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Activated and enriched "designer" biochar as sorbent in remediation of PFAS and metal contaminated soils

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Acknowledgment

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Abstract

Soil contamination has become a major environmental problem of global concern, and there is a need for effective remediation methods to counteract this problem. Immobilisation of contaminants in soil using the carbonaceous material biochar as a sorbent can make an important difference in the future, as it is both a sustainable and cost-effective remediation alternative. However, there is still much unknown about biochar's sorption capacity for various contaminants and this thesis therefore aims to contribute knowledge to this existing knowledge gap.

In order to investigate the sorption of a group of organic pollutants called per- and polyfluorinated alkyl substances (PFAS) and metals/metalloids (lead, copper, and antimony) to biochar in contaminated soil, one-step batch leaching tests were conducted, with increasing dose of biochar added. Previous research has shown that biochar has potential for improvement as a sorbent material and therefore two types of "designer" biochars were investigated in this thesis. In the PFAS contaminated soil, different activated biochars were tested and in the metal contaminated soil, biochars enriched with zero-valued iron and sulfur were tested.

In soil with low organic matter (OM) content, the addition of activated biochar gave an almost 100% reduction in PFAS leaching already at a dose of 0.5%. Sorption of PFAS in soil with high OM content required a dose of 5% to observe a clear reduction in PFAS leaching. Fully activated biochar gave the most effective PFAS sorption in both soil types. In metal/metalloid contaminated soil, biochar enriched with zero-valued iron had the best ability to sorb both lead, copper and antimony. A dose of 10% was required to get a clear effect in soil with both high and low OM content.

So far, the research on such types of "designer" biochar is scarce. The present work provides promising prospects for biochar as an effective sorbent material in soil remediation. Further research on activated biochar and iron-enriched biochar is needed to gain a better understanding of the sorption capacity and the underlying sorption mechanisms.

Sammendrag

Jordforurensning har blitt et stort, globalt miljøproblem, og der er behov for effektive behandlings metoder for å motvirke dette problemet. Immobilisering av forurensninger i jorda ved hjelp av det karbonrike sorpsjonsmaterialet biokull kan utgjøre en viktig forskjell i tiden fremover, da det både er et miljøvennlig og kostnadseffektivt behandlingsalternativ. Det er imidlertid mye som gjenstår når det gjelder kunnskap om biokulls evne til å binde ulike forurensninger i jord. Denne oppgaven har derfor som mål å bidra med kunnskap til dette eksisterende kunnskapshullet.

For å undersøke binding av en gruppe organiske forurensninger kalt per- og polyfluorerte alkyl substanser (PFAS) og metaller/metallioder (bly, kobber, og antimon) til biokull i forurenset jord, ble det gjennomført utlekkingstester (*one-step batch leaching tests*) med økende dose biokull tilsatt. Tidligere forskning har vist at biokull har et forbedringspotensiale som sorbentmateriale, og derfor ble to typer «designer» biokull undersøkt i denne oppgaven. I den PFAS forurensede jorden ble ulike varianter av aktivert biokull testet, mens i den metall/metalloid forurensede jorden ble biokull beriket med nullverdig jern og svovel testet.

I jord med lavt innhold av organisk materiale ga tilsetning av aktivert biokull en nærmest fullstendig reduksjon i PFAS-utlekking allerede ved en dose på 0,5%. Sorpsjon av PFAS i jord med høyt innhold av organisk materiale krevde en dose på 5% for å observere en markant reduksjon i PFAS utlekking. Fullstendig aktivert biokull ga mest effektiv PFAS-binding i begge jordtypene. I metall/metalloid-forurenset jord var det biokull beriket med nullverdig jern som hadde best evne til å binde bly, kobber og antimon. En dose på 10% var nødvendig for å få tydelig effekt i jord med både høyt og lavt OM innhold.

Det er foreløpig svært lite forskning på slike typer «designer» biokull, og resultatene fra oppgaven gir lovende utsikter for biokull som et effektivt sorbentmateriale for behandling av forurenset jord. Videre forskning på aktivert biokull og jernberiket biokull er nødvendig for å få en bedre forståelse for sorpsjons kapasitet og de underliggende sorpsjonsmekanismene.

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Appendix

1 Introduction

Today, the reality is characterised by climate change and continuously emerging environmental problems, and these issues are mainly caused by anthropogenic activities. During the last half of the twentieth century, anthropogenic pollution has sky-rocketed resulting in the omnipresence of chemical contaminants in the environment (Meuser, 2013). Soil, which is defined as "the top layer of the earth's crust, formed by mineral particles, organic matter, water, air and living organisms" (EC, 2006), is one environmental compartment receiving a lot of these chemical compounds, and therefore, soil contamination is an example of such an emerging environmental problem.

Soil degradation in general has already been on the EU's agenda for decades and the European Commission has listed soil contamination as the third biggest threat to soil in the Thematic Strategy for Soil Protection (EC, 2006). The Food and Agriculture Organization (FAO) of the United Nations (UN) has also increased their focus on soil contamination by raising awareness and increasing knowledge. The initiation of the annual World's Soil Day (WSD), which in 2018 was dedicated solely to soil contamination, and the publication of the first ever report on the Status of the World's Soil Resources (FAO & ITPS, 2015) are testimonies to this. One of the UNs strategic development goals (SDG15), adapted in 2015, is also concerned with land degradation aiming to "protect, restore and promote sustainable use of terrestrial ecosystems" (SDGs, 2015), reflecting the growing concern related to soil contamination and the importance of counteracting this issue now.

The most effective way of reducing a pollution is by stopping the emissions. For soil contamination these emissions are almost exclusively related to anthropogenic activities, with industry, mining, military activities, and agriculture accounting for most of the emissions (Rodríguez-Eugenio et al., 2018). In Norway, military activities with the use of small arms shooting ranges, and firefighting drill facilities at airports with the use of firefighting foam constitute two examples of major emissions of contaminants to soil. Overall, the sources of soil contamination are vast and varied and even if they are reduce or stopped, the soil is a slow-turning system (EC, 2006) and contaminants already in the ground can cause problems for years to come.

To abate these long-term challenges, a thorough soil clean-up is needed. Soil clean-up, or remediation, makes up a whole field in science with a lot of remediation options already available to counteract soil contamination. Many of these techniques are, unfortunately, expensive and time consuming, like excavation and landfilling, but luckily, new and promising techniques are emerging; like biochar remediation. Biochar has been subject to soil research since the early 2000s, primarily because it can increase soil fertility, but the discovery of biochar's ability to immobilise contaminants has recently spiked the interest in biochar.

Biochar is a carbonaceous material with a high sorption capacity for both organic and inorganic contaminants. When added to soil, biochar can therefore immobilise contaminants and prevent the contaminants from being spread from the site of contamination. Reducing spreading is key to reducing risk related to a contamination, because a large share of transport happens via the aqueous phase and this is also where contaminant exposure and uptake in organisms take place (Figure 1). The main goal of remediation is therefore to limit or stop the main rout of exposure, and for biochar soil remediation, this equates to reduce leaching of a contaminant and hence reduce the contaminant's bioavailability (Figure 3). This thesis will therefore be restricted to contamination and transport, as indicated by the red circle in Figure X.

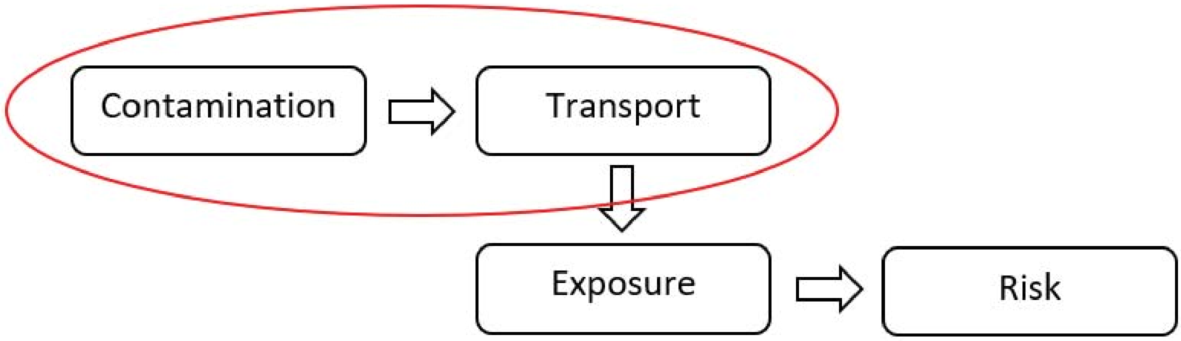


Figure 1: The connection between a contamination and risk. Red circle marks the focus of this thesis.

In addition to the aspect of contaminant immobilisation, biochar offers a possible sustainable and cost-efficient alternative to existing soil remediation methods. Biochar can be produced from resources which previously were considered waste, like crop residues and waste timber, which enables better use of resources and keeps the resources in the economy for a longer period of time. When the biochar is used to stabilise contaminated soil, this adds another dimension to the sustainability and cost-effectiveness of biochar. In addition to connecting two waste streams (waste biomass and contaminated soil) and giving them new value, biochar soil amendment mitigates climate change by sequestration of carbon. This concept is illustrated in figure X. This line of resource utilisation corresponds well with the circular economy, which is the economic model warranted in a future sustainable society.

Figure 2: Concept sketch; stabilisation of contaminated soil through remediation with biochar produced from waste timber.

However, there are some obstacles that need to be solved before biochar can become a fully competitive remediation alternative, and therefore, this master thesis sets out to solve one such obstacle by contributing knowledge to an existing knowledge gap on biochar sorption effectiveness. The sorption effectivity of both regular biochar made from waste timber and various versions of this biochar will therefore be tested in this thesis, with focus on sorption of a group of organic contaminants called per- and polyfluoroalkyl substances (PFAS) and metal contaminated soils.

2 Theory

2.1 Contaminants in pore water

Soil is, as mentioned above, a complex matrix and contaminants in soil will therefore be dispersed between minerals, organic matter (the solid phase) and water (aqueous phase) at a site of contamination. Risk related to a contaminated site is often determined by total contaminant concentrations in soil, but this approach may lead to wrong conclusions, as it does not consider the partitioning of a contaminant between solid and aqueous phase. The main problem with using total concentrations is that the actual risk is over-estimated, and the severity of a contamination may be misrepresented, because aqueous concentrations are more strongly related to environmental risk. Therefore a shift from using total contaminant concentration to contaminant pore water concentration in risk assessment is warranted (Alexander, 2000) (Ghosh et al., 2011).

Pore water denotes the water that is inside the pores on the solid particles in soil, and pore water concentrations represent the mobile and bioavailable fraction of a contaminant (Figure 3). A bioavailable or bioaccessible compound is defined by Semple et al. (2004) as a compound that is "available to cross an organism's cellular membrane", where bioavailability denotes the actual fraction freely available right now and bioaccessibility denotes both the freely available and the potential available fraction of the contaminants. Contaminant degradation, in addition to bioavailability/bioaccessibility and mobility, is also important when assessing risk related to a contamination, and all three processes occur in the aqueous phase and therefore pore water concentrations are most relevant when assessing risk.

The type of soil in which the contamination takes place is also a very important aspect regarding risk, because the soil determines the sorption of the contaminants (Hale et al., 2016) and hence the freely dissolved, aqueous fraction. The term "sorption" includes both *absorption* (dissolution in a flexible matrix) and *adsorption* (surface attraction) (Cornelissen et al., 2005)(oxforddictionaries.com 24.04.2019). The fraction of organic matter (OM) is very important in this respect. It provides the soil with a porous structure and contains a lot of functional groups and reactive sites on the OM particle surfaces, which are crucial traits for sorption of contaminants. A high fraction of organic carbon in the soil generally corresponds to a high contaminant sorption (Alexander, 2000) (NGI, 2019).

A contaminant's distribution between the solid and the aqueous phase in soil can be calculated using equation (eq) 1 and is called the distribution/partition coefficient (K_D). The K_D value is determined by the hydrophobicity and/or solubility of a compound and the sorption strength (capacity and affinity to compound) of the soil (NGI, 2019). A high K_D value indicates low solubility of a compound in the aqueous phase (or the pore water) and consequently a high fraction associated with the solid phase. Hence, a low risk of transportation and uptake. K_D is calculated by dividing a compounds concentration in soil (C_s) by the compounds concentration in the pore water (C_w) at equilibrium and the K_D will change from one soil type to the next.

$$K_D = \frac{C_s}{C_w} \qquad \text{eq 1}$$

K_D is the partitioning coefficient, C_s the concentration in soil, and C_w the concentration in water.

K_D values are widely used in management of contaminated soils, because they can predict leachability and uptake of a contaminant based on its partitioning between the solid and the aqueous phase of the soil system.

2.2 Soil remediation development

The word "remediation" denotes the action of reversing or stopping environmental damage (oxforddictionaries.com 20.02.19), which, in the context of this thesis, can equate to contaminant immobilisation. Soil remediation has been a part of contamination management for over forty years, but there has been a large development in technology since the late 1970s (Meuser, 2013, p. viii). In the beginning, soil remediation was only concerned with complete removal of the contaminants and dig-and-dump was the preferred mechanism (Meuser, 2013). This is perhaps the most intuitive way of dealing with contamination, but today the objectives of remediation are concerned with risk-reduction. As stated previously, risk is related to bioavailability, and in order to reduce the risk a contamination pose to the environment and human health, the bioavailable concentration of the contamination needs to be reduced. This seldom coincide with complete removal (Meuser, 2013).

Over the time of remediation history, new remediation techniques have developed as a reaction to the growing issue of soil contamination (Marques et al., 2009). Traditionally these techniques have been expensive and intrusive to the soil system, like soil washing and electrokinetics, but lately more cost-effective and less intrusive, *in situ*, technologies are emerging. Phytoremediation, bioremediation, and contaminant immobilisation using sorbent amendments like biochar, which is the subject of this thesis, are examples of these new remediation technologies (Meuser, 2013; Roychowdhury et al., 2019; Thapa et al., 2012). Phytoremediation is a technology where contaminants are extracted from the soil through uptake by plant roots and subsequent plant harvest (Meuser, 2013). Bioremediation decontaminates soils by microbial degradation of the contaminants and can be both *in situ* and *ex situ*. Consequently, both these remediation techniques focus on reducing total contaminant concentrations (Meuser, 2013).

Immobilisation of contaminants using sorbent amendments, however, is a soil remediation technique where only the bioavailable concentration is reduced. Contaminants in the freely available and potentially available fraction are "pulled out" of the aqueous phase and "held back" in the solid phase because of strong affinity to the amendment material (Figure 3). This may seem like a temporary solution, because the contaminants are still in the soil and the total concentration is not reduced. But if highly stable materials like biochar and activated carbon are used as sorbent materials, the contaminants can be retained in the solid phase for hundreds to thousands of years (Hale et al., 2011; Kuzyakov et al., 2009), where they are unavailable for uptake and pose no risk to environment or human-health (Semple et al., 2004).

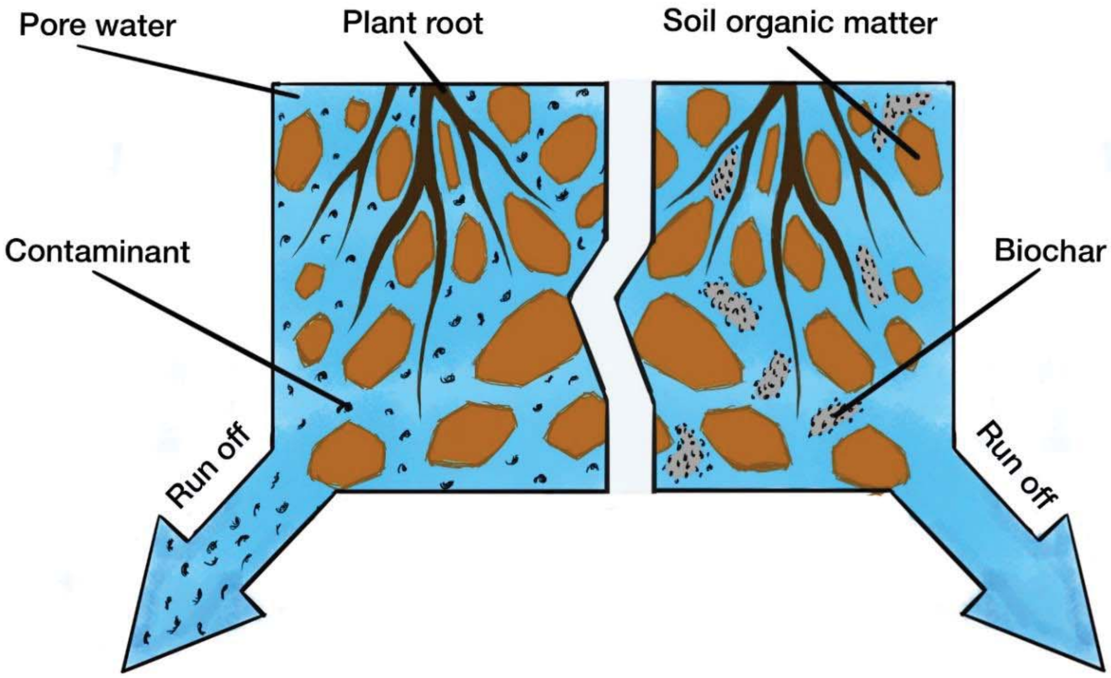


Figure 3: Contaminant distribution, up take, and leaching in soil without biochar (left) and with biochar present (right).

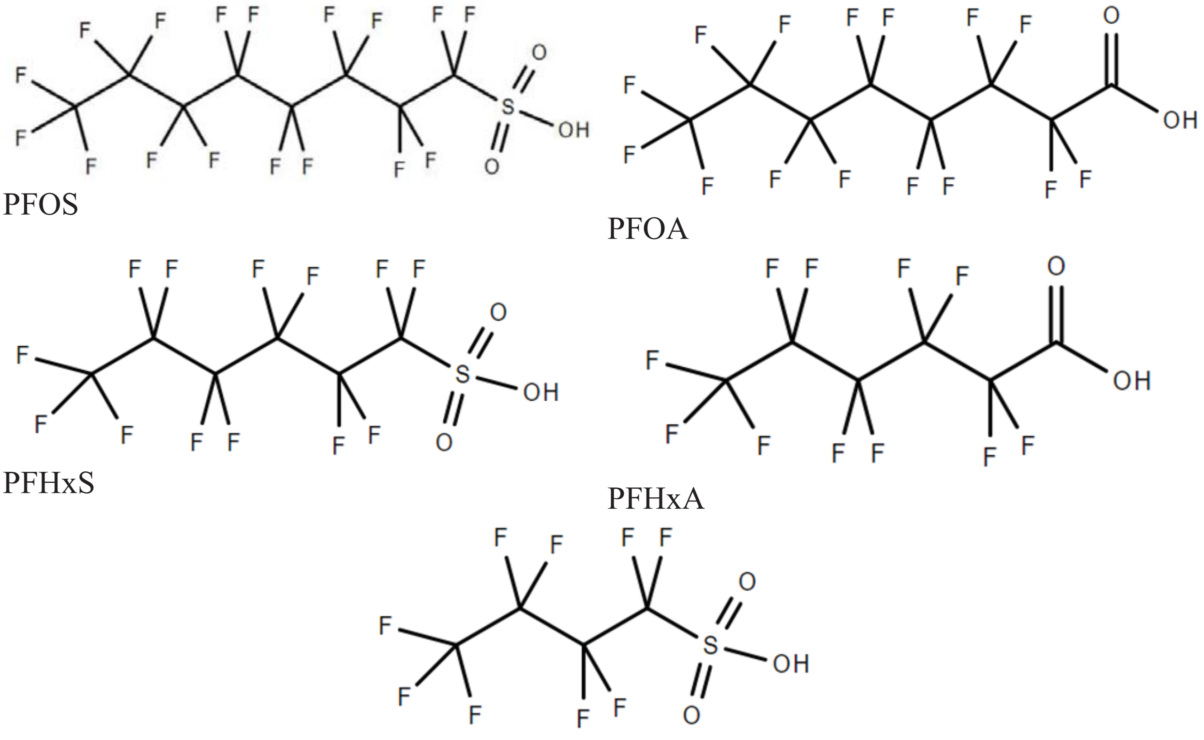
2.3 Sites and contaminants of interest

The scope of this thesis was restricted to contaminated soil from two geographic locations; Rygge Airport and Tittelsnes small arms military range. These locations were chosen because they represent big sources of anthropogenic contaminant emission. At Rygge Airport the soil was sampled from a firefighting training area/facility where firefighting foam had been used for many years, and the soil was therefore contaminated with per- and polyfluoroalkyl substances (PFAS). The firefighting foam are called aqueous film forming foams (AFFF) and are used at airports all over the world. At Tittelsnes small arms range the soil was sampled from the backstop berm (bullet trap) of the shooting range and therefore the soil was contaminated with heavy metals and antimony from spent ammunition.

2.3.1 PFAS

Per- and polyfluoroalkyl substances (PFAS), previously called per- and polyfluorinated chemicals (PFC), are a large group of organic chemicals of anthropogenic origin, with superior oil- and water-repelling properties. Because of these properties, PFAS has been widely used in industrial applications and consumer products since the 1950s (OECD, 2013). Firefighting foams (AFFF), Gore-Tex fabrics, and anti-stick Teflon kitchenware are well-known products that owe their functionality to the surface active properties of PFAS (Herzke et al., 2012; OECD, 2013). Despite their advantageous contribution to their intended areas of use, PFAS are found to persistent in the environment, have a high bioaccumulation potential, and cause adverse effect in living organisms/humans (Krafft & Riess, 2015).

The adverse effects of PFAS, which are still largely unknown, can be contributed to their molecular structure. PFAS consists of a fully (per-) or partly (poly-) fluorinated carbon chain with a functional head group, typically a carboxylic acid or a sulfonic acid/sulfonate (Figure 4). The fluorinated chain has both hydrophobic and oleophobic properties, whereas the head groups has hydrophilic properties, and overall PFAS are anionic organic compounds (Higgins & Luthy, 2006). Because PFAS are anthropogenic chemicals, they are not naturally present in the environment and hence there are no known natural enzymes able to degrade them (Krafft & Riess, 2015). Additionally, the bonds between carbon (C) and fluorine (F) in the perfluoroalkyl moiety ($-C_nF_{2n+1}$) are extremely inert and difficult to degrade/break down, making PFAS persistent in the environment. Because of this, perfluorooctanoic sulfonic acid (PFOS), which has been the most extensively produced and frequently detected PFAS in the environment, is recognised as a persistent organic pollutant (POP) and was in 2009 listed in Appendix B of the Stockholm Convention of Persistent Organic Pollutants.



PFOS

PFOA

PFHxS

PFHxA

PFBS

Figure 4: Chemical structure of perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorohexane sulfonate (PFHxS), perfluorohexanoic acid (PFHxA), and perfluorobutane sulfonate (PFBS).

Concern about PFAS presence in the environment and human exposure started in the 1970s where low concentrations of PFAS were measured in human blood serum. By the beginning of the 2000s it was evident that PFAS was omnipresent in the environment and concentrations of the chemicals were detected in water, soil, air, also in remote areas (3M Company, 2003). The adverse health effects of PFAS on humans still require a lot of research to be fully understood, but some results from studies of human exposure show that PFAS can increase cholesterol levels, increase the risk of cancer, interfere with natural hormones, and affect the immune system (ATSDR, 2018). Generally, the long-chained PFAS (> 7 C) are reported to be more toxic, bioaccumulative, and biomagnifying than the short-chained PFAS (> 7 C).

2.3.1.1 PFAS restrictions

As more and more information about the persistent, toxic, and bioaccumulative properties of PFAS has been discovered, the restrictions on production and use of these compounds has emerged and gradually become stricter. However, introduction of laws and regulations take time, and as a mitigating measure the Norwegian Environmental Protection Agency (Miljødirektoratet) has included several of the PFAS chemicals on the List of Priority Substance. This list contain chemical substances that "pose a serious threat to health or the environment" and that Norway aim to reduce and eliminate emissions of by 2020 (Mildir, 2018). PFOS was put on the List of Priority Substances in 2002, as the first PFAS, followed by perfluorooctanoic acid (PFOA) in 2007, perfluorohexane sulfonate (PFHxS) in 2017, and lastly perfluorobutane sulfonate (PFBS) was added earlier this year (2019).

So far, only PFOS is regulated through global and European legislation, for example in the Stockholm Convention on Persistent Organic Pollutants, as mentioned above, and in the EU-regulation REACH. Norwegian legislation continuously adapts to these regulations, and in March 2007 PFOS and PFOS-related compounds in firefighting foam was banned in Norway (regjeringen.no, 2010), complying with the EU directive on PFOS from 2006 (2006/122/ECOF). PFOS is also included in legislation that deals with pollution. In soil, PFOS normative values are set to 0.1 mg/kg (Forurensningsforskriften, 2004, del 1, vedlegg 1); soils containing higher concentrations are considered contaminated (hazardous waste).

Even though these regulations limited the use of PFOS and related PFAS compounds, the demand for compounds with similar properties did not decrease. PFOS was phased out, but at the same time substitution compounds without restrictions were phased in. PFBS, a short chained PFAS with 4 C, is an example of such a substitute compound (NGI, 2018). The legislation concerning PFAS is continuously changing as new knowledge is uncovered, and all the PFAS compounds mentioned in this thesis could probably be restricted by regulations in the near future. Currently both PFOA and PFHxS are on the REACH candidate list, being considered for entry on the list, and the Norwegian Environmental Agency is working on getting PFBS on the candidate list as well (NGI, 2018).

PFOS and perfluorooctanoic acid (PFOA) are the most studied chemicals of the PFAS, contributed to their extensive production and presence in the environment (EPA, 2018), and therefore most of the data available about PFAS is related to PFOS and PFOA.

2.3.2 Lead, Copper and Antimony

Even though metals in general are natural compounds in the environment, as opposed to PFAS, the presence of lead (Pb), copper (Cu), and antimony (Sb) in the environment have become problematic because of human activity. One human activity of major concern is the use of small arm shooting ranges. Pb, Cu, and Sb are important constituents of ammunition, and because spent ammunition is left in the soil of the shooting ranges (mainly in the bullet traps), these areas represent a significant input of heavy metals and metalloids into the environment (Okkenhaug et al., 2016). The Norwegian military alone, which deposited over 55.5 ton Cu, 9 ton Pb, and 0.7 ton Sb in 2016 (Utstøl et al., 2017), can be used as an example to illustrate the severity of this problem.

When left in the soil, the spent ammunition is subject to physical and chemical deterioration. New projectiles may hit and splinter old projectiles, causing physical deterioration, and corrosion of the projectiles cause chemical deterioration (Voie et al., 2010). Both types of deterioration lead to mobilisation of the metals in the soil system; either by chipping off small and mobile fractions of the projectiles or by transforming the metals and metalloid into more soluble species. Unlike organic compounds, metals and metalloids cannot be degraded, they can only be transferred from one oxidation state to another. Pb and Cu are transformed into soluble cationic forms, and Sb into soluble anionic form (Okkenhaug et al., 2016). Increased solubility corresponds to increased mobility, and thus increased transport, and therefore these compounds must be immobilised to reduce the risk associated with shooting range soil.

2.3.2.1 Metal restrictions

The adverse effect of these metals in humans are varied, but the greatest concern is related to Pb. Pb and Pb compounds are included in the List of Priority Substances (Mildir, 2018), reflecting the risk they pose to human-health and the environment. Pb is especially harmful to children, and Pb exposure have been shown to affect the development of the brain with results being for example reduced IQ and reduced attention span and increased antisocial behaviour (WHO, 2018). Pb can accumulate in the body and the World Health Organization state that “there is no known level of lead exposure that is considered safe” (WHO, 2018). Due to its toxicity, Sb is included on the list of priority pollutants of the Environmental Protection agency in the United States, but currently it is not listed in Norway (Okkenhaug, 2012). Copper is an essential mineral, but at high doses it can also have toxic effects, like Parecelsus said *it is the dose that makes the poison*.

To assess the health risk related to contaminated soil, the Norwegian Environmental Protection Agency have developed Norwegian quality guidelines for contaminated soil (TA 2553). These quality guidelines relate the degree of contamination to expected health effects, dividing contaminated soils into five classes. Class 1 represents areas where contaminant concentrations in the soil pose no risk to the environment and are set to be the normative values of the compounds, whereas soil with contaminant concentrations qualifying for class 5 are defined as very poor. Often, soils in both class 5 and 4 require remediation measurements to prevent contaminant leaching. Table 2.1 list the limits for Pb and Cu in the Norwegian quality guidelines. Limits for Sb has not yet been developed.

Table 2.1: Norwegian Quality guidelines for contaminated soil with class limits (mg/kg) for lead (Pb), antimony (Sb), and copper (Cu).

Quality guidelines	1	2	3	4	5
Description of soil	Very good	Good	Moderate	Poor	Very Poor
Limits for Pb	< 60	60 – 100	100 – 300	300 – 700	700 – 2500
Limits for Cu	< 100	100 – 200	200 – 1000	1000 – 8 500	8500 – 25 000

If contaminated soil is to be removed and put on a landfill, then the leaching limits for waste landfills set in Norwegian legislation (Avfallsforskriften) applies. A list of these limits for Pb, Sb, and Cu can be found in appendix A.

2.4 Biochar

2.4.1 What is it?

Biochar is the carbon rich, solid product of biomass combustion (thermochemical conversion) with little or no oxygen present (incomplete combustion) – a process called pyrolysis (Lehmann & Joseph, 2015). It is produced as a contribution to environmental management and is used as a non-oxidative soil application, for example in contaminant immobilisation (Hagemann et al., 2018; Lehmann & Joseph, 2015). Biochar can be produced from any kind of biomass, originating from animals or plants, but the biomass has to be sustainably sourced (Hagemann et al., 2018). This means that no new land or resources should be exploited solely for the purpose of producing biomass for biochar production. Ideally, biochar is produced from waste materials like; “crop residues, forestry waste, animal manure, food processing waste, paper mill waste, municipal solid waste, and sewage sludge” (Ahmad et al., 2014).

Biochar is only one out of several carbon-rich products of pyrolysis, generally called pyrogenic carbonaceous materials (PCM) or black carbon, and a distinction between biochar, i) char, ii) charcoal, and iii) activated carbon (AC) is beneficial for a proper understanding of the concept of biochar (Hagemann et al., 2018). i) Char is the product of natural fire and is what most people would associate with a bonfire. Char is not an intended product, but rather a by-product of (making) a fire. ii) Charcoal is generally produced in the same way as biochar, but without the necessity of sustainability, and in literature the term has previously been used interchangeably with *biochar* (Hagemann et al., 2018). The main difference between the two lies in their intended end use. Charcoal is produced "for cooking or heating, including industrial applications such as melting" (Lehmann & Joseph, 2015), and most people would probably associate it with barbequing. The distinctions are small and if someone were to put biochar on their barbeque, it would actually be classified as charcoal (Hagemann et al., 2018).

iii) Activated carbon, on the other hand, can have the same intended end use as biochar, namely soil remediation. Several studies have demonstrated ACs extreme effectiveness in contaminant immobilisation (e.g. Brändli et al., 2008), and Kupryianchyk et al. (2016) also found that it is even more effective than biochar. But AC is not a sustainable sorbent material. The carbon source in AC could be renewable biomass, waste or fossil charcoal (Hagemann et al., 2018), but due to cost and accessibility of anthracite carbon from coal mines all over the world it is most often the latter. This contribute to a large environmental footprint when employing AC remediation, because of the amount of energy and resources needed – yielding an overall negative effect compared to natural recovery of the contaminated site (Sparrevik et al., 2011). Biochar, could therefore, represents the most sustainable alternative for this type of soil remediation.

2.4.2 Biochar as a sustainable sorbent for soil remediation

In relation to environmental management, biochar has a huge potential, because biochar's production and application to soil have a multitude of positive outcomes for the environment. Lehmann and Joseph (2015) group these outcomes, or motivations for applying biochar into four groups; i) soil improvement, ii) mitigation of climate change, iii) waste management, and iv) energy production. What really makes biochar an attractive technology is the fact that these groups overlap, and when applied, several beneficial effects are achieved at the same time. In remediation of contaminated soils, for example, the main objective is soil improvement, but if the biochar is made from waste materials and the energy produced during pyrolysis is exploited, all four objectives are covered.

The climate change mitigation related to biochar is achieved by reducing greenhouse gas emissions (especially CO_2 emissions) and by carbon (C) sequestration in soil. A common trait for biochar is its high content of organic C relative to that in the biomass it was produced from (Lehmann & Joseph, 2015), which is key to reducing CO_2 emissions. Half the C captured during biomass production (photosynthesis) is preserved in the biochar during pyrolysis. Biochar is also a very stable compound and therefore the C is sequestered for thousands of years when biochar is added to soil. Biochar can thus work as a sink for C in the atmosphere, because it will take up to thousands of years before sequestered C will be broken down and rereleased back into the atmosphere as CO_2 (Kuzyakov et al., 2009).

Even though biochar is of high environmental relevance today, using biochar for soil improvement is not a new phenomenon. It dates back around eight thousand years and originates from the Amazon, where the Indians added charcoal to the soil to improve its' fertility (Mulvaney, 2011); when charcoal made from sustainably sourced biomass are left in the soil, it is called biochar (Hagemann et al., 2018). These fertile, man-made soils are often referred to as *Terra Preta de Indos* – the black soils (Lehmann & Joseph, 2015). The discovery of this application of charcoal in the 1970s spiked the scientific interest and biochar research has increased dramatically over the last decade.

Numerous studies have looked at beneficial agronomical effects of biochar, but studies of contaminant immobilisation in soil remediation is a more recent phenomenon. After the discovery of the strong sorption of contaminants to naturally occurring black carbon in sediments (e.g. Ghosh et al., 2000), AC was produced as a "clean" black carbon and was then deliberately introduced into soil/sediment to immobilise organic contaminants (Brändli et al., 2008). This field of biochar application shows great promise, but there are still some obstacles that need to be solved for biochar to become a fully competitive remediation alternative. One main obstacle is biochar's sorption effectiveness, which has been shown to be much lower than sorption to AC (Kupryianchyk et al., 2016; Oleszczuk et al., 2012).

This thesis addresses some of these current obstacles related to the use of biochar as a sorbent in soil remediation, and tries to find solutions to them, so that biochar can reach its potential as an effective, sustainable soil remediation alternative.

2.4.3 Production and properties

To investigate the sorption effectiveness of biochar and designer biochars, an introduction to production conditions and biochar properties already known is key. As previously stated, biochar is produced through pyrolysis of biomass. Consequently, biomass feedstock and pyrolysis conditions are therefore the most important factors influencing biochar properties and sorption capacity especially (e.g. Ahmad et al., 2014). Because biochar feedstock biomass can vary a lot, so can their physical and chemical properties. Biochar made from plant based biomass, for example, have high C content and low content of essential nutrients (potassium, magnesium, nitrogen), whereas the opposite is true for biochar made from manure (Lehmann & Joseph, 2015). Ahmad et al. (2014) also reported that "generally, biomass with high lignin content results in high biochar yields", lignin being an important constituent off most plant biomass.

The pyrolysis temperatures, on the other hand, has a universal, clear trend when it comes to biochar characteristics. An increase in pyrolysis temperatures lead to an increase in C content (aromatic C) and surface area (because of increase in micropore volume), in addition to a decrease in oxygen (O) and hydrogen (H) content – hence a decrease in reactive functional groups on the biochar surface (Ahmad et al., 2014). All biochars are alkaline materials, especially those produced at high pyrolysis temperature due to ash content, and when added to soil they therefore induce an increase in pH. Because biochar properties vary a lot, they should always be produced with respect to their specific use; which contaminant they are to immobilise and in what type of soil.

2.4.4 Sorption mechanism

The underlying mechanism of biochar remediation in soil is the mass transfer of contaminants from weaker sorption sites on soil particles to stronger sorption sites on biochar particles. This is illustrated in Figure 5. The mass transfer include an initial desorption process, where the contaminants leave the soil particles, followed by a diffusion in the pore water toward the biochar particles where the contaminants are finally sequestered/adsorbed (Lehmann & Joseph, 2015). The effect of biochar remediation is thus dependent on the inherent sorption strength of the soil matrix, and for optimal remediation to occur the sorption of contaminants to biochar must be much stronger that to the soil matrix (Lehmann & Joseph, 2015). Hence the $K_{D\_biochar}$ must be greater than the K_{D_soil}.

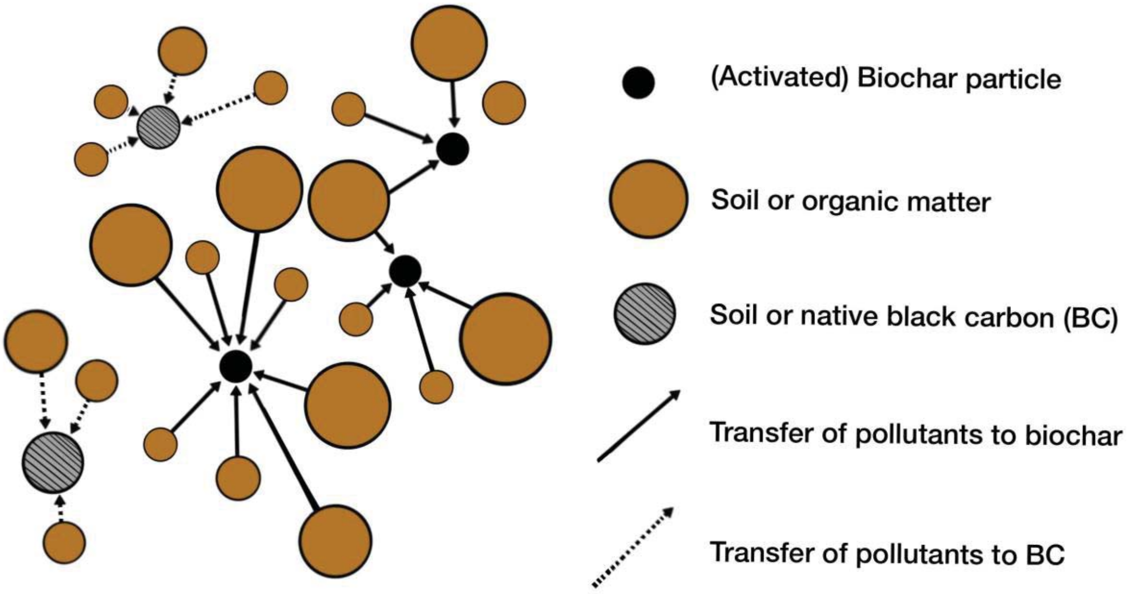


Figure 5: Sequestration of contaminants in soil after biochar or AC amendment. Illustration from (Lehmann & Joseph, 2015) with slight modifications in colour and design.

Specific sorption mechanisms on the biochar surface include partitioning or adsorption, electrostatic interactions (hydrophobic), ion exchange, and precipitation. These mechanisms are highly dependent on specific surface area (SA) and surface functional groups. Partitioning or adsorption of contaminants occur on sorption sites located inside micropores on the biochar surface and hence a high SA/pore volume equals more sorption sites. The size of these pores is in the range of 0.4 - 1.5 nm and they can easily be blocked by larger soil particles like OM if the fraction of these particles in the soil is high. However, occlusion of large molecule contaminants in the pores is also a possible sorption mechanism (Kupryianchyk et al., 2016). Pore blockage is one of three major attenuation processes affecting biochar's sorption, the second is sorption saturation. Sorption saturation is a result of limited number of sorption sites, which at high concentrations can become fully occupied. Because of this, biochar is most effective at low contaminant concentrations where sorption is approximately linear.

Electrostatic interaction is a sorption mechanism determined by van der Waals forces and is of importance for sorption of unpolar organic compounds (Ahmad et al., 2014; Kupryianchyk et al., 2016). This interaction can also be described as hydrophobic interaction because the organic compounds have a low affinity to water molecules and emigrate towards solid particles in water. Ion-exchange and precipitation are sorption mechanisms determined by polar functional groups, typically containing O. The functional groups on biochar's surface are highly determined by pyrolysis temperature and the feedstock biomass they are produced from, and generally most of them are negatively charged, with the occasional amphoteric (pH dependent) group (Ahmad et al., 2014). These mechanisms may be affected by competing ions, especially divalent calcium (Ca^{2+}), in the soil-water system. Competition for sorption sites by native compounds in the soil system is the third major sorption attenuation process for biochar (Higgins & Luthy, 2006).

Studies of biochar sorption capacity for organic and inorganic compounds in soil are scarce (Ahmad et al., 2014), but some general trends have been found. The biochar produced at high pyrolysis temperatures (≥700°C) have a great sorption capacity for organic compounds "attributed to their high surface area and microporosity" (Ahmad et al., 2014) as well as high carbonisation and aromaticity increasing the "number of sorption sites available for adsorption" (Kupryianchyk et al., 2016). Sorption of PFAS to biochar has previously been found to be highly dependent on surface area (Kupryianchyk et al., 2016). Adsorption on sorption sites inside the micropores and hydrophobic interactions are postulated to be the most important sorption mechanisms between PFAS and biochar, but this is a new science and still a lot is unknown.

Biochar produced at lower pyrolysis temperatures (≤700°C) are more effective in sorption of inorganics because they contain many polar functional groups (Ahmad et al., 2014). As mentioned in the previous chapter, Pb and Cu most often occur as cations (positively charged) in soil, whereas Sb most often occur as an oxyanion (negatively charged). Sorption of these polar compounds to biochar is therefore highly dependent on the surface functional groups, and because the shooting range soil contains both cations and anions, the amphoteric groups are especially important. Electrostatic attraction between biochar and metal ions (either cation or anion), ion exchange between exchangeable metals on biochar surface and target metals (Pb, Cu, or Sb), and precipitation of metals as insoluble species are the most important sorption mechanisms governing metal immobilisation to biochar (Ahmad et al., 2014).

Apart from the sorption mechanisms of biochar, amendments with biochar cause an increase in pH as biochar is an alkaline material. The change in pH may affect pH dependent sorption mechanisms in the soil system and create more negatively charged surface functional groups. This could increase Cation Exchange Capacity (CEC), increasing cation sorption, whereas Anion Exchange Capacity (AEC) could be reduced resulting in higher mobility of anions (Okkenhaug et al., 2013). OM (also referred to as Organic Carbon (OC)) is an important component of soil and it contributes a great deal to the soil's inherent sorption strength of contaminants. OM is shown to be affected by pH. Increase in pH affect the electrostatic attractions in the soil and cause deprotonation of organic acids, which may lead to an increase in Dissolved Organic Carbon (DOC) and further contaminant mobility. Cationic compounds in soil, like Pb, are for example very often associated with DOC in soil (Okkenhaug et al., 2016) and hence mobilised when DOC content increase.

To shortly summarise; the sorption strength/effectivity of biochar for contaminants in soil is determined by sorption capacity (number of sorption sites) and affinity to the contaminants.

2.4.5 Designer biochar – activation and enrichment

As previously stated, the use of biochar in soil remediation is thus far weakened by biochar's inferior sorption strength/effectiveness compared to other sorbents, like AC. Kupryianchyk et al. (2016), for example, found that AC amendment to contaminated soils almost completely removed PFAS from pore water, whereas biochar had small or no effect. To solve this problem, it is postulated that activation and modification of biochar should be conducted in order to increase biochar's sorption effectiveness - producing "designer" biochar.

Physical activation is a process that increase surface area and pore volume of carbonaceous materials. When these materials are exposed to an activation agent, reactive C on the surface is converted to gas (CO) in a process called gasification, resulting in opening and widening of existing pores (Lehmann 2009, p.20; Benedetti et al., 2017). Steam (H_2O) and CO_2 are often used as activation agents with the following gasification reactions:

$$C + H_2O = CO + H_2 \qquad \text{eq 2}$$

$$C + CO_2 = 2\,CO \qquad \text{eq 3}$$

Although this activation process has widely been used in production of AC, ensuring AC's high sorption effectiveness, it has not been adopted for biochar until very recently. The increase in sorption effectiveness or strength after activation is obtained by increased capacity (with a larger surface area) and affinity (a "cleaner" surface with more easily accessible sorption sites) with the contaminant (Cornelissen, 2019). Research on activated biochar is scarce and this thesis is one of few studies where activated biochar is investigated in relation to contaminant immobilisation. The effect of different degrees of activation on sorption strength/effectiveness has never (to the authors knowledge) been tested before.

Another treatment that recently has emerged in biochar research is the enrichment of biochar with other sorbent materials, like Zero Valent Iron (later referred to as ZVI or Fe^0) and sulfidated ZVI (S-ZVI). These materials have earlier been used as sorbents in contaminated soils causing effective immobilisation of Pb, Sb (Okkenhaug et al., 2016) and mercury (Hg) (O'Connor et al., 2018). When applied to contaminated sites, Fe^0 is easily oxidised in the soil forming highly reactive ferric oxyhydroxides through the following reactions (Okkenhaug, 2012):

$$\mathrm{Fe^0} + 2\,\mathrm{H_2O} + \tfrac{1}{2}\,\mathrm{O_2} \rightarrow \mathrm{Fe^{2+}} + \mathrm{H_2O} + 2\,\mathrm{OH^-} \qquad \text{eq 4}$$

$$\mathrm{Fe^{2+}} + \mathrm{H_2O} + \tfrac{1}{4}\,\mathrm{O_2} \rightarrow \mathrm{Fe^{3+}} + \tfrac{1}{2}\,\mathrm{H_2O} + \mathrm{OH^-} \qquad \text{eq 5}$$

$$\mathrm{Fe^{3+}} + 6\,\mathrm{H_2O} \rightarrow Fe(OH)_3 + 3\,\mathrm{H_3}O^+ \qquad \text{eq 6}$$

Ferric oxyhydroxides have amphoteric properties, due to variable charge of surface hydroxyl groups, enabling reaction with - and immobilisation of both cations and anions in soil (Okkenhaug et al., 2016). Sulfidation of ZVI has recently been proven to increase contaminant immobilisation by ZVI. The increased sorption is highly dependent on S/Fe ration and ZVI is supplemented by sorption mechanisms of ion exchange, complexation, and coprecipitation between FeS and $FeSH^+$ groups and metal contaminants (Li et al., 2017). Enrichment of biochar with ZVI and S-ZVI would thus probably increase the sorbents amphoteric character, resulting in better sorption of metals occurring as both cations and anions in soil. But as mentioned earlier, the area of designer biochar is novel and therefore little knowledge about effects on biochar sorption capacity exists. This highlights the relevance of this master's thesis and the need for more research like it.

2.5 Objectives and hypothesis

The overall aim of this thesis was to evaluate cost-efficient sorbent materials (read: designer biochar produced from waste timber) for PFAS and metal contaminated soil. The objectives of the thesis were therefore to investigate sorption of organic and inorganic contamination to designer biochar, and to identify the most effective sorbent and amendment dose needed to optimise biochar remediation.

PFAS contaminated soil was remediated with activated biochar and the specific objectives were to observe if the degree of activation (50%, 75%, 100%, and 125%), the pyrolysis temperature, or the activation agent (H_2O or CO_2) affected biochar's sorption effectiveness. Metal contaminated soil was remediated with zero valent iron (ZVI) and sulfur (S) enriched biochar, non-amended biochar, and pure ZVI, and the specific objectives were to compare sorption between these sorption materials and to observe if the biochar enrichments contributed significantly to biochar's sorption capacity.

Through the work of this thesis a set of hypotheses was tested, one parent hypothesis and three sub-hypotheses:

- H0: Waste timber biochar can serve as an effective sorbent for PFAS and metals/metaloids (Pb, Cu, and Sb) in contaminated soils
    - H1: Biochar effectiveness in sorbing PFAS increases with increased activation
    - H2: Metal sorption increases when using designer biochar
    - H3: Biochar effectiveness varies with soil characteristics, especially organic carbon content

Some research has already been done on this subject, but this thesis stands out in the following respects;

- it uses a sustainable sorbent (biochar instead of activated carbon),
- it uses designer biochars; testing various degrees of biochar activation and enrichments
- it uses natively contaminated soils (not spiked in the laboratory),
- it uses biochars for PFAS remediation
- it uses biochars for antimony (Sb) remediation.

3 Materials and method

To establish if biochar could work as an effective sorbent material for immobilisation of PFAS and metal contaminants in soil – which is thesis' objective – sorption tests with natively contaminated soils were conducted.

3.1 Soil samples

The soil used in experimental work of this thesis was natively contaminated soil, meaning that the soil was sampled from sites where actual contamination had occurred. The contaminant concentrations therefore represent environmental relevant concentrations. To see if factors other than biochar affected contaminant sorption, soil with different content of organic carbon was used.

3.1.1 Sampling and sample preparation

All soil sampling was done prior to the start-up of this thesis. The soil was collected from a Norwegian waste handling facility, but originally it was sampled from two different locations; Rygge Airport (59.3732 N, 10.7935 E, the 1st of July 2017) and Tittelsnes military small arms shooting range (59.7231 N, 5.5156 E, the 1st of July 2017). The soil from Rygge Airport was samples from a former firefighting training facility and the soil from Tittelsnes was sampled from, and around, a backstop berm (bullet trap). At each location soil with high total organic content (TOC) (from the upper organic horizon 10-20 cm) and low TOC (from the illuvial mineral horizon below the podzol) were collected by mixing five subsamples. The soil samples were stored cold and dark until use.

The sample preparation consisted of three parts:

- Homogenisation
- Drying
- Crushing and sieving

The high TOC soil sample from Rygge Airport amounted to 14 plastic buckets (10L). To get a representative subsample of this soil, the buckets needed to be mixed and homogenised. This was done by transferring the soil into bigger plastic tubs, where it was mixed by hand and then transferred back into the plastic buckets (Figure 6a). Further homogenisation of a smaller subsample (2 plastic buckets) was done by hand in tin containers (Figure 6b), this subsample constituted the expected volume needed in the experiment. Clay and poorly degraded organic material were torn apart and non-soil objects, like sticks, roots, and stones were taken out. All handling of the soil was done by hand while wearing gloves.

Figure 6a-c): Soil sample preparation, a) initial homogenisation of total soil sample, b) homogenisation of soil subsample, and c) crushing of soil sample.

The same procedure was done for the low TOC soil from Rygge Airport and high TOC soil from Tittelsnes, except for the pre-homogenisation which was not needed due to much smaller sample volumes. Subsamples were taken out by hand wearing gloves and transferred into tin containers. The low TOC soil from Tittelsnes was homogenised prior to the start-up of this thesis, so no further homogenisation was needed for this soil. A subsample was taken out by transferring the soil directly into the batch leach test sample bottles (ref. upcoming chapter 3.3).

After homogenisation, the samples were put in oven to dry. PFAS soils were dried at 110°C, low TOC overnight and high TOC for 2 days (d) (because extra soil had to be added due to massive soil volume reduction (high water content)). The metal soils were dried in room temperature for 4 d. Later it was discovered that the soil was not properly dry, so both high and low TOC metal soils were put in oven overnight at 40 °C. Low temperature was used to prevent changed speciation of the metal(loid) contaminants. The dried soil was then crushed and sieved to a size < 1mm (Figure 6c) to produce the required amount for the tests. This was the size fraction appropriate PFAS leaching test as defined in NS-EN 12457-2 (Standard Norge, 2003). 1.64 kg of both high and low TOC PFAS soil <1mm and 0.136 kg of both high and low TOC metal soil <1mm was needed for the sorption tests.

3.1.2 Characterisation /physio-chemical properties of the soil

Both PFAS and metal contaminated soils were part of previous (NGI) studies, and the TOC, pH, and contaminant concentrations used in this thesis was taken from this previous work. A full overview of these values can be found in appendix B, but the values relevant for this thesis is represented in Table 3.1.

Table 3.1: Physio-chemical properties of soil from Rygge airport and Tittelsnes small arms shooting range. pH, total organic carbon (TOC) content (%), and total contaminant concentrations (µg/kg and mg/kg of d.w.) (Cornelissen et al., 2018a; Cornelissen et al., 2018b).

	High TOC soil	Low TOC soil
Soil form Rygge airport		
pH	4.9	7.8
TOC content (%)	34.2	1.61
PFOS (µg/kg)	1 000	3 400
PFHxS (µg/kg)	110	200
PFHxA (µg/kg)	8.2	44
PFOA (µg/kg)	6.4	27
PFBS (µg/kg)	3.9	26
Sum PFAS* (µg/kg)	1 200	3 800
Soil from Tittelsnes small arms shooting range		
pH	7.5	8
TOC content (%)	12.6	4.7
Cu (mg/kg)	380	110
Sb (mg/kg)	210	100
Pb (mg/kg)	6 600	4 300
* Based on concentrations of 23 analysed PFAS compounds		

These PFAS soil concentrations were in the range of previously reported concentrations in soil from airport firefighting training sites. Kupryianchyk et al. (2016) reported total PFAS concentrations of 3600 µg/kg (Kjevik), 2360 µg/kg (Evenes), and 780 µg/kg (Flesland), and Hale et al. (2017) reported total PFAS concentrations from the top soil (0-2m) ranging from 96.6 µg/kg to 4240 µg/kg. Soil concentrations from five small arms shooting ranges reported in a previous study ranged from 123 – 2 900 mg/kg for Sb, 2 000 – 30 000 mg/kg for Pb, and 145 – 2 300 mg/kg for Cu (Okkenhaug et al., 2013), fitting well with the results reported in this thesis (although Sb was in the low end of the range). The Pb soil concentrations classifies the soil as hazardous waste.

3.2 Sorbent materials – the biochar

A total of 12 different sorbent materials were used during the experimental work of this thesis; 2 types of biochar, 7 types of activated biochar, 2 types of designer biochar, and 1 zero valent iron (ZVI) amendment. All biochars were produced from the same waste timber feedstock, which comprised "a mixture of demolition timber, container leases and pallets from industry, and furniture and construction wood from private persons" (Silvani et al., Submitted). The waste timber was received at the same Norwegian waste handling facility as the soil samples. The waste timber was shredded with a wood chipper before pyrolysis (Figure 7). The activated biochars were produced by NGI in collaboration with Agroscope, Switzerland, and the enriched biochars were produced by NGI in collaboration with the University of Florida. All biochars were produced prior to the thesis work.

Figure 7: Three stages of biochar production; shredded waste timber (biomass feedstock), biochar, and activated biochar (from left to right).

Several different types of biochar were used in this thesis, but they comprised two main groups: one with activated biochars (for PFAS sorption tests) and one with enriched biochars (for metal sorption tests).

3.2.1 Activated biochar

The activated biochar was produced via pyrolysis at 800-900°C in a one-step activation unit at the Agroscope Institute in Switzerland. Slightly different production conditions were employed (listed in Table 3.2) to determine which pyrolysis temperature, activation percentage, and activation agent should be used to optimise biochar sorption effectiveness. % activation denotes the amount of water that theoretically would react with for example 50% of the carbon, but this reaction is not complete and therefor 125% activation was conducted to make sure that a complete activation was reached. The biochar was dried at 110°C overnight before use.

Table 3.2: Production conditions for activated biochar via one-step activation unit.

Biochar label	Activation agent	% activation	Temperature (°C)
BC	Air (N_2)	0	900
aBC 50%	Steam (H_2O)	50	900
aBC 75%	Steam (H_2O)	75	900
aBC 100%	Steam (H_2O)	100	900
aBC 125%	Steam (H_2O)	125	900
aBC 850°C	Steam (H_2O)	100	850
aBC 800°C	Steam (H_2O)	100	800
aBC CO_2	CO_2	100	900

3.2.2 Designer biochar

The designer biochar was produced via pyrolysis at 650°C and sieved to a size between 0.25 and 1.0 mm. Afterwards the biochar was enriched with zero valent iron (ZVI) and sulphur enriched ZVI (S-ZVI) in solution. ZVI enrichment was done by adding 2.7 g $FeCl_3 \cdot 6H_2O$ to 1 g of biochar (in solution) and sulfur enrichment (S-ZVI) was done by adding 0.8 g $Na_2S_2O_4$ to Fe solution which then was added to 1 g of biochar (in solution). This was done by an external partner at the University of Florida. After production the biochar was kept in sealed plastic bags to limit the oxidation of the ZVI.

3.2.3 Characterisation

The biochars were characterised for surface area, pore volume, and element content (C and O) by external partner in Florida, and these characteristics are summarised in Table 3.3.

Table 3.3: Biochar characteristics, surface area (m^2/g) measured with N_2 and CO_2 adsorption, pore volume (cc/g), and element composition (%) of C, O, and C:O ratio.

Biochar sample	**Surface area (m^2/g)**		**Pore volume (cc/g)**		**Element content (%)**		
	N_2	CO_2	N_2	CO_2	Total C	Total O	C:O
BC	411	840	28 %	24 %	88.8	6.82	13
aBC 50%	550	744	45 %	22 %	90.6	5.87	15
aBC 75%	605	746	52 %	23 %	89	5.58	16
aBC 100%	713	750	83 %	24 %	87.7	7.98	11
aBC 125%	623	846	51 %	28 %	86.9	5.67	15
aBC 850°C	617	850	43 %	26 %	89.4	5.84	15
aBC 800°C	740	805	86 %	24 %	89.2	5.41	16
aBC CO_2	444	620	32 %	20 %	89.5	5.38	17
BC - 900	497	679.4	17%	20%	-	-	-
ZVI	58.9	136.9	21%	4.6%	-	-	-
BC-ZVI	58.1	270.4	8.8%	7.4%	-	-	-
BC-S-ZVI	14.7	-	2.7%	-	-	-	-

3.3 Experimental setup

The experimental setup of this thesis consisted of two separate parts, each part focused on one contaminant group: PFAS and metals respectively. The sorption of contaminants from soil to the sorbent materials was quantified through a standard one-step batch leaching test. This was done according to EN 12457-2 method (Standard Norge, 2003), with a few modifications. Instead of 24 hours, the equilibrium time was 14 d for PFAS test and 7 d for metal(loid) tests, the particle size was < 1mm not <4mm, the samples were put on shaking table not shaken end-over-end, and the samples were left to settle not centrifuged (Hale et al., 2017; Kupryianchyk et al., 2016; Silvani et al., Submitted).

It is important to point out that the leachate/eluate concentrations from batch leaching tests are used as a proxy for pore water concentrations in this thesis. Due to the high water-saturation and rigorous shaking used in the method, these concentrations represent a “worst case” scenario. Natural leaching would most likely never be this high, but the method is a good and widely used tool to make predictions about leachability, even though the predictions may be conservative.

3.3.1 PFAS sorption tests

The one-step batch leaching test was conducted in 0.5 L polyethylene (PE) bottles, where 40 g dry weight (d.w.) PFAS contaminated soil was amended with different doses of activated and one non-activated biochar (0%, 0.1%, 0.5%, 1%, 2%, and 5% of d.w.). Both high and low TOC soil were amended with the 8 different biochars (Table 3.3). A liquid to solid ratio of 10 (L/S, L/kg) was acquired by adding 400 mL Ultrapure water (18 MΩ). The slurry was left on shaking table 14 d, which was found to be enough time for contaminant equilibrium to occur between soil, biochar and water (Higgins & Luthy, 2006). Cornelissen et al. (2005) also found that one month was enough time for phenanthrene (PHE) to equilibrate, therefore 14 d is enough for PFAS which are much less hydrophobic than PHE. A total of 82 samples were investigated.

After shaking, the samples were left to settle for 2 d in 4°C and then filtered through 1.2 µm glass microfiber filters (Whatman, grade GF/C) (Figure 8a). pH was measured using a pH meter (WTW Inolab pH level 2) according to EN ISO 10523 and a 10 mL subsample was extracted using a syringe and filtered through a 0.45 µm polyethersulfone membrane (Figure 8b) for separate dissolved organic carbon (DOC) content was measured according to EN 1484 using a Shimadzu TOC-V CPN Total organic carbon analyzer. Then the eluates were stored at 4°C before they were sent to analysis at accredited laboratory Eurofins, where concentration of 23 PFAS compounds in the aqueous phase was quantified using LC/MS-MS following method DIN 38414-S14.

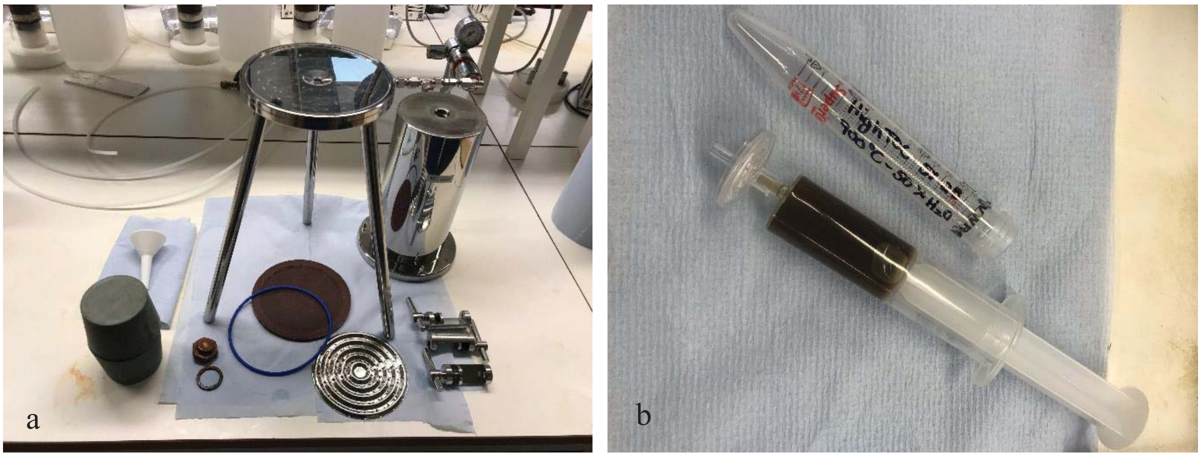


Figure 8: Filter apparatus used for a) 1.2 µm sample filtration and b) 0.45 µm sample filtration.

3.3.1.1 Quality control and assurance

Due to cost restrictions, samples were not analysed in triplicates. No analytical blanks were analysed, because prior method testing had found contaminant mass loss in PE bottles and glass microfiber filters to be negligible (Hale et al., 2017; Kupryianchyk et al., 2016).

3.3.2 Metal sorption tests

One-step batch leaching test was conducted in 60 mL glass vials, where 4 g (d.w.) metal contaminated soil (both high and low TOC) was amended with different doses of biochar, enriched biochars and ZVI (2.5%, 5%, 10%, and 20% of d.w.). L/S 10 was obtained by adding 40 mL of Ultrapure water (18MΩ) water and the slurry was left on shaking table for 7 d. After shaking, the samples were left to settle for 2 d in 4°C and then filtered through 1.2 µm glass microfiber filters (Whatman, grade GF/C) (Silvani et al., Submitted) (Figure 8a).

The eluates were filtered again through a 0.45 µm polyethersulfone membrane (Figure 8b) and divided into three subsamples; one for anion content analysis using IC 5000 Ion Chromatograph, Lachat (Zellweger analytics), one for metal(loid) content analysis using inductively coupled plasma mass spectrometry, ICP-MS (8900 Agilent QQQ), and one for DOC content analysis (EN ISO 10523). Because of small sample volume, pH was measured in the DOC subsample. Before analyses were done by external partner at the Norwegian University of Life Sciences (NMBU), the element samples were preserved with HNO_3.

3.3.2.1 Metal sorption isotherm study

To quantify sorption capacity in a "clean" system, metal sorption isotherms were determined by equilibrating the four sorbent materials with spiked metal concentrations. The spiked metal concentrations ranged from 10 µg/L to 5000 µg/L, creating the sorption isotherm, and were prepared by dilution of stock solutions containing copper nitrite ($Cu(NO_2)_2$), potassium pyroantimonate ($K[Sb(OH)_6]$), and/or lead nitrate ($Pb(NO_3)_2$) (see appendix C). Four metal stock solutions were prepared; one with 5000 µg Pb/L, one with 5000 µg Sb/L, one with 5000 µg Cu/L, and one with a mix of all three metals (5000 µg/L of each). The sorption test was conducted in 60 mL glass vials containing 50 mg sorbent material and 50 mL metal solution with increasing concentrations (L/S 1000). The samples were put on shaking table for 7 d, with further method identical to that in chapter 3.3.2.

3.3.2.2 Quality control and assurance

To control contaminant content in the sorbent materials and potentially correct this, samples containing only sorbent materials and Ultrapure water (18MΩ) were included in the batch leach test. In the sorption isotherm test metal concentration control samples were also included, to correct for inaccuracies in concentration preparation. A 250 µg/L control was therefore included for each of the four metal solutions, representing the intermediate of the diluted concentrations. The difference in analysed control concentration and the theoretical concentration (250 µg/L), which can be called the control ratio, was used to correct reduction in metal(loid) concentrations which was not a result of sorption to sorbent materials.

3.4 Data processing

All data processing and statistical analysis of this thesis was conducted using Microsoft Excel with the extension *Analysis ToolPak*, version 16.16.3 (2018).

3.4.1 Sorption capacity

To find a quantitative measure of the sorbent material's sorption capacity, contaminant equilibrium concentrations leached from the unamended, control soil samples (C_0) were compared to the equilibrium concentrations of the amended samples (C_W). The reduction in leached contaminants was found by using eq 7, giving a ratio that can also be viewed as the increase in contaminant sorption. To illustrate the relationship between amendment dose and reduction in contaminant leaching, this ratio was plotted against sorbent material dose (%). Percent reduction in leached PFAS concentration, or percentage of sorbed PFAS, was also calculated by using eq 8.

$$\frac{C_W}{C_0} \qquad \text{eq 7}$$

$$\left(1-\left(\frac{C_W}{C_0}\right)\right)\cdot\ 100 \qquad \text{eq 8}$$

C_w is the contaminant water concentration at equilibrium before amendment, and C_0 is the contaminant water concentration before amendment.

3.4.2 K_D calculations

A partitioning coefficient (K_D) (L/kg) describes the contaminant partitioning between solid and aqueous phase in a soil system. The soil concentrations measured (Table 3.1) were in reality both $C_s + C_w$ (as sampled soil contained both soil and pore water), and thus the C_w needed to be subtracted from C_s to get the "real" C_s before K_D could be calculated. And therefore, the first step in the K_D calculations was to derive the mass balance for the system (eq 10), using eq 9 as basis. It was only possible to determine K_D values for soil-water partitioning in the control samples (no sorbent amendment), because after sorbents were added it was not possible to distinguish sorption to sorbent from sorption to soil. As control samples did not contain sorbent materials, eq 11 was used instead of eq 10 for mass balance, and the K_D value was determined to be the ratio between contaminant "real" concentration in soil (ng/kg or µg/kg) and water (ng/L or µg/L) at equilibrium, calculated using eq 1. K_D calculations for the sorbent in soil required a more advanced method described in chapter 3.4.3.

$$m_{tot} = m_w + m_{soil} + m_{sorb} \qquad \text{eq 9}$$

$$m_{tot} = C_w V_w + C_s M_s + C_{sorb} M_{sorb} \qquad \text{eq 10}$$

$$m_{tot} = C_w V_w + C_s M_s \qquad \text{eq 11}$$

m_{tot} = the total mass of the contaminant in the soil (expresses as µg or mg). m_w, m_s, m_{sorb} = mass of contaminant in water, soil, and sorbent (expressed as µg or mg). C_w, C_s, C_{sorb} = concentration in water (ng/L or µg/L), soil (µg/kg), and sorbent (µg/kg) at equilibrium. V_w = volume of water (L) in sample. C_w was measured experimentally (from batch leach test) and C_{sorb} was calculated form the mass balance.

3.4.3 Freundlich isotherms

Because K_D values could not be determined for sorbent-water partitioning using the traditional sorption model, the Freundlich isotherm model was adopted (eq 12) yielding K_F (Freundlich adsorption constant) values instead. The Freundlich isotherm is a non-linear model and it has previously been found to suite biochar sorption data well, because it takes adsorption, as well as absorption, into consideration (e.g. Zhang et al., 2010; Okkenhaug et al., 2013).

$$C_{sorb} = K_F C_w^n \qquad \text{eq 12}$$

K_F is the Freundlich adsorption constant (expressed as L/kg if C_{sorb} and C_w are expressed as µg/kg and µg/L, respectively) and n is the Freundlich exponent (unit less), indicating non-linearity. Contaminant concentration in sorbent (C_{sorb}) was calculated by using a rearranged equation of the mass balance, where non-linearity was corrected for (eq 14). Eq 14 was based on eq 13, which again was derived from eq 10, but with the insertion of eq 1 and eq 12.

$$m_{tot} = C_w V_w + K_D C_w M_{soil} + K_F C_w^n M_{sorb} \qquad \text{eq 13}$$

$$Log K_F + n\, Log C_w = Log\ (m_{tot} - C_w V_w - K_D C_w M_{soil}) - Log(M_{sorb}) = \ C_{sorb} \qquad \text{eq 14}$$

Final step in the K_F determination was to run linear regression on the log C_w and log C_{sorb} data sets, giving one log K_F value for each sorption isotherm (log C_w on the X-axis and C_{sorb} on the y-axis). The linear regression analysis draws a straight line through the data plotted, based on the least square method, giving a linear equation (y = ax + b) which corresponds to the linear equation of the Freundlich isotherm model (eq 15):

$$Log\ C_{sorb} = Log K_F + n\, Log C_w \qquad \text{eq 15}$$

4 Results and discussion

The aim of performing these tests was to determine which type of biochar and which amendment dose that most efficiently immobilised PFAS or metal contaminants in soil. The results for PFAS contaminated soil and metal (Pb and Cu) and metalloid (Sb) soil are presented separately in the following subchapters. Results dealing with PFAS are presented in subchapter 4.1 and 4.2, where 4.1 is a characterisation of the soil (the control samples) and 4.2 is the effect of the amendments. Subchapter 4.3 deals with the elements (Pb, Cu, Sb), where 4.3.1 is about the metal sorption isotherm, 4.3.2 is a characterisation of the soil (the control samples), and 4.3.3 is the effect of the amendments.

4.1 PFAS contaminated soil

Control samples were used for both the high and the low TOC soil. The results from these samples described the leaching from unamended soil and were used as comparison to evaluate the efficiency of the biochar amendment. Total PFAS concentrations of PFOS, PFHxS, PFHxA, PFOA, and PFBS in soil are presented in Table 3.1 and leached PFAS concentrations (C_0) are presented in Table 4.1. PFOS constitute 57% of total PFAS leached from the high TOC soil and 82% of total PFAS leached from low TOC soil, with concentrations analysed to be 2900 ng/L and 240000 ng/L respectively. The equilibrium concentration in soil (C_s) and K_D (eq 1) values were calculated using the mass balance (eq 14). K_D values for PFOS in high TOC soil were calculated to be 335 L/kg and 4.2 L/kg in low TOC soil. Table 4.1 summarises these values. A full list of leached concentrations (C_0) of all 23 PFAS analysed can be found in appendix D.

Table 4.1: Eluate concentrations (C_w) of PFOS, PFHxS, PFHxA, PFOA, and PFBS (ng/L), soil concentrations (ng/kg), and K_D (L/kg) for unamended PFAS contaminated soils with high (34.2%) and low (1.61%) total organic carbon (TOC) content. In addition to pH and DOC (mg/L) content.

High TOC soil (34.2%)				Low TOC soil (1.61%)		
PFAS	**Soil (ng/kg)**	**Eluate (ng/L)**	**K_D (L/kg)**	**Soil (ng/kg)**	**Eluate (ng/L)**	**K_D (L/kg)**
PFOS	971 000	2 900	335	1 000 000	240 000	4.2
PFHxS	98 000	1 200	81	< 0	26 000	< 0
PFHxA	5 000	320	15	< 0	7 700	< 0
PFOA	26 180	84	319	2 000	2 800	0.80
PFBS	3 060	82	36	< 0	2 500	< 0
PFAS*	1 200	5100	-	3 800	290 000	-
pH	-	3.97	-	-	7.2	-
DOC (mg/L)	-	330	-	-	17	-

* Sum of the concentrations of 23 PFAS compounds detected in eluate.
- no reported data

The water concentrations were in the range of previously reported concentrations from similar studies, where batch leach tests with PFAS contaminated soil were conducted. Hale et al. (2017) reported total leached PFAS concentrations ranging from 3440 ng/L to 392 000 ng/L, and Silvani et al. (Submitted) (used the same soil as in this thesis) reported total leached PFAS concentrations in high TOC soil of 15 000 ng/L and 273 000 ng/L in low TOC soil. The leached PFAS concentrations of the control samples corresponded well with the concentrations in soil (Table 3.1).

PFOS, constituting 57% and 82% of the leached PFAs concentrations, was the dominant PFAS compound in the contaminated soils. This was not unexpected, as PFOS has been the main component in AFFF up until the early 2000s (Rotander et al., 2015), and PFOS was also the dominant PFAS in the above mentioned studies (Hale et al., 2017; Kupryianchyk et al., 2016). Even though the PFOS concentrations were in the range of previously reported concentrations, they far exceeded the Norwegian soil quality guidelines of 0.1 mg/kg (Forurensningsforskriften, kapittel 1, vedlegg 1).

The results also underline the persistency of PFOS in the environment. Even though the use of PFOS was heavily restricted in 2007 and its use in AFFF was banned (2.3.1.1), high PFOS concentrations were still found in the soil ten years later (sampled in 2017). The inherent stability of the PFAS and the low biodegradation (2.3.2) are key to PFAS's environmental persistence. This highlights the severity of PFAS contamination from firefighting training sites and the urgent need for effective remediation methods in order to abate this problem.

As mentioned in chapter 2.3.1, PFAS is a group of anionic compounds with high affinity for organic carbon. Higgins and Luthy (2006) discovered OC content to be the most important sediment-parameter affecting PFAS sorption, and because of this, PFAS is "pulled" out of the aqueous phase through hydrophobic interactions (van der Waals forces Hale et al.) when discharged into high TOC soil. This was evident when looking at the partitioning coefficients (K_D) of the soil (Table 4.1), where PFOS had K_D values of 335 L/kg in high TOC (34.2%) soil and only 4.2 L/kg in low TOC (1.61%) soil. K_D for low TOC soil agrees with previously reported K_D value (4.7 L/kg), whereas K_D for high TOC soil is higher than previously reported (52.1 L/kg) (Silvani et al., Submitted). If initial contaminant concentrations were similar, it would therefore be expected that the PFAS concentrations at a contaminated site, ten years after contamination, would be higher in high TOC soil than in low TOC soil. Other soil characteristics can be found in appendix E.

4.2 Effect of PFAS remediation

After conducting batch leach tests with PFAS contaminated soils and sorbent materials, it was evident that the sorbent materials increased the system's ability to sorb PFAS. The effect was, however, very different for high and low TOC soils. The biochar had a more positive effect on sorption capacity in low TOC soil than in high TOC soil. In the following subchapters results from the two soils will be presented separately and PFOS will be the only PFAS compound presented in most of the results, due to its dominance in abundance and high environmental concern.

4.2.1 Biochar remediation of low TOC soil

A significant reduction in aqueous PFAS concentrations was found for all biochars tested, with almost complete removal of PFOS from eluate at biochar doses as low as 0.5%. A clear trend was found between water concentrations (C_w) and biochar dose, reflecting an inverse proportional relationship where C_w decrease with increasing biochar dose. This relationship is illustrated in Figure 9 where the biochar dose (%) is plotted against the ratio of contaminant leached (C_w/C_0). The C_w/C_0 ratio was used instead of C_W because it depicts C_w relative to the total initial concentration C_0 (from the unamended control sample).

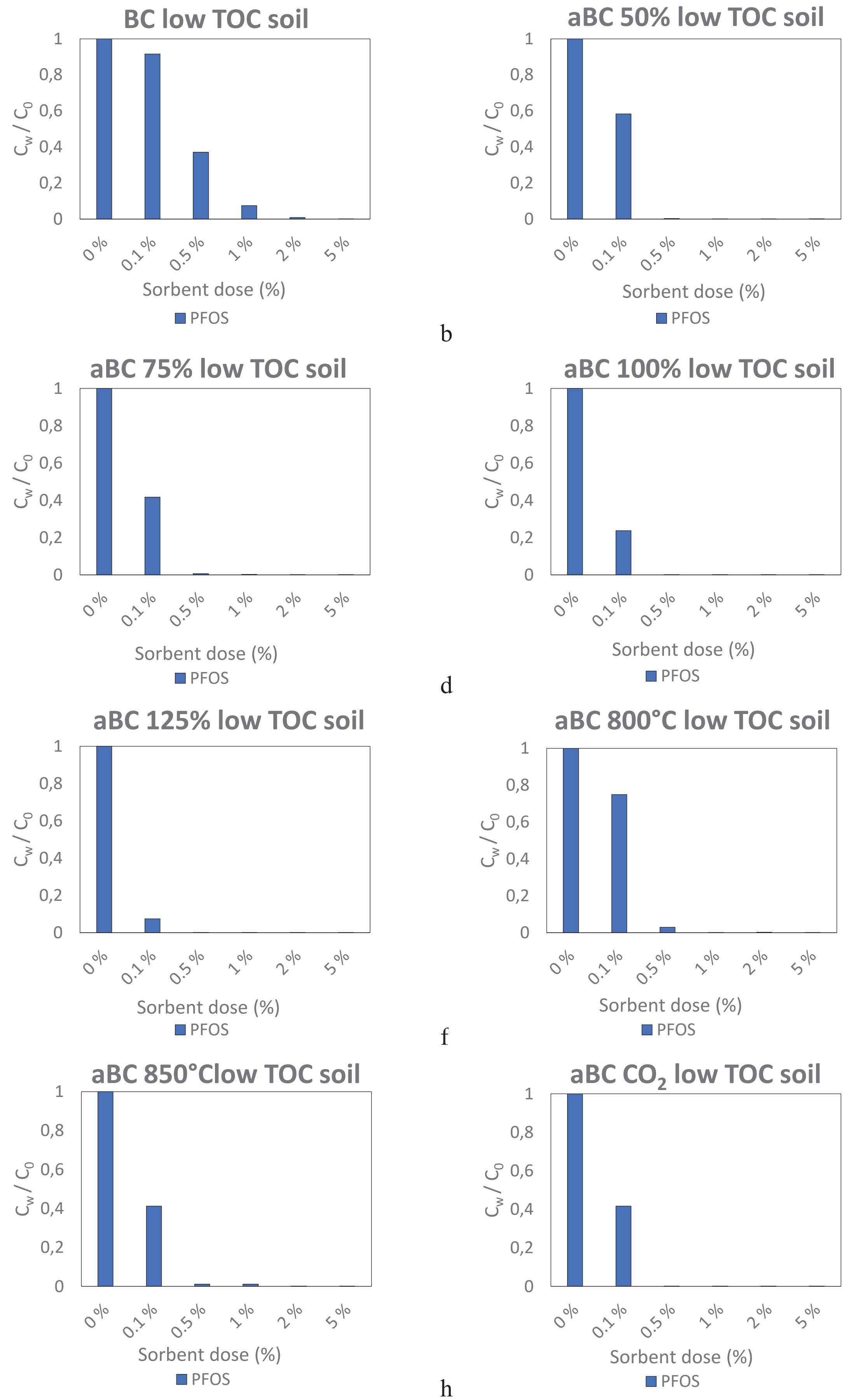


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Figure 9: Reduction in PFOS water concentrations (C_w) as a function of biochar amendment dose (%)

The graphs in Figure 9 give a clear indication of biochar's potential as an effective sorbent for PFOS immobilisation in low TOC soil remediation. The same trend can be seen for the other PFAS in figure F-1 in appendix F. The C_w of PFOS was reduced more than 99% for all biochar materials already at a dose of 0.5%, except non-activated biochar which needed a dose of 2% to achieve the same degree of reduction (Table 4.2). These results are very promising for biochar, because similar PFAS sorption effectiveness has previously only been reported for activated carbon (AC) (Hale et al., 2017). Table 4.2 shows the percentage reduction in leached concentration/sorption onto the solid phase of PFOS relative to biochar type and dose. This can be found in appendix G for PFHxS, PFHxA, PFOA, and PFBS. Based on these results, BC seems to be the least effective sorbent and that aBC125% is the most effective sorbent, although differences between the activated biochars were <1% (Table 4.2).

Table 4.2: Sorption of PFOS, as a percentage of total PFOS concentration, after amendment of low TOC soil (1.61% TOC) with 8 biochar materials at 5 different doses.

Amendment dose (%)	**BC**	**aBC 50%**	**aBC 75%**	**aBC 100%**	**aBC 125%**	**aBC 800°C**	**aBC 850°C**	**aBC CO_2**
0.1	8.33	41.67	58.33	76.25	92.5	25	58.75	58.33
0.5	62.92	99.65	99.38	99.89	99.98	97.13	98.79	99.8
1	92.50	99.95	99.74	99.96	99.98	99.87	98.88	99.95
2	99.21	99.95	99.96	99.98	99.96	99.78	100*	99.97
5	99.86	99.83	99.94	99.96	99.9	99.88	100*	99.89
* C_w <LOD, 100% sorption assumed								

To further investigate the effect of increased activation and pyrolysis temperature on biochar's sorption capacity, percent activation and pyrolysis temperature were plotted against percentage reduction in PFOS water concentrations (Figure 10). These parameters were expected to influence biochar's sorption capacity positively, because they previously have been shown to do so for other carbonaceous sorbent materials like AC (Ahmad et al., 2014). In Figure 10a, where degree of biochar activation was the independent variable, BC (0% activation), aBC 50%, aBC 75%, aBC 100%, and aBC 125% were included, and in Figure 10b, where pyrolysis temperature was the independent variable, aBC 800°C, aBC 850 °C, and aBC 100% (900°C) were included.

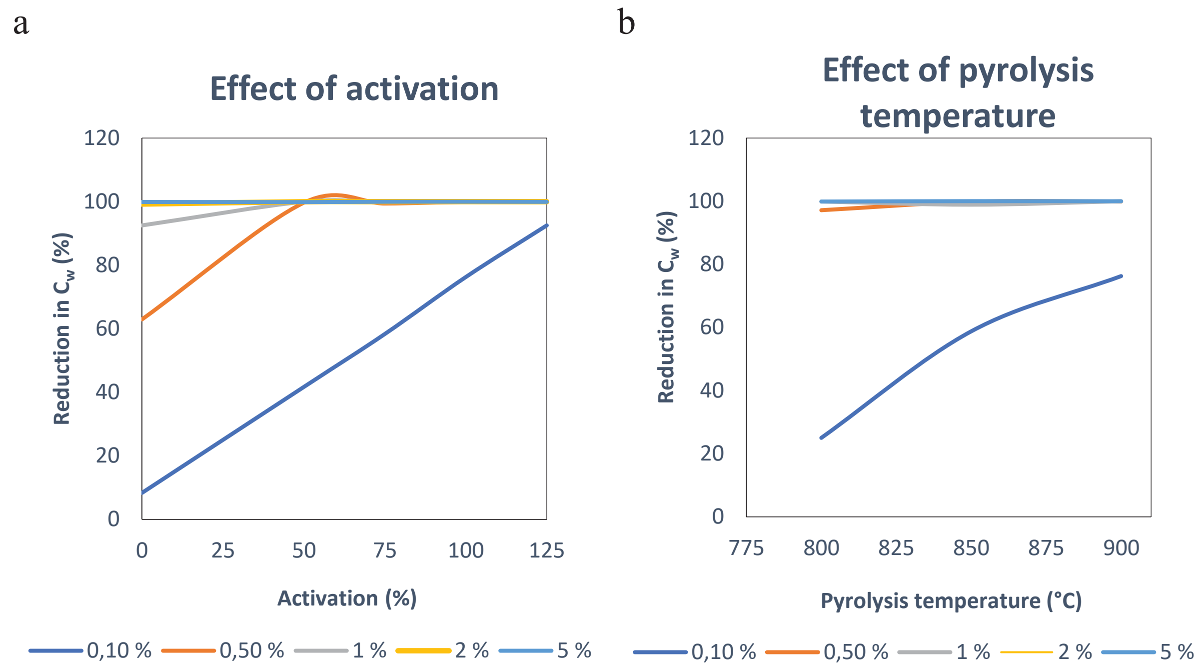

Figure 10a and b: PFOS sorption (presented as percentage reduction in pore water concentration) as a function of a) degree of biochar activation and b) pyrolysis temperature, plotted for each amendment dose (0.1%, 0.5%, 1%, 2%, and 5%).

From Figure 10 a clear trend in sorption effectiveness can be seen both related to degree of activation and pyrolysis temperature. Both graphs in Figure 10 show that an increase in the independent variable, degree of activation and pyrolysis temperature respectively, cause an increase in sorption effectiveness. These trends were, however, only visible for the lowest amendment dose of 0.1%. Due to the high effectiveness of the biochar materials, the trend in sorption for doses above 0.1% was almost a complete reduction of PFOS C_W. This is illustrated by the overlapping of the doses forming a horizontal line in the top of each graph. The lower effectiveness of BC can be seen in Figure 10a, where both 0.5% and 1% doses have lower than 99% reduction in C_W for the non-activated biochar.

A comparison between PFOS, PFHxS, and PFBS was also conducted to relate C chain length to sorption, and further if the movement of the shorter PFAS could be compared to that of PFOS. Previous studies have shown that sorption of PFAS increase with every CF_2 moiety added to the molecular structure of the compound (Higgins & Luthy, 2006), which indicates that PFOS with eight C would have a stronger sorption than PFHxS with six C and PFBS with four C. This was tested with the data from the thesis by plotting number of C in the C chain against sorption (% reduction in leached concentration) for two of the biochar materials (BC and aBC 125%); Figure 11 . BC and aBC 125% were chosen to see if the trend would be the same for the least effective biochar and one of the most effective biochars.

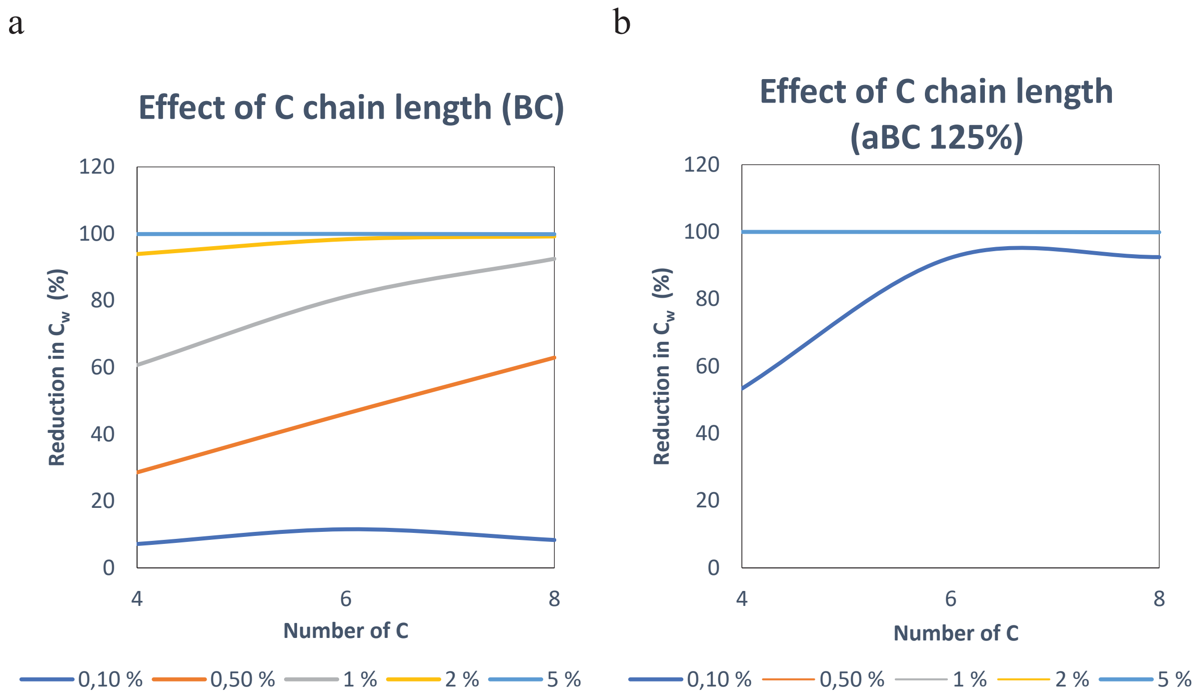

Figure 11a and b: PFAS sorption (presented as percent reduction in C_w*) for a) BC and b) aBC 125%, as a function of C chain length represented by PFBS with 4 C, PFHxS with 6 C, and PFOS with 8 C.*

From Figure 11 it looks like the expectations were met and that increased C chain length correlated with increased sorption. At 0.1% the aBC125% sorbent only caused a 50% reduction in PFBS C_w, whereas PFHxS and PFOS were reduced by 92% (ref appendix G). Higher dose of this sorbent caused almost 100% reduction in C_w regardless of C chain length. Reduction in C_w following BC amendment was dependent of C chain length at doses below 2%, with increased sorption as a result of increased C chain length. The same results were reported by Gellrich et al. (2012), but the authors also found that longer chained PFAS could displace shorter PFAS from binding sites in soil. Because the soil investigated in this thesis was dominated by PFOS, the lower sorption capacity for PFBS could therefore either be a result of short C chain or displacement by PFOS, or both.

From a remediation point of view all sorbents tested for PFAS immobilisation in low TOC soil could be recommended, but completely activated biochar (aBC125%) would probably offer the most effective contaminant sorption. However, in real world remediation costs must be considered. For this soil, the cost of activating biochar must be weighed against the cost of adding a higher dose of non-activated BC as both alternatives would give the needed remediation effect.

4.2.1.1 K_D and log K_F calculations

Because the sorbent materials were so efficient, the range of the constructed sorption isotherms were too small for proper log K_F values to be determined. Therefore, log K_D values from the lowest dose amendment (0.1%) and intermediate dose (1%) where PFOS water concentrations were completely removed, were compared to illustrate the increase in sorption capacity obtained after sorbent amendment (Table 4.3). These values can be viewed as "biochar and soil" K_D values. The K_D value for PFOS in unamended soil was calculated to be 4.2 (L/kg) (Table 4.1), corresponding to a log K_D value of 0.62.

Table 4.3: log K_D values for PFOS in low TOC soil (1.61%) after amendment with 8 biochar sorbents at amendment dose of 0.1% and 1% (of d.w.)

Amendment	0.1%	1%
BC	3.1	4.2
aBC 50%	4.0	6.4
aBC 75%	4.3	5.7
aBC 100%	4.7	6.6
aBC 125%	5.2	6.8
aBC 800°C	3.7	6.0
aBC 850°C	4.3	5.1
aBC CO_2	4.3	6.4

From Table 4.3 it is evident that sorbent amendment of 0.1% increased the soil's PFAS sorption capacity, because the K_D increased approximately 300-40 000 times (log K_D by 2.5-4.5 units) and 1% amendment dose increased the K_D by approximately 4 000 – 1 600 000 times (log K_D by 3.62-6.17 units). aBC125% caused the highest increase at both doses, demonstrating the same sorption trends as shown in the previous chapter. An increase in log K_D values ranging from 3-5 log units was also observed for the four other PFAS, but these results were more varied than for PFOS and can probably be attributed to their low soil abundance and their different sorption behaviour (Figure 11). A list of log K_D values for PFHxS, PFHxA, PFOA, and PFBS can be found in appendix H. The K_D value at 1% for BC is similar to previous reported K_D values for PFOS to biochar in soil, but K_D values for the activated biochars are similar to AC K_D (supporting information)(Kupryianchyk et al., 2016), indicating that biochar sorption can be compared to AC after activation.

The reason why optimal isotherms were not obtained was because the effect of the biochar sorbents was stronger than expected. The doses selected were expected to generate gradually reduced pore water concentration, ergo creating an isotherm, but because the biochar materials were so effective this gradual reduction was not achieved. Another reason why the sorption isotherms were not optimal may have been because natively contaminated soil was used instead of spiked PFAS solutions. As mentioned earlier natively contaminated soils were chosen because it would give a more realistic picture of PFAS sorption to biochar, and hence a more realistic reflection of what the actual soil remediation would be like. Knowledge about biochar sorption in the presence of soil is also scarce and therefore in need of further research.

4.2.1.2 Assessment of sorbent properties

The sorbent material surface area (SA), pore volume, and element composition have previously been reported to be important sorbent characteristics determining sorption effectivity (Kupryianchyk et al., 2016). To understand the differences in sorption efficiency observed for the sorbent materials, these characteristics (Table 3.3) were investigated in relation to sorption. SA found by N_2 adsorption (pores >1.5 nm) is the standard method for measuring SA and also the cheapest, but Kwon and Pignatello (2005) found that SA determined by CO_2 adsorption (0.4-1.5 nm) is better and give more realistic measurements of hydrophobic microporosity for biochar in soils. Therefore, SA based on CO_2 adsorption will be used in the following discussion.

SA in all sorbent materials used in this experiment were found to be in a similar range as SA for AC (Hale et al., 2017; Silvani et al., Submitted), which may explain the general high sorption effectiveness observed for the sorbents, but it does not explain the differences between the sorbents. SA (m^2/g) was therefore plotted against K_D values for 0.1% amendment dose to see if SA correlated with sorption (Figure 12a). C:O ratio, which can be used as a proxy for polarity and hydrophobicity of the biochar's surface, and total C, which can be used as a proxy for aromaticity (Kupryianchyk et al., 2016), were also plotted against log K_D to see if there was a correlation (Figure 12).

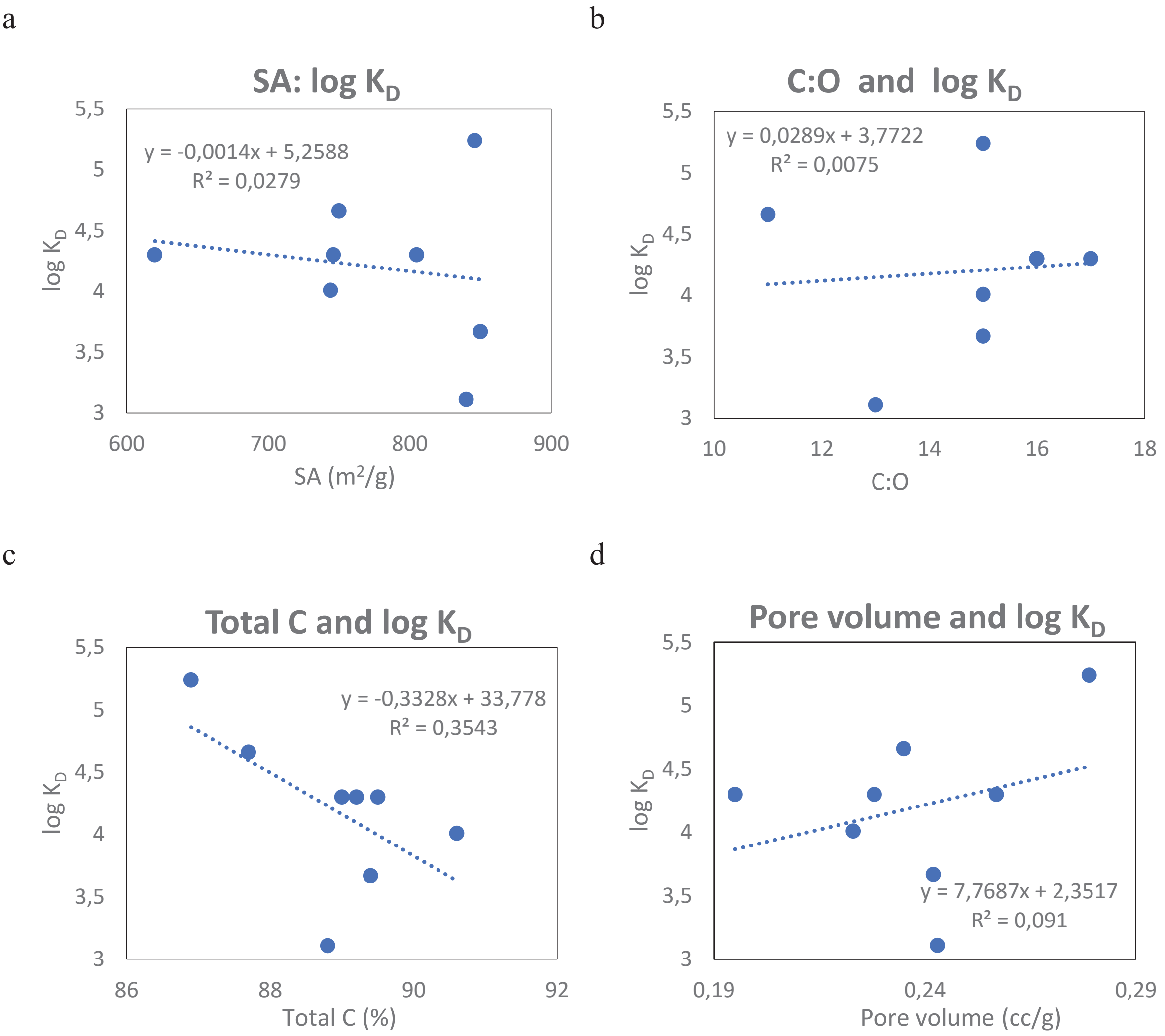

Figure 12a-d: Correlation between sorption (log K_D) and a) surface area (log SA), b) C:O, c) total C, and d) pore volume in biochar sorbents.

No clear trends were found in Figure 12 between sorption and the investigated sorbent properties. Total C (aromaticity) seemed to have a slight negative correlation with sorption (Figure 12c), which was unexpected and opposite to results from other studies (Kupryianchyk et al., 2016). However, the correlation was poor (with R^2 of 0.35) indicating that other unknown factors affected sorption more than sorbent aromaticity. Generally, there was a lot of spread in the data and no conclusions about sorption mechanisms could be made from these results.

These results show a great potential for activated biochar produced from waste timber at high pyrolysis temperature (900°C) for PFAS remediation in low TOC soil. Increasing degree of activation did increase sorption capacity with the completely activated biochar (aBC125%) being the most effective sorbent. These are new results never been reported before, highlighting the promise of activating biochar, and further research on this biochar treatment is warranted.

A distinct effect of amendment dose was observed in these results, with almost complete PFAS reduction already at a dose of 0.5% for all the activated biochars, no matter the degree of activation.

4.2.2 Biochar remediation of high TOC soil

Biochar sorbent remediation of high TOC soil contaminated with PFAS gave more varied results than in low TOC soil. The only sorbent that managed an almost complete reduction of PFOS from the water phase was the 125% activated biochar with a 98.59% reduction at amendment dose of 5%. No clear, general trend of increased PFOS sorption as a result of increased sorbent dose could be observed when plotting C_w/C_0 against sorbent dose (Figure 13). But at the highest amendment dose (5%), the PFOS C_w were visibly reduced for all biochar sorbent materials.

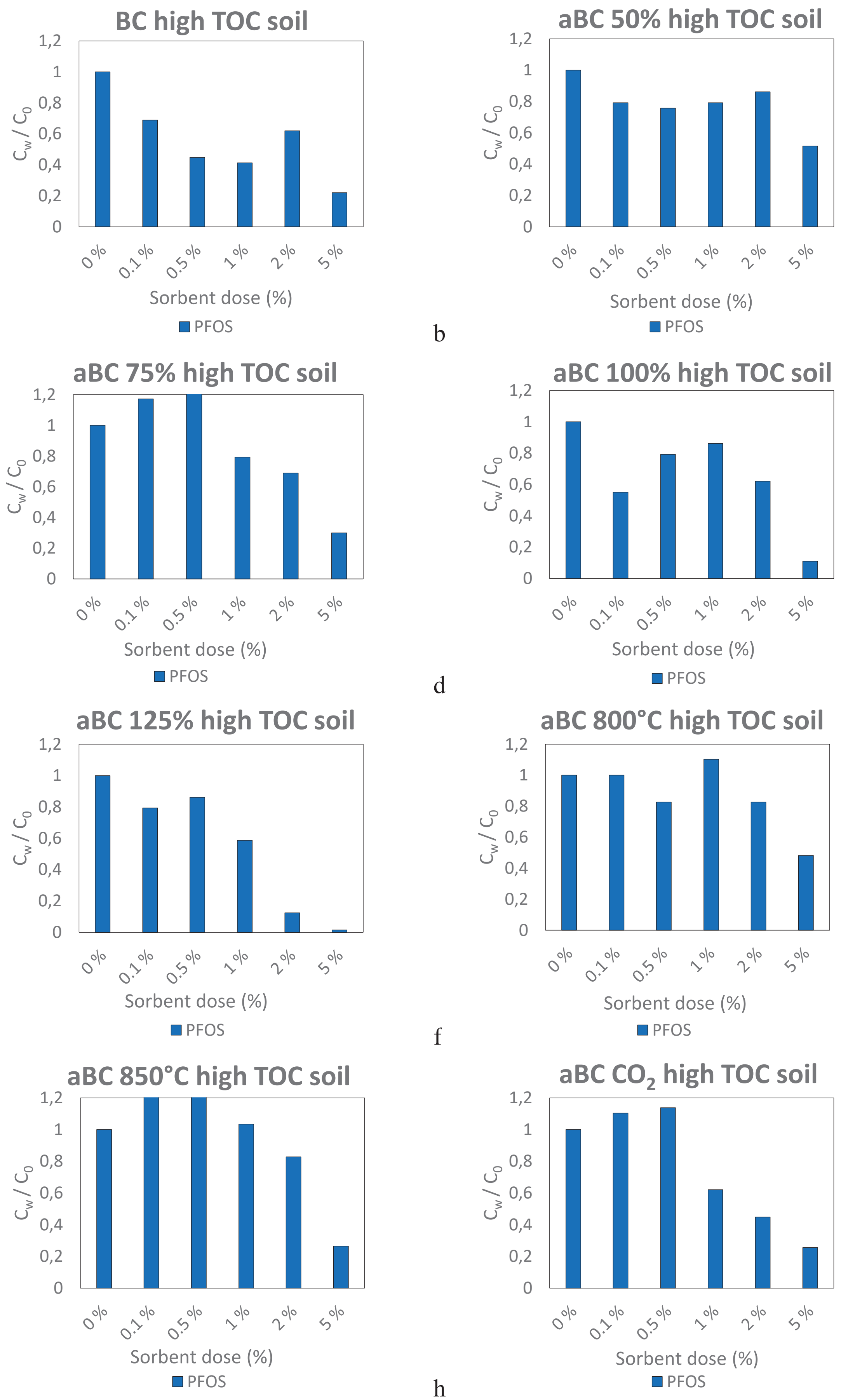

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Figure 13a-f: Reduction in eluate concentrations (Cw) as a function of biochar amendment dose (% of d.w.).

From Table 4.4 it is also apparent that the PFOS sorption capacity of the biochar materials were less effective when added to a system with high TOC content, than to a system of low TOC content. Total PFAS sorption above 60% was not reached until a dose of 5% was added for any of the biochar materials, except for aBC 125% which causes an 89.02% reduction in total PFAS concentration at amendment dose of 2% (appendix G). Some of the biochar sorbents even caused a slight increase in PFOS mobility after amendment (Table 4.4).

Table 4.4: *Sorption of PFOS as a percentage of total concentration after amendment of high TOC soil (34.2% TOC) with 8 biochar materials at 5 different doses.*

Amendment dose (%)	**BC**	**aBC 50%**	**aBC 75%**	**aBC 100%**	**aBC 125%**	**aBC 800°C**	**aBC 850°C**	**aBC CO_2**
0.1	31.03	20.69	< 0	44.83	20.69	0	< 0	< 0
0.5	55.17	24.14	< 0	20.38	13.79	17.24	< 0	< 0
1	58.62	20.69	20.69	13.79	41.38	< 0	< 0	37.93
2	37.93	13.79	31.03	37.93	87.59	17.24	30.83	55.17
5	77.93	48.28	70	88.97	98.59	51.72	83.33	74.48
< 0 indicate a mobilisation of PFOS								

Even though the general sorption of PFOS to activated biochar was less effective in high TOC soil than in low TOC soil, a complete reduction in PFOS C_w may not be required for a sufficient remediation in high TOC soil, due to its much lower initial leached PFOS C_w. By comparing a sorption effect of 58% in high and low TOC soil, the resulting C_w was 1200 ng/L for high TOC soil (obtained by 1% BC) and 100 000 ng/L for log TOC soil (obtained by 0.1% aBC75%), this point is highlighted (appendix D and G).

Non-activated biochar has previously been shown to have low sorption effect in high TOC soils (Kupryianchyk et al., 2016), but complete activation has in this thesis shown to increase biochars sorption capacity (BC vs. aBC125%). Therefore, activation of biochar looks promising, as it can immobilise PFOS in both high and low TOC soil, but further research on sorption effect related to amendment dose is suggested, as this connection was not clear form this thesis.

To explain the increased mobility of PFOS after amendment with some of the sorbent materials, pH and DOC changes was investigated. Due to its chemical structure (hydrophilic head group and hydrophobic C chain body), it is likely that both "hydrophobic and electrostatic effects influence anionic [PFAS] sorption" (Higgins & Luthy, 2006) – which both can be influenced by pH and DOC. The general trend for all sorbents was, as expected (ref chapter 2.4.3), a slight pH increase and a slight DOC decrease following increased amendment dose (figure E-1 and

E-2 in appendix E). pH and DOC measurements for the sorbents that caused an increase in PFOS mobility (aBC75%, aBC 800°C, aBC850°C, and aBC CO_2) did not deviate from these norms. This indicates that PFOS mobilisation was not affected by pH or DOC changes and PFOS mobilisation could therefore be explained by factors other than those investigated here.

The sorbent that was observed to have the highest PFOS sorption capacity (aBC125%) did, however, induce pronounced pH and DOC changes compared to the other sorbents (2 pH units increase and 4 times reduced DOC C_w) (figure E-1 and E-2 in appendix E). pH reduction has previously been reported to correlate with increased sorption for organic compounds (Higgins & Luthy, 2006), which does not fit with the results from this thesis. An explanation for the deviation from literature may be that PFOS sorption to aBC125% was so strong that opposing pH and DOC forces was not strong enough to affect PFOS sorption to any great extent. However, other soil specific factors than those investigated here could also be the explanation.

From a remediation point of view amendment with completely activated biochar at a high amendment dose (5%) would be recommended. If the cost of this remediation is justified by the effect obtained, it would be a feasible alternative in real world soil remediation.

4.2.2.1 K_D and log K_F calculations

The range of PFOS sorption isotherm was also too small for high TOC soil. Therefore, log K_D values from intermediate dose (1%) and the highest dose (5%) where PFOS water concentrations were most effectively removed, were compared to illustrate the additional sorption capacity obtained after sorbent amendment (Table 4.5). K_D value for PFOS in unamended soil was calculated to be 335 (L/kg) (Table 4.1), corresponding to a log K_D value of 2.5.

Table 4.5: log K_D values for PFOS in high TOC soil (34.2%) after amendment with 8 biochar sorbents at amendment dose of 1% and 5% (of d.w.).

Amendment	1%	5%
BC	4.7	4.4
aBC 50%	4.0	3.8
aBC 75%	4.0	4.2
aBC 100%	3.7	4.8
aBC 125%	4.4	5.7
aBC 800°C	3.6*	3.9
aBC 850°C	3.6*	4.3
aBC CO_2	4.3	4.3
* 2% amendment dose was used		

From Table 4.5 it is evident that sorbent amendment of 1% increased the soils PFAS sorption capacity by approximately 10-100 times (1.0-2.2 log units) and 5% amendment dose increased the log K_D by approximately 20-1600 times (1.28-3.15 log units). At 5% dose aBC125% was markedly better than the other biochar sorbents and the log K_D value could be compared to previous log K_D values measured for AC (Kupryianchyk et al., 2016). A list of log K_D values for PFHxS, PFHxA, PFOA, and PFBS can be found in appendix H.

For biochar remediation to have maximum effect the biochar K_D must be (much) larger than the soil K_D. Because the low TOC soil had a lower K_D than the high TOC soil, corresponding to a larger difference in soil K_D and biochar K_D, the sorption to activated biochar was more effective in low TOC soil than in high TOC soil.

4.2.2.2 Assessment of sorbent properties

The same sorbent parameters as described in chapter 4.2.1.2 were investigated to determine the most important sorption mechanism for PFOS sorption to biochar in high TOC soil.

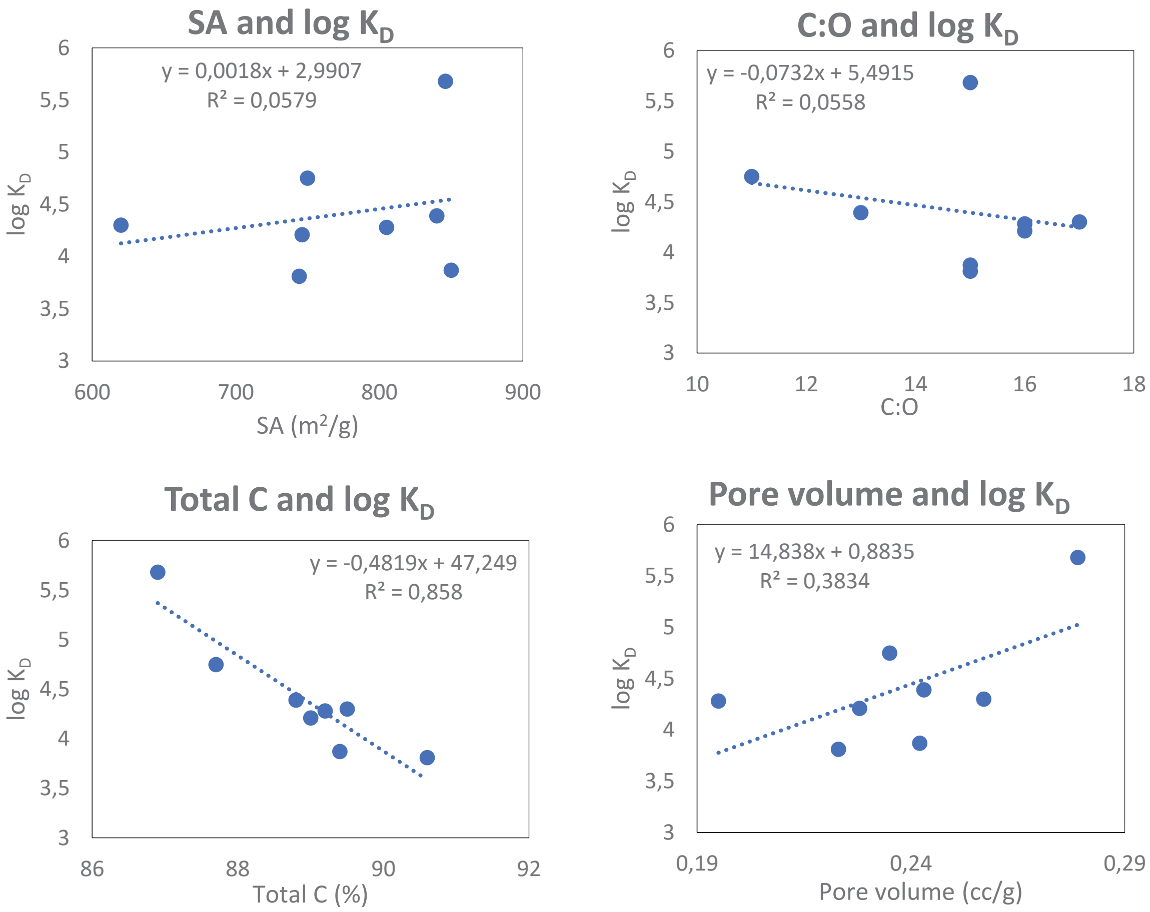


Figure 14: Correlation between sorption (log K_D) and a) surface area (log SA), b) C:O, c) total C, and d) pore volume in biochar sorbents.

In this soil, sorbent aromaticity was also found to be the most important sorbent property affecting PFOS sorption (Figure 14), but now with a prominent correlation (R^2 of 0.86). This indicating that less aromaticity gives a better sorption. These results were, as mentioned in chapter 4.2.1.2, the opposite of what was expected, and further research is warranted to get a better understanding of sorbent properties and sorption effect. Pore volume of the sorbent was also shown to be a sorbent property which could affect sorption; however, the correlation was weak (R^2 of 0.38) and no conclusion on sorption mechanism to biochar sorbents can be made from the results presented here.

Consequently, the same results related to PFOS soil remediation with activated biochar was found for both high and low TOC soil. Fully activated biochar produced from waste timber at high pyrolysis temperature (900°C), was the most effective sorbent material tested and from a remediation point of view, this would be the recommended soil amendment. If the cost of this remediation is justified by the effect obtained, it would be a feasible alternative in real world soil remediation. However, more data is needed to understand the factors determining the sorption of PFAS to these sorbents, and therefore, further research is warranted. Multiple linear regression could for example be done, to investigate if the combination of certain factors/properties could explain more of the variation in the sorption behaviour observed for the different biochars.

4.3 Sorption of Lead, Copper, and Antimony

4.3.1 Metal sorption isotherm

Sorption isotherm tests were conducted for all sorbent materials with spiked concentrations of Cu, Sb, and Pb. This was done to determine the sorption capacity of the sorbents for the three elements in a “clean system” without soil present. These results would give indications of what sorption effect could be expected in the soil remediation (ref upcoming chapters). However, a reduction in biochar’s sorption efficiency for contaminants has previously been reported when soil is present (Kupryianchyk et al., 2016), and should therefore also be expected here.

60% of the analysed samples had concentrations below the limit of quantification (LOQ) or limit of detection (LOD). Sorption isotherms of the sorbent materials could therefore not be determined properly, due to lack of data. The control samples, only containing spiked metal solution, were also analysed to contain 4-16 times lower metal concentrations than intended, indicating that solution preparation did not go as planned. The results could imply a high sorption effectivity of metals to the sorbents, as the metals were completely removed from the spiked solution, but because of the uncertainty associated with the spiked concentrations the data from this experiment is not presented here.

Inaccuracies in the stock solution preparation and the dilution series was most likely the reason why metal concentrations were much lower than expected. And during these procedures it is most likely insufficient dissolution of the metals salts that contributed most to the low spiked concentrations. The salts in the mixed metal solution, for example, needed steering over night to visibly disappear in the solution and did most likely not dissolve properly. To minimise error in later studies like this, a control of the stock solution should be included, not only one of the diluted concentrations.

4.3.2 Characterisation of unamended soil

When remediating a contaminated site, the leaching potential of the contaminants (in this case Cu, Sb and Pb) needs to be considered, because leachability determines the transport of the contaminants. The leachability of Cu, Sb, and Pb from unamended shooting range soil was determined by measuring water concentrations (C_w) of the elements in the eluate from the batch leach test. These results were then used to express the potential leaching concentration of contaminants from the soil (mg/kg), following calculations in NS-EN 12457-2 standard (Standard Norge, 2003). These concentrations are listed in Table 4.6 together with C_w (µg/L), total soil concentrations (mg/kg), and K_D values, as well as pH and DOC (mg/L) concentrations.

Table 4.6: Total concentration in soil (mg/kg), leached concentration from soil (mg/kg) and water concentrations (µg/L) of Cu, Sb, and Pb, and partitioning coefficients, K_D (L/kg) for unamended metal contaminated soils with high (12.6%) and low (4.7%) total organic carbon (TOC) content. In addition to pH and DOC (mg/L) content for the soils.

	High TOC soil (12.6%)				**Low TOC soil (4.7%)**			
	Total Soil (mg/kg)	**Leached (mg/kg)**	**Eluate (µg/L)**	**K_D (L/kg) (log K_D)**	**Total Soil (mg/kg)**	**Leached (mg/kg)**	**Eluate (µg/L)**	**K_D (L/kg) (log K_D)**
Cu	110	0.91	91	1199 (3.08)	380	0.94	94	4033 (3.61)
Sb	209	1.10	110	1899 (3.28)	207	3.40	340	607.6 (2.78)
Pb	6 600	1.10	110	59990 (4.78)	4 300	1.70	170	25284 (4.4)
pH	-	-	7.16	-	-	-	7.88	-
DOC (mg/L)	-	-	34	-	-	-	25	-

Even though the soil was classified as hazardous waste (ref chapter 3.1.2), the leaching of Pb was modest (Table 4.6), not exceeding the limit of ordinary waste landfills (Avfallsforskriften, 2004, vedlegg II, 2.3.1). These results indicate that there was a large pool of Pb in the soil, but probably due to soil properties like TOC content and pH only a small fraction of it was mobile. This is also evident from the high K_D values. The Sb leached concentrations were above the leaching limit for ordinary waste landfills (0.7 mg/kg) and must therefore be put on landfills for hazardous waste (5 mg/kg). Total Sb concentrations were much lower than Pb, but due to lower sorption capacity for this element (represented by the K_D values), especially in low TOC soil, the need to immobilise Sb and prevent element transport would be the most prominent. Leached Cu concentrations were below the leaching limits of inert waste (2 mg/kg)(Avfallsforskriften, 2004) and therefore reduction in leaching and transport of this element would be of less importance regarding remediation. Remediation focus should be on immobilisation of Pb and Sb, as the potential for leaching and further transport of these elements are high.

Compared to similar studies on shooting range soils, the K_D values reported here are in the range of previously reported K_D values from shooting range soil (Okkenhaug et al., 2018; Silvani et al., Submitted). Silvani et al. (Submitted) reported slightly lower K_D values for Pb and Sb than reported here, but the authors also found that the K_D values for Pb and Sb were higher for soil with high TOC content (10.2%) than soil with low TOC content (5.2%), indicating that OC is important in sorption of these elements. However, Okkenhaug et al. (2018) pointed out the shooting range soil may contain bullet fragments which would affect the K_D values. The solid metal(loid) bullet fragments would be analysed as a part of the total concentrations in the soil, even though it was not a result of sorption to the solid phase at equilibrium, and hence the K_D values would be misrepresented as higher being than it should.

4.3.3 Effects of soil remediation

The remediation effect of biochar, amended biochars, and zero valent iron in metal contaminated soils varied substantially, both among the sorbent amendments, as well as among the three elements. The effects of the sorbent materials will be presented individually in the following chapters and then the results will be compared to find the most effective sorbent for shooting range soil remediation. A list of all C_w and percent sorption of elements can be found in appendix I, Table I-1 and Table I-2, respectively.

4.3.3.1 Biochar (BC) sorbent

Non-enriched biochar (BC) showed little positive effect on leached metal concentrations, and the only visible reduction in C_w was observed for Cu in high TOC soil (Figure 15). Negative effect on leached metal concentrations was, however, observed for Pb and Sb in high TOC soil and Cu in low TOC soil (Figure 15), indicating that BC amendment increased the mobility of the metals rather than immobilising them.

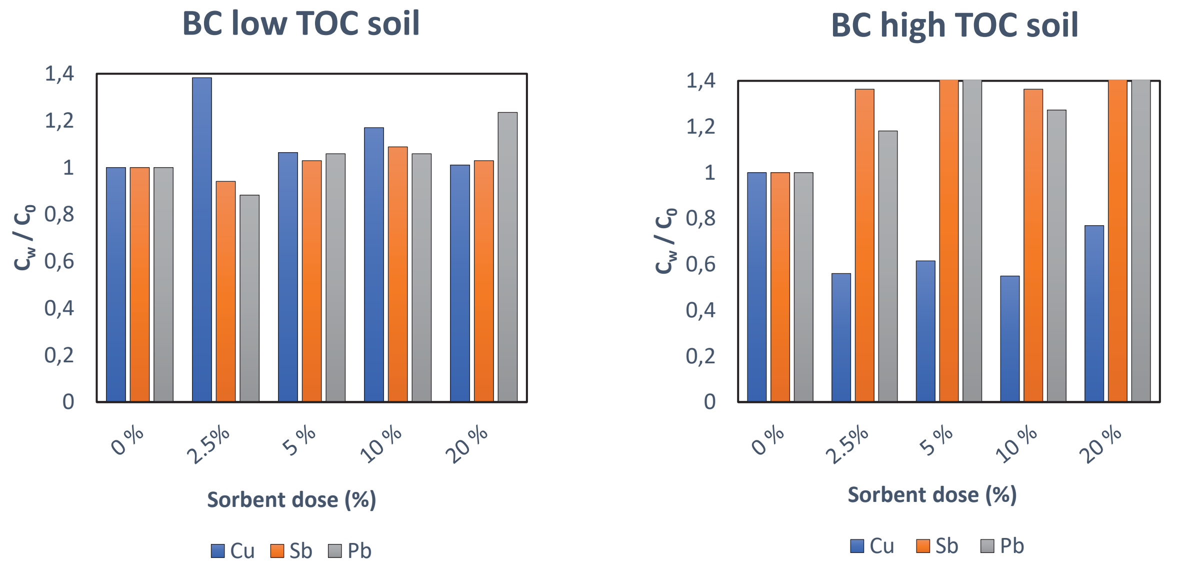


Figure 15: Reduction in leached element (Pb, Cu, and Sb) concentration as a function of biochar (BC) dose (% of d.w.) in soils with 4.7% and 12.6% TOC content respectively.

Biochar is an alkaline material (ref. chapter 2.4.3) and when added to soil it may increase pH and consequently DOC concentrations. As these parameters mainly determine the mobility of metals in soil, pH and DOC concentrations were therefore investigated to evaluate if the metal immobilisation was a result of the BC amendment or not.

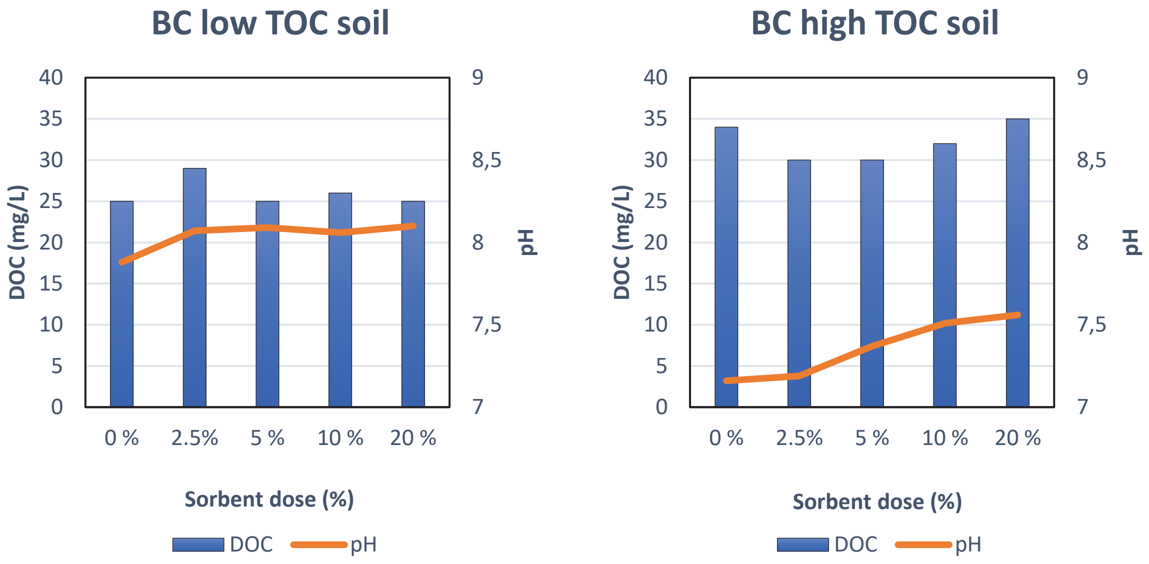


Figure 16: Changes in pH and DOC (mg/L) as a result of biochar (BC) amendment at different doses (% of d.w.) in soils with 4.7% and 12.6% TOC content respectively.

From Figure 16 it is evident that the biochar amendment caused a slight increase in pH (0.22 and 0.4 unit increase), which may explain some of the increased Sb mobility. Sb predominantly exists as an anion ($Sb(OH)_6^-$) in soil and increase in pH will lead to a reduction in positively charged surfaces in soil and AEC (ref. chapter 2.4.4), and hence increase Sb mobility. These results were supported by similar findings in previous studies (Okkenhaug, 2012). Pb mobility could be explained by an increase in DOC, because Pb, together with Cu have previously been found to have a high affinity to DOC (Okkenhaug et al., 2016). The peak in Cu C_w in low TOC soil at amendment dose of 2.5% (Figure 15), support this theory, because there is a corresponding peak in DOC in Figure 16 for the same dose. However, Pb mobility in high TOC soil was most likely not determined by DOC, because Pb C_ws were high already at initial amendment doses of 2.5% and 5% where DOC concentrations were low.

Another factor that may explain the increased Pb mobility after BC amendment is competition for sorption sites by other cations, like Ca^{2+}. This has previously been reported to increase the dissolved concentration of Pb (Klitzke & Lang, 2009). Silvani et al. (Submitted) analysed biochar made from the same waste timber as the biochar used in this thesis to contain extensive amounts of Ca^{2+} (23 g/kg). Although Ca^{2+} leached concentrations from this biochar were only analysed to be 3.97 mg/L, the biochar amendments in this thesis may have contributed with Ca^{2+} displacing Pb in the soil accounting for the Pb mobility following BC amendment.

Low sorption capacity of biochar was expected (ref. chapter 2.4.5), but the immobilisation of metals was not. Mobility of Sb and Cu may be attributed to increase in pH and DOC, but Pb mobility was likely determined by factors other than those investigated here. From a remediation point of view this sorbent material would not be recommended for shooting range soil. Cu was the only immobilised element (the least problematic element) and Pb and Sb were mobilised – the opposite of the desired effect after amendment.

4.3.3.2 Zero valent iron (ZVI) sorbent

Amendment with pure ZVI was highly effective for Sb (Figure 17), with more than 90% reduction in C_w already at amendment dose of 5% in both soils. Pb was also effectively removed from the pore water by ZVI, with 100% reduction in C_w from 10% sorbent dose for both soils (concentrations were below limit of detection and complete sorption was assumed), but in high TOC soil at amendment dose of 5%, leached Pb was only reduced by 18% to a C_w of 90 µg/L. Reduction of Cu C_w was also reduced by ZVI amendment, with maximum reduction of 75% at 5% dose in low TOC soil and 83% at 2.5% dose in high TOC soil. However, an increase in sorbent dose did not correlate with increased sorption.

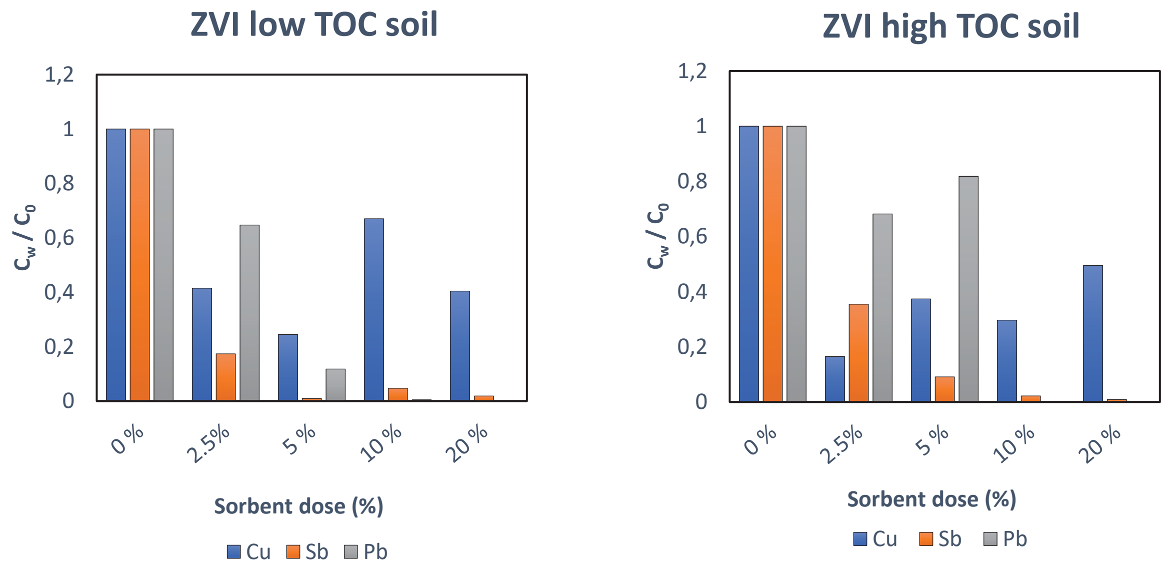


Figure 17: Reduction in leached element (Pb, Cu, and Sb) concentration as a function of zero valent iron (ZVI) dose (% of d.w.) in soils with 4.7% and 12.6% TOC content respectively.

Oxidation of zero valent iron (Fe^0) forms highly reactive, amorphous hydroxides ($Fe(OH)_3$) (ref. chapter 2.4.5), which are very strong sorbents for Sb in soil (Wilson et al., 2010). This can explain the results shown in Figure 17, where Sb C_w were effectively reduced following ZVI amendment. However, this is a highly pH dependent sorption mechanism, with maximum sorption of Sb(V) (the dominant Sb species documented in shooting range soils) at pH < 6 (Okkenhaug & Mulder, 2011). The pH in the soil before and after ZVI amendment was > 6 (Figure 18), indicating either that maximum sorption was not acquired for the 90% reduction of Sb observed in water (due to the high affinity between Sb and hydroxides), or that Sb may have been present as Sb(III) which has a wider pH sorption range (Okkenhaug & Mulder, 2011). Hydroxides can also immobilise cations as Pb and Cu in soils, but sorption of these elements are often affected by pH and DOC and to further investigate the retention/leaching of the metals, pH and DOC were therefore investigated (Figure 18).

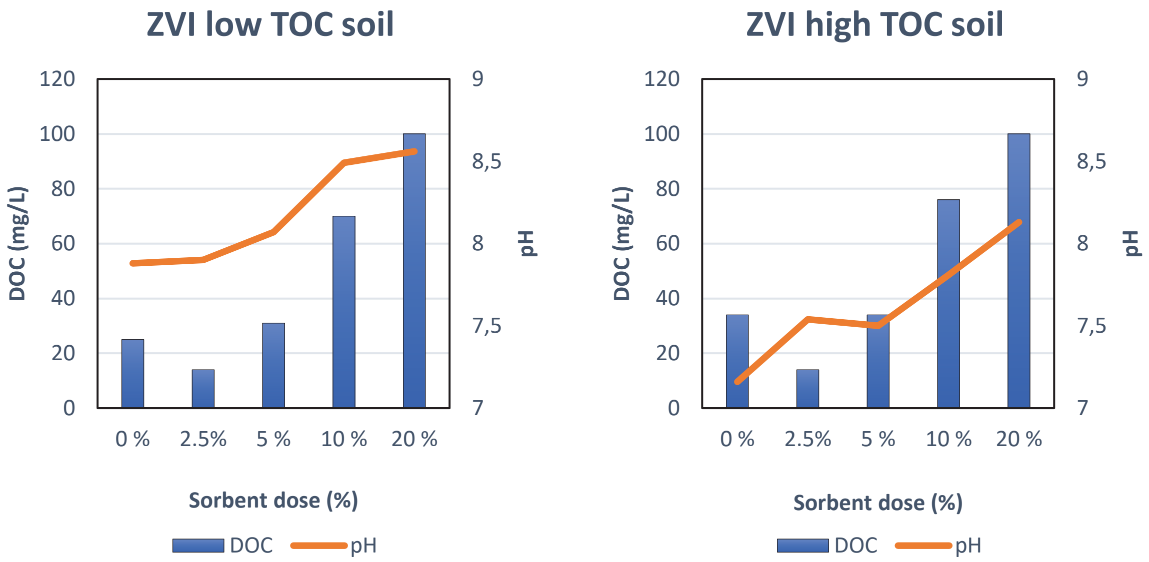


Figure 18: Changes in pH and DOC (mg/L) as a result of zero valent iron (ZVI) amendment at different doses (% of d.w.) in soils with 4.7% and 12.6% TOC content respectively.

An increase in pH was observed after ZVI amendment for both soils (0.7 and 1 units), which most likely was attributed to the initial acid-reducing oxidation of Fe^0 (eq 4 and 5). The increase in pH may explain Pb removal from the water phase, but not leaching of Cu. For both soils DOC was initially immobilised by 2.5% sorbent amendment, but then a substantially mobilisation occurred (from 30 mg/L to 100 mg/L) at highest amendment dose, suggesting that Cu may have leached from the soil due to increased DOC concentrations. However, the data does not fully overlap for DOC and Cu C_W, indicating that other factors than those investigated here affected Cu leaching. This is also the case for the peak in Pb C_W at 5% dose in high TOC.

From a remediation perspective this amendment could be recommended for shooting range soil, because leachable concentrations of both Pb and Sb were reduced to limits of inert waste at the two highest amendment doses. Cu leached concentrations were not effectively reduced, but the soil would still be below the leaching limit for inert waste landfills.

4.3.3.3 ZVI enriched biochar (BC-ZVI) sorbent

Biochar containing Fe^0 (BC-ZVI) was an effective sorbent amendment, with most prominent reduction in C_w for Sb (Figure 19). Already at a dose of 5%, the Sb C_w was reduced by 99% to 4.8 µg/L in low TOC soil and by 95% to 5.6 µg/L in high TOC soil. At 20% amendment dose in low TOC soil, the Sb C_w were, however, only reduced by 95% to 15 µg/L. Cu C_w after BC-ZVI amendment showed the same trend in sorption as for the ZVI sorbent (Figure 17) with no extra effect as a result of increased sorbent dose. Pb mobility generally decreased with increasing BC-ZVI dose, apart from the high C_w at 5% amendment dose in high TOC soil. At 20% sorbent dose the Pb C_w was reduced by 88% to 13 µg/L in high TOC soil, and at 10% sorbent dose the Pb C_w was reduced by 99% to 1.5 µg/L in low TOC soil.

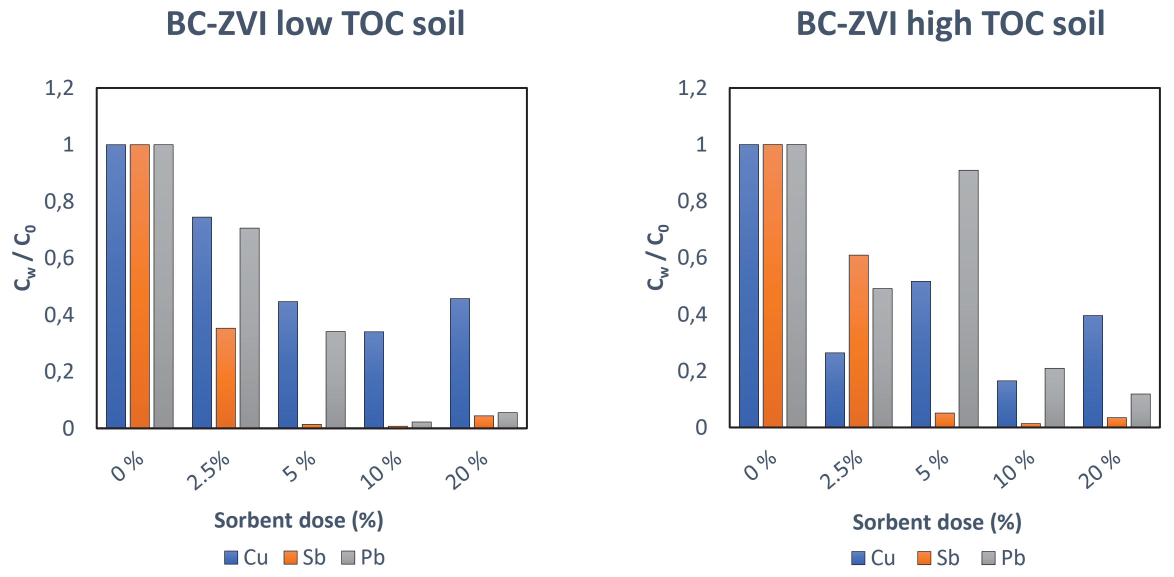


Figure 19: Reduction in leached element (Pb, Cu, and Sb) concentration as a function of ZVI enriched biochar (BC-ZVI) dose (% of d.w.) in soils with 4.7% and 12.6% TOC content respectively.

To consider if the low sorption of Cu and the high peak in Pb C_w at 5% sorbent dose in high TOC soil were results of parameters other than sorption to biochar, pH and DOC were investigated (Figure 20).

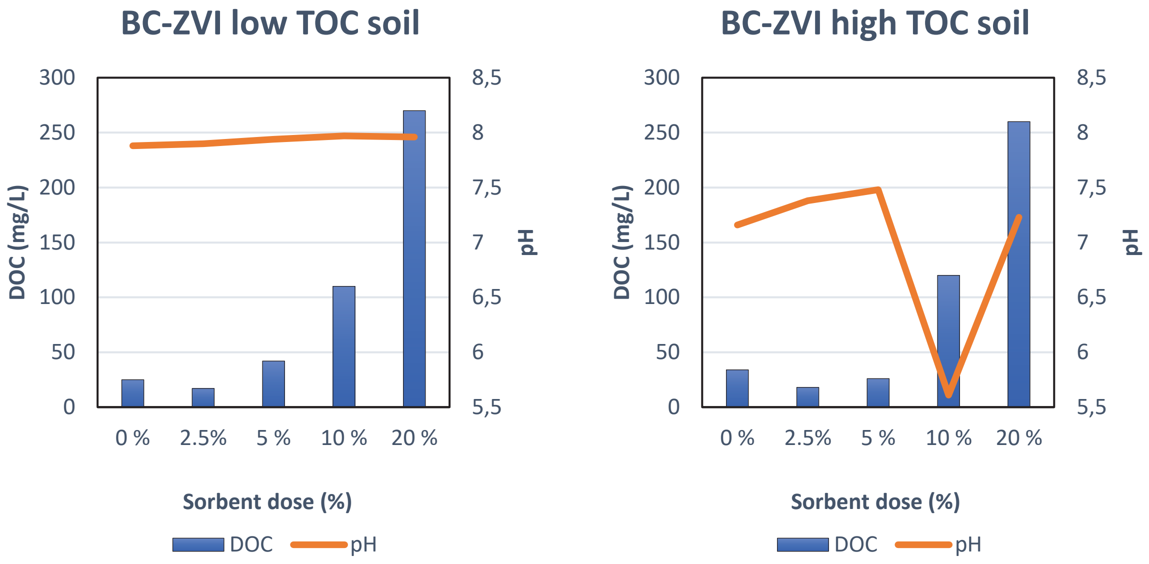


Figure 20: Changes in pH and DOC (mg/L) as a result of ZVI enriched biochar (BC-ZVI) amendment at different doses (% of d.w.) in soils with 4.7% and 12.6% TOC content respectively.

Amendment with BC-ZVI did only cause slight changes in pH for both soils (0.1 log unit), except for the drop at 10% sorbent dose in high TOC soil (Figure 20). This drop did not seem to affect element C_w (Figure 19), even though an increase in cation mobility would be expected. This pH value was therefore most likely an outlier, probably due to a measurement error. DOC had substantial increase in C_w following the two highest amendment doses for both soils (similar to ZVI), which could not be explained by the modest changes in pH. The fact that DOC C_w doubled after a doubling in sorbent dose could indicate that the sorbent itself contributed the DOC, but C_w from BC-ZVI control sample was only analysed to contain 23 mg DOC/L. The DOC mobility could therefore not be explained, but competition between DOC and Sb may explain the slightly increase in Sb C_w in low TOC soil at 20% dose. However, Sb interaction with OC is largely unknown (Okkenhaug & Mulder, 2011). High DOC C_w or the drop in pH did not correlate with the high peak in Pb C_w at 5% dose in high TOC soil or the Cu C_ws seen in Figure 19, which therefore must be explained by factors other than those investigated here.

Sorption to BC-ZVI and ZVI sorbents was similar. To investigate if the sorption to BC-ZVI was only due to ZVI or if the biochar also contributed to the sorption effectiveness, the sorbent properties were investigated. An element content analysis should be warranted for later studies, but when considering the synthesis of BC-ZVI (ref chap XX), it is legitimate to assume that less than 50% of the sorbent consisted of ZVI. Hence, BC-ZVI contained less ZVI per mass added to soil than pure ZVI, but the sorption was still similar and even better than ZVI. This indicate that the biochar in the BC-ZVI sorbent facilitates an increase sorption effect of ZVI. When comparing the surface area of the two sorbent materials it became evident that biochar had a much more porous surface than pure ZVI, with SA measured by CO_2 adsorption of 270 m^2/g compared to 137 m^2/g for ZVI. The high sorption effect of BC-ZVI could therefore be attributed to a combination of the relative high SA and the ZVI enrichment of the micropore surfaces. Treatment of biochar with ZVI like this is a novel technique and comparative results are absent.

Remediation of shooting range soil with this amendment would be considered successful, because Sb and Pb leachable concentrations were below leaching limits for inert waste landfills. Cu concentrations were below leaching limits of inert waste landfills both before and after amendment.

4.3.3.4 Fe^0 and sulfur (S) enriched biochar (BC-S-ZVI) sorbent

Biochar enriched with Fe^0 and S (BC-S-ZVI) immobilised both anionic Sb and cationic Cu effectively, Cu less than Sb. But most prominently, it caused a remarkable mobilisation of Pb (Figure 21). In both soils, 2.5% BC-S-ZVI amendment caused substantial leaching of Pb, with C_w of 740 µg/L in low TOC soil and 1200 µg/L in high TOC soil, which was 4 and 10 times higher than the initial Pb C_w. The Sb C_w was reduced by 92% at dose of 2.5% in low TOC soil and by 93% at 5% dose in high TOC soil. Further increase in sorbent dose did not markedly affect Sb C_ws, but small fluctuations were observed. Cu C_w in high TOC soil seemed to increase slightly with increasing sorbent dose.

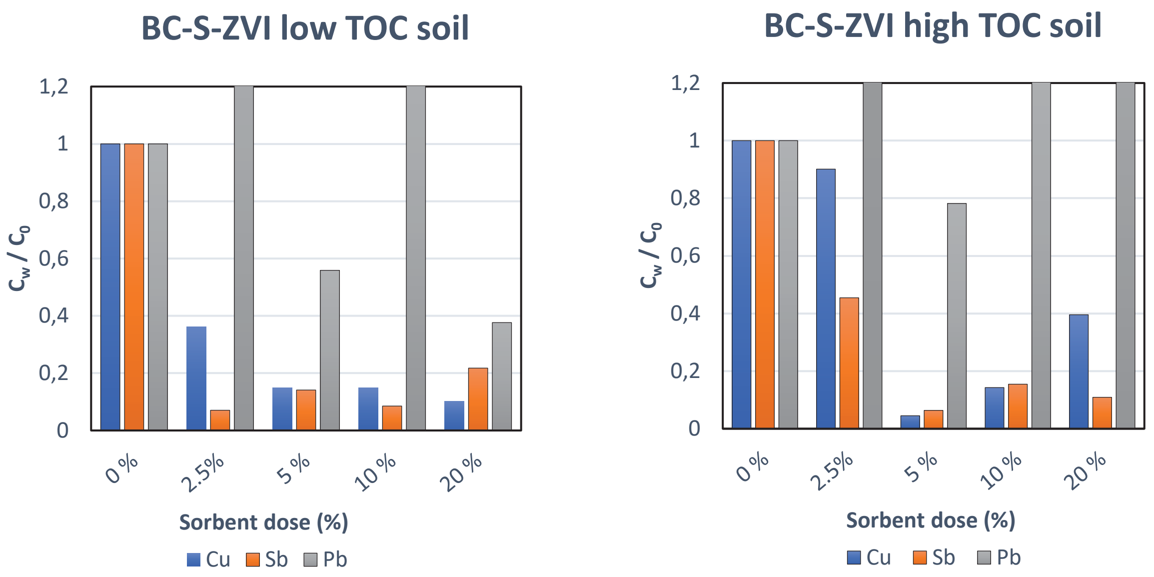


Figure 21: Reduction in leached element (Pb, Cu, and Sb) concentration as a function of S-ZVI enriched biochar (BC-S-ZVI) dose (% of d.w.) in soils with 4.7% and 12.6% TOC content respectively.

pH and DOC concentrations were plotted in Figure 22 to see if metal mobility correlated with these parameters.

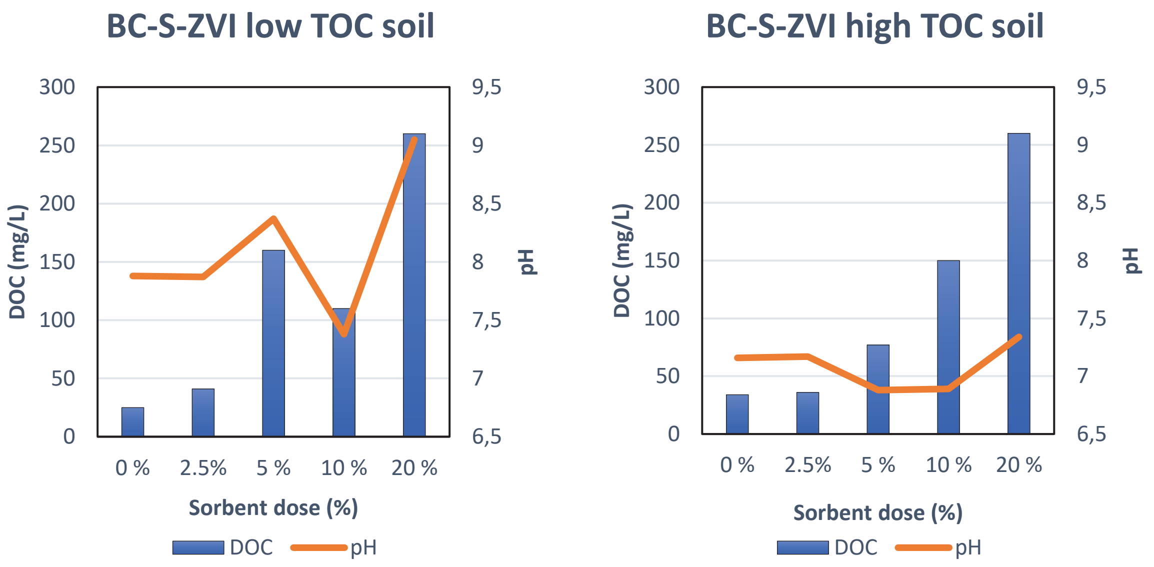


Figure 22: Changes in pH and DOC (mg/L) as a result of ZVI enriched biochar (BC-ZVI) amendment at different doses (% of d.w.) in soils with 4.7% and 12.6% TOC content respectively.

Substantial changes in both pH and DOC was observed for the low TOC samples, with a distinct overlap between the two factors (Figure 22). Two peaks in pH was observed at dose 5% and 20% in low TOC soil, which may explain the markedly reduction in Pb C_w at the same doses (Figure 21). In high TOC soil, a reduction in pH at 5% dose may also explain the slight Pb C_w reduction, but because similar pH at 10% dose did not correlate with reduced Pb C_w it is most likely not the explanation. DOC concentrations were not observed to effect Pb mobility in either soils, and the high leachability after BC-S-ZVI amendment must therefore be explained by parameters other than those investigated here. The two peaks in pH in low TOC soil mentioned above may also explain the slight increase in Sb C_w observed at 5% and 10% dose, because this would cause higher presence of OH^- groups in the soil and lower AEC (ref. chapter 2.4.4).

Generally, sulfidation of ZVI is found to increase reactivity of the sorbent and facilitate surface reactions between FeS and metals through mechanisms of ion exchange, complexation and coprecipitation (Li et al., 2017). Results in this thesis do not support Pb sorption improvement by ZVI sulfidation.

From a remediation perspective this amendment could not be warranted for shooting range soil. Even if leaching of Sb is reduced, qualifying the soil as ordinary waste (except 0.74 mg/kg at 20% dose in low TOC soil), the extensive mobilisation of Pb outweighs the positive effect of the amendment with BC-S-ZVI sorbent.

4.3.4 Comparison of sorbents

To find the most effective sorbent for remediation of shooting range soil, the sorption of each element was individually plotted against sorbent dose for all the sorbent materials. By doing this, the relative sorption effect of each element to each of the sorbents were more clearly highlighted. Comments on the success of the individual sorbents from a remediation point of view have been made in the previous chapters, but this comparison will provide a comparative overview. Figure 23 depicts the sorption of Sb to the different sorbents.

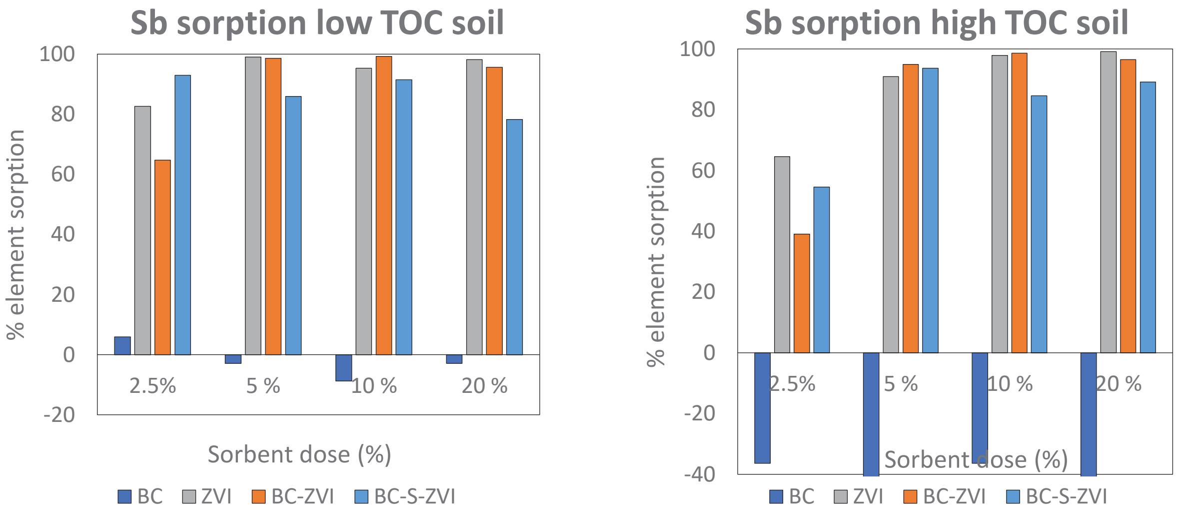


Figure 23: Percentage sorption of Sb as a function of sorbent dose for BC, ZVI, BC-ZVI, and BC-S-ZVI sorbents in low TOC (4.7%) and high TOC (12.6%) soil.

As reported in the previous results, all the sorbents, except BC, effectively immobilised Sb and this can clearly be seen in Figure 23. If only Sb immobilisation was to be considered, ZVI and both enriched biochars could therefore successfully be used in soil remediation. But in remediation of shooting range soil, Cu and especially Pb must be considered as well. Figure 24 and Figure 25 the sorption to the different sorbents of Cu and Pb respectively.

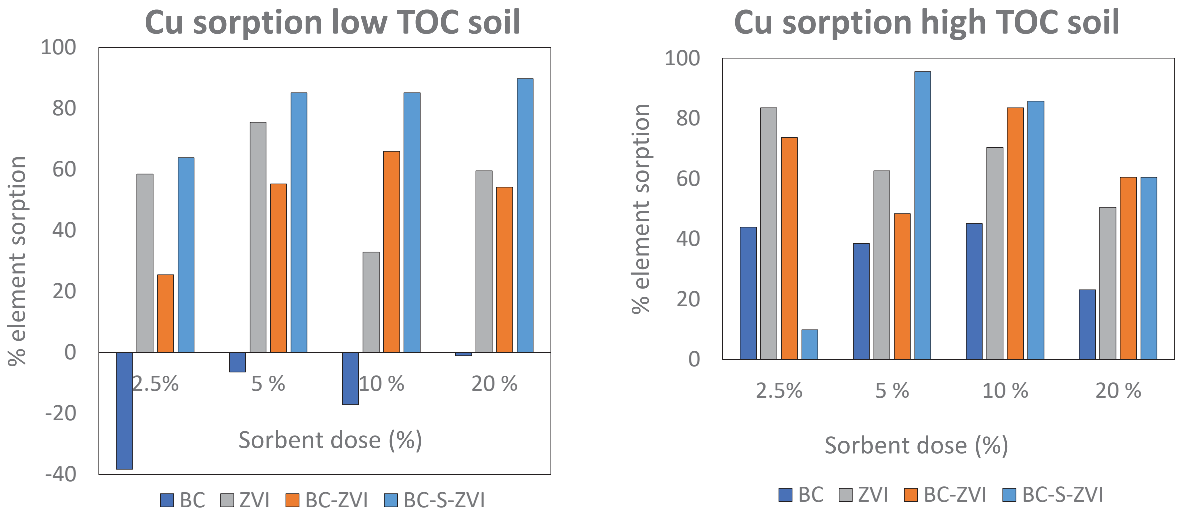


Figure 24: Percentage sorption of Cu as a function of sorbent dose for BC, ZVI, BC-ZVI, and BC-S-ZVI sorbents in low TOC (4.7%) and high TOC (12.6%) soil

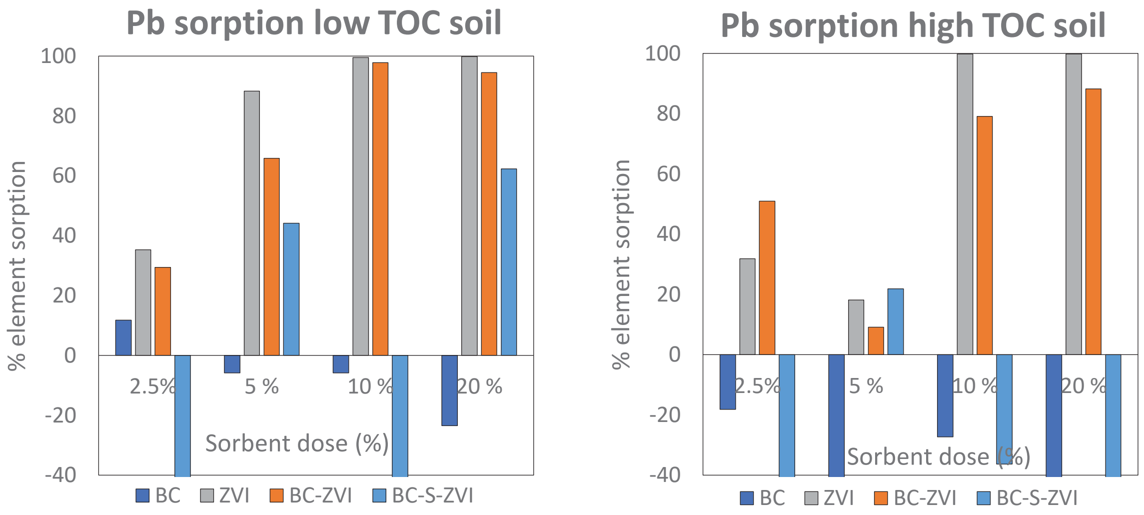


Figure 25: Percentage sorption of Pb as a function of sorbent dose for BC, ZVI, BC-ZVI, and BC-S-ZVI sorbents in low TOC (4.7%) and high TOC (12.6%) soil.

From Figure 24 and Figure 25, BC's low sorption effectiveness is evident again. For sorption of Cu BC-S-ZVI sorbent looks promising, but when considering Pb, this sorbent cause Pb immobilisation and must therefore be ruled out as a recommended sorbent in shooting range soil remediation. BC-ZVI and ZVI sorbents both cause effective immobilisation for all elements. This is not surprising for ZVI, as it has been used successfully in shooting range soil remediation in several previous studies (Okkenhaug et al., 2013; Okkenhaug et al., 2016). The strong sorption effects of BC-ZVI, however, offers new and promising results to the field of biochar remediation research. These results support one of few previous findings on increased sorption strength of Pb and Sb sorption to biochar after Fe^0 enrichment (Silvani et al., Submitted), indicating that BC-ZVI can become an effective sorbent amendment in shooting range soil remediation.

No clear effect of increased amendment dose was observed for this sorbent material. Further studies investigating dose effect on sorption of this sorbent is therefore suggested.

4.3.5 K_D calculations

Because BC-ZVI was the most promising biochar-based sorbent for contaminated soil from a shooting range, this chapter will focus on BC-ZVI.

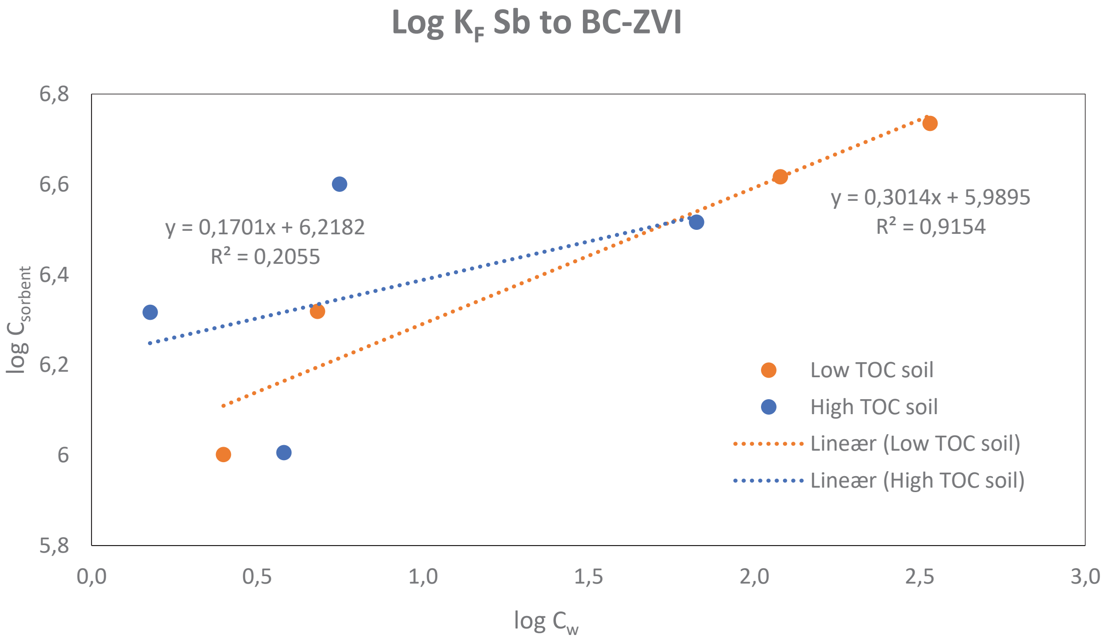


Figure 26: Partitioning of Sb between the BC-ZVI and water in high (16.2%) and low (4.7%) TOC soil.

$C_{sorbent}$ were calculated as described in chapter 3.4. From the linear regression line in Figure 26, the log K_F (intercept of y-axis) for Sb to BC-ZVI was found to be 6.22 in high TOC soil and 5.99 in low TOC soil. Compared to the initial log K_D value of the soils, 3.28 (L/kg) and 2.78 (L/kg) the sorbent amendment caused a remarkably decrease in element C_w. The R^2 for high TOC soil was however very low (0.21), indicating that the log K_F is not a good prediction for the Sb partitioning in high TOC soil. Linear regression of log $C_{sorbent}$ and log C_w for Pb in low TOC soil gave a log K_F value of 7.38, with an increase of almost 3 log units from unamended log K_D value, but the R^2 was only 31% indicating that the log K_F is not a good prediction for the Pb partitioning in low TOC soil. The linear regression for Pb and Cu can be found in appendix J. They are not included here because they had R^2 values <10%, attributed to low range in contaminant concentrations.

The use of log K_F values based on sorption isotherms like the ones used in this thesis can be questioned. In a proper sorption isotherm, depicting the partitioning of a contaminant between solid and aqueous phase, all parameters except the spiked contaminant solutions should be constant. This was not the case in the sorption isotherms constructed here. pH and DOC content varied considerably between the samples in the same isotherm, in addition to temperature and probably amount of biochar due to errors related to the practical lab procedures. Because of this, the log KF values should only be used as a guideline for expected contaminant mobility in the environment.

5 Conclusion and future perspectives

By using one-step batching leach tests, the sorption capacity of PFAS and metal(loid)s (Pb, Cu, and Sb) to activated and enriched “designer” biochars were investigated. Complete activation (125%) of biochar produced at high pyrolysis temperature (900°C) resulted in the highest sorption capacity for PFAS. An amendment dose of 0.5% was found to be sufficient in soil with low TOC content, whereas a dose of 5% was required in soil with high TOC content.

Enrichment of biochar (produced at pyrolysis temperature of 650°C) with ZVI was found to have the highest overall sorption capacity for both Pb, Cu, and Sb, owing to the material’s porous structure and the amphoteric character of the ZVI enrichments. Amendment dose of 10% was found to be required for sufficient remediation effects.

The results of this study highlight the promise of “designer” biochar as an effective, sustainable, and cost-effective alternative in soil remediation. Biomass that previously were considered waste can be brought back into the economy through the production of biochar, which then can be used to stabilise another waste material, namely contaminated soil. Contaminated soils are a growing issue worldwide and *in situ* remediation, like contaminant immobilisation using biochar, will therefore constitute an important remediation method in the times to come. Overall, biochar offers better resource utilisation and waste minimisation and is a promising product that fits well into the circular economy.

Reference list

3M Company, Moore, J., Rodricks, J., Turnbull, D. & Warren-Hicks, W. (2003). *Health and Environmental Assessment of Perfluorooctane Sulfonic Acid and its Salts*. Available at: http://multimedia.3m.com/mws/media/370351O/3m-pfos-risk-assessmt-2003.pdf (accessed: 10.05.2019).

2006/122/ECOF. (2006). *Directive 2006/122/ECOF the European Parliament and of The Council*. Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32006L0122&from=DA (accessed: 16.04.2019).

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

Alexander, M. (2000). Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environmental science & technology*, 34 (20): 4259-4265.

ATSDR. (2018). *Per- and Polyfluoroalkyl Substances (PFAS) and Your Health; What are the health effects?* In Registry, A. o. T. S. a. D. (ed.). Available at: https://www.atsdr.cdc.gov/pfas/health-effects.html (accessed: 26.04.2019).

Avfallsforskriften. (2004). *Forskrift om gjenvinning og behandling av avfall (avfallsforskriften)*. Available at: https://lovdata.no/dokument/SF/forskrift/2004-06-01-930 (accessed: 01.05.2019).

Benedetti, V., Patuzzi, F. & Baratieri, M. (2017). Gasification char as a potential substitute of activated carbon in adsorption applications. *Energy Procedia*, 105: 712-717. doi: 10.1016/j.egypro.2017.03.380.

Brändli, R. C., Hartnik, T., Henriksen, T. & Cornelissenad, G. (2008). Sorption of native polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. *Chemosphere*, 73 (11): 1805-1010.

Cornelissen, G., Gustafsson, Ö., Bucheli, T. D., Jonker, M. T., Koelmans, A. A. & van Noort, P. C. (2005). Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environmental science & technology*, 39 (18): 6881-6895.

Cornelissen, G., Silvani, L. & Smebye, A. B. (2018a). *Stabilisering av skytefeltjord forurenset med tungmetaller med biokull fra resttrevirke*. In NGI (ed.). NGI-prosjekt 20140249.

Cornelissen, G., Silvani, L. & Smebye, A. B. (2018b). *Biokull fra resttrevirke for stabilisering av jord forurenset med prefluorerte forbindelser (PFC): Sorpsjonstester*. Stabilisering av skytefeltjord - Pilot-test Oredalen. NGI.

Cornelissen, G. (2019). Conversation with Gerard Cornelissen. Oslo (08.02.2019)

EC. (2006). *Thematic Strategy for Soil Protection [SEC(2006)620] [SEC(2006)1165]/COM(2006)231 final*. Brussels.

EPA. (2018). *Basic information on PFAS*. In Agency, U. S. E. P. (ed.). PFOA, PFOS and Other PFASs. epa.gov. Available at: https://www.epa.gov/pfas/basic-information-pfas.

FAO & ITPS. (2015). *Status of the World's Soil Resources (SWSR) – Main Report.* Rome, Italy.

Forurensningsforskriften. (2004). *Forskrift om begrensning av forurensning (forurensningsforskriften)*. Available at: https://lovdata.no/dokument/SF/forskrift/2004-06-01-931/KAPITTEL_1#KAPITTEL_1 (accessed: 15.04.2019).

Gellrich, V., Stahl, T. & Knepper, T. (2012). Behavior of perfluorinated compounds in soils during leaching experiments. *Chemosphere*, 87 (9): 1052-1056. doi: 10.1016/j.chemosphere.2012.02.011.

Ghosh, U., Gillette, J. S., Luthy, R. G. & Zare, R. N. (2000). Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles. *Environmental Science & Technology*, 34 (9): 1729-1736.

Ghosh, U., Luthy, R. G., Cornelissen, G., Werner, D. & Menzie, C. A. (2011). *In-situ sorbent amendments: a new direction in contaminated sediment management*: ACS Publications.

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.

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. *Environmental Science & Technology*, 45 (24): 10445-10453.

Hale, S. E., Arp, H. P. H., Kupryianchyk, D. & Cornelissen, G. (2016). A synthesis of parameters related to the binding of neutral organic compounds to charcoal. *Chemosphere*, 144: 65-74.

Hale, S. E., Arp, H. P. H., Slinde, G. A., Wade, E. J., Bjørseth, K., Breedveld, G. D., Straith, B. F., Moe, K. G., Jartun, M. & 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.

Herzke, D., Olsson, E. & Posner, S. (2012). Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway–A pilot study. *Chemosphere*, 88 (8): 980-987. doi: http://dx.doi.org/10.1016/j.chemosphere.2012.03.035.

Higgins, C. P. & Luthy, R. G. (2006). Sorption of perfluorinated surfactants on sediments. *Environmental Science & Technology*, 40 (23): 7251-7256.

Klitzke, S. & Lang, F. (2009). Mobilization of soluble and dispersible lead, arsenic, and antimony in a polluted, organic-rich soil–effects of pH increase and counterion valency. *Journal of environmental quality*, 38 (3): 933-939. doi: 10.2134/jeq2008.0239.

Krafft, M. P. & Riess, J. G. (2015). Per-and polyfluorinated substances (PFASs): Environmental challenges. *Current opinion in colloid & interface science*, 20 (3): 192-212. doi: http://dx.doi.org/10.1016/j.cocis.2015.07.004.

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.

Kuzyakov, Y., Subbotina, I., Chen, H., Bogomolova, I. & Xu, X. (2009). Black carbon decomposition and incorporation into soil microbial biomass estimated by 14C labeling. *Soil Biology and Biochemistry*, 41 (2): 210-219.

Kwon, S. & Pignatello, J. J. (2005). Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): pseudo pore blockage by model lipid components and its implications for N2-probed surface properties of natural sorbents. *Environmental science & technology*, 39 (20): 7932-7939. doi: 10.1021/es050976h.

Lehmann, J. & Joseph, S. (2015). *Biochar for environmental management: science, technology and implementation*: Routledge.

Li, J., Zhang, X., Sun, Y., Liang, L., Pan, B., Zhang, W. & Guan, X. (2017). Advances in sulfidation of zerovalent iron for water decontamination. *Environmental science & technology*, 51 (23): 13533-13544. doi: 10.1021/acs.est.7b02695.

Marques, A. P., Rangel, A. O. & Castro, P. M. (2009). Remediation of heavy metal contaminated soils: phytoremediation as a potentially promising clean-up technology. *Critical Reviews in Environmental Science and Technology*, 39 (8): 622-654.

Meuser, H. (2013). *Soil remediation and rehabilitation: treatment of contaminated and disturbed land*, vol. 23: Springer Science & Business Media.

Mildir. (2018). *List of Priority Substances*. In Agency, N. E. (ed.): environment.no. Available at: https://www.environment.no/topics/hazardous-chemicals/list-of-priority-substances/ (accessed: 25.01.2019).

Mulvaney, D. (2011). *Green technology: an A-to-Z guide*, vol. 10: Sage.

NGI. (2018). *PFBS in the Environment: Monitoring and Physical-Chemical Data Related to the Environmental Distribution of Perfluorobutanesulfonic Acid*.

NGI. (2019). *GEOreCIRC, WP3: Eksisterende veiledere og retningslinjer for risikovurdering av spredning fra avfall of forurensede masser*.

O'Connor, D., Peng, T., Li, G., Wang, S., Duan, L., Mulder, J., Cornelissen, G., Cheng, Z., Yang, S. & Hou, D. (2018). Sulfur-modified rice husk biochar: A green method for the remediation of mercury contaminated soil. *Science of the Total Environment*, 621: 819-826.

OECD. (2013). *Synthesis paper on per- and polyfluorinated chemicals (PFCs)*. In Group, O. U. G. P. (ed.). OECD Environment, Health and Safety Publications. Paris.

Okkenhaug, G. & Mulder, J. (2011). Antimony. In Lan, R. (ed.) *Encyclopedia of Soil Science*, p. 4: Taylor and Francis.

Okkenhaug, G. (2012). *Mobility and solubility of antimony (Sb) in the environment*. Doctorial Thesis. Ås: Norwegian University of Life Sciences.

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. *Environmental science & technology*, 47 (12): 6431-6439.

Okkenhaug, G., Gebhardt, K.-A. G., Amstaetter, K., Bue, H. L., Herzel, H., Mariussen, E., Almås, Å. R., Cornelissen, G., Breedveld, G. D. & Rasmussen, G. (2016). Antimony (Sb) and lead (Pb) in contaminated shooting range soils: Sb and Pb mobility and immobilization by iron based sorbents, a field study. *Journal of hazardous materials*, 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. *Journal of soils and sediments*, 18 (11): 3310-3323. doi: 10.1007/s11368-017-1739-8.

Oleszczuk, P., Hale, S. E., Lehmann, J. & Cornelissen, G. (2012). Activated carbon and biochar amendments decrease pore-water concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. *Bioresource technology*, 111: 84-91.

regjeringen.no. (2010). *Begrensningsdirektivet - PFOS*. Available at: https://www.regjeringen.no/no/sub/eos-notatbasen/notatene/2006/jan/begrensningsdirektivet---pfos/id2431732/ (accessed: 27.04.2019).

Rodríguez-Eugenio, N., McLaughlin, M. & Pennock, D. (2018). Soil pollution: A hidden reality.

Rotander, A., Toms, L.-M. L., Aylward, L., Kay, M. & Mueller, J. F. (2015). Elevated levels of PFOS and PFHxS in firefighters exposed to aqueous film forming foam (AFFF). *Environment international*, 82: 28-34. doi: 10.1016/j.envint.2015.05.005.

Roychowdhury, R., Roy, M., Zaman, S. & Mitra, A. (2019). BIOREMEDIATION POTENTIAL OF MICROBES TOWARDS HEAVY METAL CONTAMINATION. *International Journal of Research and Analytical Reviews*, 6 (1): 1088-1094.

SDGs. (2015). *Sustainable Developement Goals*. Available at: https://sustainabledevelopment.un.org/sdgs.

Semple, K. T., Doick, K. J., Jones, K. C., Burauel, P., Craven, A. & Harms, H. (2004). *Peer reviewed: defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated*: ACS Publications.

Silvani, L., Cornelissen, G., Smebye, A. B., Zhang, Y., Okkenhaug, G., Zimmerman, A. R., Thune, G., Sævarsson, H. & Hale, S. (Submitted). Can biochar and designer biochar be used to remediate per- and polyfluorinated alkyl substances (PFAS and metal contaminated soils? *Environmental science & technology, submitted*.

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*: ACS Publications.

Standard Norge. (2003). *NS-EN 12457-2 Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction)* (accessed: 01.05.2019).

TA 2553. (2009). *Veileder: Helsebasert tilstandsklassser for forurenset grunn*. In Miljødirektoratet (ed.).

Thapa, B., Kc, A. K. & Ghimire, A. (2012). A review on bioremediation of petroleum hydrocarbon contaminants in soil. *Kathmandu university journal of science, engineering and technology*, 8 (1): 164-170.

Utstøl, S., Melnes, M., Karsrud, T. E. & Prydz, P. (2017). Forsvarssektorens miljø-og klimaregnskap for 2016. *FFI*, 17: 00741.

Voie, Ø., Strømseng, A., Johnsen, A., Rossland, H. K., Karsrud, T. E. & Longva, K. (2010). Veileder for undersøkelse, risikovurdering, opprydning og avhending av skytebaner og øvingsfelt. *FFI*: 00116.

WHO, W. H. O. (2018). *Lead poisoning and health*. In Organization, W. H. (ed.). Available at: https://www.who.int/news-room/fact-sheets/detail/lead-poisoning-and-health (accessed: 27.04.2019).

Wilson, S. C., Lockwood, P. V., Ashley, P. M. & Tighe, M. (2010). The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: a critical review. *Environmental pollution*, 158 (5): 1169-1181. doi: 10.1016/j.envpol.2009.10.045.

Zhang, H., Lin, K., Wang, H. & Gan, J. (2010). Effect of Pinus radiata derived biochars on soil sorption and desorption of phenanthrene. *Environmental Pollution*, 158 (9): 2821-2825.

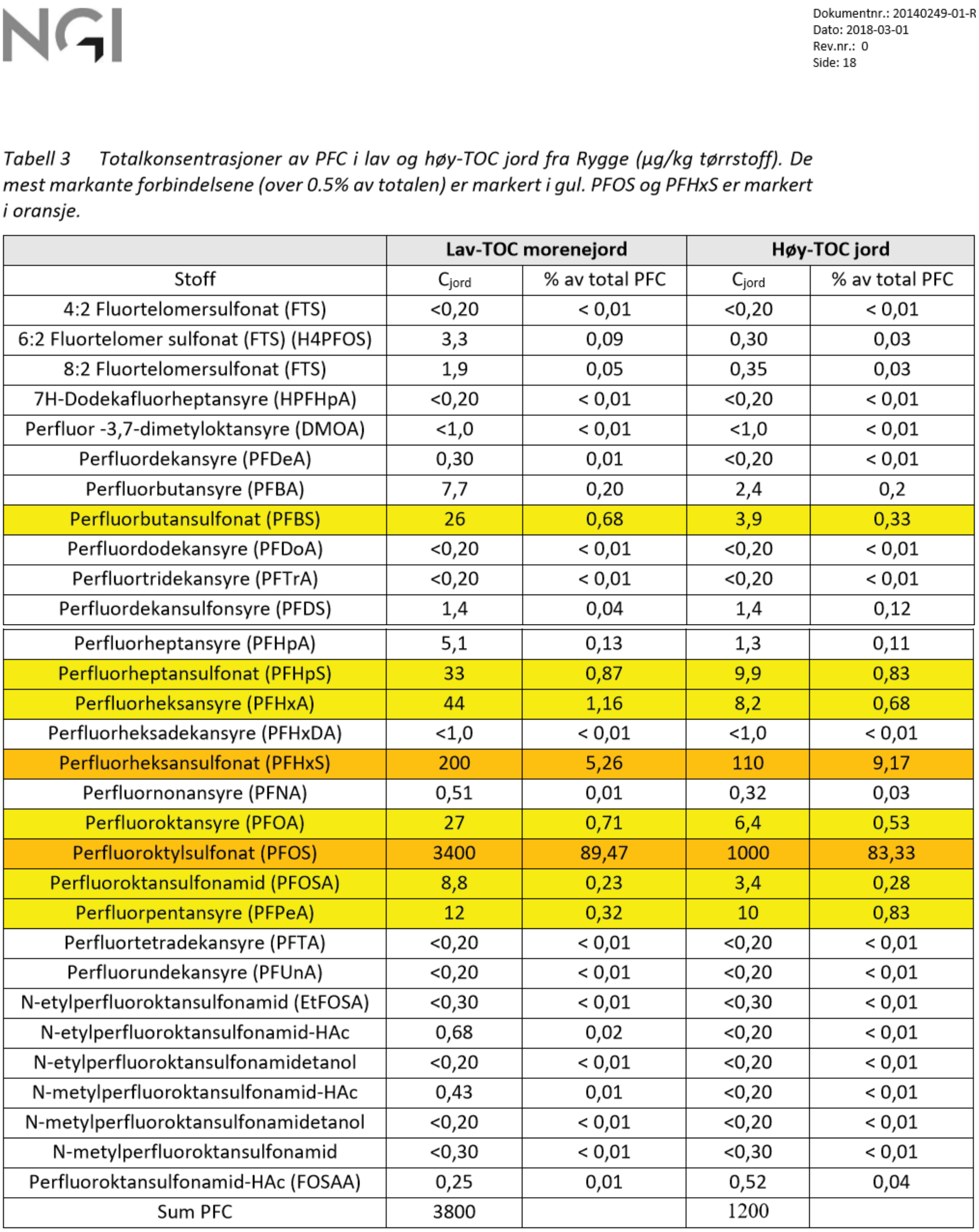
Appendix Overview

Appendix A: Leaching limits, Avfallsforskriften (2004).

Parameter	Leaching limits for inert waste landfills (mg/kg)	Leaching limits for ordinary waste landfills (mg/kg)	Leaching limits for hazardous waste landfills (mg/kg)
Copper (Cu)	2	50	100
Lead (Pb)	0.5	10	50
Antimony (Sb)	0.06	0.7	5
Only the relevant limits from batch leaching test (L/S =10) are included here			

Appendix B: Total contaminant concentrations in soil

Table B-1: Total PFAS concentrations in soil from Rygge airport (Cornelissen et al., 2018b)



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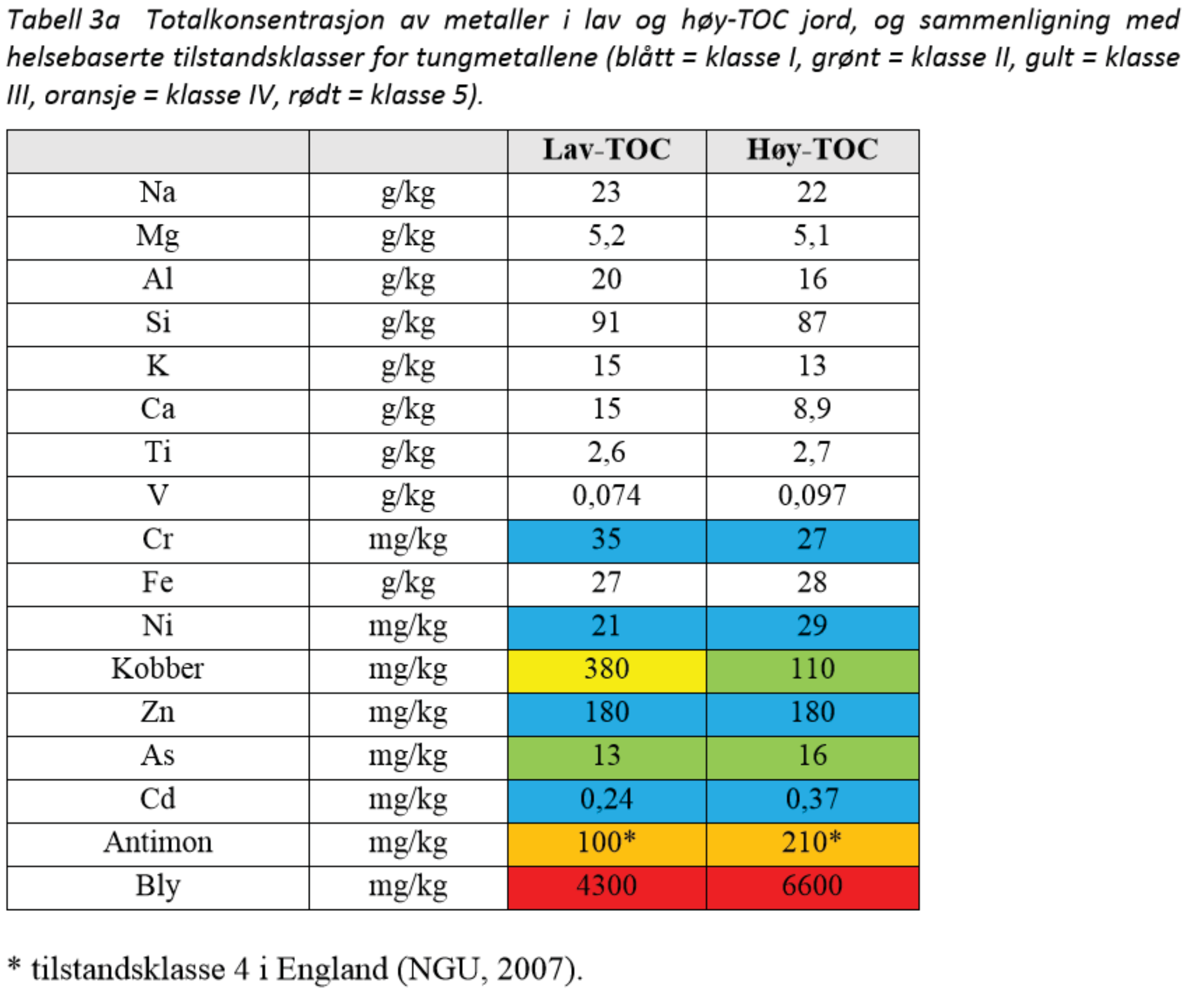
Tabell 3 Totalkonsentrasjoner av PFC i lav og høy-TOC jord fra Rygge (µg/kg tørrstoff). De mest markante forbindelsene (over 0.5% av totalen) er markert i gul. PFOS og PFHxS er markert i oransje.

	Lav-TOC morenejord		**Høy-TOC jord**	
Stoff	C_{jord}	% av total PFC	C_{jord}	% av total PFC
4:2 Fluortelomersulfonat (FTS)	<0,20	< 0,01	<0,20	< 0,01
6:2 Fluortelomer sulfonat (FTS) (H4PFOS)	3,3	0,09	0,30	0,03
8:2 Fluortelomersulfonat (FTS)	1,9	0,05	0,35	0,03
7H-Dodekafluorheptansyre (HPFHpA)	<0,20	< 0,01	<0,20	< 0,01
Perfluor -3,7-dimetyloktansyre (DMOA)	<1,0	< 0,01	<1,0	< 0,01
Perfluordekansyre (PFDeA)	0,30	0,01	<0,20	< 0,01
Perfluorbutansyre (PFBA)	7,7	0,20	2,4	0,2
Perfluorbutansulfonat (PFBS)	26	0,68	3,9	0,33
Perfluordodekansyre (PFDoA)	<0,20	< 0,01	<0,20	< 0,01
Perfluortridekansyre (PFTrA)	<0,20	< 0,01	<0,20	< 0,01
Perfluordekansulfonsyre (PFDS)	1,4	0,04	1,4	0,12
Perfluorheptansyre (PFHpA)	5,1	0,13	1,3	0,11
Perfluorheptansulfonat (PFHpS)	33	0,87	9,9	0,83
Perfluorheksansyre (PFHxA)	44	1,16	8,2	0,68
Perfluorheksadekansyre (PFHxDA)	<1,0	< 0,01	<1,0	< 0,01
Perfluorheksansulfonat (PFHxS)	200	5,26	110	9,17
Perfluornonansyre (PFNA)	0,51	0,01	0,32	0,03
Perfluoroktansyre (PFOA)	27	0,71	6,4	0,53
Perfluoroktylsulfonat (PFOS)	3400	89,47	1000	83,33
Perfluoroktansulfonamid (PFOSA)	8,8	0,23	3,4	0,28
Perfluorpentansyre (PFPeA)	12	0,32	10	0,83
Perfluortetradekansyre (PFTA)	<0,20	< 0,01	<0,20	< 0,01
Perfluorundekansyre (PFUnA)	<0,20	< 0,01	<0,20	< 0,01
N-etylperfluoroktansulfonamid (EtFOSA)	<0,30	< 0,01	<0,30	< 0,01
N-etylperfluoroktansulfonamid-HAc	0,68	0,02	<0,20	< 0,01
N-etylperfluoroktansulfonamidetanol	<0,20	< 0,01	<0,20	< 0,01
N-metylperfluoroktansulfonamid-HAc	0,43	0,01	<0,20	< 0,01
N-metylperfluoroktansulfonamidetanol	<0,20	< 0,01	<0,20	< 0,01
N-metylperfluoroktansulfonamid	<0,30	< 0,01	<0,30	< 0,01
Perfluoroktansulfonamid-HAc (FOSAA)	0,25	0,01	0,52	0,04
Sum PFC	3800		1200	

Table B-2: Total metal/metalloid concentrations in soil from Tittelsnes small arms shooting range (cornelissen et al., 2018a)



Tabell 3a Totalkonsentrasjon av metaller i lav og høy-TOC jord, og sammenligning med helsebaserte tilstandsklasser for tungmetallene (blått = klasse I, grønt = klasse II, gult = klasse III, oransje = klasse IV, rødt = klasse 5).

		Lav-TOC	**Høy-TOC**
Na	g/kg	23	22
Mg	g/kg	5,2	5,1
Al	g/kg	20	16
Si	g/kg	91	87
K	g/kg	15	13
Ca	g/kg	15	8,9
Ti	g/kg	2,6	2,7
V	g/kg	0,074	0,097
Cr	mg/kg	35	27
Fe	g/kg	27	28
Ni	mg/kg	21	29
Kobber	mg/kg	380	110
Zn	mg/kg	180	180
As	mg/kg	13	16
Cd	mg/kg	0,24	0,37
Antimon	mg/kg	100*	210*
Bly	mg/kg	4300	6600

* tilstandsklasse 4 i England (NGU, 2007).

Appendix C: The weight of salts and dilution concentrations for sorption isotherm

Table C-1: Weight of salts used to make 0.25 L stock solution (15 000 µg/L)

Salt	Weight (g)
$Cu(NO_2)_2$	0.0038
$Pb(NO_3)_2$	0.0037
$K[Sb(OH)_6]$	0.0040

Table C-2: Dilution concentrations used in sorption isotherm

Dilute concentration	5 000 µg/L	1 000 µg/L	250 µg/L	50 µg/L		
Transferred solution	0.083 L	0.010 L	0.003 L	0.0005 L	0.0001 L	
Water	0.167 L	0.040 L	0.047 L	0.0495 L	0.0499 L	

Appendix D: PFAS concentrations in the leachates

Table D-1: PFAS concentrations in leachate from high TOC soil from Rygge Airport

	(PFBS)	(PFHxS)	(PFHpS)	(PFOS)	(PFDS)	(PFBA)	(PFPeA)	(PFHxA)	(PFHpA)	(PFOA)	(PFNA)	(PFDeA)
Prøvereferanse	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
Control	84	1200	31	2900	<10	96	320	320	38	82	<10	<10
0,1% BC	78	1200	28	2000	<10	70	310	280	40	78	<10	<10
0,5% BC	77	1100	20	1300	<10	78	280	250	32	62	<10	<10
1% BC	76	1000	24	1200	<10	60	180	250	33	65	<10	<10
2% BC	67	1100	24	1800	<10	64	260	250	32	73	<10	<10
5% BC	65	490	12	640	<0,30	62	90	200	25	40	1,1	<0,30
0,1% aBC 50%	85		34	2300	<10	66	430	260	43	97	<10	<10
0,5% aBC 50%	76	1500	45	2200	<10	69	320	250	35	110	<10	<10
1% aBC 50%	66	1200	39	2300	<10	59	250	230	36	99	<10	<10
2% aBC 50%	53	950	35	2500	<10	51	230	170	29	81	<10	<10
5% aBC 50%	19	410	18	1500	<10	<20	44	56	<10	33	<10	<10
0,1% aBC 75%	87	1400	58	3400	<10	81	330	260	41	130	<10	<10
0,5% aBC 75%	62	1300	48	3600	<10	64	210	200	30	92	<10	<10
1% aBC 75%	65	1300	36	2300	<10	56	190	180	29	86	<10	<10
2% aBC 75%	52	1000	26	2000	<10	54	180	170	22	62	<10	<10
5% aBC 75%	21	310	18	870	<0,30	32	28	52	7,8	28	1,7	<0,30
0,1% aBC 100%	90	1400	32	1600	<10	64	360	290	39	87	<10	<10
0,5% aBC 100%	70	1200	35	2300	<10	74	250	210	28	76	<10	<10
1% aBC 100%	44	760	29	2500	<10	48	140	130	18	64	<10	<10
2% aBC 100%	23	420	20	1800	<10	53	64	63	<10	32	<10	<10
5% aBC 100%	8,8	98	3,1	320	<0,30	36	24	17	1,9	6,4	0,44	<0,30
0,1% aBC 125%	100	1500	39	2300	<10	80	390	290	41	110	<10	<10
0,5% aBC 125%	78	1100	46	2500	<10	82	240	240	32	92	<10	<10
1% aBC 125%	41	620	22	1700	<10	80	110	130	14	48	<10	<10
2% aBC 125%	10	71	3,4	360	<0,30	52	33	23	1,6	5,5	0,36	<0,30
5% aBC 125%	<0,30	3,5	0,33	41	<0,30	<0,60	<0,30	<0,30	<0,30	0,99	<0,30	<0,30
0,1% aBC 800C	86	1400	53	2900	<10	86	420	310	41	120	<10	<10
0,5% aBC 800C	74	1500	49	2400	<10	88	340	260	41	110	<10	<10
1% aBC 800C	66	1300	57	3200	<10	71	310	250	42	120	<10	<10
2% aBC 800C	65	1200	35	2400	<10	63	230	220	31	84	<10	<10
5% aBC 800C	37	680	21	1400	<10	50	92	110	17	47	<10	<10
0,1% aBC 850C	90	1700	62	3900	<10	93	360	260	48	140	<10	<10
0,5% aBC 850C	73	1500	57	4000	<10	67	290	240	41	130	<10	<10
1% aBC 850C	62	1400	42	3000	<10	80	240	230	37	100	<10	<10
2% aBC 850C	42	830	34	2400	<10	39	120	140	20	76	<10	<10
5% aBC 850C	18	200	11	770	<0,30	32	25	46	6,1	21	1,3	<0,30
0,1% aBC CO2	84	1500	48	3200	<10	78	290	260	41	120	<10	<10
0,5% aBC CO2	78	1400	46	3300	<10	76	270	230	35	89	<10	<10
1% aBC CO2												
2% aBC CO2	46	990	25	1800	<10	54	110	150	24	67	<10	<10
5% aBC CO2	28	640	18	1300	<10	37	55	91	14	46	<10	<10

… table continues …

	PFCA-11	(PFDoA)	(PFTrA)	(PFTA)	(PFHxDA)	(PFOSA)	4:2 (FTS)	6:2 (FTS) (H4PFOS)	8:2 (FTS)	(HPFHpA)	(PF-3,7-DMOA)	Sum PFAS
Prøvereferanse	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
Control	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	5100
0,1% BC	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4100
0,5% BC	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	3200
1% BC	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	2900
2% BC	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	3700
5% BC	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	2,5	<0,30	<0,30	<0,30	1600
0,1% aBC 50%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	3300
0,5% aBC 50%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4600
1% aBC 50%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4300
2% aBC 50%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4100
5% aBC 50%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	2100
0,1% aBC 75%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	5800
0,5% aBC 75%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	5600
1% aBC 75%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4200
2% aBC 75%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	3600
5% aBC 75%	<0,30	<0,30	<1,0	<0,30	<0,30	0,98	<0,30	1,5	1,2	<0,30	<0,30	1400
0,1% aBC 100%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4000
0,5% aBC 100%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4200
1% aBC 100%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	3700
2% aBC 100%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	2500
5% aBC 100%	<0,30	<0,30	<1,0	<0,30	<0,30	0,38	<0,30	<0,30	<0,30	<0,30	<0,30	520
0,1% aBC 125%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4900
0,5% aBC 125%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4400
1% aBC 125%	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	2800
2% aBC 125%	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	560
5% aBC 125%	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	46
0,1% aBC 800C	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	5400
0,5% aBC 800C	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4900
1% aBC 800C	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	5400
2% aBC 800C	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	4300
5% aBC 800C	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	2500
0,1% aBC 850C	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	6700
0,5% aBC 850C	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	6400
1% aBC 850C	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	5200
2% aBC 850C	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	3700
5% aBC 850C	<0,30	<0,30	<1,0	<0,30	<0,30	0,33	<0,30	0,68	0,41	<0,30	<0,30	1100
0,1% aBC CO2	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	5600
0,5% aBC CO2	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	5500
1% aBC CO2	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	3300
2% aBC CO2	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	2200
5% aBC CO2	<0,30	<0,30	<1,0	<0,30	<0,30	0,39	<0,30	0,72	0,98	<0,30	<0,30	920

Table D-2: PFAS concentrations in leachate from low TOC soil from Rygge Airport

	(PFBS)	(PFHxS)	(PFHpS)	(PFOS)	(PFDS)	(PFBA)	(PFPeA)	(PFHxA)	(PFHpA)	(PFOA)	(PFNA)	(PFDeA)
Prøvereferanse	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
Control	2800	26000	3200	240000	<10	1000	1400	7700	590	2500	45	13
0,1% BC	2600	23000	3000	220000	<10	1000	1400	7600	620	2500	59	13
0,5% BC	2000	14000	1500	89000	<10	850	1200	5800	360	1600	21	<10
1% BC	1100	4900	350	18000	<10	600	690	3000	180	710	<10	<10
2% BC	170	430	25	1900	<10	330	240	720	28	80	<10	<10
5% BC	2,7	13	3,7	330	<0,30	21	7,0	11	0,42	2,7	<0,30	<0,30
0,1% aBC 50%	2200	16000	1900	140000	<10	960	1200	5600	400	2100	31	<10
0,5% aBC 50%	160	180	14	850	<0,30	430	230	560	14	49	0,50	<0,30
1% aBC 50%	9,6	13	1,0	130	<0,30	150	34	38	0,79	2,5	<0,30	<0,30
2% aBC 50%	0,30	2,9	1,3	130	<0,30	19	1,8	1,0	<0,30	0,66	<0,30	<0,30
5% aBC 50%	<0,30	15	3,8	410	<0,30	2,9	0,53	3,8	0,34	2,6	<0,30	<0,30
0,1% aBC 75%	1900	12000	1400	100000	<10	860	1100	5000	360	1500	26	<10
0,5% aBC 75%	16	48	<10	1500	<10	140	33	58	<10	<10	<10	<10
1% aBC 75%	25	55	5,6	630	<0,30	210	61	81	2,5	9,3	<0,30	<0,30
2% aBC 75%	0,30	1,3	0,32	98	<0,30	16	1,3	0,83	<0,30	<0,30	<0,30	<0,30
5% aBC 75%	<0,30	2,3	0,68	140	<0,30	4,1	<0,30	<0,30	<0,30	0,41	<0,30	<0,30
0,1% aBC 100%	1200	5300	570	57000	<10	880	1100	3800	200	630	12	<10
0,5% aBC 100%	11	13	1,6	260	<0,30	210	47	36	0,74	1,9	<0,30	<0,30
1% aBC 100%	1,4	1,3	<0,30	91	<0,30	59	10	3,9	<0,30	<0,30	<0,30	<0,30
2% aBC 100%	<0,30	0,94	<0,30	46	<0,30	17	0,99	0,45	<0,30	<0,30	<0,30	<0,30
5% aBC 100%	<0,30	1,3	0,41	100	<0,30	1,5	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30
0,1% aBC 125%	1300	2000	150	18000	<10	890	1200	3800	130	280	<10	<10
0,5% aBC 125%	0,84	0,93	0,34	39	<0,30	130	13	2,4	<0,30	<0,30	<0,30	<0,30
1% aBC 125%	<0,30	1,3	0,51	55	<0,30	27	1,0	<0,30	<0,30	<0,30	<0,30	<0,30
2% aBC 125%	<0,30	1,7	0,79	85	<0,30	5,5	<0,30	<0,30	<0,30	0,35	<0,30	<0,30
5% aBC 125%	<0,30	7,5	2,4	250	<0,30	0,66	<0,30	<0,30	<0,30	1,2	<0,30	<0,30
0,1% aBC 800C	2200	19000	2300	180000	<10	880	1200	5700	470	2100	35	<10
0,5% aBC 800C	180	650	64	6900	<10	380	300	750	34	120	<10	<10
1% aBC 800C	20	49	4,2	320	<0,30	190	66	96	3,0	11	<0,30	<0,30
2% aBC 800C	7,5	43	6,2	520	<0,30	41	12	28	1,6	7,0	0,54	<0,30
5% aBC 800C	<0,30	7,1	2,8	280	<0,30	5,9	0,55	0,42	<0,30	1,2	<0,30	<0,30
0,1% aBC 850C	1600	11000	1400	99000	<10	790	900	3800	300	1400	22	<10
0,5% aBC 850C	120	300	26	2900	<10	370	250	530	22	70	<10	<10
1% aBC 850C	20	57	11	2700	<10	170	55	89	<10	16	<10	<10
2% aBC 850C	<0,30	<0,20	<0,30	1,7	<0,30	8,9	0,81	<0,30	<0,30	<0,30	<0,30	<0,30
5% aBC 850C	<0,30	0,50	<0,30	7,5	<0,30	1,2	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30
0,1% aBC CO2	1400	10000	1300	100000	<10	710	840	3400	260	1200	18	<10
0,5% aBC CO2	4,5	19	2,3	470	<0,30	45	14	27	1,1	5,1	<0,30	<0,30
1% aBC CO2	0,39	4,8	0,90	130	<0,30	9,2	1,4	1,5	<0,30	0,87	<0,30	<0,30
2% aBC CO2	<0,30	1,6	0,68	65	<0,30	3,4	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30
5% aBC CO2	<0,30	6,9	2,8	260	<0,30	1,0	<0,30	0,33	<0,30	1,1	<0,30	<0,30

… table continues…

	PFCA-11	(PFDoA)	(PFTrA)	(PFTA)	(PFHxDA)	(PFOSA)	4:2 (FTS)	6:2 (FTS) (H4PFOS)	8:2 (FTS)	(HPFHpA)	(PF-3,7-DMOA)	Sum PFAS
Prøvereferanse	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
Control	<10	<10	<10	<10	<10	59	<10	410	92	<10	<50	290000
0,1% BC	<10	<10	<10	<10	<10	71	<10	480	54	<10	<50	260000
0,5% BC	<10	<10	<10	<10	<10	26	<10	230	22	<10	<50	120000
1% BC	<10	<10	<10	<10	<10	<10	<10	81	<10	<10	<50	30000
2% BC	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	3900
5% BC	<0,30	<0,30	<1,0	<0,30	<0,30	1,0	<0,30	0,36	0,30	<0,30	<0,30	390
0,1% aBC 50%	<10	<10	<10	<10	<10	42	<10	320	64	<10	<50	170000
0,5% aBC 50%	<0,30	<0,30	<1,0	<0,30	<0,30	1,3	<0,30	1,6	0,52	<0,30	<0,30	2500
1% aBC 50%	<0,30	<0,30	<1,0	<0,30	<0,30	0,39	<0,30	<0,30	<0,30	<0,30	<0,30	380
2% aBC 50%	<0,30	<0,30	<1,0	<0,30	<0,30	0,50	<0,30	<0,30	<0,30	<0,30	<0,30	160
5% aBC 50%	<0,30	<0,30	<1,0	<0,30	<0,30	0,73	<0,30	0,36	0,35	<0,30	<0,30	440
0,1% aBC 75%	<10	<10	<10	<10	<10	30	<10	190	37	<10	<50	120000
0,5% aBC 75%	<10	<10	<10	<10	<10	<10	<10	<0,30	<0,30	<10	<50	1800
1% aBC 75%	<0,30	<0,30	<1,0	<0,30	<0,30	1,5	<0,30	1,2	0,62	<0,30	<0,30	1100
2% aBC 75%	<0,30	<0,30	<1,0	<0,30	<0,30	0,94	<0,30	<0,30	<0,30	<0,30	<0,30	120
5% aBC 75%	<0,30	<0,30	<1,0	<0,30	<0,30	0,41	<0,30	<0,30	<0,30	<0,30	<0,30	150
0,1% aBC 100%	<10	<10	<10	<10	<10	22	<10	110	27	<10	<50	71000
0,5% aBC 100%	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	0,48	<0,30	<0,30	<0,30	580
1% aBC 100%	<0,30	<0,30	<1,0	<0,30	<0,30	0,57	<0,30	<0,30	<0,30	<0,30	<0,30	170
2% aBC 100%	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	65
5% aBC 100%	<0,30	<0,30	<1,0	<0,30	<0,30	0,30	<0,30	<0,30	<0,30	<0,30	<0,30	100
0,1% aBC 125%	<10	<10	<10	<10	<10	<10	<10	35	<10	<10	<50	28000
0,5% aBC 125%	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	190
1% aBC 125%	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	85
2% aBC 125%	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	93
5% aBC 125%	<0,30	<0,30	<1,0	<0,30	<0,30	0,93	<0,30	<0,30	<0,30	<0,30	<0,30	260
0,1% aBC 800C	<10	<10	<10	<10	<10	60	<10	380	71	<10	<50	210000
0,5% aBC 800C	<10	<10	<10	<10	<10	<10	<10	18	13	<10	<50	9400
1% aBC 800C	<0,30	<0,30	<1,0	<0,30	<0,30	1,7	<0,30	1,9	0,65	<0,30	<0,30	760
2% aBC 800C	<0,30	<0,30	<1,0	<0,30	<0,30	0,77	<0,30	1,3	0,36	<0,30	<0,30	670
5% aBC 800C	<0,30	<0,30	<1,0	<0,30	<0,30	0,56	<0,30	<0,30	<0,30	<0,30	<0,30	300
0,1% aBC 850C	<10	<10	<10	<10	<10	40	<10	220	38	<10	<50	120000
0,5% aBC 850C	<10	<10	<10	<10	<10	<10	<10	10	<10	<10	<50	4600
1% aBC 850C	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<50	3100
2% aBC 850C	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	11
5% aBC 850C	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	9,2
0,1% aBC CO2	<10	<10	<10	<10	<10	43	<10	220	54	<10	<50	120000
0,5% aBC CO2	<0,30	<0,30	<1,0	<0,30	<0,30	0,98	<0,30	0,51	0,39	<0,30	<0,30	590
1% aBC CO2	<0,30	<0,30	<1,0	<0,30	<0,30	0,45	<0,30	<0,30	<0,30	<0,30	<0,30	150
2% aBC CO2	<0,30	<0,30	<1,0	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	<0,30	71
5% aBC CO2	<0,30	<0,30	<1,0	<0,30	<0,30	0,83	<0,30	5,9	<0,30	<0,30	<0,30	280

Appendix E: Soil characteristics

Table E-1: pH changes in soil from Rygge Airport

Amendment dose (%)	BC	aBC 50%	aBC 75%	aBC 100%	aBC 125%	aBC 800°C	aBC 850°C	aBC CO_2
High TOC soil								
0	3.97	3.97	3.97	3.97	3.97	3.97	3.97	3.97
0.1	4	3,97	4,28	3,94	3,94	4,03	4,22	4,26
0.5	4,05	4,04	4,34	4,09	4,2	4,01	4,19	4,15
1	4,13	4,19	4,16	4,32	4,52	4,06	4,23	4,32
2	4,12	4,28	4,13	4,48	4,96	4,2	4,38	4,51
5	5,05	4,64	4,46	4,68	5,88	4,44	4,67	5,08
Low TOC soil								
0	7,2	7,2	7,2	7,2	7,2	7,2	7,2	7,2
0.1	7,24	7,23	7,2	7,3	7,28	7,29	7,16	7,15
0.5	7,35	7,4	7,4	7,48	7,52	7,37	7,33	7,02
1	7,44	7,52	7,47	7,64	7,72	7,52	7,42	7,6
2	7,67	7,78	7,79	7,97	8,07	7,69	7,34	7,77
5	8,03	8,3	8,11	8,25	8,64	8,03	8,19	8,15

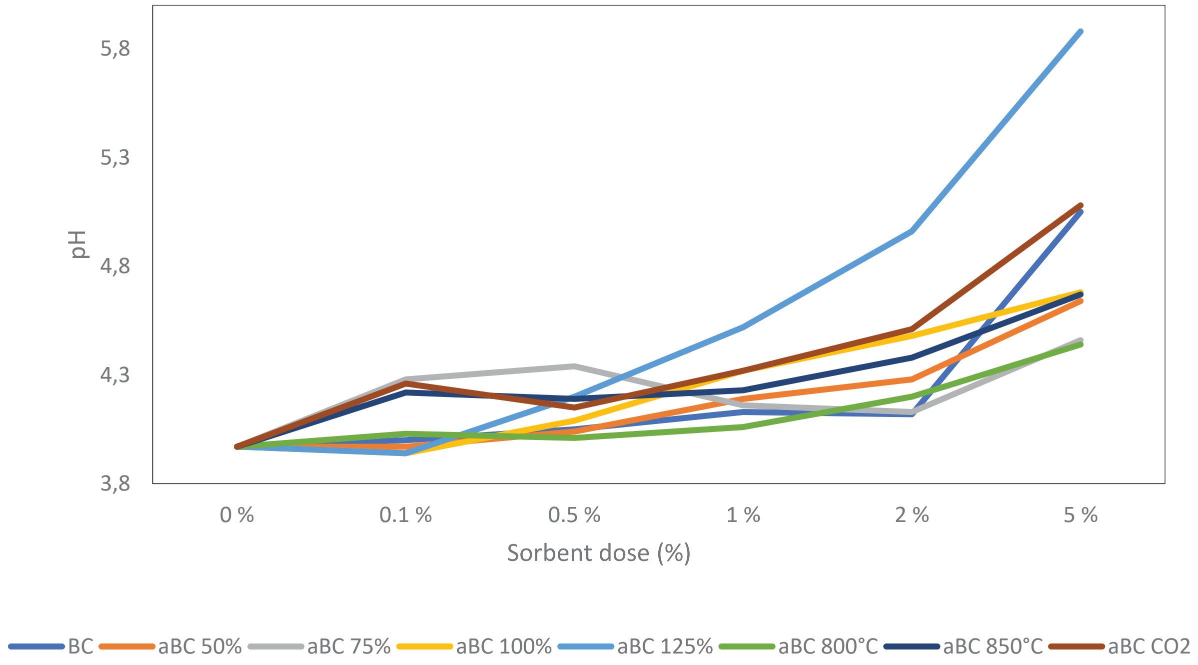


Figure E-1: pH changes in PFAS high TOC soil

Table E-2: DOC changes in soil from Rygge Airport

Amendment dose (%)	BC	aBC 50%	aBC 75%	aBC 100%	aBC 125%	aBC 800°C	aBC 850°C	aBC CO_2
High TOC soil								
0	330	330	330	330	330	330	330	330
0.1	330	510	390	520	520	400	460	270
0.5	340	480	370	440	430	390	430	370
1	310	460	440	360	350	420	380	200
2	340	420	480	320	230	380	340	270
5	190	340	350	260	74	310	450	290
Low TOC soil								
0	17	17	17	17	17	17	17	17
0.1	17	14	11	11	22	12	13	12
0.5	14	8,3	4,3	7,0	2,8	6,8	8,4	5,3
1	13	5,6	3,0	4,8	2,2	5,1	6,5	3,4
2	10	4,1	2,5	1,9	1,9	2,5	4,6	2,4
5	5,7	4,3	2,4	1,5	2,0	2,2	2,6	2,4

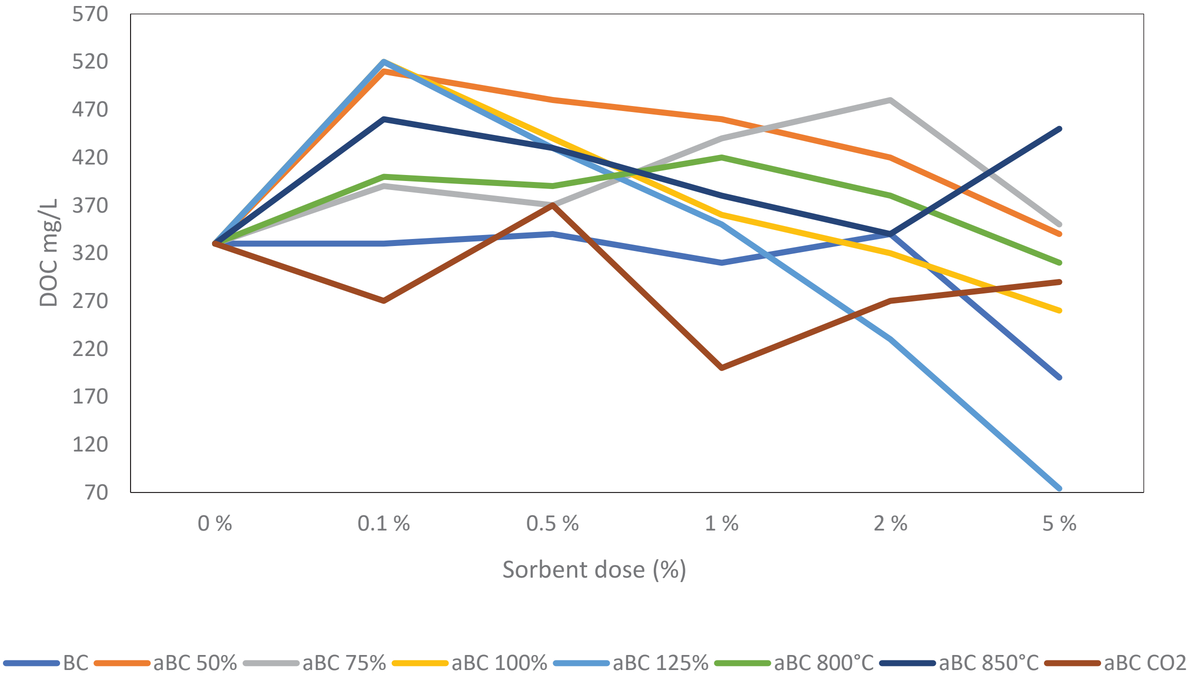
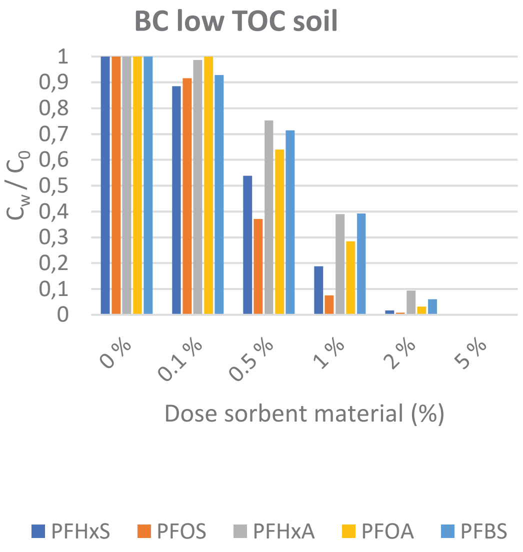


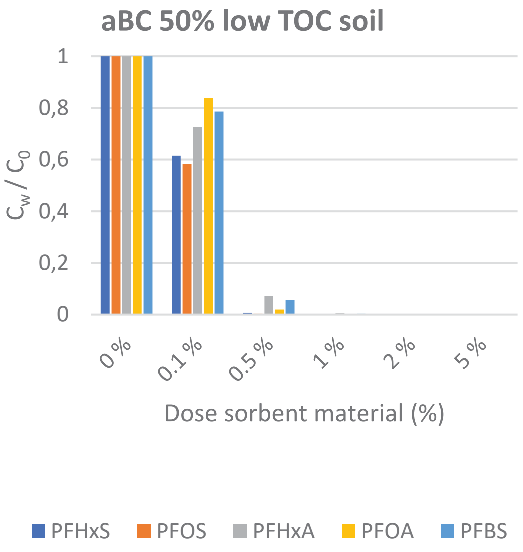
Figure E-2: DOC changes in PFAS high TOC soil

Appendix F: Reduction in PFAS water concentrations

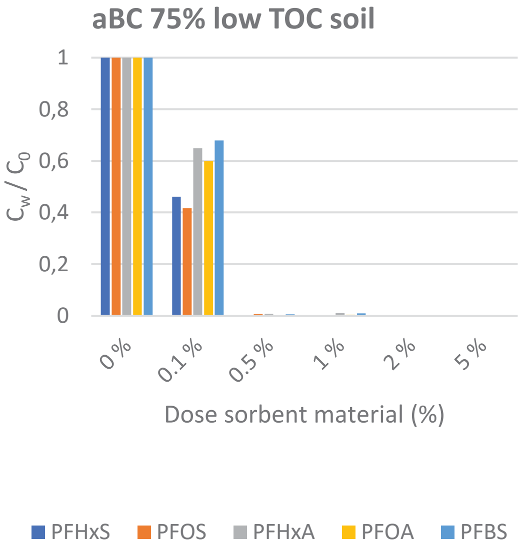
a



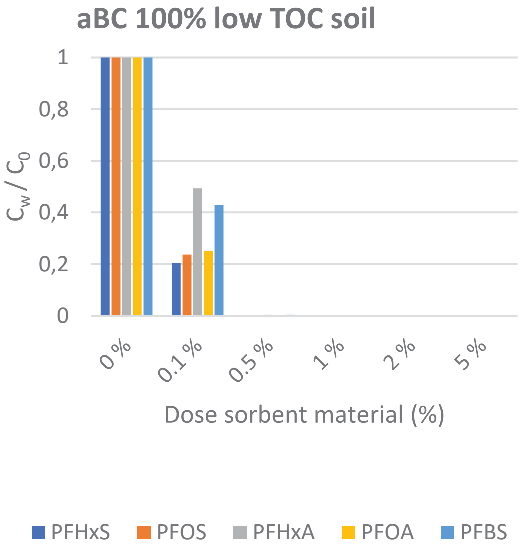
b

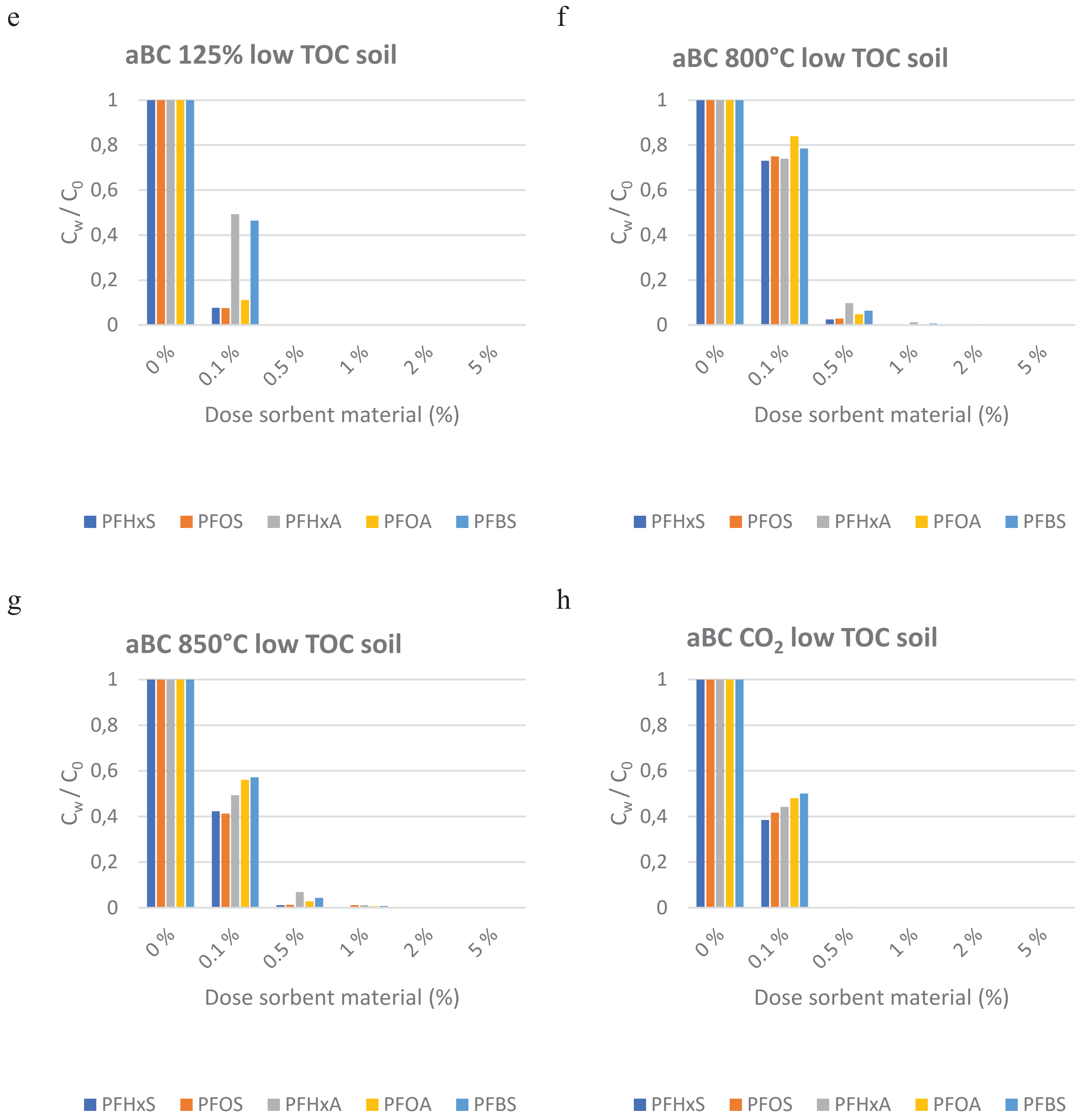


c



d




aBC 125% low TOC soil

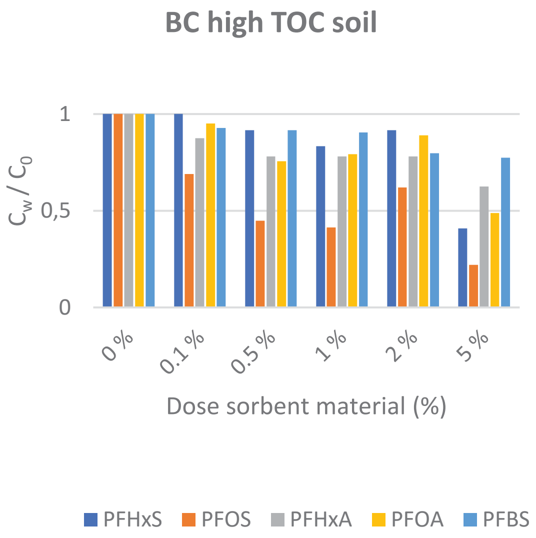
aBC 800°C low TOC soil

aBC 850°C low TOC soil

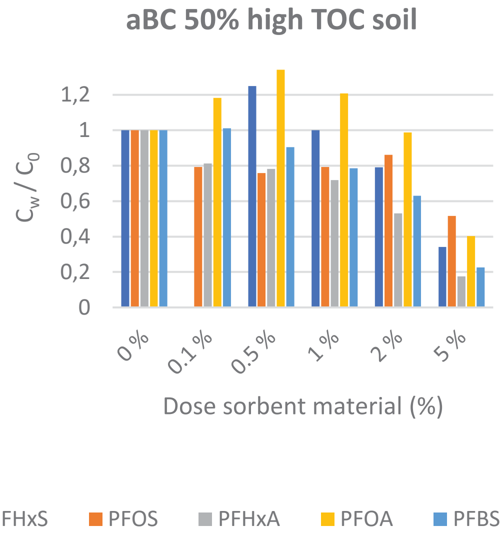
aBC CO_2 low TOC soil

Figure F-1: Reduction in PFAS water concentrations (C_w) in low TOC soil as a function of biochar amendment dose (%)

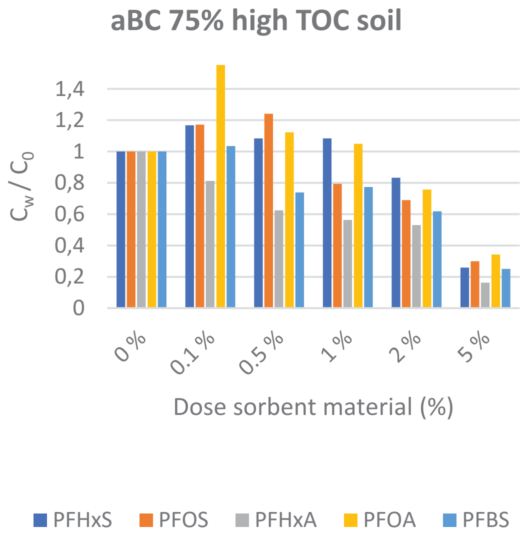
a


BC high TOC soil
C_w / C_0
1
0,5
0
0 %
0.1 %
0.5 %
1 %
2 %
5 %
Dose sorbent material (%)
PFHxS
PFOS
PFHxA
PFOA
PFBS

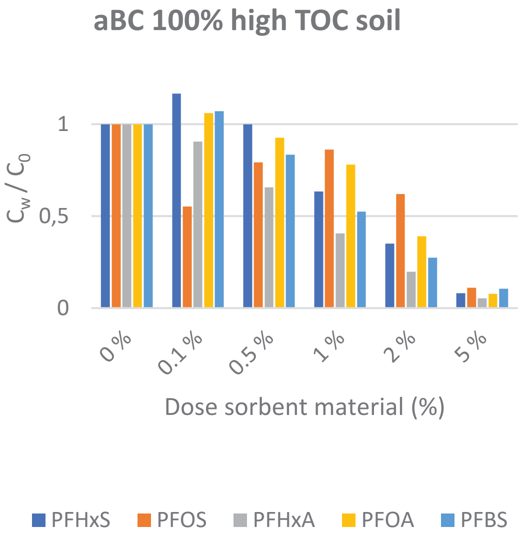
b


aBC 50% high TOC soil
C_w / C_0
1,2
1
0,8
0,6
0,4
0,2
0
0 %
0.1 %
0.5 %
1 %
2 %
5 %
Dose sorbent material (%)
PFHxS
PFOS
PFHxA
PFOA
PFBS

c


aBC 75% high TOC soil
C_w / C_0
1,4
1,2
1
0,8
0,6
0,4
0,2
0
0 %
0.1 %
0.5 %
1 %
2 %
5 %
Dose sorbent material (%)
PFHxS
PFOS
PFHxA
PFOA
PFBS

d


aBC 100% high TOC soil
C_w / C_0
1
0,5
0
0 %
0.1 %
0.5 %
1 %
2 %
5 %
Dose sorbent material (%)
PFHxS
PFOS
PFHxA
PFOA
PFBS

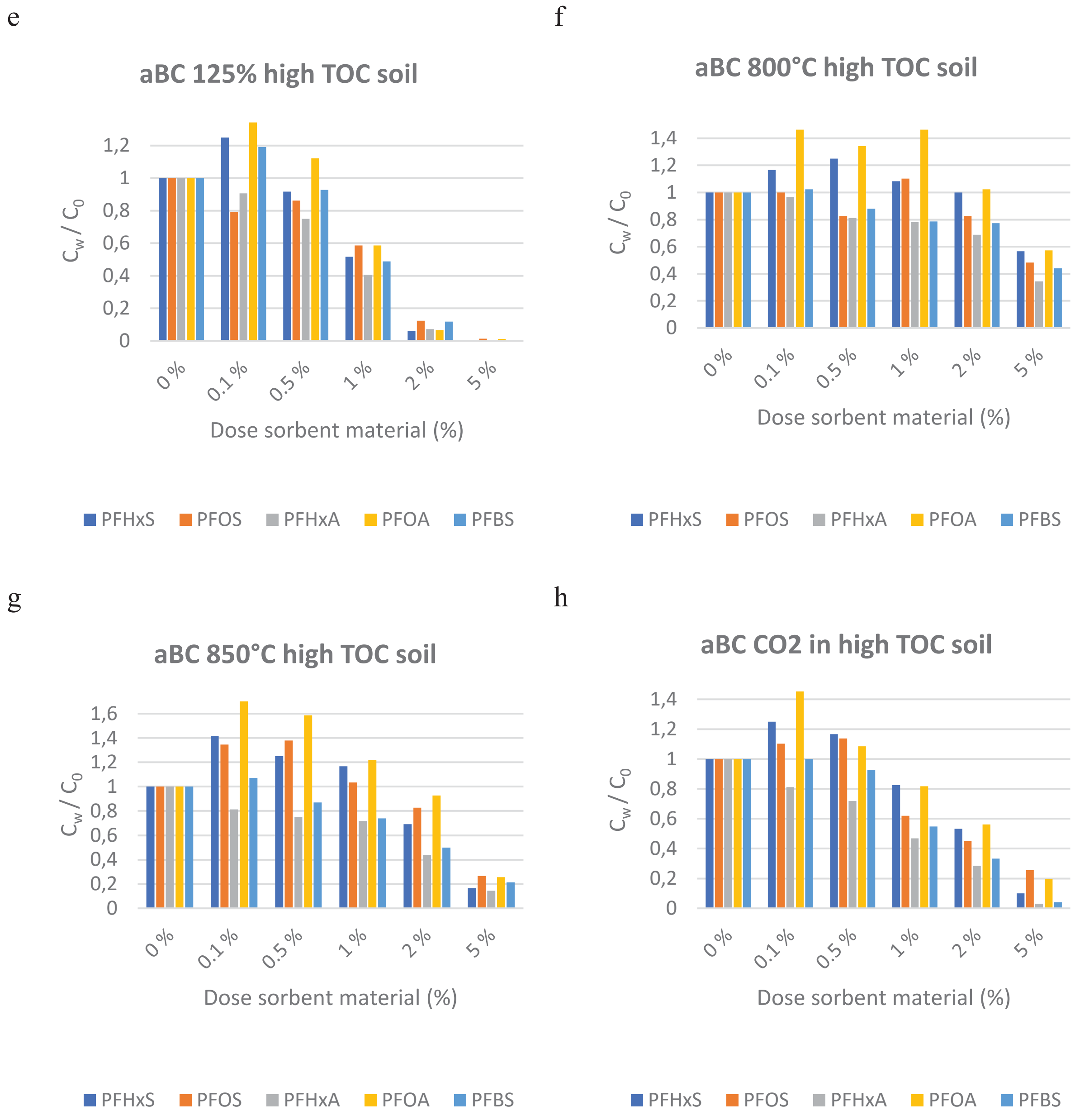


Figure F-2: Reduction in PFOS water concentrations (C_w) in high TOC soil as a function of biochar amendment dose (%)

Appendix G: % reduction in leached PFAS concentrations in high and low TOC soil from Rygge Airport

Table 0**Amendment and dose (%)**	**PFOS**	**PFHxS**	**PFHxA**	**PFOA**	**PFBS**	**Sum PFAS** (23)
BC	**Low TOC soil**					
0.1	8.33	11.54	1.3	0	7.14	10.34
0.5	62.92	46.15	24.68	36.00	28.57	58.62
1	92.50	81.15	61.04	71.60	60.71	89.66
2	99.21	98.35	90.65	96.80	93.93	98.66
5	99.86	99.95	99.86	99.89	99.90	99.87
aBC 50%	Low TOC soil					
0.1	41.67	38.46	27.27	16	21.43	41.38
0.5	99.65	99.31	92.73	98.04	94.29	99.14
1	99.95	99.95	99.51	99.9	99.66	99.87
2	99.95	99.99	99.99	99.97	99.99	99.94
5	99.83	99.94	99.95	99.9	100*	99.85
aBC 75%	Low TOC soil					
0.1	58.33	53.85	35.06	40	32.14	58.62
0.5	99.38	99.82	99.25	100*	99.43	99.38
1	99.74	99.79	99.95	99.63	99.11	99.62
2	99.96	100	99.99	100	99.99	99.96
5	99.94	99.99	100*	99.98	100*	99.95
aBC 100%	Low TOC soil					
0.1	76.25	79.62	50.65	74.8	57.14	75.52
0.5	99.89	99.95	99.53	99.92	99.61	99.8
1	99.96	100	99.95	100*	99.95	99.94
2	99.98	100	99.99	100*	100*	99.98
5	99.96	100	100*	100*	100*	99.97
aBC 125%	Low TOC soil					
0.1	92.5	92.31	50.65	88.8	53.37	90.34
0.5	99.98	100	99.97	100*	99.97	99.93
1	99.98	100	100*	100*	100*	99.97
2	99.96	99.99	100*	99.99	100*	99.97
5	99.9	99.97	100*	99.95	100*	99.91
aBC 800°C	Low TOC soil					
0.1	25	26.92	25.97	16	21.43	27.59
0.5	97.13	97.50	90.26	95.2	93.57	96.76
1	99.87	99.81	98.75	99.56	99.29	99.74
2	99.78	99.83	99.64	99.72	99.73	99.77
5	99.88	99.97	99.99	99.95	100*	99.9
aBC 850°C	Low TOC soil					
0.1	58.75	57.69	50.65	44	42.86	58.62
0.5	98.79	98.85	93.12	97.2	95.71	98.41
1	98.88	99.78	98.84	99.36	99.29	98.93
2	100	100*	100*	100*	100*	100
5	100	100	100*	100*	100*	100
aBC CO_2	Low TOC soil					
0.1	58.33	61.54	55.84	52	50	58.62
0.5	99.8	99.93	99.65	99.8	99.84	99.8
1	99.95	99.98	99.98	99.97	99.99	99.95
2	99.97	99.99	100*	100*	100*	99.98
5	99.89	99.97	100	99.96	100*	99.9
BC	**High TOC soil**					
0.1	31.03	0	12.5	4.88	7.14	19.61
0.5	55.17	8.33	21.88	24.39	8.33	37.25
1	58.62	16.67	21.88	20.73	9.52	43.14

2	37.93	8.33	21.88	10.98	20.24	27.45
5	77.93	59.17	37.50	51.22	22.62	68.63
aBC 50%	High TOC soil					
0.1	20.69	-	18.75	< 0	< 0	35.29
0.5	24.14	< 0	21.88	< 0	9.52	9.8
1	20.69	0	28.13	< 0	21.43	15.69
2	13.79	20.83	46.88	1.22	36.9	19.61
5	48.28	65.83	82.50	59.76	77.38	58.82
aBC 75%	High TOC soil					
0.1	< 0	< 0	18.75	< 0	< 0	< 0
0.5	< 0	< 0	37.5	< 0	26.19	< 0
1	20.69	< 0	43.75	< 0	22.62	17.65
2	31.03	16.67	46.88	24.39	38.1	29.41
5	70	74.17	83.75	65.85	75	72.55
aBC 100%	High TOC soil					
0.1	44.83	< 0	9.38	< 0	< 0	21.57
0.5	20.38	0	34.38	7.32	16.67	17.65
1	13.79	36.67	59.38	21.95	47.62	27.45
2	37.93	67	80.31	60.98	72.62	50.98
5	88.97	91.83	94.69	92.20	89.52	89.80
aBC 125%	High TOC soil					
0.1	20.69	< 0	9.38	< 0	< 0	3.92
0.5	13.79	8.33	25	< 0	7.14	13.73
1	41.38	48.33	59.38	41.46	51.19	45.1
2	87.59	94.08	92.81	93.29	88.10	89.02
5	98.59	99.71	100*	98.79	100*	99.10
aBC 800°C	High TOC soil					
0.1	0	< 0	3.13	< 0	< 0	< 0
0.5	17.24	< 0	18.75	< 0	11.9	3.92
1	< 0	< 0	21.88	< 0	21.43	< 0
2	17.24	0	31.25	< 0	22.62	15.69
5	51.72	43.33	65.63	42.68	55.95	50.98
aBC 850°C	High TOC soil					
0.1	< 0	< 0	18.75	< 0	< 0	< 0
0.5	< 0	< 0	25	< 0	13.10	< 0
1	< 0	< 0	28.13	< 0	26.19	< 0
2	30.83	17.24	56.25	7.32	50	27.45
5	83.33	73.45	85.63	74.39	78.57	78.43
aBC CO_2	High TOC soil					
0.1	< 0	< 0	18.75	< 0	0	< 0
0.5	< 0	< 0	28.13	< 0	7.14	< 0
1	37.93	17.5	53.13	18.29	45.24	35.29
2	55.17	46.67	71.56	43.9	66.67	56.86
5	74.48	90	97	80.49	95.95	81.96

Appendix H: Log K_D values for high and low TOC soil from Rygge Airport

	High TOC soil		Low TOC soil	
Amendment	1%	5%	0.1%	1%
PFBS				
BC	2.69	2.43	2.85	3.16
aBC 50%	3.10	3.50	3.40	5.43
aBC 75%	3.13	3.44	3.64	5.01
aBC 100%	3.63	3.9	4.09	6.27
aBC 125%	3.69		4.03	
aBC 800°C	3.10	3.07	3.40	5.11
aBC 850°C	3.22	3.53	3.84	5.11
aBC CO_2	3.58	4.34	3.97	6.82
PFHxA				
BC	2.86	2.49	1.88	2.95
aBC 50%	3.00	3.38	3.33	5.06
aBC 75%	3.30	3.42	3.49	4.73
aBC 100%	3.57	3.96	3.77	6.05
aBC 125%	3.57		3.77	
aBC 800°C	2.86	2.99	3.30	4.66
aBC 850°C	3.00	3.48	3.77	4.69
aBC CO_2	3.69	4.40	3.86	6.47
PFHxS				
BC	3.26	3.42	3.00	3.52
aBC 50%		3.55	3.68	6.19
aBC 75%		3.72	3.95	5.56
aBC 100%	3.72	4.31	4.48	7.19
aBC 125%	3.93	5.80	4.97	7.19
aBC 800°C		3.15	3.45	5.61
aBC 850°C		3.96	4.02	5.54
aBC CO_2	3.29	4.22	4.09	6.62
PFOA				
BC	3.94	3.84		3.44
aBC 50%		3.99	3.31	6.03
aBC 75%		4.10	3.86	5.46
aBC 100%	3.97	4.89	4.51	
aBC 125%	4.37	5.73	4.93	
aBC 800°C		3.69	3.31	5.39
aBC 850°C		4.28	3.93	5.22
aBC CO_2	3.87	4.43	4.07	6.49

Appendix I: Shooting range soil sorption data

Table I-1: C_w of Cu, Sb, and Pb (µg/L) in shooting range soil after amended with sorbents materials.

Amendment and dose (%)	**Cu (µg/L)**	**Sb (µg/L)**	**Pb (µg/L)**
BC	**Low TOC soil**		
2.5	130	320	150
5	100	350	180
10	110	370	180
20	95	350	210
BC-ZVI	Low TOC soil		
2.5	70	120	120
5	42	4,8	58
10	32	2,5	3,8
20	43	15	9,4
ZVI	Low TOC soil		
2.5	39	59	110
5	23	3,2	20
10	63	16	<1,5
20	38	6,3	<LD
BC-S-ZVI	Low TOC soil		
2.5	34	24	740
5	14	48	95
10	14	29	250
20	9,6	74	64
BC	**High TOC soil**		
2.5	51	150	130
5	56	190	160
10	50	150	140
20	70	220	180
BC-ZVI	High TOC soil		
2.5	24	67	54
5	47	5,6	100
10	15	1,5	23
20	36	3,8	13
ZVI	High TOC soil		
2.5	15	39	75
5	34	10	90
10	27	2,4	<LD
20	45	0,99	<LD
BC-S-ZVI	High TOC soil		
2.5	82	50	1200
5	4,1	7,0	86
10	13	17	150
20	36	12	310
Limit of detection, LD in w/V	0,956515234	0,039457169	0,449006039
Limit of quantification, LQ in w/V	3,188384114	0,131523897	1,496686796

Table I-2: % sorbed or % reduction in leached Cu, Sb, and Pb C_w in shooting range soil after amendment with sorbent materials.

Amendment and dose (%)	**Cu**	**Sb**	**Pb**
BC	**Low TOC soil**		
2.5	-38,30	5,88	11,76
5	-6,38	-2,94	-5,88
10	-17,02	-8,82	-5,88
20	-1,06	-2,94	-23,53
BC-ZVI	Low TOC soil		
2.5	25,53	64,71	29,41
5	55,32	98,59	65,88
10	65,96	99,26	97,76
20	54,26	95,59	94,47
ZVI	Low TOC soil		
2.5	58,51	82,65	35,29
5	75,53	99,06	88,24
10	32,98	95,29	100*
20	59,57	98,15	100*
BC-S-ZVI	Low TOC soil		
2.5	63,83	92,94	-335,29
5	85,11	85,88	44,12
10	85,11	91,47	-47,06
20	89,79	78,24	62,35
BC	**High TOC soil**		
2.5	43,96	-36,36	-18,18
5	38,46	-72,73	-45,45
10	45,05	-36,36	-27,27
20	23,08	-100,00	-63,64
BC-ZVI	High TOC soil		
2.5	73,63	39,09	50,91
5	48,35	94,91	9,09
10	83,52	98,64	79,09
20	60,44	96,55	88,18
ZVI	High TOC soil		
2.5	83,52	64,55	31,82
5	62,64	90,91	18,18
10	70,33	97,82	99,80
20	50,55	99,10	99,80
BC-S-ZVI	High TOC soil		
2.5	9,89	54,55	-990,91
5	95,49	93,64	21,82
10	85,71	84,55	-36,36
20	60,44	89,09	-181,82

< 0 = increase in C_w after remediation

* = C_w was under limit of detection, and 100% sorption was assumed occur

Appendix J: Partitioning of elements between BC-ZVI and water in soil

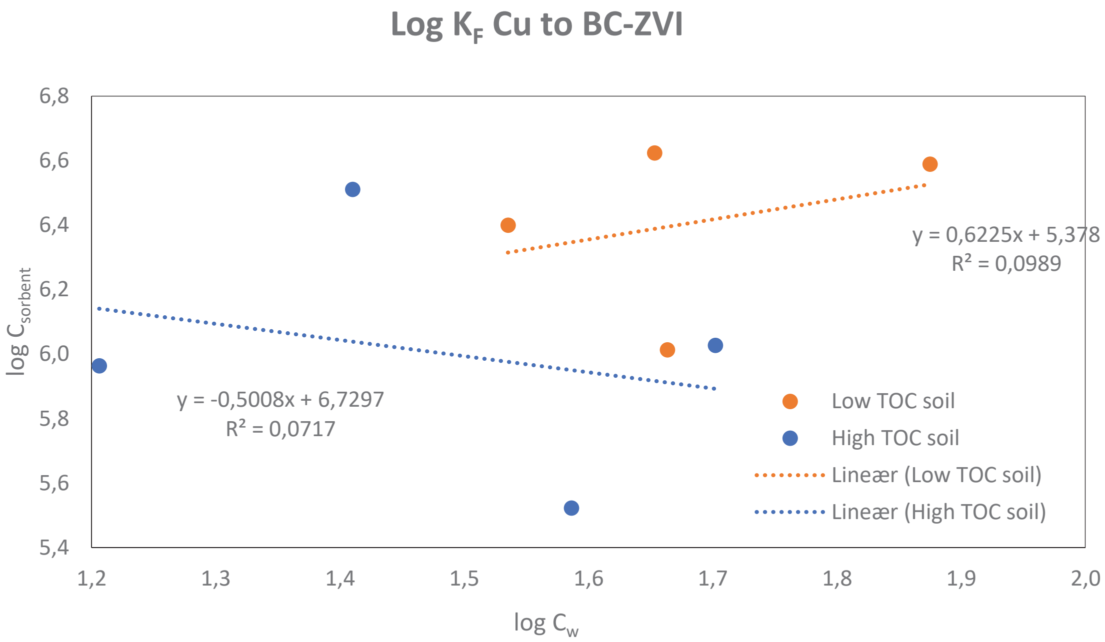


Figure J-1: Partitioning of Cu between solid and aqueous phase in high (16.2%) and low (4.7%) TOC soil.

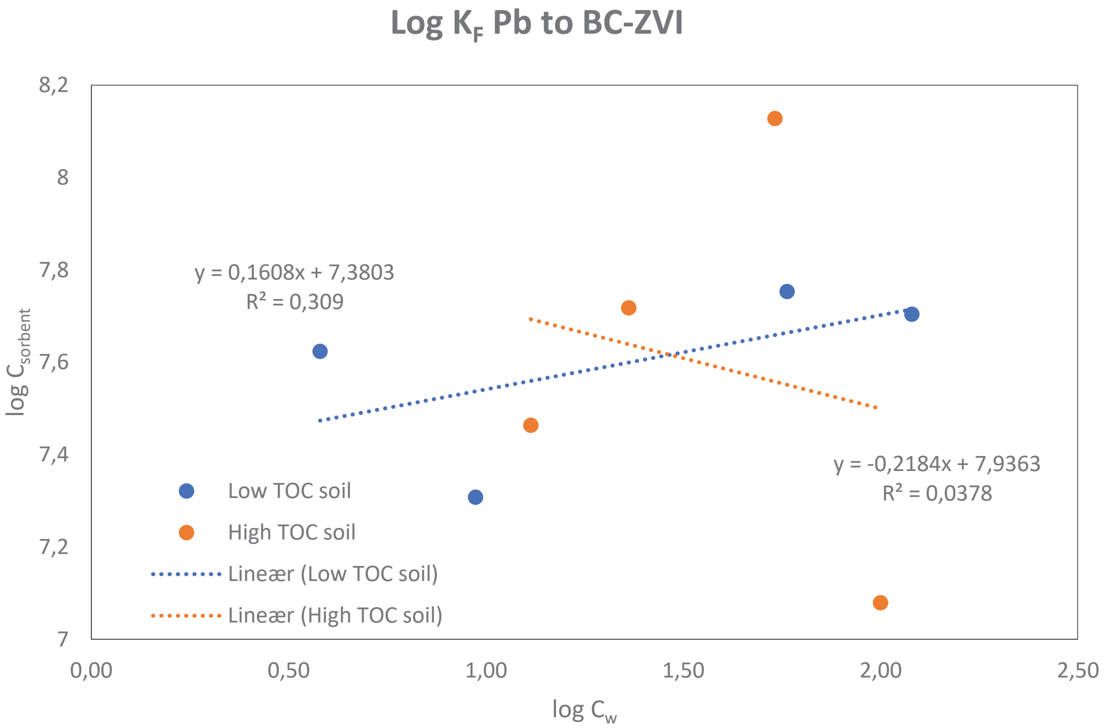


Figure J-1: Partitioning of Pb between solid and aqueous phase in high (16.2%) and low (4.7%) TOC soil.

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