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A rapidly equilibrating, thin film, passive water sampler for organic contaminants; characterization and field testing

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An ethylene vinyl acetate (EVA), thin-film passive sampler for the detection of organic compounds in marine environments is calibrated and field tested.

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ABSTRACT

Improving methods for assessing the spatial and temporal resolution of organic compound concentrations in marine environments is important to the sustainable management of our coastal systems. Here we evaluate the use of ethylene vinyl acetate (EVA) as a candidate polymer for thin-film passive sampling in waters of marine environments. Log K_{EVA-W} partition coefficients correlate well ($r^2=0.87$) with Log K_{OW} values for selected pesticides and polychlorinated biphenyls (PCBs) where Log $K_{EVA-W}=1.04$ Log $K_{OW}+0.22$. EVA is a suitable polymer for passive sampling due to both its high affinity for organic compounds and its ease of coating at sub-micron film thicknesses on various substrates. Twelve-day field deployments were effective in detecting target compounds with good precision making EVA a potential multi-media fugacity meter.

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1. Introduction

Contamination of marine and freshwater systems is of global environmental concern; however, long-term monitoring of these compounds remains a challenge (Namieśnik et al., 2005; Vrana et al., 2005). Coastal observation networks are being introduced along European and North American coastlines in order to provide continuous monitoring of environmental parameters. Currently these networks are restricted in the amount of chemical monitoring that can be conducted due to limitations in chemical sensor technology (Stuer-Lauridsen, 2005). Expanding coastal observation networks to include chemical sensors for organic contaminants in the local environment would provide essential data to both scientists and policy makers. Currently, two general strategies exist for long-term monitoring of organic pollutants in aqueous environments: discrete sampling and time-integrated or equilibrium passive sampling (Zhao et al., 2005).

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Discrete sampling in the water phase provides a snapshot of the concentration in the environment at the time of sampling (Stuer-Lauridsen, 2005). This approach suffers from the limitations of sampling artifacts, temporal deficiencies, and high costs. One solution to this problem is to increase the sampling frequency or to install sampling systems that automatically acquire a distinct number of water samples in any given period (Mayer et al., 2003; Vrana et al., 2005). However, this may be cumbersome and prohibitively expensive when implemented in long-term water quality monitoring programs.

A range of passive samplers have been successfully applied to marine systems. They are based on the free flow of an analyte from the sampled medium to a receiving phase in a sampling device and collect target compounds *in situ* without disrupting the bulk solution. They may represent a time-averaged concentration such as semi-permeable membrane devices (SPMDs) (Mayer et al., 2003; Stuer-Lauridsen, 2005; Vrana et al., 2005) in which a compound accumulates into the sampler, often non-linearly, and the final concentration in the sampler is averaged over the deployment time to estimate an average concentration of the source. These samplers often mirror uptake in organisms and can be related to bioconcentration. Equilibrium samplers contain a sorbent such as

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a thin piece of polyethylene (Adams et al., 2007) or a thin film of polymer coated onto a substrate that reaches equilibrium with the surrounding medium (Wilcockson and Gobas, 2001) and the ambient concentration can be calculated based on an equilibrium partition constant. Both samplers provide insight to the environment. When used together the samplers should yield similar estimates of concentrations in the medium provided 1) they have been well parameterized and 2) the ambient concentrations are steady over the deployment period. If ambient concentrations differ over the deployment periods or there are episodic fluctuations, the concentration estimates may diverge. The divergence is useful in assessing that the conditions above have or have not been met.

Equilibrium samplers are particularly useful in that, when calibrated, they can function as fugacity meters in the environment to help determine both the concentration and flux of target compounds in various media (Meloche et al., 2009). The calibration of thin-film devices is simpler than their time-averaged counterparts and the film may be adjusted (surface area to volume ratio) and targeted to different compounds over a given deployment period. This approach has the potential to become a reliable and cost-effective tool that may be utilized in ongoing efforts to improve the detection of priority pollutants (Allan et al., 2006). Lohmann and Muir (2010) have advocated the need for global scale monitoring strategies for organic pollutants in aquatic environments to meet national and international monitoring obligations (e.g. Stockholm Convention on Persistent Organic Pollutants).

This study reports on the calibration of an equilibrium-type passive sampler for water, comprising of micron-thick layers of the copolymer ethylene vinyl acetate (EVA) (Fig. 1). EVA was first proposed as a fugacity sampler for organic tissue by Wilcockson and Gobas (2001) and then adapted as an air-side fugacity meter by Harner et al. (2003). This study extends the application of EVA as a water-side fugacity meter to expand the application of this medium (EVA) and test its potential as a multi-media fugacity meter. EVA is elastomeric in softness and flexibility but may be processed as other thermoplastics. It has good clarity, a utilization temperature range of -60 to 55 °C, stress-crack resistance (elongation 800%) such that it can be used in deep sea environments at high pressures, is water proof (0.07% water saturation) and is resistant to UV radiation thus maintaining its integrity in surface waters. EVA is non-toxic and commonly used in drug delivery, hot glue sticks and plastic wraps. Equilibrium samplers based on polyethylene have been recently tested for marine applications (Adams et al., 2007) and are particularly effective for hydrophobic compounds. The advantages of EVA include that it can be readily spiked with internal reference compounds at exact concentrations and can then be coated onto a variety of surfaces (Harner et al., 2003; Farrar et al., 2005; Wu et al., 2008b). EVA may be readily coated at various film thicknesses at the sub-micron range to optimize sampler uptake. It is expected that EVA has an expanded range of target compounds that bridges the current gap in aquatic passive sampling due to its polar acetate group, while providing a sufficient non-polar surface area to match the chemical affinity of existing samplers.

Fig. 1. Base unit for ethylene vinyl acetate (EVA) copolymer.

EVA-water partition coefficients are reported for a suite of pesticides and polychlorinated biphenyls (PCBs) and a coastal deployment using the derived partition constants for the detection of currently used pesticides in natural waters is presented.

2. Theory

The difference in chemical potentials of an analyte across separate phases results in its net flow from one medium to another. For environmental marine monitoring, this occurs from seawater to the polymer used in the passive sampler (Huckins et al., 1990). Net movement continues until thermodynamic equilibrium is achieved or the sampling period is halted (Vrana et al., 2005). The exchange kinetics between sampler and water can be described by a first-order one-compartment model:

$$C_{S}(t) = C_{W} \frac{k_{1}}{k_{2}} \left(1 - e^{-k_{2}t} \right) \tag{1}$$

 $C_S(t)$ is the contaminant concentration in the sampler polymer as a function of time, t, C_W is the contaminant concentration in the sampled medium (i.e., seawater), and k_1 and k_2 are the uptake and offload rate constants respectively (Allan et al., 2006). Passive samplers follow one of two phases in the accumulation of organic pollutants during field deployments. These phases are kinetic or equilibrium and can be shifted by altering the sampler design (i.e. surface area and film thickness). The time to reach equilibrium for the EVA sampler is a function of the partition coefficient $K_{\text{sampler,medium}}$ and the uptake rate k_1 of the compound. Uptake follows a standard saturation curve in which the time to reach 90% of equilibrium can be expressed as (Mayer et al., 2003):

$$t_{90\%} = \frac{ln \, 10}{k_2} = K_{sampler,medium} \frac{ln \, 10}{k_1} \eqno(2)$$

In the equilibrium phase, as $(1-e^{-k_2t})$ approaches 1, and $\frac{k_1}{k_2}=K_{sampler,medium}$ Equation (1) can be reduced to:

$$C_{W} = \frac{C_{S}}{K_{EVA-W}} \tag{3}$$

where $K_{\text{EVA}-\text{W}}$ is the partition coefficient of the target analyte between EVA and water.

3. Methods

The EVA sampler is based on the principles used to monitor semivolatile organic compounds (SVOC) in the atmosphere as an alternative to high volume air sampling (Harner et al., 2003). The design consists of a thin film of EVA ($\sim 1~\mu m)$ (Elvax 40W, DuPont) on a substrate. The sampler versatility was recognized and demonstrated as it could be used to sample in either the kinetic or equilibrium phases simply by varying the thickness of the polymer coating (Harner et al., 2003; Farrar et al., 2005).

3.1. Determination of partition coefficients

The generator column method was used to measure K_{EVA-W} for a group of pesticides including several legacy organochlorine pesticides (OCPs), currently used pesticides (CUPs) and PCBs (see Fig. S1, Supplementary information). This is analogous to the methods used by Wu et al. (2008b) for the experimental determination of K_{EVA-A} for PCBs in air. In this approach, water was passed through and equilibrated with a column of 3 mm glass beads coated with EVA that had been spiked with target analytes.

The EVA solution was made by dissolving 16 g EVA in 200 mL DCM. This solution was then spiked with the target compounds (Table 1). Glass beads were coated by immersion in the EVA solution for approximately 1 min and decanting excess solution. The 'wet' beads were then immediately transferred to a large stainless steel bowl and swirled rapidly for $1{-}2$ min to allow excess DCM to evaporate and to prevent beads from clumping together (Wu et al., 2008a,b). The coated beads were loaded to the 20 mL level of a 10 mm i.d. glass column. A sub-set of the beads was retained for the determination of analyte concentration in the EVA (Cs) (see Supplementary information).

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Table 1 Log K_{OW} values of target compounds and experimentally derived values of K_{EVA-W} using the generator column method.

Log K _{ow}	$Log \; K_{EVA-W}$
2.2 ^b	2.7
2.3 ^e	2.6
2.8 ^f	2.9
3.1 ^c	3.0
3.5 ^e	3.1
3.6 ^g	4.0
3.8 ^g	4.4
3.8 ^d	3.8
4.0 ^d	3.2
4.5 ^e	4.4
5.3 ^c	6.1
2.9 ^g	3.6
1.7 ^a	2.5
2.4 ^e	3.1
5.0 ^d	5.5
4.4 ^e	4.8
5.2 ^g	5.6
4.5 ^e	5.4
5.3 ^e	6.1
5.6 ^e	6.3
	2.2 ^b 2.3 ^e 2.8 ^f 3.1 ^c 3.5 ^e 3.6 ^g 3.8 ^g 3.8 ^d 4.0 ^d 4.5 ^e 5.3 ^c 2.9 ^g 1.7 ^a 2.4 ^e 5.0 ^d 4.4 ^e 5.2 ^g 4.5 ^e 5.3 ^e

 K_{OW} values were selected based on recommended values of the Canadian National Committee for CODATA(CNC/CODATA).

- a Draber et al. (1969).
- b Liu and Qian (1995).
- ^c Kenaga and Goring (1980).
- d Bowman and Sans (1983).
- e Hansch and Leo (1987).
- ^f Finizio et al. (1991).
- g Hansch et al. (1995).

Ultra-high purity water was introduced to the top of the column at a rate of 5 mL min $^{-1}$ until the beads were completely covered. The same delivery rate was used during the collection of twelve 10 mL samples to assess $C_{\rm w}$ and to ensure that equilibrium was achieved in the generator column. Further details are provided in the Supplementary information. Experimental $K_{\rm EVA-W}$ values were calculated using $C_{\rm w}$, $C_{\rm s}$ and substituting into Equation (3). All 10 mL water samples were extracted by liquid—liquid extraction with 3 subsequent 5 mL DCM aliquots. After DCM addition, samples were agitated using a vortex mixer for 1 min before centrifugation to separate the phases and removal of the lower DCM phase into a clean boiling tube. After the third DCM rinse, the composite DCM fraction was reduced under a gentle stream of nitrogen and solvent exchanged into isooctane for analysis.

3.2. Preparation of samplers for field deployment

A coating solution of EVA was created by dissolving 2 g of EVA pellets into 100 mL of analytical grade DCM. The solution was stirred for 2 h ensuring that the EVA was completely dissolved. Pre-combusted (420 °C, 6 h) Whatman glass fiber filters (12.5 cm i.d., 0.7 um nominal retention size) were used as the coated substrates. These were baked at 420 $^{\circ}\text{C}$ for 6 h, allowed to cool to room temperature and weighed. Substrates were then dipped into the coating solution for 5 s. Upon removal, the DCM was evaporated, leaving a thin coating of EVA on the substrate with an approximate surface area of over 245 cm². The dry filters were weighed to determine the mass of the EVA. Average mass of the EVA on the sampler was 0.40 g \pm 0.01 g (density of EVA, ρ_{EVA} = 0.93 g mL $^{-1})$ which corresponds to an average film thickness of approximately 18 μm (based on the planar surface area of the filter). It should be noted that the GFFs are a fiber mesh and therefore the true film thickness along the mesh will be less than 18 μm due to the larger effective surface area of the mesh. GFFs were used (rather than beads) as a direct comparison to previous studies in air (Wu et al., 2008a,b) and to simplify the sampler-water boundary to avoid diffusion limitations in a more quiescent medium. Filters were then inserted into a solvent-rinsed stainless steel cage, wrapped in aluminum foil, placed in an airtight container and frozen until deployment. During this procedure, care was taken to ensure that the exposure of the samplers to ambient air was minimized (typically less than 5 min) in order to limit contamination. Titanium plates were also coated in a separate study (St. George, 2008) and showed no difference in EVA partitioning due to substrate.

3.3. Field deployment of EVA samplers

EVA samplers were deployed in triplicate at three stations (Station 1: 41°-26.6′N–072°-05.9′W, Station 2: 41°-22.9′N–072°-05.3′W, Station 3: 41°-19.7′N–072°-04.9′W) eastward of the channel along the Thames River Estuary (TRE)

during August 2006. This is an urbanized and industrialized tidal estuary along Long Island Sound located in southeast Connecticut (CT), USA. The Estuary is approximately 20 km long with the head of the river located in Norwich, CT. The Yantic and Shetucket Rivers comprise the major freshwater inflow to the Estuary. The watershed encompasses $3800~{\rm km}^2$. There are numerous agricultural areas within the watershed and area of the estuary, making it a good test location for investigating the application of the thin-film passive samplers for legacy and current-use pesticides.

The samplers (n=3 per station) were suspended on a stainless steel frame approximately 50 cm above the bottom sediments and left *in situ* for 12 days (Fig. S2 Supplementary information). Equilibration times were determined in the lab and ranged from 1 to 12 d for compounds with Log $K_{\rm ow}$ values between 1 and 6 (St. George, 2008), Field blanks were exposed on ship deck until the sampler entered the water. The blanks were then wrapped in pre-cleaned foil, placed in an airtight container and stored at -4 °C until ready for extraction and analysis. Sampler recovery was conducted by divers at the end of the 12 d deployment period. Once retrieved, the samplers were handled as described above. Conductivity, temperature, and depth (CTD) profiles were recorded at each station using a Seabird CTD. Bottom water salinity and temperature ranges varied only slightly between stations. Bottom water depths were 10-12 m and temperatures ranged from 18 to 20 °C.

Samplers were rinsed with de-ionized water and placed in a 125 mL sealed vessel and soaked in 120 mL analytical grade methanol (Fischer Scientific) for a 24 h period before pouring the extract into a pre-rinsed 500 mL flask. This process was repeated a second time and the extracts combined before being reduced to \sim 2 mL via rotary evaporator before transferring to a pre-rinsed centrifuge tube through 3 cm of sodium sulfate. Extracts were evaporated to approximately 0.5 mL under a gentle stream of nitrogen and then solvent exchanged to ethyl acetate followed by isooctane. Upon completion of solvent exchange, 10 μ L of Mirex (10 ng μ L $^{-1}$) was added as an internal standard. The internal standard is used to verify and quantify instrument responses. Extracts were placed in a centrifuge at 5000 RPM for 3 min to remove any EVA or sodium sulfate that may have remained in the sample. The supernatant was transferred into a GC vial and the volume further reduced to 1 mL for analysis.

4. Analysis

Extracts from laboratory samples (generator column experiments) and field samples were analyzed for current-use pesticides as per Yao et al. (2006). Briefly, phorate, α -HCH, dazoment, simazine, carbofuran, atrazine, terbufos, diazinon, disulfoton, alachlor, and metolachlor were analyzed by gas chromatography mass spectroscopy (GC-MS) in electron-ionization (EI) mode. Other CUPs: trifluralin, dimethoate, chlorothalonil, metribuzin, malathion, chlorpyrifos, dacthal and pendimethalin were analyzed by GC-MS in negative chemical ionization (NCI) mode. Legacy pesticides α -, β -, γ -, and δ -HCH, HEPT, HEPX, aldrin, dieldrin, TC, TN, CC, Endosulfan I and II, and endosulfan sulfate, the isomers of DDT and their breakdown products were also analyzed by NCI. Generator column tests were also analyzed for PCB congeners -3, -8, -15, and -18 in EI mode. For both types of analysis a J&W DB-5 30 m column (J&W Scientific, Rancho Cordova, CA), i.d. 0.25~mm, $0.25~\text{\mu m}$ film thickness was used, operated with helium as the carrier gas, connected to a Hewlett-Packard 5973 MS (in NCI mode, methane was used as the reagent gas). A 2 μ L sample was injected in splitless mode, with the split opened after 1 min. Samples were quantified by comparison to a prepared set of standards of known concentration. Peaks were quantified when S/N > 3, and when the quantifier/qualifier ratio was within 15% of the standard (Yao et al., 2006).

5. Results and discussion

5.1. Quality assurance/control

The limit of detection (LOD) was equal to the mean blank level plus three standard deviations of the mean. The instrument detection limits (DL) for the samples were calculated by extrapolation from the lowest level calibration standard to the point where the signal to noise ratio was equal to three. Calibration experiment blank levels were <10% of sample concentrations. Method

recoveries ranged from 85 to 102%. Reported concentrations were blank and recovery-corrected. Field sample blank levels were below detection for all pesticides with the exception of Trifluralin; that was as high as 7.7 pg L^{-1} . All stations showed concentrations of Trifluralin above the LOD. The standard deviation of the blanks (n = 3) was less than 1 pg L^{-1} (or $\sim 20\%$).

5.2. K_{EVA-W} determinations

Results of equilibration tests showed that the generator column came to equilibrium for all compounds with Log $K_{\rm OW}>3.5.$ Concentrations on beads for these compounds remained relatively constant. In these instances the average value of C_S and C_W was used to determine $K_{\rm EVA-W}.$ For compounds with lower $K_{\rm OW}$ values (based on results for alachlor and metolachlor), the EVA-coated beads became depleted of analyte during the time-course of the measurements. In these cases, partition coefficient determinations were based on EVA concentrations adjusted for the corresponding loss. The Log $K_{\rm EVA-W}$ values calculated from these experiments are summarized in Table 1.

A plot was constructed and used to define Log K_{EVA-W} partitioning coefficients for the 2 classes of compounds examined (Equation (4)). Strong correlations were observed ($r^2=0.87$; p<0.005) such that EVA could be an effective passive sampling material with an affinity for organic compounds that is in consistent with that of octanol for the compounds tested. The Log K_{EVA-W} versus Log K_{OW} plot yielded the following relationship:

$$Log K_{EVA-W} = 1.04 Log K_{OW} + 0.22$$
 (4)

Calibrations were in good agreement both within and among sampled pesticides and PCBs. Results indicate the effectiveness of EVA as a sampling medium for hydrophobic compounds. The relationship shows that EVA has an affinity for organic compounds slightly greater than that of octanol and other polymers used in equilibrium samplers (Adams et al., 2007) and possibly with a broader target range. These observations are in agreement with those of Golding et al. (2007, 2008) which also show the somewhat higher solubility of organic compounds in EVA compared with octanol. EVA allows both non-polar:non-polar van der Waals interactions and polar interactions at the acetate ends resulting in both stronger attractive forces and a wider range of target organics. Though a large range of hydrophobicities are represented here it would be useful to investigate additional compound classes and compounds with an extended range of K_{OW} values to test these correlations further.

5.3. Detection limits

The detection limits of the EVA sampler can be tuned to the environmental concentrations based on the amount of EVA applied and an adjustment of the surface area to maintain a thin film. Equation (4) above provides the critical parameter for field applications and $K_{\text{EVA}-W}$ can be derived using a known or estimated K_{OW} . The required mass of EVA M_{EVA} can be determined using the expected field concentration ranges (C_{W}) and the instrumental detection limits of the proposed analysis in grams or moles (N_{target}).

$$M_{EVA} = N_{target} \, \rho_{EVA} (K_{EVA-W} C_W)^{-1} \tag{5}$$

where ρ_{EVA} is the density of EVA (0.93 g cm $^{-3}$). For example, in this application the sampler contains 0.40 \pm 0.01 g EVA and the detection limits of the MS analysis are in the ng range. For this configuration, compounds with a K_{EVA-W} on the order of 10^3 have ambient detection limits in ng L^{-1} and those with a K_{EVA-W} of $>10^5$ can be detected in the $<\!pg~L^{-1}$ range.

5.4. Calculation of C_W in field tests

Experimental $K_{\text{EVA-W}}$ values (Table 1) were applied to assess C_{W} in equilibrated TRE field samples using Equation (3). Equilibrium for all target compounds was predicted to be approached within 12 days based on an 18 μ m EVA film and a diffusivity in water on the order of 0.01 cm s⁻¹. This was also confirmed experimentally in previous batch uptake experiments (Wilford et al., 2006; St. George, 2008). The mass of the target analyte detected during GC–MS analysis and the volume of EVA on the sampler was used to determine C_{S} , which was blank corrected. Blank corrections in equilibrium sampling are conceptually difficult because exposure prior to deployment is not expected to linger since the sampler re-equilibrates in the field. Here we assume that any residual blank signals are due to post-deployment exposure. This is a conservative approach and fortunately blank concentrations were not a problem.

5.5. Field testing of EVA samplers

The purpose of the field trials was to assess the experimental parameters and sample reproducibility. Results showed that over the deployment period, sample integrity was maintained and minimal visible biofouling was observed. Of the nineteen pesticides that were targeted, six were detected in the TRE. Compound concentrations are shown in Fig. 2 and are divided into two groups based on their ranges (ng L^{-1} and pg L^{-1}).

Highest average EVA-derived water concentrations across the three stations in the estuary were for metribuzin and atrazine, 110 and 72 ng L⁻¹, respectively. Atrazine and metribuzin are triazine herbicides and are commonly used to control broadleaf and grassy weeds in vegetable and field crops as well as non-cropped industrial lands (Cox, 1997). Chlorothalonil was detected at 6.8 ng L^{-1} . This is one of the most common fungicides in agricultural and household uses with lawn treatment accounting for approximately one third of its use (Cox, 1997). Water concentrations for metribuzin and atrazine reported here are in the range of reported values from water quality studies for the same study area (Garabedian et al., 1998), reflecting the ongoing use and presence of these pesticides in the estuary. In comparison with pesticide concentrations from other eastern US estuaries, the results from this study are slightly higher than mean concentrations of atrazine (48 ng L^{-1}) and chlorothalonil (2.7 ng L⁻¹) measured in the C-111 canal system and Florida Bay (Scott et al., 2002), but substantially lower than the 1.29 μ g L⁻¹ atrazine concentration detected in the Patuxent River by McConnell et al. (2004). Concentrations of these analytes varied

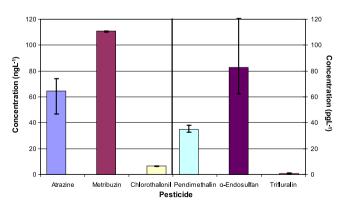


Fig. 2. Passive sampler-derived water concentrations of selected CUPs in the Thames River Estuary. Range and blank-corrected average values depicted are for a 12 d sampler deployment of the EVA sampler at three stations. Water concentrations were calculated using Equations (3) and (4); Log K_{OW} value for α -Endosulfan = 3.83 (Hansch and Leo, 1985).

only slightly between stations indicating relatively even distribution in the bottom waters of the sampled area.

The second group of CUPs detected in the pg L^{-1} range, included pendimethalin, α -endosulfan, and trifluralin. Average concentrations of pendimethalin and trifluralin were 35 and 0.91 pg L^{-1} respectively. These herbicides are used in a variety of agricultural and residential settings to control and prevent broadleaf weeds. α -Endosulfan, detected at 63–120 pg L^{-1} , is a broad-spectrum, contact insecticide and is registered for use on a wide variety of commercial agricultural settings. The concentration of α -endosulfan at Station 1 was considerably higher than at the other two stations that were closer to the mouth of the estuary. Pendimethalin and trifluralin were detected previously in the study area; however, the concentrations reported at that time were higher with maximum concentrations of 100 ng L^{-1} and 20 ng L^{-1} respectively (Garabedian et al., 1998).

The EVA sampler has a high affinity for organic compounds both polar and non-polar and may bridge the gap between current sampler polymers which tend to work optimally for a particular range of hydrophobicities. EVA shows much promise as a multimedia fugacity sampler that may be applied in diverse environmental conditions.

6. Implications and perspectives

The EVA sampler described and successfully tested here has potential for future applications in environmental research and monitoring. The sampler is flexible in that EVA can be coated onto a variety of substrates and thicknesses (down to less than a micrometer if required). EVA has been applied successfully as an equilibrium lipid and air sampler. Application of the sampler in coupled air—water lipid—water systems would allow fugacity gradients to be determined to provide an assessment of air—water exchange. If K_{OA} and K_{OW} values are known, concentrations in air and water can be calculated. By analogy, this approach can also be extended to measure chemical fugacities across sediment—water interfaces.

Future work includes determining $K_{\text{EVA-W}}$ for a broader range of target analytes, assessing $K_{\text{EVA-W}}$ as a function of temperature, salinity, and applying depuration compounds (labeled analogs spiked into the EVA prior to deployment) for field deployments in water to confirm the equilibrium status of target analytes. Analogous to the successful use of depuration compounds in passive air sampling programs, these compounds will enable the broader use of this marine passive sampler in the kinetic phase by providing an estimate of effective water sample volume. The EVA sampler meets the call for a cost-effective and simple tool for measuring persistent organic pollutants in aquatic environments (Lohmann and Muir, 2010). When used as a multi-media fugacity meter, the EVA sampler can provide additional information on inter-media equilibrium status and fluxes (e.g. air—water, sediment—water).

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Appendix. Supplementary information

Supplementary information related to this article can be found online at doi:10.1016/j.envpol.2010.10.030.

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