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Emerging investigator series: Development and Application of Polymeric Electrospun Nanofiber Mats as Equilibrium-Passive Sampler Media for Organic Compounds[†]

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Abstract

We fabricated a suite of polymeric electrospun nanofiber mats (ENMs) and investigated their performance as next-generation passive sampler media for environmental monitoring of organic compounds. Electrospinning of common polymers [e.g., polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), and polystyrene (PS), among others] yielded ENMs with reproducible control of nanofiber diameters (from 70 to 340 nm). ENM performance was investigated initially with model hydrophilic (aniline and nitrobenzene) and hydrophobic (selected PCB congeners and dioxin) compounds, generally revealing fast chemical uptake into all ENMs that was well described by a one compartment, first-order kinetic model. Typical times to reach 90% of equilibrium ($t_{90\%}$) were ~7 days under mixing conditions for all ENMs, and < 0.5 days for the best performing materials under static (i.e., no mixing) conditions. Collectively, these short equilibrium timescales suggest that ENMs may be used in the field as an equilibrium-passive sampler, at least for our model compounds. Equilibrium partitioning coefficients (K_{ENM-W} ; L kg⁻¹) averaged 2 and 4.7 log units for the hydrophilic and hydrophobic analytes, respectively. PAN, PMMA and PS were prioritized for additional studies because they exhibited not only the greatest capacity for simultaneous uptake of the entire model suite (log K_{ENM-W} ~ 1.5 – 6.2), but also fast uptake. For these optimized ENMs, rates uptake into PAN and PMMA were limited by aqueous phase diffusion to the nanofiber surface, and the rate-determine step for PS was analyte specific. Sorption isotherms also revealed that the environmental application of these optimized ENMs would occur within the linear uptake regime. We examined ENM performance for the measurement of pore water concentrations from spiked soil and freshwater sediments. Soil and sediment studies not only yielded reproducible pore water concentrations and comparable values to other passive sampler materials, but also provided practical insights into ENM stability and fouling in such systems. Further, fast uptake for a suite of structurally diverse hydrophilic and moderately hydrophobic compounds were obtained for PAN and PS, with $t_{90\%}$ ranging from 0.01 to 4 days with mixing and K_{ENM-W} values ranging from 1.3 to 3.2 log units. Our findings show

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promise for the development and use of ENMs as equilibrium-passive samplers for a range of organic pollutants across soil/sediment and water systems.

Keywords

Electrospinning; electrospun nanofiber mat (ENM); equilibrium-passive sampler; hydrophilic; moderately hydrophobic; hydrophobic; HPLC; GC/MS/MS

INTRODUCTION

Accurately measuring the abundance of organic chemical pollutants in contaminated water and sediment systems is critical for effective management and risk assessment. However, these measurements are complicated by the diverse physicochemical properties of both legacy and emerging pollutant classes, as well as variables arising from system complexity (e.g., low target concentrations, sorption to dissolved organic matter, and pollutant ionization). For this purpose, the use of passive sampling devices has increased remarkably over the last decade, particularly for the determination of the freely dissolved sediment pore water and surface water concentrations of hydrophobic contaminants.^{1–5}

To date, relatively less attention has been focused on passive samplers for hydrophilic and moderately hydrophobic contaminants.^{5–11} Alvarez *et al.*⁷ were among the first to develop and field deploy passive samplers operating in the linear uptake stage for measurement of polar compounds in surface water (the so-called Polar Organic Chemical Integrative Samplers, or POCIS). They focused on organic compounds with logarithmic octanol-water partitioning coefficients (i.e., log K_{OW} values) less than 4, with field results for two herbicides and a naturally occurring hormone yielding good agreement with conventional sampling and measurement methods. MacLeod *et al.* performed one of the first POCIS laboratory calibration for 25 pharmaceuticals and personal care products (PPCPs), which also included field deployment,¹² concluding that POCIS can be used as a quantitative tool for measuring PPCPs in water systems. Harman *et al.*¹³ and Mori *et al.*¹⁴ reviewed and summarized calibration methods and sampling rates for more than 100 hydrophilic analytes using POCIS. Both studies agreed that even though POCIS is a useful device to measure hydrophilic and moderately hydrophobic compounds in aquatic systems, there remains a lack of standardization for calibration methods, and that the use of laboratory sampling rates in field measurements can increase uncertainty when environmental time-weighted average (TWA) concentrations are calculated.

A passive sampler characterized by rapid uptake that operates in an equilibrium partitioning regime could reduce such uncertainties. Equilibrium-passive samplers hold the promise of higher precision and accuracy for field measurements because their calculations of field concentrations only depend on equilibrium partition coefficients, which can be readily measured in the laboratory. Equilibrium partitioning eliminates the need for spiking performance reference compounds, which are needed to account for sampling rates during field deployment of kinetic passive samplers. Further, shorter sampling times is highly desirable for capturing spatial and temporal variability in dynamic pollutant systems. To the best of our knowledge, only three equilibrium-passive sampler materials consisting of plastic

films have been developed to date for measurement of hydrophilic and moderately hydrophobic analytes.^{8, 9, 15} Although the uptake capacity for these materials may be lower than, for example, POCIS, their ability to achieve equilibrium over a short sampling period, even under static conditions, represents an important advance for passive environmental sampling techniques.

Here, we aim to develop a new, nanomaterial-enabled platform for equilibrium-passive sampling devices. Our approach uses electrospinning, a nanofiber fabrication method that offers superior control over the material properties exhibited by the resulting electrospun nanofiber mats (or ENM).^{16, 17} Accordingly, we investigated how the physical and chemical properties of various polymeric ENMs influence their performance as passive sampling materials toward a suite of hydrophilic (i.e., $\log K_{OW} < 2$), moderately hydrophobic (i.e., $\log K_{OW}$ ranging from 2 to 4.5), and hydrophobic (i.e., $\log K_{OW} > 4.5$) compounds. We anticipated that the high surface-area-to-volume ratio (S/V) of the nanofiber mats would promote faster uptake of target organic compounds into the ENM.^{17, 18} As has been reported for hydrophobic compounds, the size and geometry of the sampler device, often described by its S/V ratio, play an important role for uptake rates. Specifically, increasing the S/V ratio corresponds to a faster sampling device.^{18, 19} For our ENMs, this S/V ratio is inversely proportional to the nanofiber radius (i.e., $S/V = 2/r$), which we propose represents a critical design parameter for tuning and optimizing ENM performance.

To test this hypothesis, we fabricated seven ENMs from different polymers and tested their sorption performance against a suite of eight hydrophilic, four moderately hydrophobic, and ten hydrophobic compounds. Scanning electron microscopy, water contact angle and specific surface area measurements were used to characterize the fabricated ENMs. Initially, ENM performance experiments focused on aniline and nitrobenzene as model hydrophilic compounds and selected PCB congeners and dioxin as model hydrophobic compounds. Optimal ENMs from initial studies were then tested across a broader range of conditions (e.g., pH, target concentration, nanofiber diameter and in soil and sediment systems) and against a larger suite of hydrophilic and moderately hydrophobic compounds.

MATERIAL AND METHODS

ENM fabrication

We synthesized seven ENMs from ethylene-vinyl acetate (EVA); polyacrylonitrile (PAN); polyethylene terephthalate (PET); polymethyl methacrylate (PMMA); polystyrene (PS); polyvinyl acetate (PVAc); and polyvinylidene fluoride (PVDF). These polymers were selected due to their different chemical functionalities, providing materials across the spectrum from hydrophobic (e.g., PS and PVDF) to hydrophilic (e.g., PAN and PMMA) (Table S1). All ENMs were fabricated using a custom-built electrospinning apparatus described in our previous work (Figure S1).²⁰ Additional details of the polymers, the electrospinning apparatus and synthesis parameters are presented in the Electronic Supplementary Information (ESI).

ENM Characterization

ENMs were characterized via scanning electron microscopy (SEM) to measure nanofiber diameters. ENM wettability, which is a measure of their surface hydrophobicity/hydrophilicity, was examined through water contact angle measurements using a Micromeritics ASAP 2020 goniometer. The specific surface area of ENMs was determined via N₂-BET adsorption isotherm measurements. The mechanical strength and stability of ENMs in organic solvents commonly used in chemical extractions was also explored. Details on all ENM characterization equipment and methods can be found in the ESI.

Target Analyte Suite

The target hydrophilic (n=8) and moderately hydrophobic (n=4) compounds were aniline, anisole, atrazine, caffeine, benzylamine, diuron, 17 β -estradiol, nitrobenzene, phenol, p-nitrophenol, trinitrotoluene (TNT) and 1, 3, 5-trinitroperhydro-1, 3, 5-triazine (RDX). Our suite of ten hydrophobic compounds consisted of PCB1, PCB11, PCB29, PCB47, PCB121, PCB136, PCB187, PCB206, PCB209 and 2,3,7,8-tetrachlorodibenzodioxin (dioxin) (Table S2). Details on stock solutions preparation and levels are presented in the ESI.

Sorption and Uptake Experiments

Protocols for time-dependent uptake experiments were adapted from previous passive sampler development studies.^{21, 22} Initial experiments with the entire suite of ENMs were performed with aniline and nitrobenzene (model hydrophilic chemicals), as well as the entire collection of PCB congeners and dioxin (model hydrophobic chemicals) in aqueous solutions. Partition coefficients (K_{ENM-W} , L kg⁻¹) between the concentration of the chemical of interest in the ENM and the aqueous phase were used to evaluate ENM performance, as shown in eq. 1

$$K_{ENM-W} = \frac{C_{ENM}}{C_W} \quad (\text{eq. 1})$$

where C_{ENM} and C_W are the experimentally measured concentrations of the chemical in the ENM and aqueous phase, respectively. Analytical details of the measurements are provided in the ESI.

Uptake experiments were also conducted in systems containing a model soil amended with nitrobenzene (initial concentration ~10 mg L⁻¹). Experiments used a sandy loam marketed as “LBLS” (Northwood, ND and Benson, MN), which contained an organic carbon fraction of 3%.²³ Wet soil (30 g) was combined with ~0.05 g of ENM in a clean amber glass vial. Vials were tumbled end-over-end, and samples were collected after 5, 10, 15, 20 and 25 days.

As a final performance test, sediment pore water measurements of PCB contaminated sediments from the Indiana Harbor and Ship Canal (IHSC) (East Chicago, IN) were conducted. We have previously reported their PCB sediment pore water concentrations (on the order of ng L⁻¹) using PDMS fiber.⁴ Around 0.1 g of ENM was placed in a clean, amber

glass bottle (250 mL) with sediment and deionized water (~100 g), and gently shaken (80 rpm and ~25°C) for 28 days. Additional details on uptake experiments are described in the ESI.

Uptake Modeling

Analyte uptake and accumulation into the ENM was modeled using a one compartment, first-order kinetic model: ^{9, 18}

$$C_{ENW} = \frac{k_1}{k_2} \times C_w \times (1 - \exp(-k_2 \times t)) \quad (\text{eq. 2})$$

where C_{ENM} and C_w are the concentrations of the analyte in the ENM and in the water as function of time (mg L^{-1}), respectively; k_1 and k_2 are the uptake and elimination rate constants (h^{-1}), respectively; and t is time (h). Time-series of C_{ENM} and C_w data were input into eq. 2, and a non-linear least squares analysis (performed in Excel using the embedded Solver tool) was used to solve for k_1 and k_2 . Further, K_{ENM-W} can be calculated from the ratio of k_1 and k_2 , while the time required to reach 90% of equilibrium can be estimated via eq. 3. Estimation of the uncertainty of the calculated parameters was performed by the “jackknife” method.²⁴

$$t_{90\%} = \frac{\ln 10}{k_2} \quad (\text{eq. 3})$$

Analytical Methods and QA/QC

Extraction, clean up and quantification procedures for the target compounds in the aqueous and sorbent phases followed previously published methods from our group and others,^{4, 25, 26} with details presented in the ESI. Aqueous phase samples (C_w) and methanol extracted from ENM samples (C_{ENM}) were analyzed by high performance liquid chromatography with diode array detector (LC/DAD, Agilent 1100 Series HPLC) for the hydrophilic and moderately hydrophobic compounds. PCBs and dioxin aqueous phase (C_w) and hexane extracted from ENM samples (C_{ENM}) were measured using gas chromatography with tandem mass spectrometry (GC-MS/MS, Agilent 7000) in multiple reaction monitoring mode. QA/QC consisting of laboratory blanks, replicates, recoveries and surrogate recoveries, is presented in detail in the ESI.

RESULTS AND DISCUSSION

Synthesis and Characterization of ENMs

ENMs of PAN, PET, PMMA, PS and PVDF met criteria that made them most promising for application in passive sampling. These materials could be reproducibly fabricated using electrospinning, and they also showed no signs of degradation or dissolution in water across a range of pH values (from 2–12) and in various organic solvents commonly used for extraction (e.g., methanol and acetonitrile). We note that while PVAc could be fabricated by

electrospinning, it dissolved readily in methanol, and numerous attempts and approaches to fabricate EVA-ENM via electrospinning were unsuccessful. Thus these two ENMs were not further investigated.

Figure 1 shows SEM images of the five viable ENMs. All consisted of well-defined nanofibers with average diameters ranging from ~70 to 350 nm. Nanofiber diameters were relatively uniform and without beading, as evidenced by the small standard deviation associated with measured size distributions (Table 1). Further, all recipes resulted in good batch-to-batch reproducibility. For PS, for example, three replicate batches fabricated over several months produced average diameters of 150 ± 40 , 140 ± 20 and 140 ± 30 nm (Figure S2). Generally, ENMs exhibited modest N_2 -BET specific surface areas typically in the range of $5 - 30 \text{ m}^2 \text{ g}^{-1}$ (Table 1).

Measured water contact angles mostly matched expectations of polymer hydrophilicity and hydrophobicity from characteristics of their monomeric unit (Table S1). Hydrophobic ENMs (water contact angles $> 90^\circ$) were PVDF $>$ PMMA $>$ PET $>$ PS, while PAN was hydrophilic (water contact angle $< 90^\circ$). The exception was PMMA; although it contains a presumed hydrophilic carboxylate ester functional group,²⁷ the measured water contact angle of 120° suggests our PMMA-ENM behaves more as a hydrophobic material.

Simple mechanical testing indicated that all the ENMs were able to support a reasonable load, and they could be twisted and stretched without significant deformation (Figure S3). Thus, all ENMs are sufficiently robust and durable such that application in the field as a passive sampler media and subsequent handling in the laboratory during sample processing should not be prohibitive.

Trends in ENM Performance with Model Compounds

Aniline and nitrobenzene—With mixing, both model hydrophilic chemicals exhibited very fast uptake to all ENMs, shown by the minimum change in experimentally measured partition coefficients after 0.4 d (Figure 2). Thus, equilibrium partition coefficients were calculated from the average data collected from 2 to 5 days. Average K_{ENM-W} values ranged from 0.7 to 2.8 log units (L kg^{-1}), although the extent of sorption varied depending on both the ENM and the model compound target (Table S3). For example, values of K_{ENM-W} were typically ~1 log unit higher for nitrobenzene than aniline, but both compounds exhibited similar K_{ENM-W} values on PAN. We note that no inhibitory or competitive effects were observed when experiments were conducted with analyte mixtures relative to individual analyte experiments.

For aniline, the overall trend in partitioning was as follows: PAN $>$ PMMA $\approx$ PET $>$ PS $\gg$ PVDF, spanning a range of 1-log unit from the ENM with the most to least uptake capacity. Although the five ENMs exhibit different chemical properties (Table S1), aniline uptake was generally greatest on the hydrophilic ENMs (Table 1). For example, although measured water contact angles for our ENMs clustered into two groups as either hydrophilic ($40\text{--}60^\circ$) or hydrophobic ($100\text{--}140^\circ$), we observed a clear negative correlation ($p = 0.003$) between $\log K_{ENM-W}$ values and increasing water contact angles (i.e., hydrophobic surfaces; see

Figure S4). Conversely, no significant correlation was observed between the $\log K_{ENM-W}$ and ENM specific surface area from BET ($p = 0.1$).

Nitrobenzene yielded a different trend in uptake, PMMA ~ PS > PET > PAN ~ PVDF, although a similar range of 1-log unit was observed across measured partitioning coefficients. Based upon measured water contact angles, nitrobenzene uptake was greatest on moderately hydrophobic polymers (Table 1, Table S1), whereas the most hydrophilic (PAN) and most hydrophobic (PVDF) ENMs performed poorly. Unlike aniline, therefore, no significant correlation ($p = 0.25$) was found between $\log K_{ENM-W}$ values and water contact angles for nitrobenzene (Figure S4). As with aniline, no correlation was obtained between the $\log K_{ENM-W}$ and ENM specific surface area ($p = 0.6$).

For comparison, we also measured partition coefficients for aniline and nitrobenzene using conventional, commercially available passive sampling materials under the same experimental conditions. These included polystyrene beads, PDMS fiber and a low-density polyethylene (LDPE) film, many of which have been used in research and development of passive sampling materials, albeit mostly for hydrophobic compounds.^{4, 5, 28} Results showed that no uptake on LDPE was observed for either analyte, while PS beads and PDMS fibers produced aniline K_{ENM-W} values that were at least 75% smaller than those measured for the best ENMs (Figure S5). Uptake of nitrobenzene was not measurable over our standard experimental timescale for any of the commercial materials, further highlighting the dearth of passive sampling materials currently available for some polar analytes outside of POCIS.

PCBs and Dioxin—Because PVDF performed most poorly toward aniline and nitrobenzene and our goal was to identify materials suitable for passive samplers targeting chemicals with a broad range of $\log K_{OW}$ values, PVDF was not considered in studies with PCBs and dioxin. Once again, the remaining four ENMs exhibited relatively fast equilibration times (< 0.5 d) for both selected PCB congeners and dioxin under mixing conditions in the laboratory (Figure S6). Average K_{ENM-W} values from samples collected at 0.5 and 1 day ranged from 3.2 to 6.4 log units ($L\ kg^{-1}$) across the ENMs (Figure 3, Table S4), which are comparable to estimated partition coefficients previously reported for commercially available passive sampler materials (e.g., POM film, PDMS glass fiber and LDPE film).^{1, 29}

Unexpectedly, we observed a decrease in the K_{ENM-W} on all ENMs for highly chlorinated congeners (e.g., see results for PCBs 187, 206 and 209 in Figure 3). Others have also observed this phenomenon and several explanations have been proffered. These include insufficient time for the system to achieve equilibrium between phases, differences in the extraction processes and thickness of the sampling materials,^{30, 31} and physicochemical properties of materials and analytes,⁹ while still others did not provide an explanation.³² We speculate that the reduction in partition coefficients for these congeners may be due to these highly hydrophobic congeners not completely dissolving into aqueous solution, such that our reported K_{ENM-W} values may not actually reflect the extent of their partitioning into ENMs. Thus, these PCB congeners were removed from further analysis.

Generally, the overall trend in partitioning for PCBs and dioxin was as follows: PMMA $\approx$ PS > PET > PAN (Figure 3, Table S4). PAN yielded the lowest equilibrium partition coefficients, as might be expected for the uptake of strongly hydrophobic targets on a hydrophilic substrate (Table 1). Conversely, more hydrophobic PMMA (water contact angle $\approx 120^\circ$) yielded the highest equilibrium partition coefficients. A significant correlation was found between the equilibrium partition coefficients and the water contact angle for PCB congeners 1 to 121 ($p < 0.05$), but no significant correlation was found for PCB136 nor dioxin ($p > 0.05$) (Figure S7). Further, no significant relationship existed between $\log K_{ENM-W}$ values and ENM surface area. For PCB congeners 1 to 136 and dioxin, positive correlations between $\log K_{ENM-W}$ and $\log K_{OW}$ ($p < 0.05$) were observed for each ENM (Figure S8). Thus, ENM hydrophobicity (as water contact angle) and/or compound K_{OW} values generally predict ENM performance toward PCBs and dioxin.

Modeling Uptake Rates and Timescales for Model Compounds into ENMs

Because of rapid PCB and dioxin uptake (i.e., equilibrium was generally achieved during the first two sampling periods), we elected to focus our efforts to model analyte uptake to our polar model compounds, nitrobenzene and aniline. Time-dependent experimental C_w and C_{ENM} data, and resulting equilibrium partition coefficients, were well-described by the one compartment, first-order kinetic model (eq. 2; see Figure S9), as others have also observed for passive sampler materials.^{9, 18, 33} Accordingly, using model outputs for k_2 we calculated $t_{90\%}$ values for the 5 ENMs, with estimates ranging from 0.01 ± 0.01 to 7.3 ± 1.2 days for aniline and nitrobenzene under mixing conditions in the laboratory (Table S3).

The longer time to achieve equilibrium for PMMA ($t_{90\%} = 1.2 \pm 0.06$ and 7.3 ± 1.2 days for nitrobenzene and aniline, respectively) is likely related to its larger diameter compared to other ENMs such as PAN and PS (Table 1). Indeed, we observed a positive correlation ($p < 0.025$) between $t_{90\%}$ and nanofiber diameter for both aniline and nitrobenzene across the suite of ENMs investigated (Figure 4). Such a relationship implies that thinner nanofibers can produce faster uptake rates and in turn will require less time to reach equilibrium in the field, consistent with conventional wisdom that a higher S/V (or in this case 2/r) ratio corresponds to a faster sampling device.^{18, 19, 34} Notably, there was no relationship between $t_{90\%}$ and K_{ENM-W} , suggesting that faster uptake rates do not negatively impact ENM sorption capacity.

Additional uptake experiments were conducted using PAN, PMMA and PS without mixing (i.e., static conditions). These systems, intended to mimic passive sampling conditions in the field, resulted in nearly equivalent K_{ENM-W} values when compared to results from well-mixed systems, and time-dependent uptake once again followed the one compartment, first-order model (eq. 2, Table S3). Because no change in the sorption capacity was observed between mixing and static conditions, we conclude that changes in the uptake kinetics do not affect ENM sorption capacity (Table S3).

Changes in $t_{90\%}$ values between mixed and unmixed systems lend insight into the rate-determine steps in analyte sorption on ENMs. For example, PAN and PMMA exhibited longer equilibrium times in unmixed relative to mixed systems (Table S3), presumably due to their larger nanofiber diameters or smaller S/V ratios. (Figure 4). This increase is

consistent with diffusion across the aqueous boundary layer being rate-limiting in analyte uptake. In contrast, PS produced a mixed result, where uptake rates of aniline were the same with and without mixing, while $t_{90\%}$ values for nitrobenzene increased three-fold in static relative to well-mixed systems (Table S3). Thus, rate controls for PS appear analyte dependent. We note that water boundary rate-limiting uptake into LDPE strips has been reported for hydrophobic compounds ($\log K_{OW} > 4.5$) under low flow conditions.^{35–37}

Influence of Nanofiber Diameter on ENM Performance—To further evaluate the effect of nanofiber diameter on uptake rates, we fabricated two larger diameter variations of PS ENMs (with average diameters of 300 and 560 nm) and compared their performance toward nitrobenzene under static conditions with that of our standard 140 nm diameter PS ENM (Figure 5). Measured K_{ENM-W} values were invariant across all nanofiber diameters (Table S5). Although we cannot directly compare our ENM with plastic sheets as passive sampler materials, this independence of equilibrium partition coefficient with respect to material thickness has also been demonstrated for LDPE.³⁸

A decrease in uptake kinetics was observed with increasing nanofiber diameter. Utilizing eqs. 2 and 3, values of $t_{90\%}$ increased from 0.03 ± 0.01 to 0.5 ± 0.07 days with an increase in diameter from 140 to 560 nm. Recall, for 140 nm nanofibers, $t_{90\%}$ values were equivalent in mixed and unmixed systems. For PS ENMs, therefore, these diameter-dependent uptake data may suggest a shift in the rate determining step from solid-phase to aqueous-phase diffusion above some critical nanofiber diameter. Nevertheless, this behavior is consistent with the established relationship between the uptake rate and the surface area-to-volume (S/V) ratio of the sampling device,¹⁹ where a high S/V ratio results in a faster diffusive exchange between both phases.¹⁸

Collectively, these results illustrate the promise of electrospinning for tailoring the fabrication of a sampling device with short equilibration times without diminishing overall (per unit mass) sorption capacity, as the same K_{ENM-W} values were obtained for all PS nanofiber diameters explored (Figure 5). Moreover, these relative short equilibration times, even for the static experiments, strongly suggest that our ENMs can be deployed as equilibrium-passive samplers in the field and over timescales considerably shorter than the 20 to 40 day sampling periods typically utilized for water and sediment pore water passive samplers.

Influence of System on the Performance of Optimal ENMs

From the experiments with model compounds, PAN, PMMA and PS were selected as the most promising material for further development as passive sampling materials. PMMA and PS yielded the highest K_{ENM-W} values toward our model compounds, on average 2.2 ± 0.7 log units (Table S3). PAN was also included, in part because it showed a slightly better performance toward aniline than the rest of the ENMs, but also due to how commonly it is used for electrospinning and its ease of fabrication.³⁹

Influence of pH on ENM Performance—We found that K_{ENM-W} were generally independent of pH for both aniline (i.e., anilinium cation) and nitrobenzene (Figure S10). We specifically tested the effect of pH on the sorption capacity on PMMA and PS because

preliminary sorption experiments indicated that both ENMs yielded, in general, the highest K_{ENM-W} values for these two compounds. While further work is merited, a slight pH dependence observed for aniline at low pH may reflect different modes of uptake on PMMA and PS. For example, PMMA exhibited more uptake at lower pH values, where a greater fraction of the aniline mass is positively charged (roughly ~20% of total aniline mass is positively charged at pH 5.5. $pK_a = 4.9$). Meanwhile, aniline uptake is essentially independent across pH on PS, but notably lower than on PMMA. We propose that the greater net uptake of aniline on PMMA, as well as the slight pH-dependence in partition coefficients in more acidic regimes, reflects a favorable role for electrostatic or specific binding interactions in uptake. In contrast, uptake of aniline on PS may be limited to only hydrophobic exclusion (presumably localized to the aromatic ring of aniline) and nonspecific interactions (e.g., van der Waals), the driving force for which would be independent of pH.

Sorption Isotherms to Establish ENM Capacity—Isotherm experiments using PAN, PMMA and PS with aniline and nitrobenzene assessed whether ENM application at environmentally relevant concentrations would be limited by their uptake capacity. Linear sorption isotherms were obtained for aniline and nitrobenzene on all ENMs (Figure S11), allowing ENM-water equilibrium partition coefficients to be calculated from linear regression analyses of the isotherm slope. This value was comparable to those calculated at each sampling point during aforementioned time-dependent uptake experiments (Table S3).

Isotherm results indicate that ENMs operate in a linear uptake regime, where K_{ENM-W} values are independent of the aqueous concentration, up to ~25 mg L⁻¹ (for our model compounds). This linear concentration range far exceeds concentrations likely to be encountered at contaminated sites where ENMs would be deployed. Thus, during field deployment, partitioning of polar targets should scale linearly with the dissolved concentration in surface or sediment pore water and not be subject to a saturation regime that would complicate accurate analysis of field concentrations. Moreover, this behavior suggests aniline and nitrobenzene uptake occurs primarily via absorption (i.e., bulk uptake into nanofibers rather than surface adsorption-limited). Indeed, we found no significant correlation ($p > 0.1$) between K_{ENM-W} values and ENM surface area (Figures S4 and S7), as might be expected for an adsorptive process.

Freely-Dissolved Pore Water Measurements in Soil and Sediment Systems

Pore water nitrobenzene concentrations in spiked soils using PMMA and PS are shown in Figure 6a. The pore water concentration was calculated using the mass of the chemical accumulated in the ENM (m_i), the mass of the ENM used in the experiment (m_{ENM}), and the K_{ENM-W} values measured in our aqueous-phase uptake experiments (Table S3) according to eq. 4.

$$C_{Pwi} = \frac{m_i}{m_{ENM}} \times K_{ENM-W} \quad (\text{eq. 4})$$

Both ENMs achieved rapid equilibrium with pore water nitrobenzene (~ 1 day), as we have previously demonstrated in aqueous systems. Effectively, PMMA and PS were equivalent in their performance, with equilibrium pore water concentrations ranging between 1.7 and 2.9 mg L⁻¹ for these samples. However, an important practical distinction is that PS was far more resistant to fouling from organic matter in these sterilized soil systems. After 5 d of mixing with soil, PS was considerably easier to clean of debris and wash than PMMA (Figure S12). For example, after a gentle mechanical cleaning with a paper towel and a light rinse with a small volume of DI water [for which loss of nitrobenzene was minimal (< 5%)], the PS was nearly the same color as when freshly synthesized. SEM images of the rinsed PS also revealed no residual soil particles or organic residues (Figure S12). In contrast, PMMA remained covered in soil and organic particles that were observable to the naked eye. More aggressive washing necessary to clean PMMA possibly led to loss of compounds in the wash water, which we believe contributed to the slightly greater relative standard deviation (RSD) of the pore water concentration for PMMA (~20%) relative to PS (~10%).

With anthropogenically impacted sediment from the IHSC, 28 d experiments with PMMA and PS revealed the occurrence of many individual PCB congeners based on detection with gas chromatography. However, here we report only the congeners for which we had already measured equilibrium partition coefficients (Table S4). Sediment pore water concentrations (from eq. 5) for our nine PCB congeners (PCB1, 11, 29, 47, 121, 136, 187, 206 and 209) ranged from 0.2 to 230 ng L⁻¹. It is most probable that the calculated concentrations of PCBs 187, 206 and 209 are overestimated due to our low equilibrium partition coefficients obtained for those three congeners. Both PMMA and PS performed similarly, with no significant difference observed between their measured sediment pore water concentrations (Figure 6b), although PS was once again easier to clean than PMMA. Further, these individual PCB concentrations are within the range and follow the same trend among congeners for published sediment pore water concentrations for the same IHSC sediment but using PDMS fiber (range from 0.4 to 60 ng L⁻¹).⁴ Further, PMMA and PS proved to be more sensitive than PDMS fiber; while it was possible to detect PCBs 206 and 209 on ENMs, these congeners were not amenable to analysis via PDMS fiber.

Uptake of Hydrophilic and Moderately Hydrophobic Compounds

As a final test of our ENMs, uptake experiments under mixing conditions with ten additional hydrophilic and moderately hydrophobic compounds on PAN and PS were performed. Concentration uptake curves (Figure S13) revealed fast uptake, as described before with our model compounds. In general, equilibrium partition coefficients were measured from samples collected after 1 day. Most $\log K_{ENM-W}$ values were similar to those measured for aniline and nitrobenzene, with an average of 2.0 ± 0.7 log units. Larger values (i.e., > 2.7 log units) were occasionally observed; this was the case for 17 β -estradiol on both PAN and PS, as well as for TNT and anisole on PS (Table 2, Figure S13).

Again, hydrophilic and moderately hydrophobic compound uptake into PAN and PS was well-described by the one compartment, first-order kinetic model. Calculated values of $t_{90\%}$ ranged from 0.01 ± 0.01 to 4.2 ± 0.3 days, consistent with PAN and PS exhibiting relatively short equilibration times with the suite of analytes tested. We note that uptake rates, and

consequently $t_{90\%}$ values, for some analytes depended on the ENM tested. For example, anisole uptake occurred 3-fold faster on PS than on PAN, whereas p-nitrophenol uptake was 30 times faster on PAN than PS. Interestingly, for these two analytes the ENM with the higher K_{ENM-W} value also exhibited the faster uptake rate, a scenario ideal for development of an equilibrium-passive sampler. This was not always the case, however. For example, TNT uptake was faster on PAN, but PS produced the greater sorption capacity. Nevertheless, results with this analyte suite reveal the potential for producing not only a fast, but also a high capacity equilibrium-passive sampling device from polymeric ENMs.

Reasonably strong correlations ($R^2 = 0.83$ and $p < 0.05$) were obtained when the equilibrium partition coefficients of all investigated analytes (except PCB187, 206 and 209) were plotted as a function of K_{OW} , hexadecane-water ($K_{hexadecane-w}$)⁴⁰ partition coefficient, and the dissolution constant (D, see ESI for calculations),¹⁵ as shown in Figure 7. $K_{hexadecane-w}$ has been suggested by others to better predict equilibrium partition coefficients of moderately and hydrophobic compounds into sorbent materials,^{41, 42} and D expresses the distribution of both the neutral and the ionic fraction of the analyte between the K_{OW} for the basic analyte and for the acidic analyte.¹⁵

We note that $\log K_{ENM-W}$ values for our moderately hydrophobic compounds on PAN were relatively insensitive to these descriptors, whereas PS seemed to show a better correlation across all of the analytes tested and the descriptors used. This suggests that PAN may be most promising for rather constant performance across a range of polar targets, while classical paradigms for hydrophobic partitioning may govern uptake capacity on PS. Nevertheless, this correlation analysis suggests that it may be possible to estimate with a low degree of uncertainty the equilibrium partition coefficients on PAN and PS for a diverse type of analytes using these chemical properties.

CONCLUSIONS

Electrospun nanofiber mats (ENMs) provide a promising sorbent for passive sampling materials targeting organic contaminants in water and sediment environments. ENMs possess nanoscale features, but also exist as a robust bulk, macroscopic material. Their tunable nanofiber properties (e.g., diameter and surface area) make them ideal for applications that rely on uptake rate and pollutant partitioning. High surface area-to-volume ratios (S/V) can lead to improved uptake rates and shorter times to achieve equilibrium. For passive sampling, these ENM performance characteristics translate into shorter field deployments and easier analytical detection.

Across several polymers considered, PAN, PMMA and PS ENMs were most promising. They exhibited rapid (with and without mixing) uptake with $t_{90\%}$ values from 0.008 to 7 days and equilibrium partitioning coefficients ranging from 1.3 to 6.4 log units ($L\ kg^{-1}$) for hydrophilic, moderately hydrophobic and hydrophobic targets alike. From results with model compounds, these materials provide comparable performance or better to commercially available passive sampling materials and more traditional research alternatives, although a direct comparison to POCIS remains needed. Indeed, POCIS and ChemcatcherTM generally show higher equilibrium partitioning coefficients, from 1 to 4 log

units for hydrophilic and moderately hydrophobic compounds, but sometimes there is no accumulation of the analytes into their different sorbent phases (e.g., Triclosan and Dicamba), ^{21, 33} and with longer time to reach equilibrium. ³³

We contend, therefore, that these ENMs have the potential to be applied to a broad spectrum of pollutant targets, simultaneously, with only a single sorbent material. We also demonstrated ENM performance in complex settings (e.g., soil and sediment), while also revealing important practical considerations associated with their use; for example, PS had limited organic matter fouling relative to PMMA in soil and sediment.

While the results shown here are promising, further improvement on selectivity and capacity, are likely needed. Further, device scale up with integration of ENMs into a passive sampling device, and ultimately field demonstration and validation, will be needed to fully realize the promise of ENMs as next-generation passive sampling materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Environmental Significance

Effectively measuring both legacy and emerging pollutants in aquatic and sediment environments is challenging because of their range of properties, occurrence, and spatial and temporal variability. Passive sampling is a promising approach, but current commercially available sampling materials have some limitations, especially for hydrophilic and moderately hydrophobic compounds. This work, which blends fundamental and practical considerations, lays the foundation for improving measurement of organic pollutants in complex environmental compartments using a nanotechnology-enabled equilibrium-passive sampler that performs well toward a diverse suite of organics relative to more traditional, commercial materials.

Figure 1. SEM images of fabricated ENMs at low (left) and high (right) magnification. Corresponding recipes and characterization of these ENMs are provided in Table S1.

Figure 2.

Uptake curves with mixing (top) and without mixing (bottom) for aniline (a, c) and nitrobenzene (b, d) with our five ENMs. The error bars represent one standard deviation from two (w/mixing) and three (static) replicate uptake experiments. Laboratory set up: pH ~ 6.5 (DI water), initial concentrations of aniline: 2 mg L^{-1} and nitrobenzene: 3 mg L^{-1} , ENM loading $\sim 1.5 \text{ g L}^{-1}$. Please note the difference in the x-axis scale for experiments with and without mixing. The light gray area in panels a and b notes a shorter, zoomed in time scale. Lines simply connect data points.

Figure 3.

Average equilibrium partition coefficients in log units ($L \cdot kg^{-1}$) for PAN, PET, PMMA and PS for our model hydrophobic compounds. Uncertainties represent the standard deviation from at least two replicate experiments. Values are also shown in Table S4. Laboratory set up: pH ~ 6.5 (DI water), initial concentrations from 0.25 to 5 $ng \cdot L^{-1}$, ENM loading ~ 3 $g \cdot L^{-1}$.

Figure 4.

Time to reach 90% equilibrium ($t_{90\%}$) for (a) aniline and (b) nitrobenzene versus nanofiber diameter of our ENMs. Void circles correspond to mixing experiments, while black triangles are under static conditions. $t_{90\%}$ was calculated from eq. 3 (Table S3), and the nanofiber diameters are shown in Table 1. Line represents the linear regression from the mixing experiments (void circles). See the y-axis break in b).

Figure 5.

Nitrobenzene uptake into PS as a function of nanofiber diameter. Data are shown for PS with 140, 300 and 560 nm, and uptake experiments were conducted statically (without mixing). For comparison, data for the 140 nm (our standard PS recipe) are also shown from experimental systems where uptake experiments were actively mixed. $t_{90\%}$ s were calculated from the non-linear least squares regressions (Table S5). The curves show the non-linear least squares regression from the one compartment-first-order kinetic model. Laboratory set up: pH ~ 6.5 (DI water), initial concentrations of nitrobenzene: 3 ng L^{-1} , ENM loading $\sim 1.5 \text{ g L}^{-1}$.

Figure 6.

Measurements in heterogeneous systems of (a) nitrobenzene pore water concentrations versus time in systems with a model spiked soil, and (b) individual PCB sediment pore water concentrations from IHSC sediment, both using PMMA and PS. IHSC measurements were carried out for 28 days. Error bars represent the standard deviation from two replicate uptake experiments. Lines simply connect data points.

Figure 7.

Average equilibrium partition coefficients of PAN (top panels) and PS (bottom panels) versus octanol-water (K_{OW}) and hexadecane-water ($K_{hexadecane-w}$)⁴⁰ partition coefficients, and dissolution constant (D)¹⁵ for our hydrophilic, moderately hydrophobic and hydrophobic analyte suite. When no error bar is visible, the bars are smaller than the data symbol. Uncertainties represent the standard deviation from at least two replicate experiments. Compounds with uptake into ENMs of less than 5% of the total available mass were not included in the regression (Table 2), as well as PCBs 187, 206, and 209 due to their uncertainty in the measured equilibrium partition coefficients.

Table 1

Physical and chemical properties for ENMs investigated herein.

Property	PAN	PS	PMMA	PET	PVDF
Average diameter (nm) ^a	160 ± 30 (n = 7)	140 ± 30 (n = 4)	340 ± 50 (n = 6)	70 ± 20 (n = 4)	50 ± 10(n=5)
Surface area (m ² /g)	12 ± 0.50	27 ± 3.5	6.1 ± 1.4	7.1 ± 2.2	16 ± 0.2
Water contact angle (°)	44 ± 6.2	109 ± 9.9	119 ± 5.1	117 ± 7.5	135 ± 5.4

^aFiber diameters were measured from SEM images using ImageJ software. Typically, 100 nanofiber diameters were measured per ENM sample, allowing size distributions to be calculated for all synthesized materials. n = number of replicate syntheses.

Table 2

Summary of average and model ENM-water equilibrium partition coefficients and $t_{90\%}$ for the 10 hydrophilic and moderately hydrophobic compounds with PAN and PS ENMs (log units, $L\ kg^{-1}$) under mixing conditions.

Analytes	PAN		PS	
	Log K_{ENM-W} ($L\ kg^{-1}$)	$t_{90\%}$ (day)	Log K_{ENM-W} ($L\ kg^{-1}$)	$t_{90\%}$ (day)
	Measured	Model	Measured	Model
Aniline (n=10)	1.9 ± 0.06	1.9 ± 0.04	1.5 ± 0.03	1.5 ± 0.01
Anisole (n=6)	1.9 ± 0.04	1.9 ± 0.01	3.1 ± 0.05	3.0 ± 0.02
Atrazine (n=4)	1.2 ± 0.1 ^a	1.1 ± 0.01	1.6 ± 0.01	1.6 ± 0.01
Benzylamine (n=6)	2.0 ± 0.03	2.0 ± 0.01	1.3 ± 0.06	1.3 ± 0.01
β-Estradiol (n=6)	3.2 ± 0.2	3.4 ± 0.02	3.2 ± 0.1	3.2 ± 0.01
Caffeine (n=6)	1.3 ± 0.05 ^a	1.3 ± 0.02	1.3 ± 0.07 ^a	1.2 ± 0.02
Diuron (n=6)	1.4 ± 0.02 ^a	1.4 ± 0.01	1.3 ± 0.1 ^a	1.4 ± 0.1
Nitrobenzene (n = 10)	1.9 ± 0.1	1.9 ± 0.01	2.8 ± 0.01	2.8 ± 0.01
Phenol (n=6)	1.7 ± 0.02 ^a	1.6 ± 0.01	1.7 ± 0.03 ^a	1.7 ± 0.01
p-Nitrophenol (n=6)	1.7 ± 0.06	1.8 ± 0.01	1.6 ± 0.1	1.7 ± 0.1
RDX (n=6)	1.8 ± 0.03 ^a	1.9 ± 0.01	1.8 ± 0.1 ^a	1.8 ± 0.01
TNT (n=6)	1.9 ± 0.03	1.9 ± 0.01	2.8 ± 0.01	2.7 ± 0.02

^a Less than 5% of the total aqueous mass was sorbed to the ENM.