



Sewage sludge biochars as effective PFAS-sorbents

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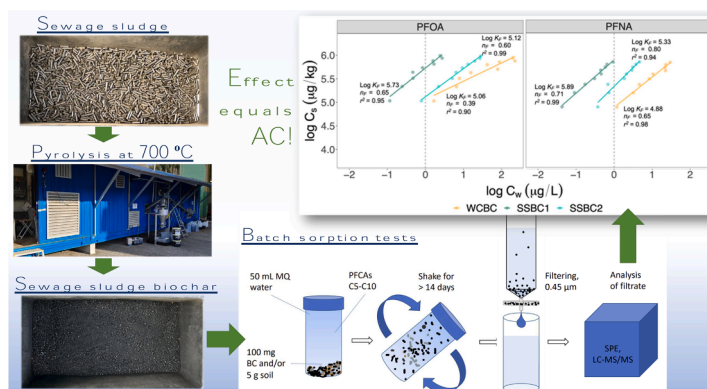
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HIGHLIGHTS

- Sorption isotherms for six perfluorinated carboxylic acids to sewage sludge biochars.
- Sorption effectiveness better for sewage sludge biochars than wood-based biochar and similar to activated carbons.
- Availability of pore volume and surface area within large enough pore size range identified as key factor.
- Attenuation effect from competition with similar compounds stronger than attenuation from soil organic matter.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of sewage sludge to produce biochar-based sorbents for per- and polyfluoroalkyl substances (PFAS) removal from water and soil may be an economically and environmentally sustainable waste management option. This study compared the sorption of six perfluorinated carboxylic acids (PFCAs) by two sewage sludge biochars (SSBCs) and one wood chip biochar (WCBC), dry pyrolyzed at 700 °C. Batch sorption tests were conducted by adding individual PFCAs and a PFCA-mixture to pure biochars and mixtures of biochar and a sandy soil (1.3% TOC). PFAS-sorption to the SSBCs exhibited log-linear biochar-water distribution coefficients ($\log K_d$), comparable to those previously reported for commercial activated carbons (e.g., 5.73 ± 0.02 for perfluorooctanoic acid at 1 µg/L). The strong sorption of PFCAs was attributed to the SSBCs relatively high pore volumes in the pore size range that can accommodate these compounds. Sorption was attenuated by the presence of soil (by factors 3–10), by the presence of a mixture of PFCAs (by factors of 6–532) and by both together (by factors of 8–6581), indicating strongly competitive sorption between PFCA-congeners, and less severe sorption

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attenuation by soil organic matter. These findings could enable sustainable value chains for SSBs in soil remediation and water filtration solutions.

1. Introduction

Per- and polyfluorinated alkyl substances (PFAS) are a large group of synthetic compounds that are currently undergoing a group restriction process in Europe (European Commission, 2020) due to their collective tendency to contaminate water, food chains and soils at trace concentrations over intergenerational timescales (Hale et al., 2020). Point-sources of PFAS contamination include paper mills (Langberg et al., 2021; Lee et al., 2020), landfills (Masoner et al., 2020), fire-fighting training facilities (Filipovic et al., 2015), and fluorochemical plants (Gebbinck et al., 2017). Two of the most widely used and distributed compounds, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), are listed under the Stockholm Convention as persistent organic pollutants (POPs). After decades of use, PFAS are ubiquitous in soils, groundwater, and surface water (Rankin et al., 2016). This puts wastewater treatment plants under pressure to adequately treat waste streams to avoid further proliferation of PFAS chemicals (Lenka et al., 2021).

Perfluorinated carboxylic acids (PFCA) and perfluorinated sulfonic acids (PFSA) are two PFAS groups of the highest environmental concern. These differ in structure according to their respective functional groups. The combination of a $(CF_2)_n$ tail that is both hydrophilic and lipophilic, and an ionizable hydrophilic head group, makes understanding the fate of PFCAs and PFSAs in the environment more complex than that of legacy POPs (Arp et al., 2006; Cabrerizo et al., 2018). The same is true for the abatement of their environmental risk. Thus, research is needed to develop effective tools for remediating PFAS-contamination. Adsorption technology is among the most promising tools for the energy- and cost-effective treatment of contaminated soils and waters (Ahmad et al., 2014; Alhashimi and Aktas, 2017; Beesley et al., 2011; Hale et al., 2017). To this end, sorbents must be identified that show strong affinity to PFAS. Previous research has postulated that high surface area, porosity, and carbon content are important for sorption of organic contaminants (Ahmad et al., 2014; Cornelissen et al., 2005; Hale et al., 2016; Zimmerman et al., 2004). Today, activated carbon (AC), generally from fossil coal sources like anthracite, is the most common sorbent used for soil remediation because of its high porosity and carbon content (Hagemann et al., 2018). However, AC can be costly and chemical- and energy-intensive to produce (Ahmed et al., 2019).

The application of biochar as a sorbent is relatively novel (Beesley et al., 2011; Hale et al., 2011), and even more so is the use of sewage sludge for biochar production (Khan et al., 2013; Regkouzas and Diamadopoulos, 2019; Tang et al., 2018). The main advantage of biochar over AC is its greater sustainability, as shown in an end-point life-cycle analysis (Sparrevik et al., 2011), due to its potential for carbon sequestration (Smith, 2016) and reduced use of chemicals and reliance on coal mines (Zheng et al., 2019). Biochar is often produced from wood-based sources (Hale et al., 2016). However, from a circular economy perspective, it may be even more attractive to use lightly contaminated waste as a substrate to make biochar sorbents. Sewage sludge can be expensive and problematic to dispose of in landfills because of significant concentrations of toxic metals, microplastics, pathogens, and organic contaminants (Propp et al., 2021; Raheem et al., 2018). Incineration of sewage sludge releases substantial amounts of greenhouse gases (GHG), fly ashes, and PAHs (Huang et al., 2022). Thus, the pyrolysis of sewage sludge into biochar could offer the possibility of a more sustainable waste management alternative to landfilling or incineration, as it would both remove many of the contaminants present in the sludge, including much of the PFAS (Sajjadi et al., 2019), and produce a sorbent for PFAS.

An expected challenge for substituting SSBC for AC as a PFAS sorbent

is a lower carbon content, porosity and surface area compared to AC or wood-based biochars, as these three factors usually contribute to stronger sorption (Leng et al., 2021). This was the case in an investigation of PFAS removal from contaminated water by one sewage sludge biochar and one wood-based biochar by Kundu et al. (2021), who found that the wood-based biochar had a better PFAS removal effect due to a higher surface area. In addition, an important consideration when placing sorbents in organic matter (OM)-rich soils is that certain pore sizes are prone to blockage by large organic molecules (Sorengard et al., 2019; Sørmo et al., 2021). There is a general agreement that the presence of organic pollutants and/or soil organic matter has the greatest effect in weakening (“attenuating”) the sorption of PFAS and other organic compounds to biochar, activated carbon and other carbonaceous geosorbents (Higgins and Luthy, 2006; Kwon and Pignatello, 2005; Teixeira et al., 2013; Zareitalabad et al., 2013). Large organic molecules kinetically limit the sorption of PFAS through steric hindrance, i.e., obstructing the entrances of biochar pores (Mahinroosta and Senevirathna, 2020; Pignatello et al., 2006). Furthermore, smaller humic molecules can compete with PFAS for surficial sorption sites, thus reducing the sorption capacity of biochar (Du et al., 2014). These mechanisms have been shown to attenuate sorption by factors of 7–150 compared to sorption in pure water (Cornelissen and Gustafsson, 2004; Hale et al., 2009; Teixeira et al., 2013).

To investigate the potential of biochars derived from sewage sludge to be sustainable PFAS sorbents, the present work studies for the first time to our knowledge (i) aqueous sorption of a range of PFCA compounds of varying concentrations and comparing their relative sorption strengths to SSBCs and biochar made from clean wood chips (WCBC), (ii) effects of perfluorinated carbon chain-length on PFCA sorption to SSBCs, and (iii) attenuation effect of competing sorbates and the presence of soil on PFCA sorption to biochars. The results of this work will aid in realizing the potential for valorization of sewage sludge biochars as sorbents in the remediation of PFAS-contaminated soil and water.

2. Methods

2.1. Biochar sorbents

2.1.1. Feedstock

Three feedstocks were selected for biochar production: dewatered sewage sludge from the Gardermoen wastewater treatment plant (60.170 N, 11.114 E) located in Ullensaker northeast of Oslo, Norway (SSBC1); the digestate from anaerobically digested sludge and food waste from Lindum waste handling company (59.691 N, 10.271 E), Drammen, Norway (SSBC2); and commercially available clean wood chips (WCBC) from fresh additive-free mixed softwood timber mainly of spruce and pine (Hallingdal Trepellets, Ål, Norway). The feedstocks were dried (SSBC1 and SSBC2) or shredded (WCBC) and compressed into 8 mm pellets before pyrolysis.

2.1.2. Pyrolysis

The biochars were produced at Lindum AS (Drammen, Norway) by slow pyrolysis at 700 °C and a residence time of 20 min for WCBC and SSBC2, and 40 min for SSBC1 using Biogreen© technology. Details on the pyrolysis process can be found in the supporting information (SI). A biochar sub-sample (100 g) was taken by random grab-sampling from the bulk volume (~5 kg). The biochars were crushed using a ball mill (Retsch ISO 9001) at 50 rpm for 5 min, then sieved into fine-powdered biochar (diameters <1 mm).

2.1.3. Biochar characterization

Total surface area (SA) and pore volume (PV) were determined by nitrogen (N₂) and carbon dioxide (CO₂) gas sorptiometry at -195.8 °C and 0 °C, respectively, using a Quantachrome Autosorb 1 surface area analyzer according to the methods described by [Kwon and Pignatello \(2005\)](#) and interpreted using density functional theory (DFT). Analyses of the biochar total elemental composition were performed in triplicate according to DIN 51732. Total carbon (C) was analyzed by the dry combustion method at 1030 °C described by [Nelson and Sommers \(1982\)](#). Total nitrogen (N) was determined according to the *Dumas* method ([Bremmer and Mulvaney, 1982](#)) by the same principles as that of total C. Other major elements (Ca, Fe, K, Mg, Na) were determined by NO₃-digestion at 260 °C in an Ultraclave from Milstone, followed by dilution and analysis using an Agilent Triple QQQ 8800 ICP-MS with an ICP-OES. In these analyses, the NJV 94-5 and NCS ZC 73007 certified reference materials were used for quality control purposes.

2.2. Soil

Soil used for batch sorption tests was an unaged, sandy Eutric Cambisol sampled in a 1 m³ bulk from the B horizon (40–160 cm depth) in a remote agricultural field, 17 km South of Uppsala, Sweden (59.733 N, 17.667 E). The bedrock in the area consists of weathered and partly metamorphosed granitoids, while the vegetation is hemiboreal forest in combination with agricultural lands where food grains and ryegrass are grown. The bulk sample was homogenized before a subsample taken by random grab sampling (1 kg, 10–20 scoops). The soil carbon content was determined through dry combustion according to ISO10694 (1995) using an elemental analyzer for macro samples (TruMac® CN, Leco corp, St. Joseph, MI, USA). The soil was dried at 100 °C for 24 h, and then crushed and sieved to < 2 mm before use in the batch test.

2.3. Chemicals

Six perfluorinated carboxylic acids (PFCAs) were selected as target sorptives for the batch sorption test experiments: perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA), which have from 4 to 9 CF₂ moieties, respectively. Stock solutions of each PFCA were prepared from pure compound salts/liquids (95%) bought from Sigma Aldrich (Oslo, Norway) that were dissolved in methanol (MeOH, SupraSolv, 99%) acquired from VWR Chemicals (Trondheim, Norway).

The following chemicals were used for sample extraction and analysis: ammonium acetate (NH₄Ac, ≥98%) and LC-MS grade MeOH (>99.9%) bought from VWR Chemicals (Trondheim, Norway); formic acid (FA, 96%) acquired from Sigma Aldrich (Oslo, Norway); and ¹³C₈-perfluorooctanoic acid (¹³C₈-PFOA, 99%), purchased from Cambridge Isotope Laboratories.

Purified water, Milli-Q grade (MQ, 18 MΩ), was produced with a Q-option Elga Labwater system from Veolia Water systems LTD UK.

2.4. Batch sorption tests

Batch sorption tests were prepared with a liquid-to-solid mass ratio (L/S) of 500 v/w for biochar and water solution, and 10 v/w for soil amended with 2% (w/w) biochar and water solution. The tests were based on the European standard CEN EN 12457, with modifications as described in [Hale et al. \(2017\)](#) and [Kupryianchuk et al. \(2016\)](#). The different batch test categories prepared were: 1) biochar spiked with six individual PFCAs at 10 concentrations (BC-single), 2) biochar spiked with a cocktail of the six PFCA target sorptives in triplicate (BC-mix), 3) soil-biochar mixtures spiked with PFOA at 6 concentrations (BC-S-PFOA), 4) soil-biochar mixtures spiked with the PFCA cocktail at 6 concentrations (BC-S-mix), 5) soil spiked with six individual PFCAs in triplicate (soil-single), and 6) soil spiked with the PFCA cocktail in

triplicate (soil-mix). The concentration range used to construct sorption isotherms spanned four orders of magnitude with single concentration points ([Table S6](#)) and was based on the approach suggested by [Kreyling et al. \(2018\)](#), where statistical evidence is provided that the amount of single concentration points maximized over a large range is preferable over having a smaller number of replicated points, when the aim is to discern patterns of a numeric response variable along continuous drivers, in this case regression analysis of sorption as a function of concentration over a wide concentration range. Special attention was paid to ensure that the concentrations spiked were below the critical micelle concentrations (CMC) of the different PFCAs ([Bhatarai and Gramatica, 2011](#); [Ding and Peijnenburg, 2013](#)) and that the samples contained < 1% MeOH. All samples were prepared in 50 mL polypropylene (PP) centrifuge tubes that were pre-rinsed three times with 50% MeOH.

Batch tests were shaken end-over-end (9 rpm) and/or agitated on a shaking table (160 rpm) at room temperature (23 °C) for 14 days, which has been shown sufficient for equilibration ([Kupryianchuk et al., 2016](#)). Following this period, samples were filtered through a 0.45 μm Minisart® regenerated cellulose syringe filter into PP tubes using the methods described in [Sorengard et al. \(2019\)](#). Soil samples were centrifuged to settle as many particles from suspension as possible prior to filtration.

2.5. Sample extraction and analysis

The batch test filtrates were prepared for analyte quantification by solid phase extraction (SPE) according to the methods described by [Arvaniti et al. \(2012\)](#) using a Phenomenex Strata-X RP® 200 mg/6 mL cartridge, followed by elution with 100% MeOH. The internal standard used was ¹³C₈-PFOA. A more detailed overview of the SPE protocol and QA/QCs is in the supplemental formation provided. The eluted samples were analyzed by UPLC®-MS/MS using an Acquity ultra-performance liquid chromatography (UPLC®) I-Class system connected to a Xevo TQ-S triple quadrupole mass spectrometer, equipped with an ESI Z spray working in negative mode (ESI⁻). PFAS were separated in a Kinetex C18 chromatographic column (30 × 2.1 mm, 1.3 μm) connected to a C18 (2 × 2.1 mm i.d.) security guard, both obtained from Phenomenex (Torrance, CA, U.S.). Milli-Q water with 2 mM NH₄Ac (A) and pure MeOH (B), were used as mobile phases. Information about chromatographic conditions and MS parameters are summarized in the SI. Data analysis and descriptive statistics did not include non-quantifiable data (i.e., < limit of quantification).

pH and conductivity were measured with a WTW inoLab pH meter and WTW LF538 conductivity meter, respectively, in a slurry of biochar and water (1:500) and biochar-soil-water (1:5) after stirring (15 min) and then settling (>24 h) before measurement (n = 3).

2.6. QA/QC

Several QA/QC procedures were considered during sample preparation and analysis. Contamination that may have arisen during preparation of samples and from laboratory materials was evaluated through the analysis of sample and procedural blanks. One procedural blank per batch of samples was prepared by spiking the internal standard (IS) directly into the SPE cartridge and eluting with methanol. Two blank samples were prepared by bringing 50 mL pH 3 MQ water (sample matrix), spiked with IS, through the extraction protocol. During analysis, solvent blanks (MeOH), and a standard mixture of the target sorptives at 10 ppb, were injected every 15–20 samples in order to monitor potential cross-contamination, carryover, and to assure maintenance of sensitivity. The injection needle was washed with a solution of MeOH:MQ (50:50; v/v) 0.1% FA before and after each injection. To correct for potential PFCA-loss when filtering the batch tests, spiked blanks of each compound were prepared in triplicate for each PFCA.

To ensure accuracy and precision, a 10-point calibration curve ranging from 0.01 to 50 ng/mL was prepared in methanol. The

Table 1

Surface area (SA) and pore volume (PV) interpreted using DFT, elemental composition (C, H, N, Ca, Mg, and Fe), and ratios for the sewage sludge biochars (SSBC1 and SSBC2) and the clean wood chips biochar (WCBC).

Biochar sorbent	CO ₂ sorption (pores 0.4–1.5 nm)		N ₂ sorption (pores > 1.5 nm)		Main elements (%)			Elemental ratios		Other elements (g/ kg)		
	Surface area (m ² /g)	Pore volume (cm ³ /g)	Surface area (m ² /g)	Pore volume (cm ³ /g)	C	H	N	H/C	C/ N	Ca	Mg	Fe
SSBC1	165	0.047	97	0.153	29.6	1.24	1.13	0.04	26	21	5.30	23
SSBC2	87	0.027	84	0.133	13.5	1.05	0.82	0.08	16	26	4.70	180
WCBC	683	0.186	261	0.160	91.4	1.01	0.69	0.01	133	8	0.91	0.1

correlation coefficient for all compounds remained above 0.98. The instrumental limits of quantification (iLOQs) were calculated for each target analyte as ten times the signal from the baseline noise (S/N ratio) and ranged from 0.01 to 2 ng/mL (Table S5). The method LOQs (mLOQs) were estimated accordingly by using pre-extraction spiked samples and ranged from 0.1 to 5 ng/mL (Table S5). Complete instrument programming, parameters and QA/QC samples are summarized in the SI. Signals below LOQ were achieved for the lowest batch test concentration points, and as a result, these data had to be removed from the data analysis.

2.7. Data analysis

Statistical analyses were carried out using the ggplot2 package (Wickham, 2016) in RStudio IDE (2022.02.0–443), R v.4.1.2.

As the sorption of PFCA to biochar was non-linear (Hale et al., 2016), the Freundlich equation was used to describe the sorption isotherms (Schwarzenbach et al., 2005; Yin et al., 2022) such that:

$$\log C_s = \log K_F + n_F \times \log C_w \quad (1)$$

where C_s is the sorbed PFCA concentration in $\mu\text{g}/\text{kg}$, K_F is the Freundlich distribution coefficient in $(\mu\text{g}/\text{kg})/(\mu\text{g}/\text{L})^{n_F}$, n_F is the dimensionless coefficient of non-linearity, and C_w is the equilibrium aqueous PFCA concentration in $\mu\text{g}/\text{L}$. As the sorbed PFAS concentration was not analyzed directly, C_s at equilibrium was calculated assuming 100% mass balance.

For those batch tests prepared in triplicate (BC-mix, soil-mix and soil-PFOA), distribution coefficients (K_d) between soil and/or biochar (C_s) and filtered water (C_w) were calculated assuming a linear sorption model by dividing the mean C_s by the mean C_w :

$$K_d = \frac{C_s}{C_w} \quad (2)$$

Note that at $C_w = 1 \mu\text{g}/\text{L}$, $K_d = K_F$, as inserting Eq. 2 into Eq. 1 gives $\log K_d = \log K_F + (n_F - 1) \log C_w$, and at $1 \mu\text{g}/\text{L}$ the “ $(n_F - 1) \log C_w$ ” term equals 0. Thus, the $\log K_F$ values reported here can be directly compared to $\log K_d$ values at $1 \mu\text{g}/\text{L}$ reported in the literature.

Modeling of soil-inclusive sorption isotherms (BC-S-mix and BC-S-PFOA) at equilibrium were done using the Freundlich model (Eq. 1) where $\log C_s$ is the mass of PFCA sorbed to biochar and soil together and $\log C_w$ is the aqueous PFCA concentration.

Since the BC-single batch tests were expected to exhibit stronger sorption than BC-mix spiked cocktails, BC-soil-mix spiked cocktails and BC-soil-PFOA, dimensionless attenuation factors (AF) were calculated for each PFAS by dividing the distribution coefficient (K_d) for the BC-single samples ($K_{d,BC\text{-}single}$) at the highest spiked concentration by the distribution coefficient of the other batch test types containing biochar with soil and/or other PFAS at the same spiked concentration of each PFCA (BC-mix, BC-S-PFOA, BC-S-mix = $K_{d,BC-x}$):

$$AF = \frac{K_{d,BC\text{-}single}}{K_{d,BC-x}} \quad (3)$$

The resulting AF represents the factor by which biochar samples sorb each individual PFAS greater than the biochars in the presence of soil

and/or a mixture of other PFAS.

3. Results and discussion

3.1. Soil and biochar characterization

The soil contained 1.3% total organic carbon (TOC), the pH was 5.38 ± 0.02 , the cation exchange capacity (CEC) was $2.63 \pm 0.06 \text{ cmol}_c/\text{kg}$. Additional soil parameters can be found in Table S8.

The surface area (SA) of WCBC ($683 \text{ m}^2/\text{g}$) was approximately six times greater than that of SSBC1 and SSBC2 (165 and $87 \text{ m}^2/\text{g}$, respectively) for ultrananopores mainly between 0.4 and 1.5 nm (CO₂ absorption). WCBC also had the highest pore volume (PV) $0.186 \text{ cm}^3/\text{g}$, followed by SSBC1 ($0.047 \text{ cm}^3/\text{g}$), and SSBC2 ($0.027 \text{ cm}^3/\text{g}$). For nanopores largely > 1.5 nm (N₂ absorption), the SA of WCBC ($261 \text{ m}^2/\text{g}$) was approximately three times higher than that of SSBC1 and SSBC2 (97 and $84 \text{ m}^2/\text{g}$, respectively). The same trend as for the CO₂ PV was seen for PV in the N₂ pore range: WCBC ($0.160 \text{ cm}^3/\text{g}$) > SSBC2 ($0.133 \text{ cm}^3/\text{g}$) > SSBC1 ($0.153 \text{ cm}^3/\text{g}$). A summary of the main biochar characterization parameters, including H/C and N/C ratios, is presented in Table 1, and the total element composition are in Table S9.

3.2. Sorption isotherms

The Freundlich isotherms and fitting parameters of individually spiked PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA adsorption to WCBC, SSBC1 and SSBC2 are presented in Fig. 1 and Table 2. All values reported are in units of $(\mu\text{g}/\text{kg})/(\mu\text{g}/\text{L})^{n_F}$ for K_F and of $(\mu\text{g}/\text{kg})/(\mu\text{g}/\text{L})$ for K_d . Overall, log-linear fits were very strong (r^2 mostly > 0.9) except those for PFPeA and PFHxA ($r^2 < 0.3$ and $p > 0.05$) adsorption onto two of the biochars (SSBC2 and WCBC). One possible explanation for these poor fits is because ionic interactions may be more important for sorption of these short-chain PFCA relative to hydrophobic interactions for the longer-chain-PFCA. The contribution of these two processes to the partitioning could increase the variation in K_d values compared to when hydrophobic interactions dominate. This may be so because ionic sorption is highly dependent on accessible ion exchange sites and competing counter-ions in the test system (Gagliano et al., 2020; Sigmund et al., 2022). As a consequence, correlations that did not meet the $p > 0.05$ threshold have been removed from the main discussion (these data are presented in the supporting information). For the remaining four PFCA, the highest sorption coefficients were observed for the two sewage sludge biochars (SSBCs: SSBC1 and SSBC2). $\log K_F$ ranged from 4.10 to 6.00 for SSBC1, 3.30–5.61 for SSBC2, and 3.98–5.22 for WCBC and increased from the shortest to the longest CF₂ chain.

To the best of our knowledge, there is no current literature available reporting distribution coefficients for PFCA sorption to any SSBCs. However, the $\log K_d$ -values for PFOA sorbed to the SSBCs (5.12–5.73) were equivalent to, or higher than, $\log K_d$ -values for PFOA to commercially produced activated carbons (AC) tested in previous studies: > 5.60 (Kupryianchyk et al., 2016), 4.45 (Hansen et al., 2010), and 4.74–5.42 (Silvani et al., 2019), all at $C_w = 1 \mu\text{g}/\text{L}$. $\log K_d$ for PFOA at $1 \mu\text{g}/\text{L}$ for WCBC (4.44 ± 0.05) was also higher than that for other previously studied biochars: 4.00 for PFOS to pine sawdust biochar (\log

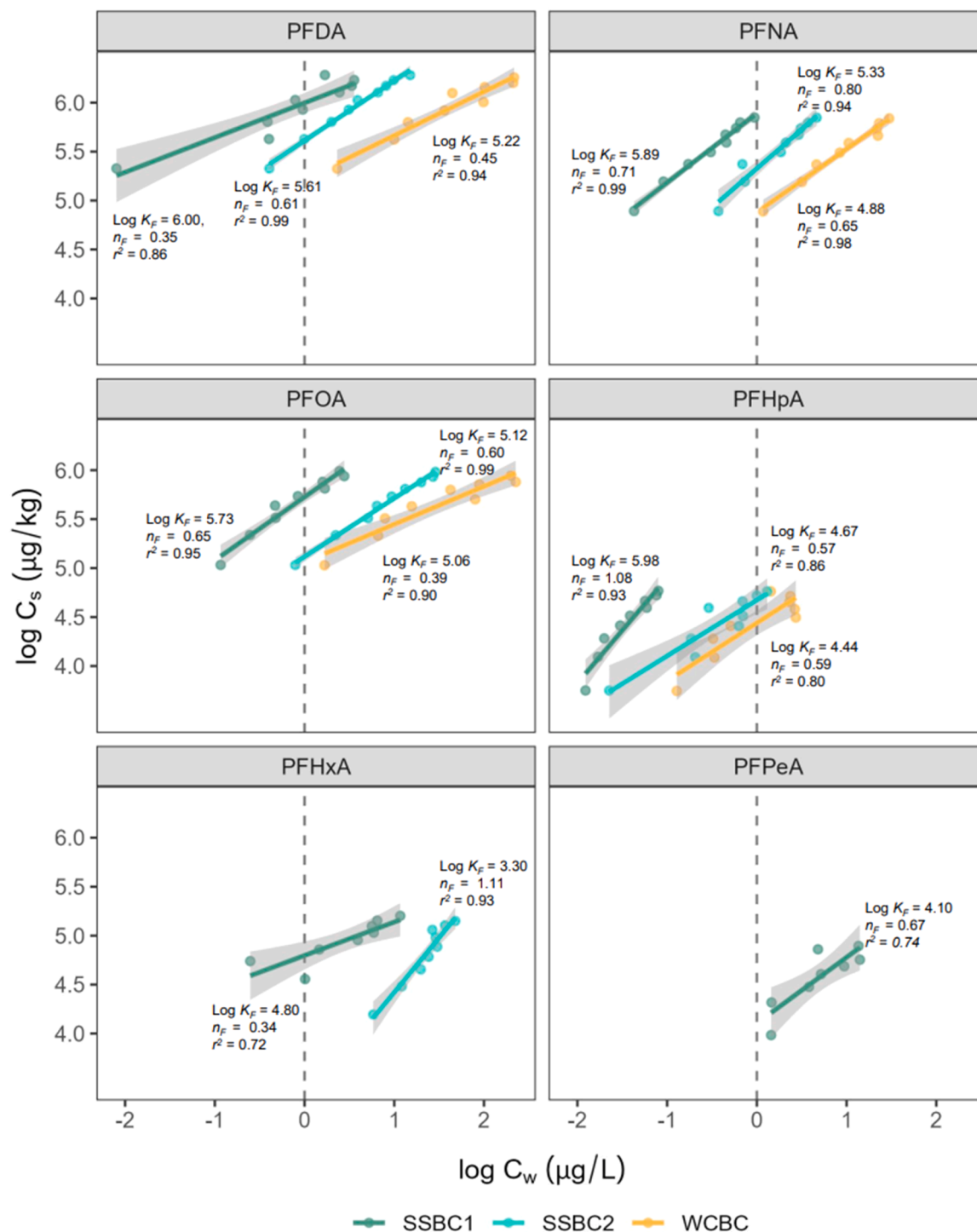


Fig. 1. Sorption isotherms of PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA on biochars produced at 700 °C from clean wood chips (WCBC), digested sludge Lindum (SSBC2) and Ullensaker sludge (SSBC1). The dashed vertical line represents $\log K_d = \log K_d = 1 \mu\text{g/L } C_w$. Non-significant isotherms ($p < 0.05$) have been removed from this plot. A 95% confidence interval, based on the regression statistics, is shown around each regression line.

$K_d < 0.5$ for PFOA) and 0.2 for PFOA to pea straw biochar, both pyrolyzed at 750 °C (Askeland, 2019).

On average, non-linearity coefficients, n_F , were 0.64 ± 0.23 . This average is close to the 0.61 median value found for sorption of legacy POPs to pyrogenic materials from 21 other studies (Cornelissen et al., 2005). Also, non-linear isotherms with n_F -values between 0.3 and 0.7 were observed for PFAS sorption to AC (Kupryianchyk et al., 2016; Silvani et al., 2019).

3.3. PFAS sorption and biochar chemical composition relationships

3.3.1. Relationships between K_F and biochar surface area and pore volume

High internal surface area (SA) and pore volume (PV) are generally desirable for strong sorption of organic contaminants (Ahmed et al., 2020; Hale et al., 2016). The higher SA and PV of WCBC compared to the SSBCs (Table 1) suggests that the wood-based WCBC would have a greater number of active sorption sites and the highest pore-filling capacity (i.e., PV) compared to the SSBCs. However, the cumulative pore

Table 2
Freundlich distribution coefficients ($\log K_F$) in units of ($\mu\text{g}/\text{kg}/(\mu\text{g}/\text{L})^n$) and non-linearity coefficients (n_F) with standard deviations and linear regression coefficients for BC-single isotherms ($n = 9$) and PFOA isotherms in soil (BC-S-single, $n = 6$) and in soil with a cocktail spike of other PFAS (BC-S-mix, $n = 6$).

PFCA	CF ₂ moieties	D_{eff}^1 (nm)	D_{max}^2 (nm)	Single-compound sorption experiments (BC-single)				SSBC1				SSBC2				WCBC			
				n	$\log K_F^3$	n_F	r^2	p	$\log K_F^3$	n_F	r^2	p	$\log K_F^5$	n_F	r^2	p	$\log K_F^5$	n_F	r^2
PFPeA	4	0.45	0.96	9	4.10 ± 0.13	0.67 ± 0.16	0.74	6 × 10 ⁻³	3.30 ± 0.15	1.11 ± 0.11 ⁴	0.06	7 × 10 ⁻¹	0.30	1 × 10 ⁻¹	4.44 ± 0.05	0.59 ± 0.11	0.80	1 × 10 ⁻³	
PFHxA	5	0.50	1.08	9	4.80 ± 0.06	0.34 ± 0.09	0.72	7 × 10 ⁻³	4.67 ± 0.06	0.57 ± 0.09	0.93	2 × 10 ⁻⁵	0.04	6 × 10 ⁻¹	5.06 ± 0.08	0.39 ± 0.05	0.90	1 × 10 ⁻³	
PFHpA	6	0.56	1.19	9	5.98 ± 0.17	1.08 ± 0.11 ⁴	0.93	3 × 10 ⁻⁵	5.12 ± 0.02	0.60 ± 0.02	0.86	3 × 10 ⁻⁴	0.80	9 × 10 ⁻⁵	4.88 ± 0.04	0.65 ± 0.04	0.98	4 × 10 ⁻⁷	
PFOA	7	0.61 ³	1.36 ³	9	5.73 ± 0.02	0.65 ± 0.05	0.95	6 × 10 ⁻⁶	5.33 ± 0.03	0.80 ± 0.07	0.94	2 × 10 ⁻⁸	0.94	9 × 10 ⁻⁵	5.22 ± 0.07	0.45 ± 0.04	0.94	2 × 10 ⁻⁵	
PFNA	8	0.67	1.42	9	5.89 ± 0.02	0.71 ± 0.03	0.99	8 × 10 ⁻⁸	5.61 ± 0.02	0.61 ± 0.02	0.99	3 × 10 ⁻⁸	0.94	4 × 10 ⁻⁷	3.45 ± 0.21	0.88 ± 0.09	0.96	6 × 10 ⁻⁴	
PFDA	9	0.72	1.54	9	6.00 ± 0.04	0.35 ± 0.05	0.86	3 × 10 ⁻⁴	4.91 ± 0.06	0.39 ± 0.03	0.97	3 × 10 ⁻⁴	0.82	1 × 10 ⁻²					
Attenuation experiments (BC-S-single and BC-S-mix)																			
PFOA				6	5.16 ± 0.03	0.62 ± 0.03	0.99	3 × 10 ⁻⁵	5.08 ± 0.10	0.46 ± 0.08	0.90	4 × 10 ⁻³	0.96	6 × 10 ⁻⁴					
PFOA				6	5.00 ± 0.05	0.39 ± 0.03	0.98	1 × 10 ⁻⁴	4.91 ± 0.06	0.39 ± 0.03	0.97	3 × 10 ⁻⁴	0.82	1 × 10 ⁻²					

¹Effective cross-sectional diameter of the PFCA molecule (Inoue et al., 2012)

²Maximum diameter of the PFCA molecule (Inoue et al., 2012)

³Retrieved from Inoue et al. (2012). D_{eff} and D_{max} for the other PFCA listed were derived by linear interpolation and extrapolation of PFCA molecular sizes provided in the Inoue et al. study

⁴Not statistically different from 1

⁵ $\log K_F = \log K_d = 1 \mu\text{g}/\text{L}$

size distributions shown in Fig. 2 indicate that nearly 80% of the SA and 60% of the PV in WCBC resided in the ultra-micropore range (<0.7 nm). These pores are too small for PFCA to diffuse into considering that the perfluorinated chains of PFAS are large and helical (Mifkovic et al., n. d.). PFCA with 4–9 CF₂ moieties range 0.45–0.72 nm in effective cross-sectional diameter (D_{eff}) and 0.96–1.54 nm in maximum diameter (D_{max} , Table 2) (Inoue et al., 2012). Large sorbate molecules can be excluded from small pore spaces due to high tortuosity and restricted diffusion (Piai et al., 2019; Yang et al., 2006).

For WCBC, SA and PV resided almost exclusively in pores < 3 nm. By contrast, SA and PV for the SSBCs increased steadily up to 35 nm, the method pore-size cutoff. The higher porosity of the SSBCs > 3 nm compared to that of WCBC is a plausible explanation for the stronger sorption measured for the SSBCs.

Greater PFAS sorption capacity was observed for the SSBC1 compared to the SSBC2 biochar. This difference cannot be explained by SA and PV as these parameters were roughly equal for both sludge-based chars (Fig. 2, Table 1). We tentatively attribute this to the higher carbon content of SSBC1 (30%) compared to that of SSBC2 (14%), suggesting stronger hydrophobic interactions between the SSBC1 carbonaceous matrix for PFAS. Previous findings indicate that carbon content can be a predictor of charcoal and soil sorption affinity for PFAS (Fabregat-Palau et al., 2021; Hale et al., 2016; Zareitalabad et al., 2013) and other hydrophobic organic contaminants (HOCs) (Cornelissen et al., 2005; Kupryianchyk et al., 2016; Wang et al., 2016).

3.3.2. Relationships between K_F and PFCA chain length

In accordance with previous studies (Ahmed et al., 2020; Fabregat-Palau et al., 2021; Sorengard et al., 2019), K_d increased with increasing length of the perfluorinated chain (Table 2). This can be attributed to increasing hydrophobic interactions with PFAS of longer chain length (Vo et al., 2022; Zhang et al., 2021). Due to the perfluorinated tail's high surface area and low Van der Waals interactions, the free energy of cavity formation required to dissolve PFCA in water increases with each additional CF₂ moiety (Arp et al., 2006). Generally, water cavity formation energy and van der Waals interactions have been considered less important for sorption of short-chain PFAS (<C6), but are, however, more important for long-chained PFAS (>C6) (Du et al., 2014). The chain length dependency on sorption found in this study indicates that hydrophobic interactions dominate PFCA in sorption to biochars, in accordance with previous literature (Ahmed et al., 2020; Fabregat-Palau et al., 2021; Sorengard et al., 2019).

3.3.3. Relationships with H/C and C/N ratios

The higher H/C and lower C/N ratios for the SSBCs (H/C = 0.04 and 0.08 for SSBC1 and SSBC2, respectively; C/N = 26 and 16 for SSBC1 and SSBC2, respectively) compared to that of WCBC (H/C = 0.01 and C/N = 133) suggest that the WCBC matrix was more aromatic, containing a relatively high level of condensed carbon moieties, whereas the SSBCs contained more polar functional groups (e.g. carboxyl, hydroxyl, carbonyl, and amines). Some studies have found that lower H/C and C/N ratios can enhance PFAS sorption by aiding in pore-filling by electrostatic interactions (Du et al., 2014; Fabregat-Palau et al., 2021; Saeidi et al., 2020). In addition, a low C/N ratio can be indicative of more positively charged functional groups such as amines in the periphery of the condensed carbon structure. Amines are protonated at environmentally relevant pHs (pK_a 6–11, (Juranić, 2014)), which could contribute to anion-exchange with the negatively charged carboxylate head-groups of PFCA (Deng et al., 2010). However, to the best of our knowledge, no data exists on how nitrogen speciation changes during pyrolysis of sewage sludge. Therefore, a lower C/N ratio is only indication of nitrogen-containing functional groups. The higher H/C and lower C/N ratios for the SSBCs may thus have contributed to the relatively higher PFAS sorption by these biochars compared to that of WCBC. However, more data would be needed to test this relationship statistically.

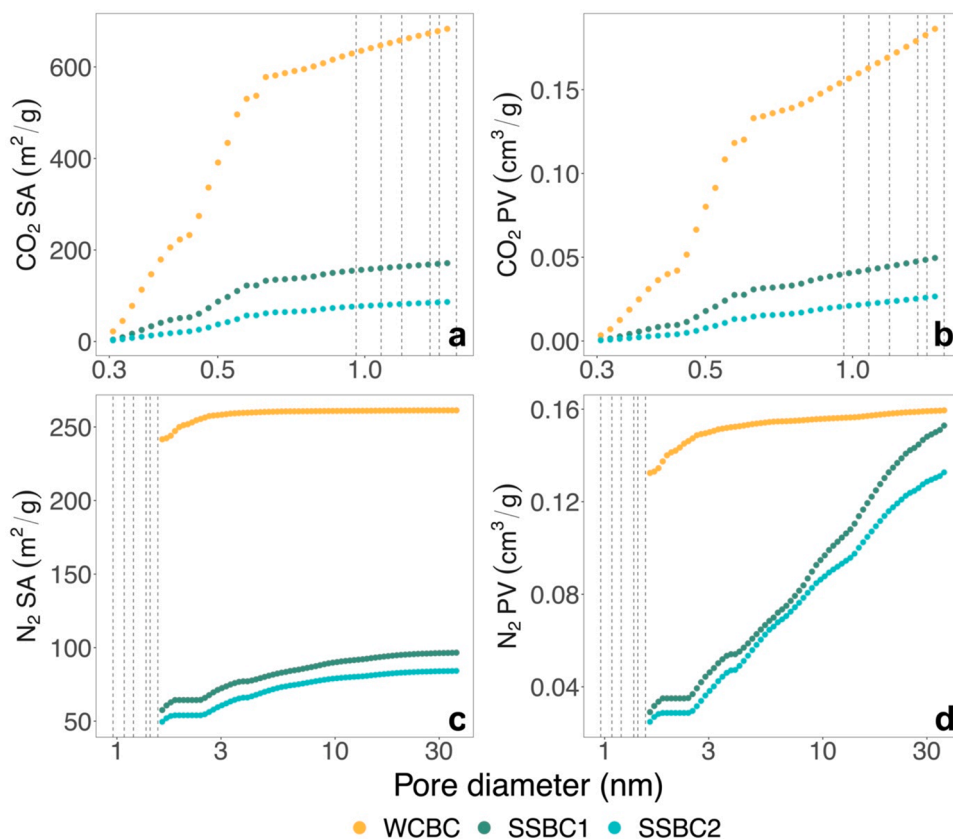


Fig. 2. Cumulative surface area (SA) and pore volume (PV) for pore diameters ranging between 0.4 and 1.5 nm (a and b), and pores > 1.5 nm (c and d) using DFT theory. The dashed vertical lines represent the maximum diameter of the PFCAs tested (Table 1).

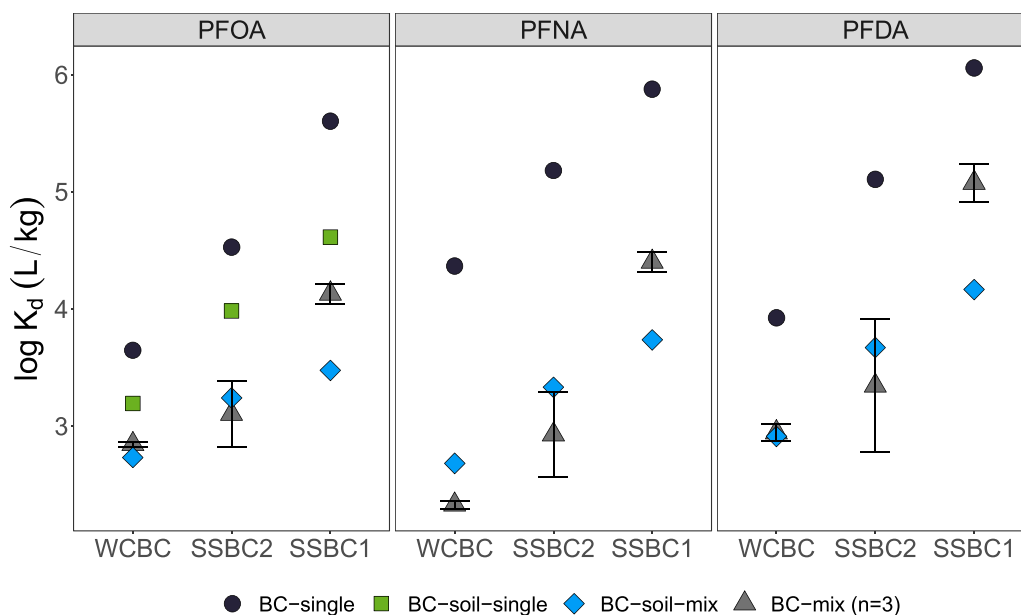


Fig. 3. Log K_d in each batch test category calculated at the highest isotherm concentration point in triplicate batch tests (Table S6). Error bars show the standard deviation of triplicate datapoints.

3.3.4. Relationships with Fe, Ca, and Mg

Total Fe concentration was especially high in SSBC2, 18%, versus 3.3% and 0.01% for SSBC1 and WCBC, respectively (Table 1). Thus, the Fe concentration could have affected the surface morphology of SSBC2 which had the lowest porosity. Iron can be important for PFAS sorption

(Lu et al., 2016; Zhang et al., 2022), however, SSBC2 PFAS sorption was always somewhat lower than that of SSBC1. The concentrations of Ca and Mg were three to six times greater in the sludge biochars than in WCBC (Table 1). It has been shown that most Ca is mostly insoluble after pyrolysis (Limwikran et al., 2018). Therefore, bridging by divalent

Table 3

Attenuation factors (*AF*) calculated using Eq. (3) and the respective log K_d -values at the highest isotherm concentration in triplicate batch tests (Table S6). Log K_d -values are shown as single values (for $n = 1$) or the geometric mean with standard deviation ($n = 3$).

PFCA	Batch test category	<i>n</i>	WCBC		SSBC2		SSBC1	
			log K_d^*	<i>AF</i>	log K_d^*	<i>AF</i>	log K_d^*	<i>AF</i>
PFPeA	BC-mix	3						
PFHxA	BC-mix	3					2.50 ± 0.14	42
PFHpA	BC-mix	3					3.14 ± 0.13	532
PFOA	BC-mix	3	2.84 ± 0.02	6	3.17 ± 0.28	23	4.13 ± 0.09	29
PFNA	BC-mix	3	2.33 ± 0.03	109	3.03 ± 0.36	140	4.40 ± 0.08	29
PFDA	BC-mix	3	2.95 ± 0.07	9	3.60 ± 0.57	32	5.09 ± 0.16	9
PFPeA	BC-S-mix	1						
PFHxA	BC-S-mix	1	2.19				2.40	55
PFHpA	BC-S-mix	1	2.21	249			2.05	6581
PFOA	BC-S-mix	1	2.73	8	3.24	19	3.47	134
PFNA	BC-S-mix	1	2.68	48	3.33	71	3.73	138
PFDA	BC-S-mix	1	2.91	10	3.67	27	4.16	78
PFOA	BC-S-sing	1	3.19	3	3.98	4	4.61	10

Standard deviations are the geometric standard deviation average.

K_d values can only be compared across batch test categories for the same PFCA compound because each compound was spiked at different concentrations. Standard deviations are the geometric standard deviation average.

cations is unlikely to contribute significantly to the greater PFCA sorption seen for the SSBCs (Higgins and Luthy, 2006).

3.4. Sorption attenuation

Fig. 3 shows how the biochar sorption affinity measured for single PFCA compounds ($K_{d,BC-single}$, calculated at the highest concentration points of each isotherm, ~10 mg/L total PFCA, data in Table S6) was attenuated by the presence of soil ($K_{d,BC-soil}$), and/or the presence of multiple PFCA compounds (Fig. 3, $K_{d,BC-mix}$ and $K_{d,BC-S-mix}$). For the three biochars, *AF*s ranged from 3 to 10 (median = 4) for (single spiked) PFOA with soil and biochar (BC-S-single), 6–532 (median = 29) for PFAS cocktail with biochar (BC-mix), and 8–6581 (median = 63) for PFAS cocktail with biochar and soil (BC-S-mix) (Table 3). Thus, though the presence of soil weakened PFAS sorption to the biochars to a certain extent, sorption appeared to be more strongly attenuated by the presence of other PFAS. This indicates that sorption attenuation is to a larger extent a result of competition for binding sites between similar compounds rather than a result of pore blockage and binding site competition from dissolved soil organic carbon molecules. However, it should be noted that the degree of sorption attenuation by soil might differ depending on soil type, as was shown by Askeland et al. (2020) who demonstrated that the amendment effect of biochar was higher in a sandy clay loam compared to a loamy sand.

These data are the first published attenuation factors for the sorption of PFAS to sewage sludge and wood biochars, thus, they cannot be directly compared to literature values. However, previous literature found *AF*s in the same order of magnitude; 10 for phenanthrene on black carbon isolated from contaminated sediments in the presence other PAHs (Cornelissen and Gustafsson, 2006), 32 for DDT on lignite-based fossil AC in the presence and absence of soil (Hale et al., 2009), and 100–500 for sulfamethazine (SMT) on hardwood biochar in the presence of soil (Teixido et al., 2013), both in experiments similar to the ones in this study.

It is possible that the *AF*s in the presence of soil derived after 14 days in this study would have been reduced by increasing contact times. Hale et al. (Hale et al., 2009) found that sorption of DDT onto AC was no longer attenuated by the presence of soil after 26 months of continuous agitation. This suggests that sorption of organic contaminants onto porous materials in the presence of soil is a kinetically limited slow diffusion process and restriction of pore-throats by soil constituents may be alleviated over time. Competition between various PFAS is probably not diminished by contact time though.

4. Environmental implications

This study is the first to show that biochars from raw and digested sewage sludge can be used as effective sorbents for PFAS in most environmental contexts, with efficiencies similar to or better than those of AC. High porosity in the right size range and carbon content were probably the most important parameters responsible for the high sorption strengths observed for the sludge-derived biochars, along with some possible influences of amine functional groups. However, to validate these findings, further studies are recommended using a larger variety of sewage sludge-derived biochars and relating their PFAS sorption to more detailed SSBC characteristics. Further, as the results showed poor sorption of short chain PFAS (PFPeA, PFHxA, and PFHpA), an increasing and substantial threat to drinking water quality (Neuwald et al., 2022), more research is needed to find ways to sustainably remove these during wastewater treatment.

Sorption was more strongly attenuated by the presence of other PFCAs than the presence of soil and was most severely attenuated by the presence of both soil and other PFCAs. This has implications for their usefulness as sorbents for soil remediation as well as for their application in filter solutions for complex contaminant mixtures. Additional tests are needed to determine the effectiveness of these biochars in soils of different compositions (especially sorption strength of the soil itself and organic matter content) and for in situ soil remediation and wastewater treatment, such as by column tests, lysimeters, or in water treatment filters. Further research should also examine a larger range of biochar samples made at different pyrolysis temperatures to identify the characteristics ideal for PFAS sorption, such as surface area, pore volume, carbon content, and mineral contents (mainly Ca and Fe). Finally, studying the effect of activation of sludge chars on sorption strength could be useful for the further improvement of their sorption characteristics.

SSBCs can contribute to reducing the demand for AC in a range of applications. Taking a circular approach, PFAS-contaminated sludges from water treatment plants or agricultural land could be pyrolyzed locally, eliminating the PFAS and then using the SSBC as a sorbent to treat PFAS-contaminated soils or wastewater. The potential for carbon sequestration and increased commercial valorization of sewage sludge is a promising environmentally and economically sustainable alternative to AC sorbents.

The present work shows how novel and sustainable value chains can be created by pyrolyzing sewage sludge to produce sorbents with an effectiveness for binding per- and polyfluoroalkyl substances (PFAS) that rivals that of commercial activated carbons. This has important implications for wastewater treatment and soil stabilization as it

demonstrates how problematic waste fractions can be upcycled to valuable materials that can contribute to dealing with the threat of hazardous materials spreading in the environment.

CRedit authorship contribution statement

Katinka M. Krahn: Methodology, Investigation, Formal analysis, Writing – original draft. **Gerard Cornelissen:** Supervision, Project administration, Funding acquisition, Conceptualization, Methodology, Writing – review & editing. **Gabriela Castro:** Methodology, Investigation, Formal analysis, Writing – review & editing. **Hans Peter H. Arp:** Supervision, Project administration, Funding acquisition, Visualization, Writing – review & editing. **Alexandros G. Asimakopoulos:** Supervision, Data curation, Validation, Writing – review & editing. **Raoul Wolf:** Software, Visualization, Writing – review & editing. **Rune Holmstad:** Resources, Funding acquisition. **Andrew R. Zimmerman:** Investigation, Writing – review & editing. **Erlend Sørmo:** Supervision, Funding acquisition, Conceptualization, Methodology, Resources, Investigation, Formal analysis, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2022.130449](https://doi.org/10.1016/j.jhazmat.2022.130449).

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