



# Assessment of marine sediment remediation efficiency with SPME-based passive sampling measurement

Ian J. Allan <sup>\*</sup>, Violette Raffard, Alfhild Kringstad, Kristoffer Næs

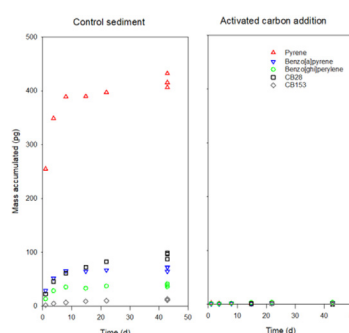
Norwegian Institute for Water Research (NIVA), Gaustadalléen 21, NO-0349 Oslo, Norway



## HIGHLIGHTS

- Suitability of an ex-situ SPME method to evaluate sediment remediation strategies
- AC and anthracite amendments to reduce the availability of PAHs in contaminated sediment
- Distribution of chlorinated compounds may be affected by the presence of coal tar pitch in sediment.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 4 August 2020

Received in revised form 8 November 2020

Accepted 8 November 2020

Available online 21 November 2020

Editor: Jay Gan

### Keywords:

Sediment

Polycyclic aromatic hydrocarbons

Passive sampling

Solid phase microextraction

Activated carbon

Remediation

## ABSTRACT

Passive sampling has been shown to be a suitable procedure to assess the risk of contaminated sediments through the measurement of freely dissolved concentrations ( $C_{Free}$ ) and remedial actions involving amendments such as activated carbon (AC). Here we report results of the application of simple, solvent-free solid phase micro extraction methodology (SPME) to assess the performance of different materials for the remediation of selected Norwegian harbour sediments contaminated with polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). AC amendments enabled a reduction of the availability of PAHs and/or PCBs by a factor of ten to over one hundred in Aker Brygge sediments (Oslo) and sediments from Elkembukta, impacted by industrial emissions of PAHs with/from coal tar pitch. Another material, anthracite, slightly less effective in this set of experiment than AC, showed nonetheless great promise as capping material. The SPME data are put in perspective with equilibrium measurements of  $C_{Free}$  for PAHs and organochlorines with silicone rubber in other Elkembukta sediments collected in the vicinity of those used for the remediation experiments. A reduction of sediment  $C_{Free}$  for pyrene, benzo[a]pyrene and benzo[ghi]perylene in inner Elkembukta sediment from on average 407, 6.3 and 0.82 ng L<sup>-1</sup> to values of or below 1.3, 0.15 and 0.076 ng L<sup>-1</sup>, respectively can be expected upon remediation with AC. For the outer, less contaminated Elkembukta sediment,  $C_{Free}$  would reduce from 36, 0.81 and 0.13 ng L<sup>-1</sup> to value of or below 0.06, 0.03 and 0.005 ng L<sup>-1</sup> for these three compounds, respectively. Differences in pattern of PAH and organochlorine contamination of inner and outer Elkembukta sediments are discussed.

© 2020 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Aquatic sediments in harbours or in the vicinity of industrial plants can be contaminated with high concentrations of hydrophobic organic compounds such as polycyclic aromatic hydrocarbons (PAHs),

<sup>\*</sup> Corresponding author.

E-mail address: [ian.allan@niva.no](mailto:ian.allan@niva.no) (I.J. Allan).

polychlorinated biphenyls (PCBs) or other industrially-produced chemicals and often require some form of remediation. Passive sampling methodologies have increasingly been applied for the assessment of the risk these chemicals pose to benthic and aquatic organisms as well as possible transfer and spread from the contaminated areas (Greenberg et al., 2014; Lydy et al., 2014). Passive sampling devices are used to estimate freely dissolved contaminant concentrations (Booij et al., 2016) or sediment-water fluxes (Eek et al., 2010; Fernandez et al., 2014), often in a sediment remediation context. Since organism exposure, toxicity and release of contaminants from bed sediment are directly linked to freely dissolved concentrations ( $C_{Free}$ ), a reduction in  $C_{Free}$  assessed with passive samplers has been used as an acceptable endpoint for evaluating the efficiency of remediation strategies e.g. (Beckingham and Ghosh, 2013; Hale and Werner, 2010). Contaminant sorption to sediment and particularly to the organic carbon present in the sediment dictates the availability of chemicals and their ability to be (rapidly) released into pore water to compensate changes in freely dissolved concentrations (Cornelissen et al., 2005).

Amendment of sediments with strongly sorbing materials such as activated carbon has been shown to be very efficient in reducing freely dissolved hydrophobic organic contaminant concentrations in sediments (Ghosh et al., 2011; Patmont et al., 2015). These can be added on their own or as mixtures with other materials such as clay. They can be mixed into the sediment biologically active layer or applied as a thin cap. The efficiency of sediment remediation with activated carbon addition has been assessed with passive samplers as well as with bioaccumulation experiments using benthic organisms. In both cases, strong reductions in the (bio)availability of non-polar organic contaminants such as PAHs, PCBs, DDTs or PCDD/Fs are shown (Beckingham and Ghosh, 2013; Ghosh et al., 2011; Patmont et al., 2015; Thomas et al., 2014; Zimmerman et al., 2005). Passive sampling measurements can be found in different formats and implemented in the field with in situ deployments or in the laboratory with batch measurements to measure  $C_{Free}$  or accessible concentrations (Reichenberg and Mayer, 2006). A relatively common procedure involves bringing in contact a sufficiently large volume of sediment to be tested with a passive sampler with a sorption capacity that minimises potential for depleting the sediment (Mayer et al., 2000). These methodologies also need to ensure that the measurement is conducted at equilibrium. When working with milligrams to grams of polymers such as silicone rubber, these need to be exposed to volumes of sediment up to litres in order to fulfil non-depletion measurement validity criterion. To fulfil the equilibrium criterion, the sediment slurry-passive sampler exposure is often agitated to help equilibrium between the contaminant concentration in the sampler and that in the sediment is reached rapidly (Smedes et al., 2013). The use of different passive sampler formats can also affect sensitivity or limits of detection of the methodology, time to equilibrium or depletion. The use of silicone rubber membrane for example may offer improved sensitivity but the larger sampler mass used is more likely to result in depletion in the sediment and longer equilibration times than when using a SPME fibre with a volume of polydimethylsiloxane phase in the  $\mu\text{L}$  range. The loss of sensitivity of the SPME fibre may be compensated by the direct injection of the entire amount of target analytes absorbed (Ghosh et al., 2014; Jonker et al., 2018). In cases of remediation with addition of a sorption phase, this mixing of the sediment may contribute to increasing the effectiveness of the amendment by promoting the transfer of chemicals from the sediment to the newly-added sorption material. With these points in mind, it appears useful to be able to apply a passive sampling methodology that reduces the amount of sediment needed, of solvents used in the laboratory, and that can easily be applied in a high number of replicate or treatment options.

In this study, we have applied a simple methodology based on the use of solid-phase microextraction (SPME) fibres with a polydimethylsiloxane sorbent phase to investigate the availability of PAHs and organochlorinated compounds in selected coastal/harbour sediments

upon amendments with various potential remediation materials. In this methodology, a direct insertion of SPME fibre into sediment for exposure is followed by a solvent-free single-step extraction/analysis by gas chromatography-mass spectrometry (GC/MS). This procedure was applied to three different sediments, one from Aker Brygge marina in Oslo and two from Elkembukta (inner and outer) in Kristiansand fjord (Norway). A long exposure to Aker Brygge sediment was used to assess SPME accumulation pattern and decide an appropriate exposure time for subsequent exposures. SPME exposures to Elkembukta sediments were conducted for 4.5 day. SPME measurements were undertaken prior to and post remediation to assess the efficacy of the addition of strongly sorbing materials. We also report  $C_{Free}$  measurements for PAHs and organochlorinated compounds undertaken with silicone rubber in eight sediment samples collected on a transect across inner and outer Elkembukta in the vicinity of sampling locations for sediments used in the remediation experiments. The treatment efficiencies obtained with SPME fibres, expressed as a proportional reduction in  $C_{Free}$  can be applied to these measurements. The Aker Brygge marina is the site of an old shipyard of Oslo and sums of 19 PAHs and 9 PCBs were  $46 \mu\text{g g}^{-1}$  and  $767 \text{ ng g}^{-1}$ , respectively (Allan et al., 2012). The sediment outside the Elkem Carbon industrial site in Kristiansand (inner Elkembukta) is contaminated with high levels of PAHs as results of coal tar pitch emissions/discharges from the factory over the years ( $\Sigma_{16}\text{PAHs} \sim 100\text{--}300 \mu\text{g g}^{-1}$ ) (Næs et al., 2014). The area referred to as outer Elkembukta is part of wider fjord named Fiskåbukta and shows lower but still elevated levels of PAHs ( $\Sigma_{16}\text{PAHs} \sim 55 \mu\text{g g}^{-1}$ ).

## 2. Materials and methods

### 2.1. Materials

Solid phase microextraction fibres and manual injection plunger were from Supelco/Sigma-Aldrich (Norway). SPME fibres were composed of a pure polydimethylsiloxane (PDMS) coating with a  $30 \mu\text{m}$ -diameter ( $0.132 \mu\text{L}$  PDMS). Sheets of AlteSil™ silicone rubber ( $500 \mu\text{m}$ ) were purchased from Altecweb (UK) and cut into small 0.5 or 0.8 g pieces. Analytical-grade solvents including dichloromethane, ethyl acetate, methanol and pentane were obtained from Rathburn (UK). Cyclohexane was from J.T. Baker (USA). Sodium azide ( $\text{NaN}_3$ ) used a biocide was purchased from Sigma-Aldrich.

Ultrapure water (Option 3, Elga™) was used for PRC spiking and preparation of  $\text{NaN}_3$  stock solution. Analytical-grade standards for 16 US EPA PAHs and their deuterated analogues were from Chiron AS (Norway). Purities were  $>99\%$  for PAHs and  $>99.5\%$  for deuterated PAHs. Analytical and recovery standards for PCBs were of similar grade and obtained from LGC/Promochem (UK). FluoroPCBs used as performance reference compounds (PRCs), pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) were from Chiron AS. PRCs were acenaphthene- $\text{d}_{10}$ , fluorene- $\text{d}_{10}$ , phenanthrene- $\text{d}_{10}$ , chrysene- $\text{d}_{12}$ , benzo[a]pyrene- $\text{d}_{12}$ , and F-PCBs 3, 28, 52, 105 and 156. Recovery standards for PAHs were naphthalene- $\text{d}_8$ , biphenyl- $\text{d}_{10}$ , acenaphthylene- $\text{d}_8$ , dibenzothiophene- $\text{d}_8$ , pyrene- $\text{d}_{10}$ , benz[a]anthracene- $\text{d}_{12}$  and perylene- $\text{d}_{12}$ , and PCBs 30, 53 and 204, respectively.

### 2.2. Sediments collection

Aker Brygge sediments (Oslo, Norway) were collected by grab sampling at a sampling location with coordinates of 59.908034 and 10.725284 in 2009. Sediments were then kept a 4–5 °C until use (some days later). Sediments from Kristiansand were collected in an area that has been the subject of much investigation over the years as a result of the presence of PAH-contaminated sediments in Elkembukta. Sediment sampling locations for equilibrium measurements of  $C_{Free}$  with AlteSil™ silicone rubber can be found elsewhere (Olsen et al., 2018). The two most recent sediment batches from inner and outer Elkembukta were collected in 2019 from two locations representative

of respective contamination in the two areas. Multiple consecutive grab sampling (down to 10 cm beneath sediment-water interface) with a Van Veen grab sampler was used to assemble a sufficient volume of sediment to be able to conduct all planned testing. Each batch of sediment was approximately 15 L and these were kept in large plastic tubs at 4–5 °C until use.

### 2.3. Additional sediment characterisation

Total sediment concentrations of PAHs and PCBs as well as total organic carbon content were measured at a commercial laboratory (Eurofins). TOC was obtained through combustion (method reference NF EN 15936 - Method B). Water content (method EN 12880: 2001-02) and particle size distribution were also measured.

### 2.4. Sediment supplementation with remediation materials

Aker Brygge sediment was supplemented with powdered activated carbon (Darco® G60, 100 mesh from Sigma-Aldrich) and fine olivine sand (provided by North Cape Minerals AS). The batch of sediment was first thoroughly homogenised with a paint mixer prior to splitting into three portions. The first portion was the control sediment with no addition while the two other fractions were supplemented with activated carbon (5% wv) or olivine sand (10% wv). The AC dosage here is different to that used with Kristiansand sediments principally because there was a 10-year gap between the timing of these experiments. Sediment batches placed in glass jars were then thoroughly homogenised to ensure complete mixing of the added material with the sediment. Sediments were kept at 4–5 °C for a month before SPME measurements were undertaken. It is worth considering the potential (physical) toxicity of AC when amending sediments with relatively high proportions of AC (Jonker et al., 2009).

Elkembukta (inner and outer) sediments collected in 2019 were also homogenised with a drill mixer until the sediment batches became smooth slurries. Sediments (700 mL) were then subsampled into 1 L glass jars and supplemented with the remediation materials to achieve a remediation material concentration level of 20 g L<sup>-1</sup>. Remediation materials to be evaluated in this study consisted of activated carbon and anthracite powder. The Aquasorb™ CP1- F highly porous powdered activated carbon was from Jacobi and kindly provided by Geir Markussen (Sparks AS). The calcined anthracite powder was collected from filters within the Elkem plant. Over 90% of the anthracite powder had a particle size below 20 µm. Two different treatments were undertaken for each sediment-remediation material pairs. The first treatment consisted of stirring the sediment samples for 24 h at 100 rpm on an orbital shaker. Sediment batches were then kept statically at 4–5 °C for 5 weeks until the SPME measurement was undertaken. This treatment was proposed to simulate more realistic conditions of remediation material-sediment interaction. A second set of samples were continuously shaken at room temperature for 8 weeks prior to SPME measurement. This treatment was expected to maximise the potential efficiency of the remediation material by maximising the transfer of PAHs from the sediment to the remediation material. Control batches for inner and outer Elkembukta sediments were also subjected to these treatments.

### 2.5. SPME measurement

The principle of the measurement involved direct exposure of the PDMS coating of the SPME unit to the sediment for a period of time in a static position. The exposure was conducted in a GC vial and homogenised sediments (1.8–2.0 g wet weight sediment) were added to the GC vial with the help of a custom-made plastic pipette with a wide opening. In experiments with Aker Brygge sediments, a tiny layer of water was added on top of the sediment to avoid the surface drying over the 42 d exposure. This was not deemed necessary for the

Kristiansand sediments since exposures were restricted to 4.5 days. It was decided based on the uptake curves in the Aker Brygge sediments that 4.5 days would be sufficient to observe a substantial PAH accumulation when exposed to Kristiansand sediments, thereby allowing us to obtain treatment efficiency results without needing to wait for 42 days. The spring on the SPME needle was removed to be able to continuously expose the PDMS coating to the sediment. A screw cap GC vial with a septum was used to allow sealing the exposure system and avoid damaging the PDMS coating when dismantling the system. Once the vial ready with the sediment, the SPME needle was used to punch through the septum before exposing the PDMS coating to the sediment. The vial was then placed on a stable surface on a rack until the end of the exposure. At the end of the exposure, the cap was unscrewed and before retracting the PDME fibre into the needle, its surface was rinsed with ultrapure water and a wetted lint-free tissue to remove any residual sediment particles. The efficiency of this procedure was visually assessed with the use of a magnifier. Once the fibre clean and ready for injection, it was retracted into the needle, the end of the needle covered with aluminium foil and the syringe was placed at –20 °C until injection.

For the Aker Brygge sediment, uptake curves for exposure times up to 42 days were obtained, with the 42 d exposures conducted in triplicate. For each of the treatments for the Kristiansand sediments, single exposures were conducted over 4.5 d in triplicate. An experiment was also conducted with the control sediment to obtain PAH accumulation profiles in the SPME fibre with time over 11 d and assess whether it remained linear over the chosen 4.5 d exposure.

### 2.6. GC/MS analysis of SPME fibres

PAHs and PCBs absorbed into the SPME fibres were quantified by manual injection of the SPME fibre directly into the injector of a HP-6890 Plus gas chromatograph linked to a HP 5973 mass selective detector. The GC/MS method was adapted from a method previously published (Allan et al., 2016a). The MS detector was operated in single ion monitoring mode with electron impact ionisation at 70 eV. PAHs were separated on a 30 m DB-5 column with an internal diameter of 0.25 mm and a film thickness of 0.25 µm (from Agilent JW Scientific, Santa Clara, USA) and with a helium flow of 1 mL min<sup>-1</sup>. The splitless injection volume was 1 µL. The GC oven temperature programme was as follows: held for 2 min at 60 °C before increasing to 250 °C at a rate of 7 °C min<sup>-1</sup>. The final stage was an increase to 310 °C at a rate of 15 °C min<sup>-1</sup> (held for 6 min). Injector, transfer line, ion source and quadrupole temperatures were set to 300, 280, 230 and 150 °C, respectively. Quantification of individual PAHs and PCBs in pg per fibre was performed through the use of a 5-point calibration curve based on 1 µL-injections.

### 2.7. Equilibrium measurement with AlteSil™ silicone rubber

The initial cleaning of the silicone rubber and removal of oligomers was through Soxhlet extraction with ethyl acetate for 50 h. The silicone rubber was then cut into small pieces of 0.5 and 0.8 g prior to further soaking in methanol. All silicone rubber samplers were spiked with a set of performance references compounds (PRCs) with the help of a co-solvent methodology (with methanol and water as co-solvents) according to procedures described earlier (Allan et al., 2013; Booij et al., 2002). Volumes of co-solvents however were adjusted to the small size of the samplers. Once the PRC spiking was undertaken, samplers were wiped and stored in a clean glass jar at –20 °C until further use.

Approximately 1 L of sediment from each sampling location was placed in glass jars. These were supplemented with a biocide (NaN<sub>3</sub>) to achieve a final concentration of ~1 g L<sup>-1</sup>. One silicone rubber sampler was placed in each glass jars at the start of the exposure. Glass jars were then placed on an orbital shaker at 150 rpm at 20 °C for 6 weeks. Samplers were retrieved with tweezers, rinsed with ultrapure water, dried with a clean tissue and placed in a 50 mL glass vial for extraction with

45 mL pentane. Blank/control samples and samplers were also used to assess initial PRC concentrations and initial contamination with PAHs and PCBs. Recovery standards were added during the pentane extraction step. After 24 h, the silicone rubber samplers were removed from the pentane with solvent-rinsed tweezers and the pentane evaporated to 2 mL with a gentle stream of nitrogen. Extracts were first split into two volumes. The fraction for PAH/PRC analysis was cleaned up using gel permeation chromatography (dichloromethane as mobile phase). The final extract was reduced to ~200  $\mu$ L prior to analysis; the other fraction was treated with  $2 \times 1$  mL concentrated sulfuric acid; was reduced in volume, and was analysed for PCBs, pentachlorobenzene and hexachlorobenzene. Analysis was performed on an Agilent 7890A gas chromatograph coupled to an Agilent 5975c inert XL EI/CI quadrupole mass spectrometer operated in SIM mode with electron impact ionisation (70 keV) and has been described elsewhere (Allan et al., 2013; Allan et al., 2016b).

Most PRCs (deuterated PAHs and some fluoroCBs) were fully dissipated from the samplers during exposure. Only F-CB156 remained in the samplers with fractions of 0.14 to 0.32 of initial levels. Higher dissipation of that PRC was for sediment batches presenting a higher organic carbon content. Freely dissolved concentrations were calculated from contaminant masses accumulated and silicone rubber-water partition coefficients,  $K_{pw}$  (Smedes et al., 2009) for all compounds except CB138 and CB180 with highest  $K_{pw}$  and most likely closest to that of F-CB156.  $\log K_{pw}$  values for target compounds and PRCs are given in Table SI-1. As explained in SI, for these two compounds,  $C_{Free}$  was calculated from the sampling rates estimated from PRC dissipation kinetics, under the assumption that the only limiting factor to reaching full PRC depletion was the exposure time (Booij and Smedes, 2010; Rusina et al., 2010). Differences between estimated  $C_{Free}$  values using this procedure and when assuming equilibrium were between a factor of 1.2 and 2.5 (see Tables SI-2 and SI-3). We also tried to ensure the mass of SR was sufficiently low to avoid any depletion issues. Based on Eq. (1) from Jonker et al. (2020), we calculated the mass of sediment needed to expose 0.5 g of SR in order to remain below the 5% depletion level. These masses for the eight sediments were below the amount of sediment added to our jars with 1 L of sediment.

### 3. Results and discussion

#### 3.1. Efficiency of remediation of Aker Brygge sediments

The first sediment used for evaluating the SPME methodology was the Aker Brygge sediment. This is because total and dissolved PAH and PCB concentrations in Aker Brygge sediment previously measured are high (Allan et al., 2012). This helps with maximising the detectability of the chemicals with the SPME measurement as well as the potential to observe a significant decrease in availability of the contaminants since we are working far from limits of quantification (0.07–0.4 pg fibre for most compounds). Accumulation curves for selected PAHs and PCBs over a 42-d period are shown in Fig. 1 and detailed data are given in Table SI-4. Most PAH compounds and PCB congeners could be detected after 1 d exposure. The accumulation curves appear generally to follow a fast rate of accumulation followed by a plateauing which is consistent with a static passive sampler exposure in sediments. Despite the small volume of the SPME fibre, it is difficult to distinguish whether the plateauing is the result of equilibrium or whether the fibre has depleted the local environment of chemicals. At the start of the accumulation, it is likely that the mass of chemical absorbed is proportional to the  $C_{Free}$  in sediment. For pyrene, the PAH with the highest freely dissolved concentration in the sediment, the mass absorbed in the SPME fibre is close to 400 pg after 42 days while these remain in the tens of pg for the other compounds shown in Fig. 1. The triplicate measurements undertaken after 42 d showed a very low method variability. On average, the relative standard deviation of triplicate measurements was 9% for PAHs and PCBs. Contaminant masses accumulated in SPME fibres exposed to sediments after sand and AC amendments are given in Tables SI-5 and SI-6, respectively. Interestingly and as expected, masses of PAHs and PCBs accumulated in the SPME fibres exposed for 42 days to the Aker Brygge sediment supplemented with sand show no significant differences with the mass accumulated when exposed to the original sediment ( $t$ -test at  $P < 0.05$ ). This is not surprising since sand has little capacity to bind these hydrophobic organic contaminants and these tests show that 10% addition of fine sand has no effect on the availability of contaminants in the Aker Brygge sediment. The addition of activated

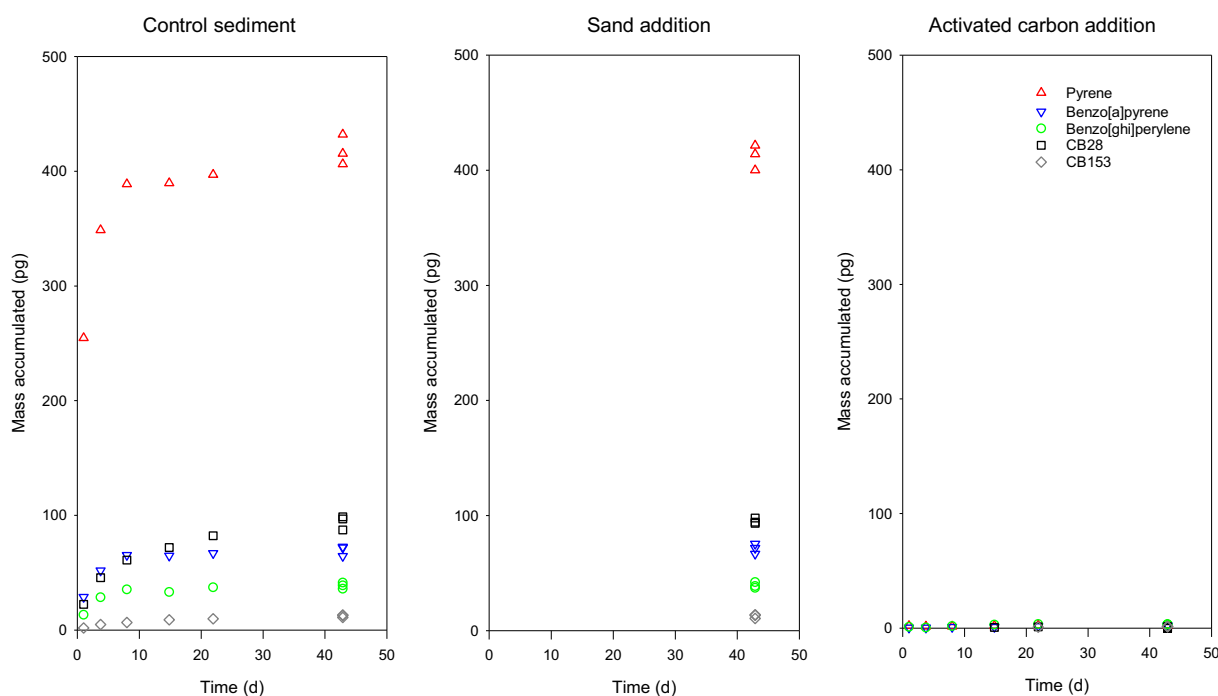


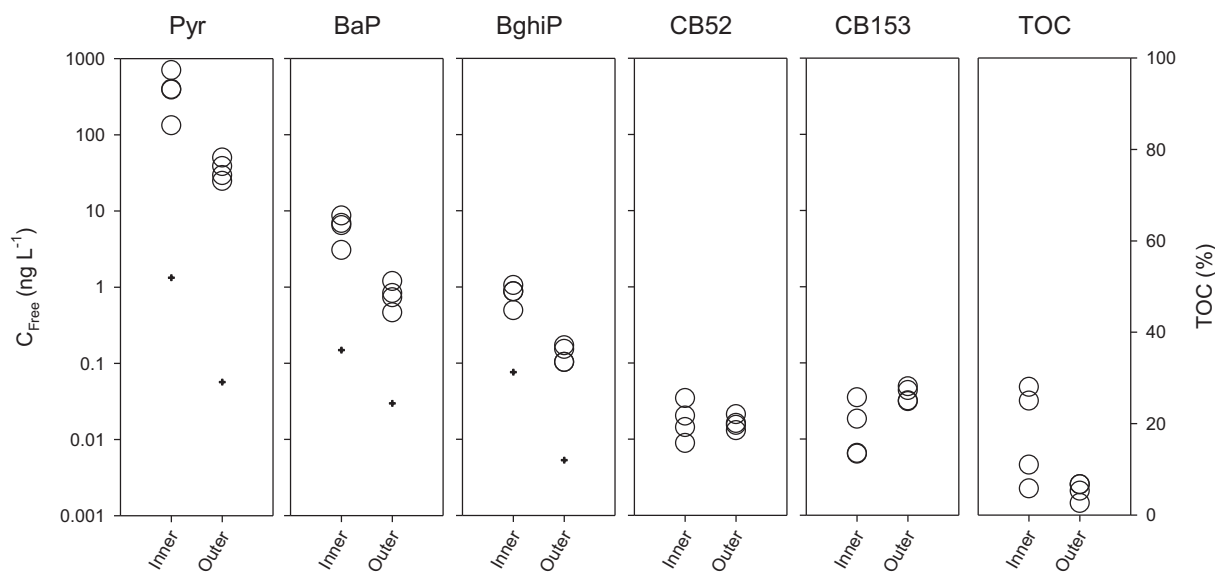
Fig. 1. Accumulation of selected PAHs and PCBs into SPME fibres exposed statically for up to 42 days to Aker Brygge sediments with no supplementation and following activated carbon or fine olivine sand amendments. The SPME measurement was conducted one month after addition of AC and sand.

carbon however has a very significant impact on the freely dissolved concentration of PAHs and PCBs in this sediment. The average reduction in contaminant mass accumulated in SPME fibres over 42 d for compounds whose concentrations were above limits of quantification in SPME fibres exposed to sediment supplemented with activated carbon was a factor of 25. Concentrations for all PAHs and PCBs reduced by a minimum of 75% for all chemicals. The highest reduction was observed for pyrene and CB28 and was approximately a factor of 200. Jia et al. showed similar levels of efficiency of AC addition to DDT-contaminated sediments (Jia et al., 2016). Rakowska et al. also used a SPME to quantify the reduction in availability of PAHs and PCBs in contaminated sediments following AC addition (Rakowska et al., 2014). They found 4% (w/v) powdered AC to be most effective and presented their results as a ratio of fluxes of contaminants to the SPME fibre (treated vs control) since the flux to the SPME is expected to be proportional to the  $C_{Free}$ . Abel et al. demonstrated that AC added at the 1% level in Finnish sediments was much more effective at lowering the PCB burden in *L. variegatus* than a 0.1% supplementation (Abel et al., 2017). The apparent decrease in PCB bioavailability of an order of magnitude is in line with the drop in  $C_{Free}$  for PCBs in Aker Brygge sediment we observe. In general, reductions in contaminant availability are in line with what can be expected from AC amendment with these dosage and contact time (Rakowska et al., 2012).

### 3.2. Freely dissolved concentrations in Kristiansand fjord sediments

A large amount of sediment data is available for the Kristiansand location near Elkembukta as a result of the continual concern with the PAH contamination of the area and potential need for remediation activities. Detailed sediment chemical and toxicological characterisation and detailed mapping of the contamination have been conducted in the past. Freely dissolved concentrations of PAHs and PCBs were measured in three batches of sediment from the two fjord areas for sediment samples collected in 2013 (Næs et al., 2014). This work was repeated on eight sediment samples collected on a transect from the inner Elkembukta towards the outer Elkembukta with results presented here. A map with sediment sampling location is given in Fig. SI-1. In these sediments, highest PAH concentrations were found for those from inner Elkembukta (Sites 1–4) with lower levels of contamination found for outer Elkembukta (Sites 5–8) (Olsen et al., 2018). Freely

dissolved concentrations estimated with equilibrium sampling with AlteSil™ silicone rubber show a similar pattern (Table SI-7). Regarding the measurement itself, near complete dissipation of performance reference compounds was observed for exposures to all eight sediment batches. This indicates that most compounds were sampled at equilibrium. Estimated  $C_{Free}$  for the eight sediments for selected PAHs and PCBs are shown in Fig. 2. Data from each sampling location are shown as individual points on the figure. Four sediment batches belonged to the inner Elkembukta plot and four to the “outer” plot. The fourth sample from outer Elkembukta, presented a contaminant level close to the lesser contaminated outer bukta sediments and a lower total organic carbon content, despite being situated close to inner Elkembukta (Figs. 2 and SI-1). The median of freely dissolved concentrations of pyrene, benzo[a]pyrene and benzo[ghi]perylene for the inner Elkembukta sediment is an order of magnitude higher than for the outer sediment batches. This is representative of data for all PAHs. The  $C_{Free}$  for the sum of 16 US EPA PAHs was highest for a batch of inner Elkembukta sediment close to  $4 \mu\text{g L}^{-1}$  and decreased to under  $0.3 \mu\text{g L}^{-1}$  for the sampling site furthest away from Elkembukta. These increased freely dissolved PAH concentrations are in agreement with total sediment concentrations and higher contamination level in sediment of inner Elkembukta as the recipient of contaminants from the industrial plant. The median of  $C_{Free}$  values measured for PAHs in inner Elkembukta sediments collected in 2017 is within a factor of three lower than  $C_{Free}$  for a batch of Elkembukta sediment collected in 2013 (TOKS1 sediment in Table SI-8). For the outer sediment, the difference with sediment collected in 2013 (TOKS 2) was larger and a factor of 2–11. There were no major differences in methodology between 2013 and 2017, so differences could be due to the variability in PAH contamination of Elkembukta. Total PAH concentrations in Elkembukta sediments (Table SI-9) are classified as high or very high, in other words, level IV or V according to the Norwegian sediment risk assessment guidelines (Olsen et al., 2018). Freely dissolved PAH concentrations in inner Elkembukta sediments are two orders of magnitude higher than those estimated for Danube sediments with a similar polymer/methodology (Rusina et al., 2019). These values are also an order of magnitude lower than those obtained for Haringen harbour, the Western Scheldt estuary (Hansweert) or the Eastern Wadden Sea (Smedes et al., 2013). Values of  $C_{Free}$  estimated for PAHs in inner Elkembukta are also over a factor of one hundred over those measured by SPME fibres in sediments



**Fig. 2.** Freely dissolved concentrations of pyrene (PYR), benzo[a]pyrene (BaP), benzo[ghi]perylene (BghiP), CB52 and CB153 measured with AlteSil™ silicone rubber in sediment samples from inner ( $n = 5$ ) and outer Elkembukta ( $n = 3$ ) collected in 2017. The total organic carbon content (TOC, %) is also shown. Crosshair symbols represent concentrations that may be achieved through AC-amendment based on SPME results.

of the German Bight (Niehus et al., 2019). They also remained a factor of ten higher than those measured in contaminated Dutch harbour sediments (Booij et al., 2003). These comparisons clearly demonstrate the high PAH contamination levels of the Elkembukta sediments.

The pattern of  $C_{Free}$  for PCBs deviates from that observed for PAHs since any PCBs contamination in the area is not associated with PAHs and coal tar pitch contamination of inner Elkembukta. Observed  $C_{Free}$  values for PCBs as exemplified by data for CB52 and CB153 in Fig. 2, tend to be lower for the inner sediments than for the outer sediments. This difference is even clearer or more pronounced if looking solely at inner Elkembukta sediments with a clearly higher TOC (Fig. 2). The average of whole sediment concentrations for inner Elkembukta ( $n = 3$ ) are either higher or in the same range as those measured for the outer area ( $n = 5$ ) for 7 indicator PCBs. There may be different explanations for this. Although not strictly apparent from the whole sediment concentrations of PCBs, there may be higher contamination levels for chlorinated compounds in the outer Elkembukta as a result of releases from other industries in the vicinity. These higher total concentrations are able to sustain higher  $C_{Free}$  in the sediment. One explanation may be that our ratio of OC to SR was not large enough considering the strongly sorbing nature of the OC in these sediments. In these conditions, the sediment OC may not be able to replenish sufficiently (fast) chemicals lost to the SR (Ghosh et al., 2014). This is unlikely however since we estimated that 0.5 g SR was low enough to enable under 5% depletion for sediments with 3% amorphous organic carbon. This was the sediment with lowest OC content, furthest away from emission source of coal tar pitch and most likely to contain natural amorphous organic carbon. Another possible explanation is that the carbonaceous material/coal tar pitch emitted by the plant, initially free of PCBs may have a strong capacity to sorb PCBs. Our agitated exposure setup for the silicone rubber samplers likely promotes an increased transfer of PCBs from natural sediment particles and sorption to this carbonaceous phase. This is also apparent in Fig. 3 where the apparent  $C_{Free}$  for pentachlorobenzene and hexachlorobenzene are clearly lower for the inner sediment batches than for the outer Elkembukta sediments with lower amounts

of coal tar pitch (Fig. 2). While we do not have whole sediment concentrations for PeCB and HCB, it is generally expected that outer Elkembukta sediment may be more contaminated with chlorinated compounds such as HCB than the inner Elkembukta location, sheltered from chlorinated chemical contamination sources in the fjord (nickel smelter). It therefore cannot be ruled out that the differences in  $C_{Free}$  for these two compounds is the result of different levels of contamination, rather than the influence of the carbonaceous phase in the sediment. It is also possible that contamination of inner Elkembukta sediments with coal tar pitch from the industrial plant, initially free of these two chemicals may induce sorption of these two compounds to this additional organic carbon phase. It will occur when this material deposits and mixes within the bottom sediments. This phenomenon may be accelerated by the mixing during  $C_{Free}$  measurement in the laboratory.

### 3.3. Kristiansand fjord sediment remediation efficiency

According to the Norwegian sediment quality classification guidelines, total sediment concentrations of most of the 16 US EPA PAHs in the Elkembukta sediment batch used for the SPME testing fall in the level IV and V categories. For example, concentrations of 32, 28, 13, 6.3 or 5.6 mg kg<sup>-1</sup> dry weight for fluoranthene, pyrene, chrysene, indeno[1,2,3-*cd*]pyrene and benzo[ghi]perylene, respectively are in the highest category of contamination (level V). Total PAH concentrations in the outer Elkembukta sediment batch are a factor of 4.5 on average (range of 2.9 for benzo[ghi]perylene to 6.7 for fluoranthene) lower than those in inner Elkembukta sediment and mostly in category IV.

The efficiency of two potential remediation materials for in situ application to inner and outer Elkembukta sediments was tested using the SPME procedure. Fig. 4 presents a comparison of masses of selected PAHs accumulated in SPME fibres exposed over 4.5 d to control and remediated inner and outer Elkembukta sediments. The mean and standard deviation of triplicate SPME for PAHs for each sediment treatment are given in Tables SI-10 and 11 for inner and outer Elkembukta sediments, respectively. Limits of detection and quantification for the SPME measurements are provided in Table SI-12. These sediments were continuously agitated from the moment the additive was added until the analysis with SPME was performed. The reduction in masses absorbed in SPME for six PAHs achieved with AC is in the range of a factor of 14–630 and 11–305 for inner and outer Elkembukta sediments, respectively. The reduction for the anthracite addition treatment is less significant with factors of 2–6 and 8–37 observed for inner and outer Elkembukta sediments, respectively. Anthracite appears more effective for the lesser contaminated sediment.

The simplicity of the methodology allowed us to evaluate a higher number of scenarios or treatment with replication than with for example the silicone rubber procedure mentioned above. The efficiency of the treatments is however not given as freely dissolved concentration but as an efficiency relative to the control sediment with no remediation and can be viewed as a proportional reduction in  $C_{Free}$ . Rakowska et al. also used such a procedure, with the efficiency defined as ratio of fluxes to the SPME fibre observed with treatment over than obtained in the control sediment (Rakowska et al., 2014). Fig. 5 shows the proportional reduction in availability of 17 PAHs in inner and outer Elkembukta upon AC or anthracite under differing agitation conditions and treatment time. It is clear that the AC treatment allows reducing  $C_{Free}$  in Elkembukta sediments more effectively than the anthracite. The reduction in  $C_{Free}$  with AC is mostly a factor of 10 to over a 100 (see Fig. 2 for expected improvements in  $C_{Free}$  for selected PAHs). The static and longer treatment with anthracite appears to improve efficiency observed with agitation. This is the opposite to the results observed for the AC supplementation. In general, improvements are greatest for the least hydrophobic PAHs with the lowest reductions in  $C_{Free}$  observed for the most hydrophobic PAHs. This is not surprising as the transfer to and subsequent binding to the sorption material will suffer more hindrance for

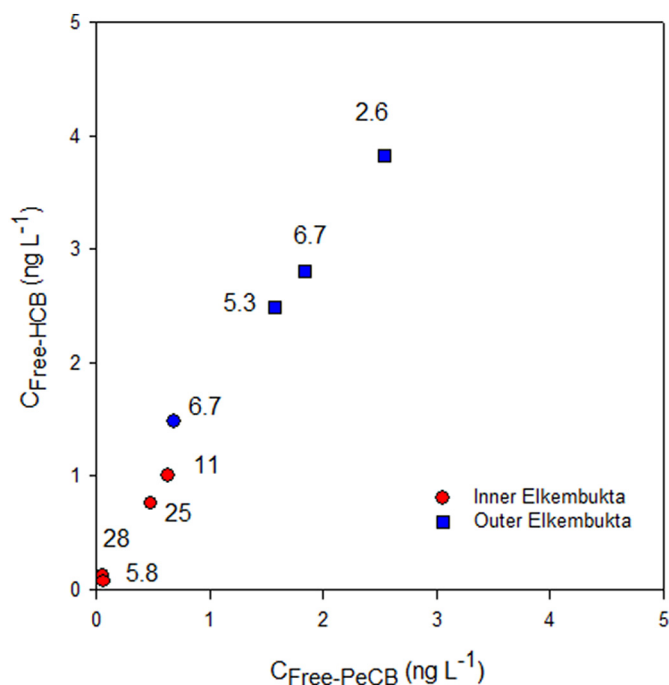
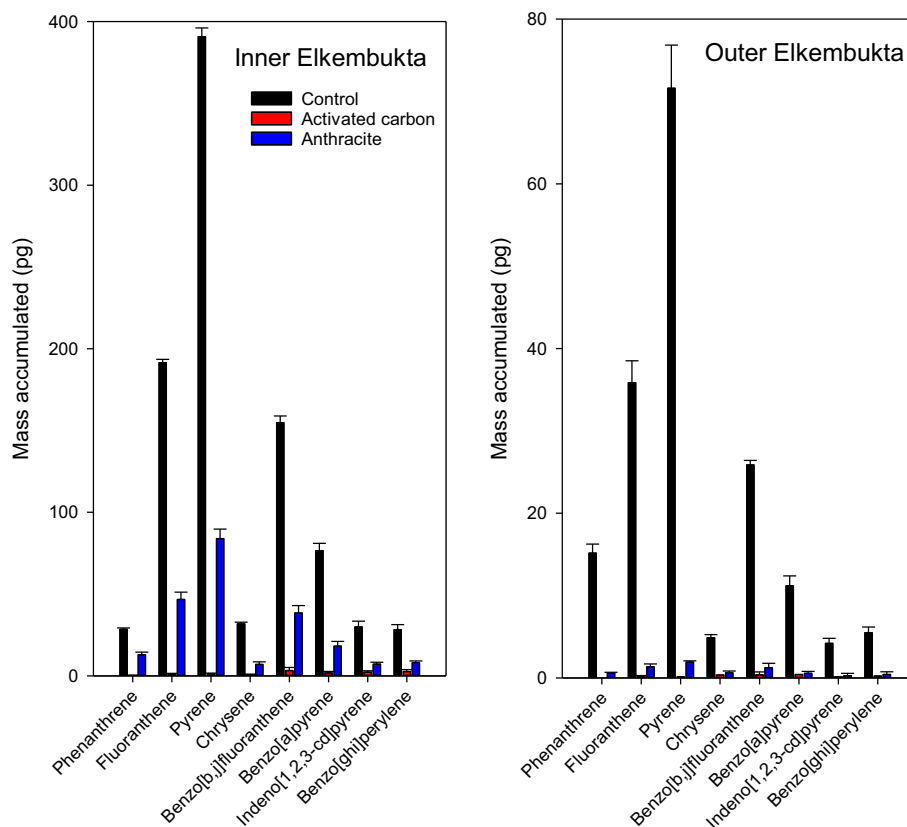


Fig. 3. Freely dissolved concentrations of pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) in the 8 sediment batches from inner and outer Elkembukta obtained through equilibrium sampling with AlteSil™ silicone rubber. Numbers indicated close to the symbols are TOC content of the sediment batches (% dry weight).



**Fig. 4.** Masses of selected PAHs accumulated in SPME fibres exposed statically to inner and outer Elkembukta sediment for 4.5 days prior to and following addition of activated carbon and anthracite powder. Sediments were continuously agitated following supplementation. Error bars correspond to standard deviation of triplicate measurements.

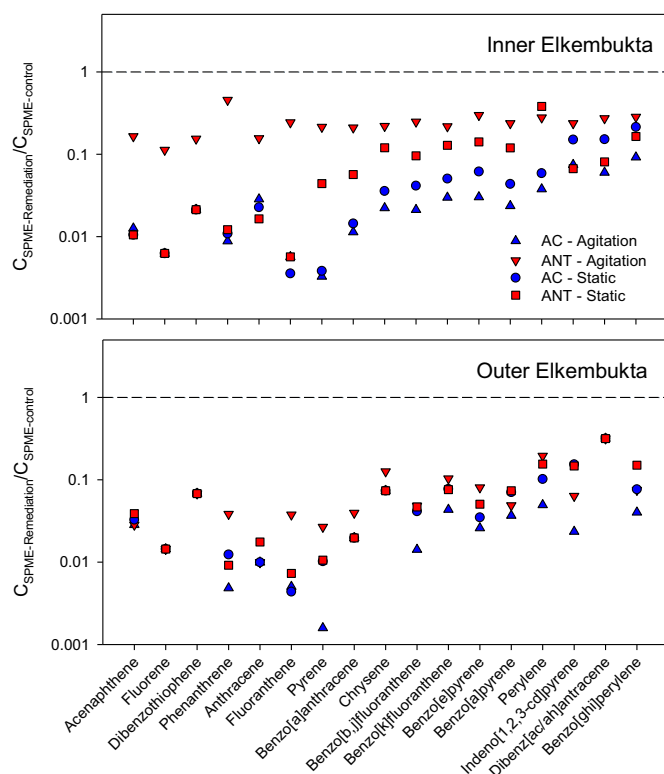
the more hydrophobic and less soluble chemicals. The efficiency of the AC addition for outer sediments is similar in proportion to that obtained for inner Elkembukta sediments. For these sediments with lower total PAH concentrations and less available PAHs (compared with inner sediments), the efficiency of the anthracite and AC treatments are much more similar (Fig. 5). As for inner Elkembukta sediments, the efficiency of the treatment appears higher for the less hydrophobic PAHs. Rakowska et al. found calculated apparent first-order adsorption rates to granulated activated carbon lower for the more hydrophobic PAHs in line with our relative efficiencies for the different PAHs (Rakowska et al., 2014).

In general, it is difficult to distinguish whether differences in efficiency of the treatments are the result of the level of agitation of the sediment post remediation or of the remediation material-sediment contact time. Since assays were not amended with a biocide, biodegradation of the PAHs cannot be excluded particularly for the treatments that were agitated at room temperature. This factor may have contributed to the improved results for the AC treatments under agitation but cannot be observed for the anthracite one. Re-assessing  $C_{Free}$  after a year may provide some insight into the efficiency that could be expected with the application of AC and anthracite amendments on a longer-term basis. Hale and Werner (2010) did not find major differences in efficiency of AC amendments between continuously and briefly mixed supplementation (Hale and Werner, 2010). However, the authors expected more significant differences for sediments with more available PAHs. Rakowska et al. found that desorption of PAHs from sediments was helped by mixing intensity and this was explained by the fragmentation of sediment aggregates (induced by the turbulent mixing) and dissolved organic matter-mediated transport (Rakowska et al., 2017). In that study, PAH desorption rates were found to be lower for the more hydrophobic PAHs. We can expect that in our study the maximum reduction in availability of these PAHs expected

upon AC amendment has not been reached and will continue to reduce over longer AC-sediment contact time.

### 3.4. Comparison of SPME and SR-estimated $C_{free}$

While it may be possible to model the SPME accumulation to estimate a freely dissolved PAH concentration, it was not the purpose of this work (Shen and Reible, 2019). Fig. SI-2 presents accumulation curves for selected PAHs in SPME fibres exposed to the inner Elkembukta control sediment for 10.5 days. Uptake curves show a fast accumulation over the first few hours or days followed by a slower accumulation and/or plateauing for certain compounds in agreement with Fig. 1 for Aker Brygge sediments. Masses of PAHs accumulated over 10.5 days are assumed to be close to the value at equilibrium. Since the volume of PDMS of the SPME fibre is extremely small it is possible that the plateauing observed is indicative of PAH concentrations in PDMS reaching equilibrium with those in the sediment. This may not be surprising since such SPME fibres are expected to be the fastest to reach equilibrium when the sediment is constantly mixed (Jonker et al., 2018). Under static conditions, time to equilibrium is expected to be longer and is partly dependent on the volume of the sampler, which in our case is very low. The amounts of PAHs absorbed by the SPME fibre are negligible in comparison with the amounts of PAHs added to the GC vial for the measurement as shown in Table SI-14. This would support that the SPME fibre as a result of its extremely low volume does not deplete the system. Using literature values of PDMS-water partition coefficients (DiFilippo and Eganhouse, 2010) for Supelco SPME fibres, we estimated  $C_{free}$  from SPME measurements for inner and outer Elkembukta sediments (details in Supporting Information) and compared them with data generated with AlteSil™ SR (Fig. SI-3). A very good agreement is generally observed since most datapoints are very close to the 1:1 relationship. Some data deviate from this relationship



**Fig. 5.** Ratio of masses of PAHs accumulated in SPME fibres ( $C_{SPME}$ ) exposed to remediated inner and outer Elkembukta sediment over those prior to activated carbon (AC) and anthracite (ANT) amendment with sediment remediation undertaken under constant agitation and under static conditions. Note that remediation times differed for the different tests. When data were below limits of quantification, these were used to calculate ratios.

and this could be due to the comparison of sediment batches that are not identical, (bio)degradation of the lighter PAHs during the SPME measurements, or the mass of these PAHs reaching maximum solubility in the PDMS.

#### 4. Conclusions

The SPME methodology presented above appears useful to assess the availability of organic contaminants in sediments. This simple and solvent-less procedure can be implemented on a wide scale with adequate replication. Masses of contaminants absorbed by the SPME fibre can be viewed as a proxy for the freely dissolved contaminant concentration  $C_{Free}$  or the flux of contaminant to the SPME fibre that the sediment is capable of sustaining. This is very helpful for those with an interest to evaluate the efficiency of remediation materials such as activated carbon under various treatment scenarios. Here, we demonstrated the possibilities with three contaminated sediments. In the case of activated carbon supplementation, we demonstrated a reduction in availability of PAHs and PCBs by one to over two orders of magnitude. The results obtained with the anthracite material were also very promising and are worthy of more work to assess the possibility of its use for sediment remediation. This SPME procedure could easily be applied in boxcore experiments or for depth profiling in intact sediment cores. In case an actual determination of  $C_{Free}$  with passive samplers is needed, while the equilibrium measurement with silicone rubber described above is suitable, we also showed that SPME fibres.

#### CRediT authorship contribution statement

**Ian J. Allan:** Methodology, Conceptualization, Investigation, Formal analysis, Writing - original draft, Supervision. **Violette Raffard:**

Investigation, Formal analysis, Methodology, Writing - review & editing. **Alfild Kringstad:** Investigation, Formal analysis, Supervision. **Kristoffer Næs:** Writing - review & editing, Conceptualization, Resources, Project administration.

#### 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.

#### Acknowledgements

We would like to acknowledge Elkem AS and the Norwegian Research Council through NIVA's strategic institutional initiatives for financing parts of this work.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.143854>.

#### References

- Abel, S., Nybom, I., Mäenpää, K., Hale, S.E., Cornelissen, G., Akkanen, J., 2017. Mixing and capping techniques for activated carbon based sediment remediation—efficiency and adverse effects for *Lumbriculus variegatus*. *Water Res.* 114, 104–112.
- Allan, I.J., Ruus, A., Schaanning, M.T., Macrae, K.J., Næs, K., 2012. Measuring nonpolar organic contaminant partitioning in three Norwegian sediments using polyethylene passive samplers. *Sci. Total Environ.* 423, 125–131.
- Allan, I.J., Harman, C., Rannekleiv, S.B., Thomas, K.V., Grung, M., 2013. Passive sampling for target and nontarget analyses of moderately polar and nonpolar substances in water. *Environ. Toxicol. Chem.* 32, 1718–1726.
- Allan, I.J., Christensen, G., Bæk, K., Evensen, A., 2016a. Photodegradation of PAHs in passive water samplers. *Mar. Pollut. Bull.* 105, 249–254.
- Allan, I.J., O'Connell, S.G., Meland, S., Bæk, K., Grung, M., Anderson, K.A., et al., 2016b. PAH accessibility in particulate matter from road-impacted environments. *Environ. Sci. Technol.* 50, 7964–7972.
- Beckingham, B., Ghosh, U., 2013. Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field. *Chemosphere* 91, 1401–1407.
- Booij, K., Smedes, F., 2010. An improved method for estimating in situ sampling rates of nonpolar passive samplers. *Environ. Sci. Technol.* 44, 6789–6794.
- Booij, K., Smedes, F., van Weerlee, E.M., 2002. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* 46, 1157–1161.
- Booij, K., Hoedemaker, J.R., Bakker, J.F., 2003. Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments. *Environ. Sci. Technol.* 37, 4213–4220.
- Booij, K., Robinson, C.D., Burgess, R.M., Mayer, P., Roberts, C.A., Ahrens, L., et al., 2016. Passive sampling in regulatory chemical monitoring of nonpolar organic compounds in the aquatic environment. *Environ. Sci. Technol.* 50, 3–17.
- 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. *Environ. Sci. Technol.* 39, 6881–6895.
- DiFilippo, E.L., Eganhouse, R.P., 2010. Assessment of PDMS-water partition coefficients: implications for passive environmental sampling of hydrophobic organic compounds. *Environ. Sci. Technol.* 44, 6917–6925.
- Eek, E., Cornelissen, G., Breedveld, G.D., 2010. Field measurement of diffusional mass transfer of HOCs at the sediment-water interface. *Environ. Sci. Technol.* 44, 6752–6759.
- Fernandez, L.A., Lao, W., Maruya, K.A., Burgess, R.M., 2014. Calculating the diffusive flux of persistent organic pollutants between sediments and the water column on the Palos Verdes Shelf Superfund Site using polymeric passive samplers. *Environ. Sci. Technol.* 48, 3925–3934.
- Ghosh, U., Luthy, R.G., Cornelissen, G., Werner, D., Menzie, C.A., 2011. In-situ sorbent amendments: a new direction in contaminated sediment management. *Environ. Sci. Technol.* 45, 1163–1168.
- Ghosh, U., Kane Driscoll, S., Burgess, R.M., Jonker, M.T., Reible, D., Gobas, F., et al., 2014. Passive sampling methods for contaminated sediments: practical guidance for selection, calibration, and implementation. *Integr. Environ. Assess. Manag.* 10, 210–223.
- Greenberg, M.S., Chapman, P.M., Allan, I.J., Anderson, K.A., Apitz, S.E., Beegan, C., et al., 2014. Passive sampling methods for contaminated sediments: risk assessment and management. *Integr. Environ. Assess. Manag.* 10, 224–236.
- Hale, S.E., Werner, D., 2010. Modeling the mass transfer of hydrophobic organic pollutants in briefly and continuously mixed sediment after amendment with activated carbon. *Environ. Sci. Technol.* 44, 3381–3387.



- Jia, F., Liao, C., Xue, J., Taylor, A., Gan, J., 2016. Comparing different methods for assessing contaminant bioavailability during sediment remediation. *Sci. Total Environ.* 573, 270–277.
- Jonker, M.T., Suijkerbuijk, M.P., Schmitt, H., Sinnige, T.L., 2009. Ecotoxicological effects of activated carbon addition to sediments. *Environ. Sci. Technol.* 43, 5959–5966.
- Jonker, M.T., Van Der Heijden, S.A., Adelman, D., Apell, J.N., Burgess, R.M., Choi, Y., et al., 2018. Advancing the use of passive sampling in risk assessment and management of sediments contaminated with hydrophobic organic chemicals: results of an international ex situ passive sampling interlaboratory comparison. *Environ. Sci. Technol.* 52, 3574–3582.
- Jonker, M.T., Burgess, R.M., Ghosh, U., Gschwend, P.M., Hale, S.E., Lohmann, R., et al., 2020. Ex situ determination of freely dissolved concentrations of hydrophobic organic chemicals in sediments and soils: basis for interpreting toxicity and assessing bioavailability, risks and remediation necessity. *Nat. Protoc.* 15, 1800–1828.
- Lydy, M.J., Landrum, P.F., Oen, A.M., Allinson, M., Smedes, F., Harwood, A.D., et al., 2014. Passive sampling methods for contaminated sediments: state of the science for organic contaminants. *Integr. Environ. Assess. Manag.* 10, 167–178.
- Mayer, P., Vaes, W.H.J., Wijmker, F., Legierse, K.C.H.M., Kraaij, R., Tolls, J., et al., 2000. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environ. Sci. Technol.* 34, 5177–5183.
- Næs, K., Håvardstun, J., Oug, E., Beyer, J., Bakke, T., Heiaas, H., et al., 2014. Oppdatert risikovurdering av sediment og overvåking med vekt på PAH av det nære sjøområdet til Elkem i Kristiansand i 2013. RAPPORT L.NR. 6664. Norwegian Institute for Water Research, Oslo, Norway, p. 107 (pages).
- Niehus, N.C., Brockmeyer, B., Witt, G., 2019. Bioavailability and distribution of PAHs and PCBs in the sediment pore water of the German Bight and Wadden Sea. *Mar. Pollut. Bull.* 138, 421–427.
- Olsen, M., Næs, K., Schaanning, M., Øxnevad, S., Håvardstun, J., Allan, I., et al., 2018. Tiltaksplan for forurenset sjøbunn utenfor Elkem Carbon AS, Kristiansand. Norwegian Institute for Water Research (NIVA), Oslo, Norway (pp. 113 pages).
- Patmont, C.R., Ghosh, U., LaRosa, P., Menzie, C.A., Luthy, R.G., Greenberg, M.S., et al., 2015. In situ sediment treatment using activated carbon: a demonstrated sediment cleanup technology. *Integr. Environ. Assess. Manag.* 11, 195–207.
- Rakowska, M., Kupryianchyk, D., Harmsen, J., Grotenhuis, T., Koelmans, A., 2012. In situ remediation of contaminated sediments using carbonaceous materials. *Environ. Toxicol. Chem.* 31, 693–704.
- Rakowska, M.I., Kupryianchyk, D., Koelmans, A.A., Grotenhuis, T., Rijnaarts, H.H., 2014. Equilibrium and kinetic modeling of contaminant immobilization by activated carbon amended to sediments in the field. *Water Res.* 67, 96–104.
- Rakowska, M.I., Smit, M.P., Kupryianchyk, D., Qin, J., Koelmans, A.A., Rijnaarts, H.H., et al., 2017. Turbulent mixing accelerates PAH desorption due to fragmentation of sediment particle aggregates. *J. Soils Sediments* 17, 277–285.
- Reichenberg, F., Mayer, P., 2006. Two complementary sides of bioavailability: accessibility and chemical activity of organic contaminants in sediments and soils. *Environmental Toxicology and Chemistry: An International Journal* 25, 1239–1245.
- Rusina, T.P., Smedes, F., Koblizkova, M., Klanova, J., 2010. Calibration of silicone rubber passive samplers: experimental and modeled relations between sampling rate and compound properties. *Environ. Sci. Technol.* 44, 362–367.
- Rusina, T.P., Smedes, F., Brborić, M., Vrana, B., 2019. Investigating levels of organic contaminants in Danube River sediments in Serbia by multi-ratio equilibrium passive sampling. *Sci. Total Environ.* 696, 133935.
- Shen, X., Reible, D., 2019. An analytical model for the fate and transport of performance reference compounds and target compounds around cylindrical passive samplers. *Chemosphere* 232, 489–495.
- Smedes, F., Geertsma, R.W., Zande, Tvd, Booij, K., 2009. Polymer–water partition coefficients of hydrophobic compounds for passive sampling: application of cosolvent models for validation. *Environ. Sci. Technol.* 43, 7047–7054.
- Smedes, F., Van Vliet, L.A., Booij, K., 2013. Multi-ratio equilibrium passive sampling method to estimate accessible and pore water concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in sediment. *Environ. Sci. Technol.* 47, 510–517.
- Thomas, C., Lampert, D., Reible, D., 2014. Remedy performance monitoring at contaminated sediment sites using profiling solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers. *Environ Sci Process Impacts* 16, 445–452.
- Zimmerman, J.R., Werner, D., Ghosh, U., Millward, R.N., Bridges, T.S., Luthy, R.G., 2005. Effects of dose and particle size on activated carbon treatment to sequester polychlorinated biphenyls and polycyclic aromatic hydrocarbons in marine sediments. *Environmental Toxicology and Chemistry: An International Journal* 24, 1594–1601.