Evaluation of methods to determine adsorption of polycyclic aromatic hydrocarbons to dispersed carbon nanotubes

Berit Glomstad¹ · Lisbet Sørensen² · Jingfu Liu³ · Mohai Shen^{3,4} · Florian Zindler^{1,5} · Bjørn M. Jenssen¹ · Andy M. Booth²

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Abstract A number of methods have been reported for determining hydrophobic organic compound adsorption to dispersed carbon nanotubes (CNTs), but their accuracy and reliability remain uncertain. We have evaluated three methods to investigate the adsorption of phenanthrene (a model polycyclic aromatic hydrocarbon, PAH) to CNTs with different physicochemical properties: dialysis tube (DT) protected negligible depletion solid phase microextraction (DT-nd-SPME), ultracentrifugation, and filtration using various types of filters. Dispersed CNTs adhered to the unprotected polydimethylsiloxane (PDMS)-coated fibers used in nd-SPME. Protection of the fibers from CNT adherence was investigated with hydrophilic DT, but high PAH sorption to the DT was observed. The

efficiency of ultracentrifugation and filtration to separate CNTs from the water phase depended on CNT physicochemical properties. While non-functionalized CNTs were efficiently separated from the water phase using ultracentrifugation, incomplete separation of carboxyl functionalized CNTs was observed. Filtration efficiency varied with different filter types (composition and pore size), and non-functionalized CNTs were more easily separated from the water phase than functionalized CNTs. Sorption of phenanthrene was high (< 70%) for three of the filters tested, making them unsuitable for the assessment of phenanthrene adsorption to CNTs. Filtration using a hydrophilic polytetrafluoroethylene (PTFE) filter membrane (0.1 µm) was found to be a simple and precise technique for the determination of phenanthrene adsorption to a range of CNTs, efficiently separating all types of CNTs and exhibiting a good and highly reproducible recovery of phenanthrene (82%) over the concentration range tested (70–735 µg/L).

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✉ Andy M. Booth
andy.booth@sintef.no

¹ Department of Biology, Norwegian University of Science and Technology, NO-7491, 7491 Trondheim, Norway

² SINTEF Ocean, NO-7465, 7465 Trondheim, Norway

³ State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

⁴ Present address: School of Environment, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Key Laboratory for Environmental Pollution Control, Henan Normal University, Xinxiang 453007, China

⁵ Present address: Aquatic Ecology and Toxicology Section, Centre for Organismal Studies (COS), University of Heidelberg, Im Neuenheimer Feld 504, 69120 Heidelberg, Germany

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Introduction

Carbon nanotubes (CNTs) have many possible applications, including composite materials in electronics (De Volder et al. 2013; Petersen et al. 2011) and in medicine (Kesharwani et al. 2015). CNTs also interact strongly with hydrophobic organic compounds (HOCs) (Glomstad et al. 2016; Kah et al. 2011, 2014; Yang and Xing 2010; Yang et al. 2006b; Zindler et al. 2016), making them interesting sorbents, e.g., in water treatment (Mauter and Elimelech 2008; Yu et al. 2014). Concurrent with an increase in CNT production and use is a

growing concern regarding their environmental effects (Alloy and Roberts 2011; Edgington et al. 2010; Schwab et al. 2011). Furthermore, the high adsorption capacity of CNTs and other carbon nanomaterials (CNMs) for HOCs has been shown to influence HOC fate, bioavailability, and toxicity in the environment (Baun et al. 2008; Glomstad et al. 2016; Schwab et al. 2013; Shen et al. 2014, 2012; Zindler et al. 2016).

While hydrophobic, pristine CNTs are prone to agglomeration and sedimentation in freshwater (Pan and Xing 2008), stable CNT dispersions can be formed under certain conditions. CNT physicochemical properties (e.g., surface oxygen content) and environmental factors (e.g., natural organic matter, NOM) have been reported to enhance CNT dispersibility (i.e., the dispersed CNT concentration) and dispersion stability (Hyung et al. 2007; Schwyzer et al. 2012). The increased available specific surface area (SSA) of dispersed CNTs enhances adsorption of HOCs compared to agglomerated CNTs (Zhang et al. 2012). CNTs dispersed in aquatic matrices may therefore have increased potential for influencing the fate of co-adsorbed HOCs. Assessing HOC adsorption to agglomerated rather than dispersed CNTs could lead to an underestimation of their environmental effects.

In recent years, several studies have investigated the adsorption of polycyclic aromatic hydrocarbons (PAHs) to CNTs (Cho et al. 2008; Glomstad et al. 2016; Kah et al. 2011, 2014; Wang et al. 2009; Yang et al. 2006a, b; Zhang et al. 2012; Zindler et al. 2016), with phenanthrene being one of the most frequently used compounds (Apul et al. 2012). The adsorption of other HOCs to a range of CNTs with different physical and chemical properties has also been studied [e.g., (Carabineiro et al. 2011, 2012; Chen et al. 2007; Cho et al. 2011; Dai et al. 2009; Huffer et al. 2015; Schwab et al. 2014)]. Most studies have focused on agglomerated rather than dispersed CNTs, although a few studies using CNTs dispersed by sonication have been reported (Kah et al. 2014; Zhang et al. 2012). Studying dispersed CNTs is challenging because of the difficulty in separating the dispersed CNTs from the water phase prior to determination of the freely dissolved PAH concentration in the water phase (C_{free}) and the PAH concentration adsorbed by CNTs (C_{CNT}) (Petersen et al. 2016; Yang et al. 2011). Centrifugation has commonly been employed in adsorption studies to sediment agglomerated CNTs before the supernatant is withdrawn and C_{free} determined (Cho et al. 2008; Kah et al. 2011; Wang et al. 2009; Yang et al. 2006a, b). A few studies have also used centrifugation to assess PAH adsorption to dispersed CNTs (Linard et al. 2015; Su et al. 2013). However, centrifugation may not be sufficient to fully sediment well-dispersed CNTs, possibly causing errors in the determination of C_{free} and C_{CNT} .

Solid phase extraction (SPE) using polyoxymethylene sheets has been reported to successfully determine PAH adsorption to partly dispersed CNTs but requires a 28-day equilibrium period (Kah et al. 2011, 2014; Zhang et al. 2012).

Negligible depletion solid phase microextraction (nd-SPME) has also been used to study HOC adsorption to aqueous suspensions of the fullerene C_{60} (Hu et al. 2008, 2010) but has, to our knowledge, not been validated for CNTs. Here, a negligible fraction of the target analyte proportional to C_{free} is extracted onto the fiber without affecting the equilibrium between C_{free} and the adsorbent (Heringa and JLM 2003). While separation of dispersed CNTs from the water phase is avoided, nd-SPME could lead to the adherence of PAH-loaded CNTs to the fiber, causing an overestimation of C_{free} .

In a different approach, filtration has been used to study the adsorption of, e.g., the herbicide diuron to CNTs (Schwab et al. 2014), and to investigate the adsorption of HOCs, including the PAH phenanthrene, to suspended agglomerates of C_{60} (Baun et al. 2008). No studies have evaluated the use of filtration to study PAH (or HOC) C_{free} in the presence of different types of CNTs. The importance of understanding the HOC adsorption to dispersed CNTs and the need to develop appropriate separation techniques has previously been highlighted (Pan and Xing 2008). However, no systematic evaluation of methods to determine C_{free} in the presence of CNTs has been performed. Furthermore, the separation efficiency of centrifugation and filtration is likely to depend on CNT physicochemical properties (e.g., diameter and surface oxidation) which influence their dispersion state (Schwyzer et al. 2012). The role of CNT properties on the suitability of different separation techniques has not been considered to date.

We have evaluated different methods for studying the adsorption of the model compound phenanthrene to CNTs, with a focus on identifying the most reliable way of determining C_{free} values of phenanthrene remaining in the water phase. Three methods for determining C_{free} were evaluated; (i) dialysis tube (DT) protected nd-SPME (DT-nd-SPME), (ii) ultracentrifugation, and (iii) filtration. The objective for the ultracentrifugation and filtration methods was a complete separation of dispersed CNTs from the water phase. A suite of CNTs, including one single-walled CNT (SWCNT), two non-functionalized multi-walled CNTs of different diameters and lengths (MWCNT-15 and MWCNT-30), and two functionalized MWCNTs (MWCNT-OH and MWCNT-COOH), was included in the study to ensure that the method would be suitable for a range of CNTs exhibiting varying physicochemical properties. CNT dispersions were prepared in the presence of environmentally relevant concentrations of NOM to increase the environmental relevance of the study and enhance the dispersion of CNTs.

Materials and methods

A schematic overview of the nd-SPME, DT-nd-SPME, ultracentrifugation, and filtration methods evaluated for their suitability in the determination of C_{free} and subsequent calculation of C_{CNT} is presented in Fig. 1.

Fig. 1 Overview of the methods evaluated for the determination of CNT adsorption of phenanthrene (C_{CNT}). The method encircled with dotted lines is the final method developed for determination of phenanthrene C_{free} in the presence of different types of CNTs

Chemicals and materials

A suite of five different CNTs (SWCNT, MWCNT-15, MWCNT-30, MWCNT-OH, and MWCNT-COOH (purity > 95%) was purchased from Timesnano (Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences). Phenanthrene ($\geq 99.5\%$) and pyrene (> 99%) (included in evaluation of nd-SPME) were purchased from Sigma-Aldrich and stock solutions prepared in methanol. Fluorene-*d*10 was supplied by Chiron AS. Suwannee River natural organic matter (SR-NOM; Reference Aquatic NOM; Catalog number 2R101N) was purchased from the International Humic Substance Society (IHSS). The organic solvents, methanol (Fluka Analytical), dichloromethane (Rathburn Chemicals Ltd.), *n*-hexane (Fluka Analytical), acetonitrile (Fluka Analytical), and isopropanol (Lab Scan), were of analytical grade and tested in-house for any impurities before use. Polydimethylsiloxane-coated (PDMS)-fused silica fibers (diameter 110 μm , coating thickness 30 μm) was purchased from Polymicro Technologies (Switzerland). Hydrophilic cellulose ester membrane DT was purchased from Spectrum Laboratories, Inc.

CNT characterization

CNT properties as specified by the manufacturer are available in Table S1 in the Supplementary Data. Several CNT parameters, including outer diameter and purity (transmission

electron microscopy, TEM), surface chemistry (X-ray photoelectron spectroscopy, XPS), and specific surface area (SSA; calculated by Brunauer-Emmett-Teller method), were further verified by in-house characterization.

Media and media-NOM preparation

Two freshwater media, commonly used in aquatic ecotoxicity tests, EPA moderately hard reconstituted water (MHRW) (U.S. Environmental Protection Agency 2002) and OECD algal growth media TG201 (OECD 2011), were used throughout the study. These media were selected in order to ensure that the methods being evaluated would subsequently be appropriate for use in standardized aquatic ecotoxicological tests (freshwater algae and *Daphnia magna*). It has been shown that dispersed CNT concentrations are positively related to NOM concentration [e.g., (Kennedy et al. 2008; Smith et al. 2012)]. In order to achieve improved dispersion of the CNTs, the NOM concentration utilized in the current study is at the higher end of the range found in natural waters (Thurman 1985). The preparation of media containing SR-NOM (nominally 20 mg/L), further referred to as media-NOM or MHRW-NOM and TG201-NOM, has been previously reported (Glomstad et al. 2016) and is summarized in the Supplementary Data. Briefly, SR-NOM was stirred into the media for 24 h to maximize dissolution, followed by filtration to remove any residual particulate NOM that could represent an alternative adsorption site for the organic pollutants.

Preparation and quantification of CNT dispersions

Details on the CNT dispersion procedure have been previously published (Glomstad et al. 2016; Zindler et al. 2016). Briefly, bath sonication (Bandelin Sonorex Super RK 510H, 640 W, 35 kHz) was used to prepare 0.2-L stock dispersions of CNTs (100 mg/L) in media-NOM. The CNT stock dispersions were then added to 1.8 L of media-NOM, giving a final CNT concentration of 10 mg/L. A settling period of 24 h was applied to allow natural settling of any undispersed CNTs. This also allowed the settling of large CNT agglomerates which could influence subsequent UV-vis absorbance measurements as previously described (Cerrillo et al. 2015; Li et al. 2006; Petersen et al. 2016). The preparation of and use of media solutions took place at room temperature (20 ± 2 °C). In cases where the CNT dispersions were not used immediately, they were stored in the dark at 4 °C.

A spectral analysis was conducted to verify the absorbance maxima of both the studied CNTs and background media solutions in order to identify a wavelength where the influence of other matrix components (e.g., NOM and PAHs) on the absorbance was minimized. The dispersed CNT concentration (after 24 h settling) was determined by measuring absorbance at 800 nm with UV-vis spectrophotometry (Hitachi U-2000) using quartz cuvettes (3.5 mL; 10 mm light path, Hellma Analytic). A series of external calibration standards with known CNT concentrations was used to generate individual UV-vis calibration curves for each of the CNTs. At the selected wavelength, no significant absorbance by the two media solutions, the media-NOM solutions or PAH solutions, was observed. As the CNTs were dispersed in media-NOM, blank samples consisted of media-NOM without CNTs. The limit of detection (LOD) and limit of quantification (LOQ) were calculated as the blank mean (MHRW-NOM or TG201-NOM) plus three (LOD) or ten (LOQ) times the standard deviation (SD). Dispersed CNT concentrations were determined immediately after preparation of the dispersions or immediately before use if the dispersions had been stored.

Negligible depletion solid phase microextraction approaches

Another model PAH, pyrene, was used in addition to phenanthrene in evaluation of the nd-SPME method. Although pyrene was not used in the evaluation of other methods presented herein, the pyrene nd-SPME data provide important supplementary information to that generated for phenanthrene. Preliminary studies showed that CNTs adhered to the PDMS-coated fibers used as the extraction medium in the nd-SPME studies and affect the determination of C_{free} . To protect the PDMS-coated fibers, hydrophilic cellulose ester membrane DT with a molecular weight cutoff of 0.5–1.0 kD and a width of 10 mm was used. The DT was cut into 3-cm pieces

and rinsed in deionized water before use. The PDMS-coated fibers were carefully cut into pieces of 1 cm (using a surgical scalpel) and rinsed in acetone before use. The fibers were placed inside DT filled with a few drops of deionized water before the DT ends were folded and closed with metal clam clips (Fig. S1, Supplementary Data). The extraction units were prepared daily and kept in deionized water until use.

To determine the PAH equilibration time for DT-nd-SPME, extraction of phenanthrene and pyrene (100 µg/L) at various time points, 1, 2, 4, 6, and 10 days, was performed. Linearity of the method was investigated in the range 5–100 µg/L. Extraction was performed in individual solutions and mixtures of pyrene and phenanthrene to evaluate the possibility of using DT-nd-SPME for analysis of PAH mixtures. The effect of NOM on the extraction efficiency was investigated by performing the extraction in the presence and absence of NOM. This was performed both with and without DT protection (using DT of 15 cm). Comparison of PAH extraction onto the PDMS-coated fibers using DT-nd-SPME and nd-SPME was used to investigate the effect of DT on the extraction. Furthermore, liquid-liquid extraction (LLE) of the MHRW solutions with dichloromethane (3×20 mL) followed by gas chromatography mass spectroscopy (GC-MS) analysis was performed to estimate the loss of pyrene after extraction with nd-SPME and DT-nd-SPME. Uptake equilibrium studies showed that the adsorption equilibrium of PAHs onto the DT protected PDMS-coated fibers was established after 2 and 4 days for phenanthrene and pyrene, respectively (Fig. S2, Supplementary Data). To ensure equilibrium, and to standardize the method, an extraction time of 5 days was therefore implemented in all studies.

The detailed DT-nd-SPME method is presented in the Supplementary Data. Preliminary studies showed no effect of NOM on extraction of PAHs onto PDMS-coated fibers, with or without DT (Fig. S3, Supplementary Data). Therefore, all tests for validation of the DT-nd-SPME method were performed in MHRW. Validation of the method was performed in the absence of CNTs. Briefly, the extraction units were inserted into the sample solutions (MHRW spiked with PAHs) and extracted for 5 days. The fiber was then removed and placed in *n*-hexane for desorption (24 h) prior to analysis by GC-MS to determine PAH concentration.

Ultracentrifugation

Visual inspection of CNT dispersions after performing regular centrifugation (Eppendorf Centrifuge 5804 R, 2200×g, 30 min) showed that this was not sufficient to sediment the suite of CNTs tested. Therefore, ultracentrifugation was employed for further testing. Dispersions of each CNT type were placed in 36-mL centrifugation tubes and centrifuged at 40,000×g for 30 min and 50,000×g for 30 min (T-865 Fixed Angle Rotor, Sorvall™ WX Ultracentrifuge, Thermo

Scientific). After centrifugation, the supernatant was carefully removed using a glass pipette, taking care not to resuspend settled CNTs. UV-vis absorbance measurements of the supernatant (800 nm) were performed to assess the separation efficiency of CNTs from water phase.

Filtration

A glass vacuum filter flask setup was employed for filtration of CNT dispersions. Several filter membrane materials were investigated, including polycarbonate (PC, pore size 0.1 μm), mixed cellulose ester (MCE, 0.2 μm), polyvinylidene fluoride (PVDF, 0.2 μm), and hydrophilic polytetrafluoroethylene (PTFE, 0.1 μm). In addition, two glass fiber filters (GF/F, 0.7 μm , GF-75, 0.3 μm) were evaluated. The selected filters were assessed for (i) their ability to retain CNTs and (ii) the degree of sorption of phenanthrene to the filter. The CNT dispersions were placed in the glass tower, gently drawn through the filter, and the filtrate collected in 20-mL glass vials placed inside the Erlenmeyer filter flask. Removal of CNTs was evaluated based on UV-vis absorbance measurements (800 nm) of the filtrate. Single replicates of each CNT type were used for all filters except for PTFE where triplicate samples were filtered owing to the promising data generated by the single replicate. Blanks (TG201-NOM) were filtered to verify that the filtration process itself did not contribute to the measured absorbance.

Sorption of phenanthrene to the filters was evaluated by determining the phenanthrene concentration in the filtrate after filtration of solutions with known phenanthrene concentrations. Analysis was performed either by solid phase extraction (SPE; Bond Elut® PPL columns, 500 mg, Agilent Technologies Inc.) of the filtrate followed by GC-MS or by direct injection of the filtrate using high-performance liquid chromatography with photodiode-array UV detection (HPLC-UV) (Glomstad et al. 2016; Zindler et al. 2016). Details on the chemical analysis are provided in Supplementary Data. Quantification of target analytes by GC-MS offers the lowest limits of detection and is therefore necessary for samples with low C_{free} concentrations. Where C_{free} of the target analyte is sufficiently high, HPLC-UV represents the quickest and least expensive method for quantification.

Results and discussion

CNT properties and dispersibility

A summary of the CNT physicochemical properties determined by in-house characterization is presented in Table 1. Significant differences in mean diameter, SSA, and surface oxygen content were observed between the suite of CNTs tested. SWCNT exhibited a much smaller outer diameter and

a higher SSA (483.7 m^2/g) than the MWCNTs. MWCNT-30 had a somewhat higher SSA (177.4 m^2/g) than the other MWCNTs ($\sim 140 \text{ m}^2/\text{g}$); however, this was not statistically significant. MWCNT-COOH had the highest surface oxygen content (5.7%) followed by MWCNT-OH (3.9%). The non-functionalized CNTs had lower surface oxygen content as expected ($< 2.0\%$). Differences in CNT dispersibility were also observed, with final dispersed concentrations increasing in the order SWCNT (0.7 mg/L) $<$ MWCNT-15 = MWCNT-30 (1.6 mg/L) $<$ MWCNT-OH (2.9 mg/L) $<$ MWCNT-COOH (6.0 mg/L). The results are in good agreement with other studies which have shown that outer diameter and oxygen-containing surface functional groups increase CNT dispersibility (Schwyzer et al. 2012). Initial characterization of the CNT dispersion using dynamic light scattering (DLS) to determine particle size distributions and polydispersity index resulted in large uncertainties in the measurements. This is consistent with the findings of other studies with high aspect ratio CNTs (Petersen and Henry 2012), which is due to DLS employing modeling assumptions based on monodisperse spheres. The different dispersion concentrations generated for each CNT type also represent an additional uncertainty when attempting to compare DLS data. No further assessment of CNT particle size distribution was conducted in the current study.

Dialysis tube protected negligible depletion solid phase microextraction

SEM images of the PDMS-coated fibers collected after exposure to CNT dispersions revealed significant quantities of CNTs adhered to the fiber surface (Fig. S4, Supplementary Data). Preliminary studies using pyrene and phenanthrene with unprotected PDMS-coated fibers in the presence of CNTs also indicated little or no adsorption of phenanthrene to CNTs had occurred (Fig. S5, Supplementary Data). In some cases, the determined C_{free} was higher in the presence of CNTs than when no CNTs were present. Phenanthrene adsorption by CNTs is well documented (Kah et al. 2011; Yang et al. 2006b). While Yang et al. (2006b) studied adsorption by CNTs using classical two-phase batch experiments, Kah et al. (2011) investigated both centrifugation and a three-phase system using a polyoxymethylene passive sampler. In all studies, high adsorption of the target PAH to the selected CNTs was observed. This is in contrast to the negligible level of phenanthrene adsorption calculated in the three-phase system investigated in the current study. As seen in relation with the SEM images, this supports the suggestion that the adherence of phenanthrene-loaded CNTs to the PDMS-coated fibers generates erroneously low C_{CNT} values when phenanthrene desorbs from the CNTs in the *n*-hexane. Given that the principle of the nd-SPME approach is based upon adsorption of negligible amounts of the target PAH, and considering the high

Table 1 Physicochemical properties of the CNTs

CNT	Average diameter (nm)	Length (μm) ^a	Specific surface area (m^2/g)	Surface oxygen content (%)	Surface carbon content (%)
SWCNT	$2.4 \pm 1.1\text{a}$	5–30	$483.7 \pm 23.5\text{a}$	1.6	98.4
MWCNT-15	$14.8 \pm 5.6\text{b}$	~ 50	$140.5 \pm 0.4\text{b}$	1.5	98.5
MWCNT-30	$16.6 \pm 8.6\text{c}$	10–30	$177.4 \pm 3.0\text{b}$	2.0	98.0
MWCNT-OH	$14.3 \pm 5.8\text{b}$	~ 50	$140.2 \pm 2.8\text{b}$	3.9	96.1
MWCNT-COOH	$20.3 \pm 7.5\text{d}$	~ 50	$139.7 \pm 3.5\text{b}$	5.7	94.3

Variations are presented as standard deviations. Different letters in the columns indicate statistically significant differences among the CNTs (ANOVA: $p > 0.05$)

^a Supplied by the manufacturer

adsorption affinity of CNTs towards PAHs, any adherence of PAH-loaded CNTs onto the PDMS-coated fibers will significantly influence the data generated.

Although, nd-SPME has been used to determine PAH adsorption to C_{60} by inserting the PDMS-coated fibers directly into C_{60} dispersions (Hu et al. 2008), the role of PAH-loaded C_{60} adherence to the PDMS-coated fibers was not investigated in the study. The current study shows that adherence of PAH-loaded CNTs to the PDMS fiber can lead to an overestimation of the true C_{free} value. Modification of the method is necessary for use in PAH-CNT adsorption studies and should be evaluated for other CNMs such as C_{60} . The DT-nd-SPME method showed promising features, as a linear relationship between PAH uptake onto the PDMS-coated fiber (C_{fiber}) and C_{nominal} was observed for both phenanthrene and pyrene in the concentration range tested (5–100 $\mu\text{g/L}$; Fig. S6). This showed that C_{fiber} , when protected inside the DT, was directly proportional to PAH C_{nominal} in the MHRW media. In the presence of CNTs, C_{fiber} can therefore be related to C_{free} . DT-nd-SPME also proved to be suitable for extraction of phenanthrene and pyrene mixtures, as no difference in the amount of either PAH extracted onto the PDMS-coated fiber was observed (Fig. S7, Supplementary Data). This indicates that DT-nd-SPME has potential for studying the adsorption of a range of PAHs (and possibly other organic compounds) to CNTs, either individually or as mixtures.

A comparison of PAH extraction onto the PDMS-coated fibers with and without DT protection showed that the use of DT influenced the amount of PAH extracted onto the fibers. A significant reduction in C_{fiber} was observed when using DT-nd-SPME as compared to nd-SPME (Fig. S3, Supplementary Data). However, these data were generated in initial studies using 15-cm DTs rather than the 3-cm DTs used in the rest of the study. Therefore, the influence of DT protection on pyrene extraction was further investigated using 3-cm DTs. Again, a large decrease in C_{fiber} was observed with DT-nd-SPME compared to nd-SPME (Fig. 2a). Furthermore, the C_{free} determined from DT-nd-SPME by LLE after 5 days of extraction showed a significant reduction in pyrene C_{free} (> 70%) compared to nd-SPME (Fig. 2b). The decrease in pyrene C_{free} occurred at both

the C_{nominal} values tested (1 and 100 $\mu\text{g/L}$) and is attributed to sorption onto the DT. Pyrene sorption to the DT appeared to be concentration dependent and did not result in a complete depletion of the solution, indicating an equilibrium was established between C_{free} pyrene and DT-sorbed pyrene. Sorption of PAHs to the DT could theoretically be reduced by significantly decreasing the amount of DT used and/or by increasing the water sample volume. However, reduction in DT length is not feasible unless other sealing techniques are identified, and increasing water volume presents challenges regarding sample throughput and waste volumes. The degree of adsorption to the DT is also likely to be highly dependent on the specific PAH being studied. The high sorption of PAHs to the DT will affect the overall partitioning equilibrium in the system, possibly leading to a desorption of CNT-bound PAHs as C_{free} is reduced and a new equilibrium becomes established.

Separation of CNTs from the water phase

A complete removal of dispersed CNTs from the water phase is necessary to achieve an accurate determination of

Fig. 2 **a** Concentration of pyrene on PDMS-coated fiber with and without DT protection at C_{nominal} 100 $\mu\text{g/L}$. Error bars represent standard deviation of replicate samples ($n = 3$). **b** Pyrene concentration in the water determined by LLE after extraction with nd-SPME or DT-nd-SPME. Error bars show standard deviation for replicate samples with DT protection ($n = 2$). A significant reduction in the C_{fiber} (**a**) and C_{free} (**b**) was seen when using DT-nd-SPME compared to nd-SPME

phenanthrene C_{free} in the water phase and a subsequent calculation of C_{CNT} through mass balance. Therefore, the separation efficiency of ultracentrifugation and filtration was investigated in the current study using the suite of CNTs.

Ultracentrifugation Absorbance measurements of the CNT dispersion supernatant after ultracentrifugation are presented in Fig. S8 in the Supplementary Data. Ultracentrifugation showed good removal of four of the five CNTs from the water phase. No absorbance was detected for the non-functionalized CNTs, while an absorbance of 0.004, slightly above LOD, indicated that low concentrations of MWCNT-OH remained after the procedure. In contrast, the supernatant remaining after ultracentrifugation of MWCNT-COOH exhibited a relatively high absorbance (0.017), which was well above the LOQ. Approximately 10% of the initial MWCNT-COOH concentration remained in the supernatant after ultracentrifugation, showing that MWCNT-COOH could not be efficiently removed by ultracentrifugation. In previous studies, standard centrifugation (1500–3000×g) has been employed to sediment dispersed CNTs (Linard et al. 2015; Su et al. 2013). The CNTs used in these studies were, however, non-functionalized. In the current study, even ultracentrifugation could not successfully separate dispersions of –COOH functionalized CNTs, indicating the efficiency of (ultra)centrifugation is highly dependent on CNT physicochemical properties. Furthermore, the dispersion technique employed (i.e., sonication) and the presence of dispersants (e.g., NOM) are likely to influence CNT dispersion state and their sedimentation efficiency (Cerrillo et al. 2015).

Ideally, any centrifugation method employed should offer a consistent level of separation efficiency, irrespective of CNT properties. At the very least, studies employing (ultra)centrifugation for the removal of dispersed CNTs from an aqueous phase should verify the method for its applicability for a broad range of CNT types and for the specific dispersion and media conditions employed in the study. However, centrifugation techniques do offer some advantages over nd-SPME and filtration by being independent of the target HOC analyte. While the suitability of both nd-SPME and filtration needs to be evaluated for individual analytes, centrifugation is suitable for all HOCs. Ultracentrifugation was not considered a suitable separation technique for the CNT suite tested in the current study owing to the incomplete separation observed for the functionalized MWCNTs. An improved removal of CNTs may be achieved by increasing the ionic strength of the solution immediately prior to ultracentrifugation. Increased ionic strength promotes agglomeration of CNTs (Petersen et al. 2016; Yang et al. 2011), which could aid in their sedimentation during ultracentrifugation. However, change in ionic strength and agglomeration state may result in PAH desorption and should therefore be evaluated further.

Filtration The absorbance measured in the filtrate, after filtration of CNT dispersions through a range of different filter types, is presented in Fig. 3. The sorption of phenanthrene to the filters is presented in Fig. 4. Filtration has been used to study diuron adsorption to dispersed CNTs (Schwab et al. 2014) and phenanthrene adsorption to C_{60} agglomerates (Baun et al. 2008). To our knowledge, this is the first study that systematically evaluates the efficiency of a range of filters for removing dispersed CNTs and tests their adsorption towards a model compound. No absorbance was measured in blank samples (no CNTs present) after filtration with any of the filters, showing that the filtration step itself did not contribute to any measured absorbance. The efficiency of filters to retain CNTs clearly depended on both CNT type and filter type (Fig. 3). All filter types could effectively remove the SWCNTs, while the two non-functionalized MWCNTs could be removed effectively except by the glass fiber filters. The two functionalized MWCNTs, in particular MWCNT-COOH, were more difficult to remove by filtration, with high absorbance measured for four (MCE, PVDF, GF/F, and GF-75) out of the six filters tested. Assessment of all CNT and filter combinations indicated that only two filters, PC and PTFE, could adequately retain all five CNT types. No absorbance could be detected for any CNT after filtration by PC, and MWCNT-COOH exhibited only a slight absorbance (0.005) when the PTFE filters were used. In a previous adsorption study, PTFE filters with a pore size of 0.45 μm were used for the separation of dispersed CNTs (Schwab et al. 2014) and the current study suggests such filters can be appropriate for specific CNT types. SWCNTs were efficiently removed by GF filters with pore sizes up to 0.7 μm , but all of the MWCNTs had low retention capacities. This indicates that GF filters are suitable for studies addressing PAH adsorption to SWCNTs only. Similarly, PC, MCE, PVDF, and PTFE filter membranes, with pore sizes up to 0.2 μm , all proved to remove SWCNTs and non-functionalized MWCNTs efficiently from the water phase but not the functionalized MWCNTs. However, the results

Fig. 3 Absorbance measured at 800 nm in the filtrate of the CNT dispersions after filtration of five types of CNTs through various filters. Error bars represent the standard deviation of replicate samples using PTFE filters ($n = 3$). For all other filters, only single samples were prepared and analyzed ($n = 1$). Dotted lines show limit of detection (LOD) and limit of quantification (LOQ)

show only filters with a pore size of 0.1 μm were capable of effectively retaining all CNT types and therefore these filters have the broadest application.

To investigate if the detected amount of MWCNT-COOH after filtration with the PTFE filter could significantly affect the determination of C_{free} , the concentration of MWCNT-COOH at LOQ was calculated and the contribution of CNT-bound phenanthrene to C_{free} estimated using adsorption data for MWCNT-COOH calculated in our previous study (Glomstad et al. 2016). The MWCNT-COOH concentration at the LOQ corresponded to < 2% of the initial MWCNT-COOH concentration. The estimated contribution to C_{free} was < 4% over the phenanthrene concentration range of 6–800 $\mu\text{g/L}$. The contribution of phenanthrene adsorbed by MWCNT-COOH detected in the filtrate to the measured C_{free} is considered negligible, and both PC and PTFE are suitable for determination of C_{free} .

A number of factors could be contributing to the differences in filtration efficiency observed between CNT types. Although all CNT dispersions were prepared with identical nominal concentrations (10 mg/L), the dispersed concentrations determined after the 24-h settling period (i.e., the dispersibility) varied significantly due to the physicochemical properties of the different CNTs. The non-functionalized CNTs exhibit the greatest degree of agglomeration and settling (Petersen et al. 2016, 2011), leading to lower final dispersed concentrations. The propensity for a particular CNT to form agglomerates will aid in its retention on a filter, possibly explaining the observed high degree of retention for the non-functionalized CNTs. It is also possible that there are differences in the proportion of individually dispersed CNTs, with those forming small or loose agglomerates being trapped more efficiently during filtration. Again, increasing the ionic strength of the solution prior to filtration should promote CNT agglomeration and may result in improved retention (Yang et al. 2011).

The difference in dispersed concentration was also considered as a possible factor influencing filtration efficiency. SWCNT was present in the lowest concentration (0.7 mg/L), yet was most easily removed by filtration. In contrast, MWCNT-COOH was present in the highest concentration (6.0 mg/L) and proved the most difficult to remove from the aqueous phase (Fig. 3). To investigate if the concentration of dispersed CNTs affected the efficacy of the filtration, the influence of both dispersion dilution and the use of a secondary filtration of the filtrate was performed with MWCNT-COOH using selected filters that showed insufficient separation of this particle, MCE, PVDF, and GF-75 (Fig. S9, Supplementary Data). Neither dilution nor secondary filtration resulted in a satisfactory increase in CNT retention. This indicates initial CNT concentration does not significantly influence filtration efficiency and is consistent with the findings of a previous study (Yang et al. 2011).

The CNT dispersion method can have a significant impact on the final dispersion properties and aggressive dispersion techniques can damage the CNTs (Cerrillo et al. 2015; Hennrich et al. 2007; Stegen 2014). Although SEM images of the pristine CNTs showed they all exhibited lengths significantly above 1 μm (Fig. S10), suggesting the potential for high retention on filters with pore sizes in the range 0.1–0.2 μm , this is not consistent with results in the current study. However, a detailed assessment of the mean CNT lengths was not conducted in the current study. The use of a low-energy bath sonicator (as opposed to high-energy probe sonication) should ensure the formation of CNT fragments is minimized, consistent with previous studies into CNT damage and breakage (Cerrillo et al. 2015; Hennrich et al. 2007; Stegen 2014). While it is also possible that other carbonaceous fragments could be present in some of the samples, the common CNT synthesis method suggests significant differences between the different CNT types are unlikely. It is suggested that differences in CNT retention are predominantly driven by their surface chemistry and its role in dispersibility.

In addition to effectively retaining the CNTs, filters must also have a low sorption potential for the target analytes. The current study investigated the sorption of phenanthrene, as a model PAH, to the filters. A low phenanthrene recovery (< 30%) was observed for three of the filters (PC, MCE, PVDF; Fig. 4), indicating they have high adsorption affinities for phenanthrene. Nearly 100% adsorption of phenanthrene was observed for the MCE filter. This is somewhat surprising as cellulose ester membrane filters have previously been used to assess phenanthrene adsorption to suspended agglomerates of C_{60} (Baun et al. 2008). The reason for the contrasting results observed is unknown but shows that testing of selected filters is important to avoid erroneous measurements. A high

Fig. 4 Sorption of phenanthrene by various filters. A high sorption by the filters would impede further analysis of the filtrate to determine C_{free} . Error bars represent the standard deviation of triplicate samples for the PTFE filters ($n = 3$) and of duplicate samples for all other filter types ($n = 2$)

recovery was seen for the glass fiber filters (> 93%) and the PTFE filter membrane (~ 80%).

Although the PC filter retained all CNT types well, the high sorption of phenanthrene made this filter unsuitable for subsequent determination of phenanthrene C_{free} . The two glass fiber filters exhibited the lowest degree of adsorption but could not efficiently retain CNTs owing to their large pore sizes (0.3 and 0.7 μm , respectively). Considering the two criteria for selecting an appropriate filter, CNT retention and low phenanthrene adsorption, the PTFE filter membrane exhibited the best overall performance. To investigate the suitability of the PTFE filter further, phenanthrene recovery was tested at concentrations ranging from 70 to 735 $\mu\text{g/L}$ (Fig. 5). The filtration method showed very high precision regarding recovery values, with a coefficient of variation (CV) of < 2.3% for the six replicates tested at each concentration. Furthermore, the recovery ($82.5 \pm 1.5\%$) was very similar over the concentration range tested. A recovery of > 80% is considered to be acceptable, especially considering the high precision of the method. However, adsorption to the filter may vary for different PAHs, with increased adsorption likely for larger, more hydrophobic PAHs (e.g., pyrene) despite the hydrophilic nature of the filter. A lower recovery could still be acceptable provided that the PAH loss can be adequately corrected for, either through a predictable loss in the filtration step as observed in the current study or by the use of internal standards. Importantly, the method should be verified when applied to new target analytes, with the most appropriate filter being selected optimized on a case-by-case basis.

Filtration using 0.1- μm hydrophilic PTFE membrane proved to be a simple, time- and cost-efficient method for separating a range of CNTs from the water phase prior to determination of phenanthrene C_{free} . Subsequent to validation, the method has been successfully applied to investigate phenanthrene adsorption to dispersed CNTs (Glomstad et al.

Fig. 5 Percentage of phenanthrene sorbed to PTFE filter membrane at different phenanthrene C_{nominal} . Error bars represent the standard deviation of replicate samples ($n = 6$). The percentage of phenanthrene sorbed was highly reproducible over the range of C_{nominal} tested

2016; Zindler et al. 2016). Adsorption isotherms were established and fitted to the Dubinin-Ashtakhov model that has previously been used in several other studies to describe PAH adsorption to CNTs (Kah et al. 2014; Yang et al. 2006a; Yang and Xing 2010). The determined adsorption capacity was somewhat higher than that observed in other studies using agglomerated or partly agglomerated CNTs (Kah et al. 2011; Yang et al. 2006a) but was consistent with previous studies reporting higher adsorption capacities of PAHs for dispersed CNTs (Zhang et al. 2012). As the method was applicable to a range of CNTs, the study could evaluate the influence of CNT physicochemical properties on phenanthrene adsorption and subsequently the effect on bioavailability and toxicity to the freshwater algae *Pseudokirchneriella subcapitata* (Glomstad et al. 2016) and *D. magna* (Zindler et al. 2016).

Conclusions

The current study shows that PAH adsorption to dispersed CNTs, using phenanthrene as a model compound, can be accurately determined using simple filtration methods. A 0.1- μm hydrophilic PTFE filter membrane efficiently separated a suite of dispersed CNTs with a range of physicochemical properties from the water phase without significantly retaining the dissolved phenanthrene. The resulting aqueous samples contained negligible quantities of CNTs allowing for accurate determination of phenanthrene C_{free} values. Ultracentrifugation was unable to fully sediment all of the studied CNT types from the water phase, limiting its use as a broadly applicable approach for CNT-PAH adsorption studies. The nd-SPME and DT-nd-SPME approaches evaluated highlighted significant problems with the adherence of CNTs to the PDMS-coated fibers and sorption of PAHs to the dialysis tubing, which negatively influence the determination of accurate C_{CNT} values. In addition, filtration offers a time and cost benefit to the other methods evaluated, especially the nd-SPME techniques. Filtration also has potential for investigating the adsorption of other HOCs, as a wide range of filter materials is available. However, careful selection of filters based on their composition and pore size is necessary to achieve efficient separation of CNTs from the water phase while minimizing PAH/HOC sorption to the filter. As sorption to the filter can vary for different target analytes, it is necessary to validate all filters for their suitability prior to use in adsorption studies.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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