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Passive sampling for spatial and temporal monitoring of organic pollutants in surface water of a rural-urban river in Kenya

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HIGHLIGHTS

- Silicone rubber was used to monitor for hydrophobic organic compounds in a rural-urban tropical river.
- Polynuclear aromatic hydrocarbons (PAHs) and phthalates were quantified from silicone rubber extracts.
- Pollution hot-spots were identified.
- Use of performance reference compounds revealed variation in site–specific deployment conditions.

GRAPHICAL ABSTRACT

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ABSTRACT

Passive sampling is an emerging monitoring strategy for surface waters and can be applied in a range of environments including remote locations. Silicone rubber (SR) as a robust single-phase passive sampler was applied to characterize the spatial and temporal variability of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) and three phthalates, namely, dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and bis(2–ethylhexyl)phthalate (DEHP) in a tropical river traversing rural and urban catchments. OCPs and PCBs were not detected. Up to 31.8 ng/L of freely dissolved concentrations of PAHs were quantified and were dominated by the lower molecular weight members. Mean concentrations of DBP, BBP and DEHP were 72.6 ng/L, 3.9 ng/L and 7.1 ng/L respectively. However, in sampling for phthalates using SR, quality control and assurance remains the key challenge and must always be ensured. Spatial variability in concentrations was evident and could be related to land use. Temporal variability was not significant.

1. Introduction

Passive sampling continues to gain acceptance as an emerging monitoring strategy of surface waters due to its uncomplicated deployment and time-integrative character as compared to the conventional grab sampling. Furthermore, passive sampling devices (PSDs) pre-concentrate the analytes of interest in situ from large volumes of water that yield concentrations above the instrumental limits of detection/quantification (Schulze et al., 2011; Booij et al., 2016).

PSDs are deployed for a user–defined period, for instance one month, during which they passively accumulate contaminants from the water phase and they therefore collect all information from episodic and non–episodic events. This is not possible when using conventional

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monitoring strategies unless expensive and energy–consuming water sampling methods are used. Passive sampling therefore offers an alternative cost–effective monitoring strategy and can be applied even in remote locations. Additionally, passive sampling yields freely dissolved concentrations (c_w) as opposed to concentrations when using grab sampling. Fractions bound to suspended particulate matter or to dissolved organic carbon are not measured or irrelevant due to either their exclusion by the diffusion-limiting layer, slow transport through it, or poor uptake by the receiving phase. c_w is indicative of the bioavailable fraction of a contaminant and therefore can be used to quantify the effective concentration gradient for diffusive transport and partitioning (Gorecki and Namiesnik, 2002; Schulze et al., 2011) as well as to estimate bioaccumulation and (eco)toxic effects (Mayer et al., 2014; Münze et al., 2015).

Several PSDs have been developed and applied in monitoring organic contaminants in surface waters. For example, the biphasic semipermeable membrane device and single–phase low-density polyethylene, silicone rubber (SR) and polydimethylsiloxane (PDMS) have been used to monitor hydrophobic organic contaminants (HOCs) including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) (Vrana et al., 2001; Allan et al., 2009, 2013). Among the single–phase PSDs, SR is robust having high diffusion coefficients and low transport resistances implying that uptake of a compound is controlled by the water boundary layer, a stagnant layer of water around the sampler (Rusina et al., 2007).This presents opportunities for manipulation of deployment conditions by choosing locations with high flow rates and therefore maximize compound uptake by SR.

In this study, SR was applied in a tropical river traversing rural and urban catchments to char-acterize the spatial and temporal variability of PAHs, PCBs, OCPs and three phthalates, namely, dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and bis(2ethylhexyl)phthalate (DEHP).

The considered surface water is the Sosiani river, one of the tributaries of river Nzoia that lies in Uasin Gishu County, Kenya. The section of the river under study traverses through forests, agricultural fields and Eldoret town, the fifth largest urban center in Kenya. Eldoret lies at an altitude of 2085 m above sea level and receives 1270–1790 mm/a rainfall. It has a population density nearly 900 persons per square kilometer. The town has emerged as an important commercial, agricultural and industrial center and has an estimated growth rate of 7% per annum. The Sosiani river is impacted by pollution from agricultural fields, urban surface runoff, directly discharged domestic sewage from slum dwellings, treated municipal sewage, car washes, runoff from solid waste dumpsites, among others. With the varied sources of pollution coupled to the knowledge gap on HOCs, it is therefore important to investigate the fate of these compounds, since the river is not only a habitat for various organisms but also a source of water mainly for livestock and urban agriculture.

2. Experimental

2.1. Reagents and materials

Solvents, and chemicals used are listed in section S1 of the Supplementary data. Before field deployment the samplers were spiked according to the procedure given by Smedes and Booij (2012) with the following performance reference compounds (PRCs): [D_{10}]acenaphthene, [D_{10}]fluorene, [D_{10}]phenanthrene, [D_{10}]anthracene, [D_{10}]pyrene, [D_{12}]chrysene, [D_{12}]perylene, [D_4]DEHP, PCB 29, PCB 54, PCB 77 and PCB 81.

2.2. Description and preparation of SR sheets

AlteSil™ silicone sheets, translucent 300 × 300 mm, 0.5 mm thick were obtained from Altec Products Ltd., Victoria/UK. They were prepared according to the procedure outlined in Smedes and Booij (2012). Briefly, the membranes were cut into 5.5 cm × 9 cm strips and pre-cleaned by soxhlet extraction in ethylacetate during five days to remove oligomers and other impurities. PRCs were then spiked onto the membranes by equilibrating in a methanol-water mixture during one week and thereafter, the membranes were dried with lint–free tissue and stored at 4 °C until use.

2.3. Sampling sites and campaigns

The membranes were deployed along Sosiani river, Kenya (0°3′S and 0°55′N, 34°55′E and 35°31′E; see Fig. 1). As its name suggests in the local dialect, the river is rocky and turbulent and can therefore be considered to be well mixed especially during low flows from December to February. This period marks the dry season with 25.4 mm average rainfall, mean temperature highs of 25 °C and lows of 11 °C and average water depths of 0.8 m. There are negligible non–point inputs due to overland flow and given the stable environmental conditions, the fate of analytes in the river is therefore governed principally by temperature fluctuations and hydrodynamics. Potential groundwater inputs are not known but unlikely due to the shallowness of the river.

Seven sampling stations were selected to reflect varying levels of land use, from the relatively undisturbed locations at R1 and R2 to U7, downstream of the wastewater outfall. Two sampling campaigns were carried out in January–February 2014 at all sampling stations and in December 2014–January 2015 at stations U5 and U6. Detailed information on the sampling stations (geographic coordinates, water depths, surrounding land use) is given in Table S2.

Given the low water depth, the samplers could not be deployed in standard cages thus a home- made solution was designed as follows: The membranes were secured equidistant from each other using a knotted polypropylene rope. The rope was then first anchored onto boulders those were readily available at the river bed to ensure that the samplers remained immersed in water at approximately two–thirds depth from the water surface then further fastened onto wooden pegs at the river banks. Field exposure duration was 35 d and 30 d during the first and second field campaigns respectively. During retrieval, the membranes were first rinsed in river water to remove excess fouling and debris then they were patted dry with lint–free tissue, wrapped in pre–cleaned aluminium foil and transported in a cooler box at 4 °C. The samplers were stored at −20 °C until extraction.

2.4. Extraction and analysis

Samplers were extracted twice in 150 mL methanol at room temperature during a total of 24 h. The extracts were concentrated to 2 mL in a Turbovap evaporator (Zymark) then 20 mL ethylacetate were added and further concentrated to 2 mL. The extracts were cleaned and dried in a glass syringe packed with anhydrous sodium sulfate and eluted with 6 mL ethyl acetate. The extracts were further concentrated to 1 mL under a cold gentle stream of nitrogen then they were transferred to a 1 mL-glass vials and analyzed by gas chromatography–mass spectrometry (GC–MS). Details of the analysis and the recoveries are given in section S3. Additionally, fabrication and field controls were used and processed similarly to the field-exposed samplers.

2.5. Calculation of freely dissolved concentrations

The uptake rate of an analyte from the water phase by a passive sampler generally follows first order kinetic approach to equilibrium, and is dependent on the physicochemical properties of the analyte and deployment conditions. The amount of analyte sorbed onto SR (m_t) after an exposure duration t is used to calculate c_w of the target analytes as