reference	PFOS			PFOA		
		log K_F (μg kg^{-1}) (μg L^{-1})$^{-n}$	n	r^2	log K_F (μg kg^{-1}) (μg L^{-1})$^{-n}$	n	r^2
BC in low TOC soil	This study	3.38	0.54	0.85	2.08	0.56	0.86
aBC in low TOC soil	This study	5.49	0.59	0.82	5.42	0.78	0.98
aBC in high TOC soil	This study	5.00	0.88	0.77	4.74	0.93	0.73
GAC	Hansen et al. 2010	5.86[a]	0.50	0.99	4.45[a]	0.29	0.93
Mixed wood biochar	Kupryianchyk et al. 2016	4.61	0.87	–	3.02	0.90	–
Paper mill water biochar	Kupryianchyk et al. 2016	4.41	0.64	–	3.01	0.73	–
AC	Kupryianchyk et al. 2016	>5.60[b]	–	–	>5.60[b]	–	–

This study: biochar (BC) in low TOC soil; and activated biochar (aBC) in low and high TOC soil. BC in the high TOC soil is not given as there was no additional sorption.
Literature: AC = (coal based)-activated carbon, PAC = powder activated carbon, GAC = granular activated carbon, MW = mixed wood biochar, PMW = paper mill waste biochar.
[a] Values extrapolated.
[b] Complete removal of PFOS and PFOA in the water phase.

3.7. Remediation efficiency for shooting range soils

BC significantly reduced the concentration of Pb and Sb in leachate compared to the unamended control (Fig. 2a–d; $p < 0.05$), but there was no significant difference ($p < 0.05$) between amendment doses. Amending 20% BC to the low TOC soil led to reductions of 61 and 12% for Pb and Sb concentrations. By contrast, amending 20% of the iron enriched designer biochar, Fe-BC, had a much stronger effect on leaching, with reductions of 98% for Pb (significant difference between doses, $p < 0.05$) and 47% for Sb (without a dose effect). Fig. 2a–d shows the ratio between C and C_0^{-1} for Pb and Sb following BC and Fe-BC amendment to the low and high TOC soils, along with the pH. The DOC content in the corresponding batches is shown in Fig. S8a–d. The concentration ratio of all the other metals in the leachate water is reported in Fig. S9–12. Fig. 2a–d shows that both BC and Fe-BC effectively decrease Pb and Sb concentrations in the soil leachate; their performances being dependant on the metal/metalloid and the soil type. In the high TOC soil, the amendment of 20% BC resulted in the removal of 40% and 90% Pb and Sb, respectively (no significant effect of the doses; $p < 0.05$). In contrast (and as for the low TOC soil), the amendment of 20% Fe-BC led to an improved effect for Pb (reduction of 75%), but a lower effect for Sb (60% reduction). There was a significant effect of Fe-BC amendment dose for Pb ($p < 0.05$), but not for Sb ($p < 0.05$).

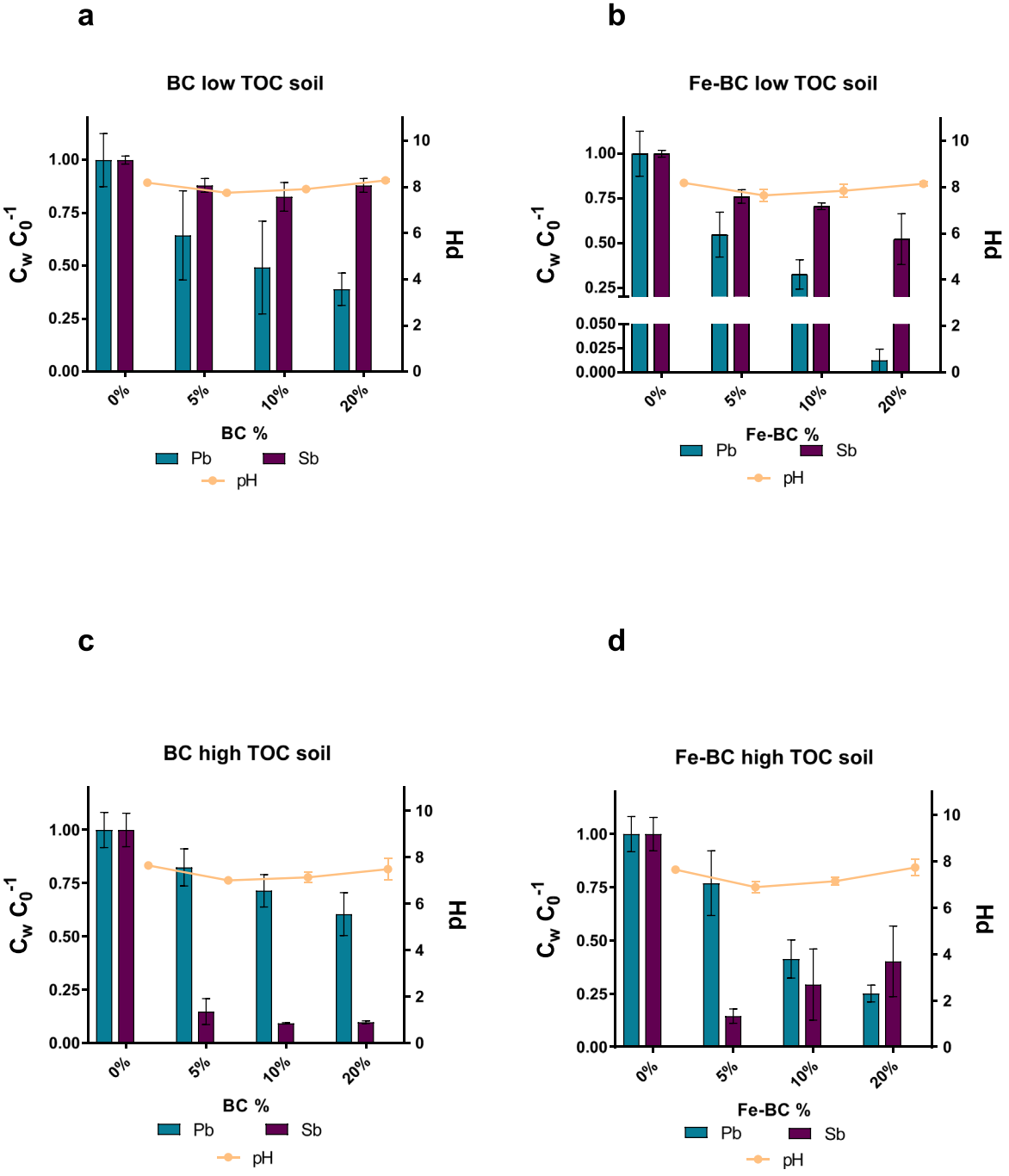

Fig. 2. a–d. Trend of $C_w C_0^{-1}$ for Pb and Sb along with pH after a) BC and low TOC soil, b) Fe-BC and low TOC soil, c) BC and TOC soil and d) Fe-BC and high TOC soil. Where C_w is the metal/metalloid concentration in the leachate at equilibrium after the amendment and C_0 is the metal/metalloid concentration in the leachate before amendment. [Standard deviations calculated on 3 replicates].

Previous studies (Shen et al., 2019; Van Poucke et al., 2019) have shown that pH is an important parameter in the sorption of Pb onto biochar where precipitation has been speculated to be the key mechanism operating (Shen et al., 2019). As shown in Fig. 2a–d, an increase in biochar dose did not result in an increase in pH and this may be the reason why Pb sorption is not affected by dose. The positive effect of the Fe-BC for both low and high TOC soils is in accordance with previous work (Trakal et al., 2016). Trakal et al. (Trakal et al., 2016) reported that Fe oxides contained on the biochar surface increase the sorption of Pb where the best effects were seen for the iron enriched biochar with a well-defined structure. The use of Fe-BC had a positive effect on the sorption of Sb in the low TOC soil. As will be discussed below, (Section 3.7.1) Fe based biochars can effectively sorb metals/metalloids such as Sb (which is in turn related to speciation (Okkenhaug et al., 2016; Okkenhaug et al., 2013)) owing to the direct interactions with the amorphous iron oxides (Mariussen et al., 2012; Okkenhaug et al., 2013) on the biochar surface (Vithanage et al., 2015).

3.7.1. Shooting range soil: metal/metalloid speciation

Sorption isotherms were constructed for PFAS based on the clear relationship between leachate concentrations and biochar amendment dose. However for metals, results were mixed. In some cases there was very little effect of the different amendment doses, and in some cases concentrations were higher following amendment. Owing to these uncertainties, isotherms were not constructed for the metals.

Geochemical modelling was carried out in order to assess the metals' speciation in the leachate water with and without biochar amendment. Modelling of the control and amended low and high TOC soil (5% BC and 5% Fe-BC) showed that Pb was primarily associated to fulvic acid (97–100%). According to the simulation, Sb exclusively occurred as Sb $(OH)_6^-$ (99.999%) which suggests a low association of Sb with organic materials, as previously reported (Okkenhaug et al., 2018). A previous laboratory study by Tella and Pokrovski (Tella and Pokrovski, 2012) showed that the complexation of $Sb(OH)_6^-$ with DOM at neutral to basic pH (as used in these simulations) was low (<5%). The modelling showed no difference in speciation or association between amended and unamended systems. This suggests that the reduction in metal concentration is caused by stronger sorption to the solid phase, and not by changes in speciation in the liquid phase or by precipitation. Sorption of metals/metalloids to solid biochar mainly takes place on surface functional groups, especially oxygen containing functional groups, including iron oxides (Mariussen et al., 2012; Okkenhaug et al., 2013; Belzile et al., 2001). Sorption is most likely caused by electrostatic attractions and less by precipitation, since the latter mechanism would probably have led to changes in speciation in the liquid phase (Ahmad et al., 2012). These findings are in line with Okkenhaug et al. (Okkenhaug et al., 2016), who reported that dissolved Pb in porewater mainly occurred as Pb bound to DOC and Sb mainly occurred as $Sb(OH)_6^-$ (99.99%) (Okkenhaug et al., 2016; Okkenhaug et al., 2013).

The ability of the iron based materials to sorb metals/metalloids (both cations and oxyanions such as As and Sb) has previously been reported to occur mainly on amorphous iron oxides (Mariussen et al., 2012; Okkenhaug et al., 2013; Belzile et al., 2001) due to their ability to form surface complexes with both cationic and anionic substances with hydroxyl groups (Mariussen et al., 2012). Mariussen and coworkers (Mariussen et al., 2015) reported better sorption performance of charcoal when combined with iron hydroxide, with an increased selectivity for Pb and Sb.

Previous studies have suggested that pH is one of the most important factors affecting the mobility and adsorption of metals in water and porewater (Mariussen et al., 2012; Okkenhaug et al., 2013; Mariussen et al., 2018). For example, an increase in pH led to an increase in Sb soil mobility due to a reduction in the anion exchange capacity of the soil (Okkenhaug et al., 2013). However, the pH was stable in these tests, as also observed by Mariussen et al. (Mariussen et al., 2012), implying that pH did not affect sorption (Fig. S13a in SI). The DOC was also found to be stable during the tests (Fig. S13b) implying that sorption was independent of DOC concentration.

3.8. Implications and recommendations

The results from this study support the use of biochar as a sustainable and climate-friendly sorbent amendment material for PFAS and metal contaminated soils. Both types of soil have a high societal relevance especially as monitoring programmes and regulation for PFAS become more stringent, and alternative remediation strategies are needed. Producing biochar from waste timber provides an opportunity to add value to organic waste and turn it in to a resource. By amending metal and PFAS contaminated soil with the newly created resources, the subsequent reduction in leaching provides a further environmental benefit. Following sorbent amendment it may be possible to leave the soil in place if clean up targets are reached. In cases where they are not reached and the soils must be disposed of at a landfill, stabilizing pollutants with biochar will likely reduce the cost of disposal. If the amendment of, for example 10% biochar, can reduce leaching to a level that complies with a lower grade waste (ordinary rather than hazardous), landfill costs will be reduced. The climate change mitigation effect of biochar comes as an important co-benefit (Sparrevik et al., 2011), provided that the biochar is made in a clean manner with low emissions of greenhouse gases and aerosols (Smebye et al., 2017).

In order to maximize remediation effectiveness, the type of biochar used, as well as the soil properties must be taken into consideration. Designer biochars should be developed in order to meet the remediation goals for the particular soil in question. For metal and metalloid soil remediation, iron enrichment can be optimized for various shooting range soils, and for PFAS contaminated soils the level of activation should be controlled in order to produce a material that can optimally sorb the contaminant concentration in the presence of native TOC. It must be kept in mind that activation brings along an environmental "cost" in the form of lower biochar yield, and lower energy generation of the process (Hagemann et al., 2018). It also increases the cost of the biochar and this cost should be weighed against the benefits of stronger sorbent effectiveness.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.133693.

References

Ahmad, M., Lee, S.S., Yang, J.E., Ro, H.M., Lee, Y.H., Ok, Y.S., 2012. Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil. Ecotoxicol. Environ. Saf. 79, 225–231.

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99, 19–33.

Amstaetter, K., Eek, E., Cornelissen, G., 2012a. Sorption of PAHs and PCBs to activated carbon: coal versus biomass-based quality. Chemosphere 87 (5), 573–578.

Amstaetter, K., Eek, E., Cornelissen, G., 2012b. Sorption of PAHs and PCBs to activated carbon: coal versus biomass-based quality. Chemosphere 87 (5), 573–578.

Armitage, J.M., MacLeod, M., Cousins, I.T., 2009. Comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources. Environ. Sci. Technol. 43 (15), 5830–5836.

Belzile, N., Chen, Y.W., Wang, Z., 2001. Oxidation of antimony (III) by amorphous iron and manganese oxyhydroxides. Chem. Geol. 174 (4), 379–387.

Brändli, R.C., Breedveld, G.D., Cornelissen, G., 2009. Tributyltin sorption to marine sedimentary black carbon and to amended activated carbon. Environ. Toxicol. Chem. 28 (3), 503–508.
Carlsson, P., Christensen, J.H., Borgå, K., Kallenborn, R., Pfaffhuber, K.A., Odland, J.Ø., ... Pawlak, J.F., 2017. Influence of climate change on transport, levels, and effects of contaminants in northern areas. Arctic Monitoring and Assessment Programme.
Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B., Hay, A.G., 2011. Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. Bioresour. Technol. 102 (19), 8877–8884.
Clausen, J.L., Bostick, B., Korte, N., 2011. Migration of lead in surface water, pore water, and groundwater with a focus on firing ranges. Crit. Rev. Environ. Sci. Technol. 41 (15), 1397–1448.
Cornelissen, G., Gustafsson, Ö., 2006. Effects of added PAHs and precipitated humic acid coatings on phenanthrene sorption to environmental black carbon. Environ. Pollut. 141 (3), 526–531.
Cornelissen, G., Pandit, N.R., Taylor, P., Pandit, B.H., Sparrevik, M., Schmidt, H.P., 2016. Emissions and char quality of flame-curtain" Kon Tiki" kilns for farmer-scale charcoal/biochar production. PLoS One 11 (5), e0154617.
European Union Council directive/31/EC of 26 April 1999 on the landfill of waste Off. J. Eur. Communities (1999) (or Council of the European Union, Council directive 1999/31/EC of 26 April 1999 on the landfill of waste. In Official Journal of the European Communities, 16/7/1999; L182/1−19.
Filella, M., Belzile, N., Chen, Y.W., 2002. Antimony in the environment: a review focused on natural waters: II. Relevant solution chemistry. Earth Sci. Rev. 59 (1–4), 265–285.
Ghosh, U., Luthy, R.G., Cornelissen, G., Werner, D., Menzie, C.A., 2011. In-Situ Sorbent Amendments: A New Direction in Contaminated Sediment Management.
Giller, K.E., Witter, E., Mcgrath, S.P., 1998. Toxicity of heavy metals to microorganisms and microbial processes in agricultural soils: a review. Soil Biol. Biochem. 30 (10−11), 1389–1414.
Guo, W., Lu, S., Shi, J., Zhao, X., 2019. Effect of corn straw biochar application to sediments on the adsorption of 17α-ethinyl estradiol and perfluorooctane sulfonate at sediment-water interface. Ecotoxicol. Environ. Saf. 174, 363–369.
Gustafsson, J.P., 2012. Visual Minteq ver. 3.0; KTH.
Hagemann, N., Spokas, K., Schmidt, H.P., Kägi, R., Böhler, M., Bucheli, T., 2018. Activated carbon, biochar and charcoal: linkages and synergies across pyrogenic carbon's ABCs. Water 10 (2), 182.
Haines, A., Amann, M., Borgford-Parnell, N., Leonard, S., Kuylenstierna, J., Shindell, D., 2017. Short-lived climate pollutant mitigation and the sustainable development goals. Nat. Clim. Chang. 7 (12), 863.
Hale, S., Hanley, K., Lehmann, J., Zimmerman, A., Cornelissen, G., 2011. Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. Environ. Sci. Technol. 45 (24), 10445–10453.
Hale, S.E., Arp, H.P.H., Slinde, G.A., Wade, E.J., Bjørseth, K., Breedveld, G.D., Høisæter, Å., 2017. Sorbent amendment as a remediation strategy to reduce PFAS mobility and leaching in a contaminated sandy soil from a Norwegian firefighting training facility. Chemosphere 171, 9–18.
Hansen, M.C., Børresen, M.H., Schlabach, M., Cornelissen, G., 2010. Sorption of perfluorinated compounds from contaminated water to activated carbon. J. Soils Sediments 10 (2), 179–185.
Heier, L.S., Lien, I.B., Strømseng, A.E., Ljønes, M., Rosseland, B.O., Tollefsen, K.E., Salbu, B., 2009. Speciation of lead, copper, zinc and antimony in water draining a shooting range—time dependant metal accumulation and biomarker responses in brown trout (Salmo trutta L.). Sci. Total Environ. 407 (13), 4047–4055.
Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. 40 (23), 7251–7256.
Hockmann, K., Tandy, S., Studer, B., Evangelou, M.W., Schulin, R., 2018. Plant uptake and availability of antimony, lead, copper and zinc in oxic and reduced shooting range soil. Environ. Pollut. 238, 255–262.
http://ec.europa.eu/environment/water/water-framework/index_en.html (11/02/2019).
http://www.miljodirektoratet.no/no/Publikasjoner/2016/September-2016/Tiltaksplan-for-arbeidet-med-per–og-polyfluorerte-stoffer-i-perioden-2016-2018/ (18/01/19).
Jeffery, S., Abalos, D., Prodana, M., Bastos, A.C., Van Groenigen, J.W., Hungate, B.A., Verheijen, F., 2017. Biochar boosts tropical but not temperate crop yields. Environ. Res. Lett. 12 (5), 053001.
Koelmans, A.A., Meulman, B., Meijer, T., Jonker, M.T., 2009. Attenuation of polychlorinated biphenyl sorption to charcoal by humic acids. Environ. Sci. Technol. 43 (3), 736–742.
Kupryianchyk, D., Hale, S.E., Breedveld, G.D., Cornelissen, G., 2016. Treatment of sites contaminated with perfluorinated compounds using biochar amendment. Chemosphere 142, 35–40.
Lindstrom, A.B., Strynar, M.J., Libelo, E.L., 2011. Polyfluorinated Compounds: Past, Present, and Future.
Lorenz, K., Lal, R., 2014. Biochar application to soil for climate change mitigation by soil organic carbon sequestration. J. Plant Nutr. Soil Sci. 177 (5), 651–670.
Mariussen, E., Ljønes, M., Strømseng, A.E., 2012. Use of sorbents for purification of lead, copper and antimony in runoff water from small arms shooting ranges. J. Hazard. Mater. 243, 95–104.
Mariussen, E., Johnsen, I.V., Strømseng, A.E., 2015. Selective adsorption of lead, copper and antimony in runoff water from a small arms shooting range with a combination of charcoal and iron hydroxide. J. Environ. Manag. 150, 281–287.
Mariussen, E., Johnsen, I.V., Strømseng, A.E., 2018. Application of sorbents in different soil types from small arms shooting ranges for immobilization of lead (Pb), copper (cu), zinc (Zn), and antimony (Sb). J. Soils Sediments 18 (4), 1558–1568.
Milne, C.J., Kinniburgh, D.G., Van Riemsdijk, W.H., Tipping, E., 2003. Generic NICA—Donnan model parameters for metal-ion binding by humic substances. Environ. Sci. Technol. 37 (5), 958–971.
Ochoa-Herrera, V., Sierra-Alvarez, R., 2008. Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. Chemosphere 72 (10), 1588–1593.
Okkenhaug, G., Amstätter, K., Lassen Bue, H., Cornelissen, G., Breedveld, G.D., Henriksen, T., Mulder, J., 2013. Antimony (Sb) contaminated shooting range soil: Sb mobility and immobilization by soil amendments. Environ. Sci. Technol. 47 (12), 6431–6439.
Okkenhaug, G., Gebhardt, K.A.G., Amstaetter, K., Bue, H.L., Herzel, H., Mariussen, E., ... Mulder, J., 2016. Antimony (Sb) and lead (Pb) in contaminated shooting range soils: Sb and Pb mobility and immobilization by iron based sorbents, a field study. J. Hazard. Mater. 307, 336–343.
Okkenhaug, G., Smebye, A.B., Pabst, T., Amundsen, C.E., Sævarsson, H., Breedveld, G.D., 2018. Shooting range contamination: mobility and transport of lead (Pb), copper (Cu) and antimony (Sb) in contaminated peatland. J. Soils Sediments 18 (11), 3310–3323.
Pandit, N.R., Mulder, J., Hale, S.E., Martinsen, V., Schmidt, H.P., Cornelissen, G., 2018. Biochar improves maize growth by alleviation of nutrient stress in a moderately acidic low-input Nepalese soil. Sci. Total Environ. 625, 1380–1389.
Pignatello, J.J., Kwon, S., Lu, Y., 2006. Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): attenuation of surface activity by humic and fulvic acids. Environ. Sci. Technol. 40 (24), 7757–7763.
Schmidt, H.P., Taylor, P., Eglise, A., Arbaz, C., 2014. Kon-Tiki flame curtain pyrolysis for the democratization of biochar production. Biochar J. 1, 14–24.
Shen, Z., Hou, D., Jin, F., Shi, J., Fan, X., Tsang, D.C., Alessi, D.S., 2019. Effect of production temperature on lead removal mechanisms by rice straw biochars. Sci. Total Environ. 655, 751–758.
Silvani, L., Vrchotova, B., Kastanek, P., Demnerova, K., Pettiti, I., Papini, M.P., 2017. Characterizing biochar as alternative sorbent for oil spill remediation. Sci. Rep. 7, 43912.
Skaar, J.S., Ræder, E.M., Lyche, J.L., Ahrens, L., Kallenborn, R., 2018. Elucidation of contamination sources for poly-and perfluoroalkyl substances (PFASs) on Svalbard (Norwegian Arctic). Environ. Sci. Pollut. Res. 1–8.
Smebye, A.B., Sparrevik, M., Schmidt, H.P., Cornelissen, G., 2017. Life-cycle assessment of biochar production systems in tropical rural areas: comparing flame curtain kilns to other production methods. Biomass Bioenergy 101, 35–43.
Sparrevik, M., Saloranta, T., Cornelissen, G., Eek, E., Fet, A.M., Breedveld, G.D., Linkov, I., 2011. Use of Life Cycle Assessments to Evaluate the Environmental Footprint of Contaminated Sediment Remediation.
Stahel, W.R., 2016. The circular economy. Nat. News 531 (7595), 435.
Strømseng, A.E., Ljønes, M., Bakka, L., Mariussen, E., 2009. Episodic discharge of lead, copper and antimony from a Norwegian small arm shooting range. J. Environ. Monit. 11 (6), 1259–1267.
Tella, M., Pokrovski, G.S., 2012. Stability and structure of pentavalent antimony complexes with aqueous organic ligands. Chem. Geol. 292, 57–68.
Tittlemier, S.A., Pepper, K., Seymour, C., Moisey, J., Bronson, R., Cao, X.L., Dabeka, R.W., 2007. Dietary exposure of Canadians to perfluorinated carboxylates and perfluorooctane sulfonate via consumption of meat, fish, fast foods, and food items prepared in their packaging. J. Agric. Food Chem. 55 (8), 3203–3210.
Trakal, L., Veselská, V., Šafařík, I., Vítková, M., Číhalová, S., Komárek, M., 2016. Lead and cadmium sorption mechanisms on magnetically modified biochars. Bioresour. Technol. 203, 318–324.
Van Poucke, R., Allaert, S., Ok, Y.S., Pala, M., Ronsse, F., Tack, F.M.G., Meers, E., 2019. Metal sorption by biochars: a trade-off between phosphate and carbonate concentration as governed by pyrolysis conditions. J. Environ. Manag. 246, 496–504.
Vithanage, M., Rajapaksha, A.U., Ahmad, M., Uchimiya, M., Dou, X., Alessi, D.S., Ok, Y.S., 2015. Mechanisms of antimony adsorption onto soybean stover-derived biochar in aqueous solutions. J. Environ. Manag. 151, 443–449.
Werner, D., Higgins, C.P., Luthy, R.G., 2005. The sequestration of PCBs in Lake Hartwell sediment with activated carbon. Water Res. 39 (10), 2105–2113.
Xu, X., Schierz, A., Xu, N., Cao, X., 2016. Comparison of the characteristics and mechanisms of Hg (II) sorption by biochars and activated carbon. J. Colloid Interface Sci. 463, 55–60.
Yu, Q., Zhang, R., Deng, S., Huang, J., Yu, G., 2009. Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: kinetic and isotherm study. Water Res. 43 (4), 1150–1158.
Zareitalabad, P., Siemens, J., Hamer, M., Amelung, W., 2013. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater–a review on concentrations and distribution coefficients. Chemosphere 91 (6), 725–732.
Zhang, X., Wang, H., He, L., Lu, K., Sarmah, A., Li, J., Huang, H., 2013. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. Environ. Sci. Pollut. Res. 20 (12), 8472–8483.