# Assessing the transport of PAH in the surficial sediment layer by passive sampler approach

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## HIGHLIGHTS

- Pore water concentration gradients of a set of PAHs were measured by passive samplers.
- The diffusivities of PAHs in the sediment were measured using tracer compounds.
- The investigated PAHs were fluorene, fluoranthene and pyrene.
- The selected tracer compounds were 2H-labelled versions of the same PAHs.
- The diffusive fluxes in the sediment and near the interface were calculated.

## GRAPHICAL ABSTRACT
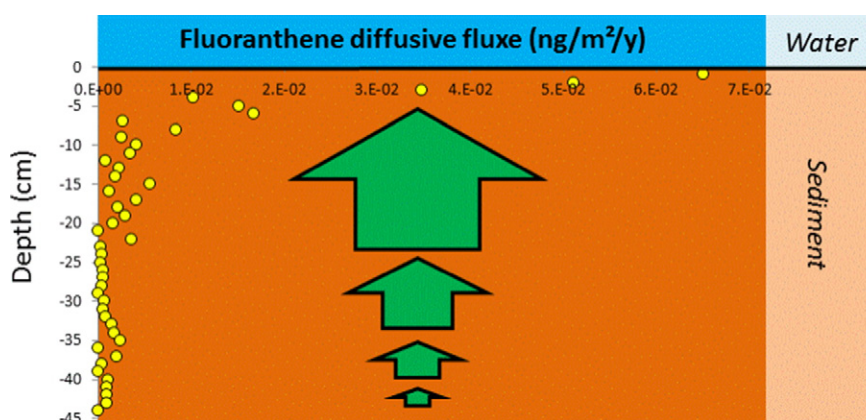


## ARTICLE INFO

## ABSTRACT

A new method based on passive samplers has been developed to assess the diffusive flux of fluorene, fluoranthene and pyrene in the sediment bed and across the sediment-water interface. The dissolved compound concentration gradient in the sediment in the vertical direction was measured at the outlet of a storm water pond by using polyethylene strips as passive samplers. Simultaneously, the dissipation of a set of tracer compounds preloaded in the passive samplers was measured to estimate the effective diffusion coefficients of the pollutants in the sediment. Both measurements were used to evaluate the diffusive flux of the compounds according to Fick's first law. The diffusive fluxes of the 3 studied compounds have been estimated with a centimetre-scale resolution in the upper 44 cm of the sediment. According to the higher compound diffusion coefficient and the steeper concentration gradient in the surficial sediment layer, the results show that the net flux of compounds near the sediment interface (1 cm depth) is on average 500 times higher than in the deep sediment, with average fluxes at 1 cm depth on the order of 5, 0.1 and 0.1 ng/m$^2$/y for fluorene, fluoranthene and pyrene, respectively.
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## 1. Introduction

The concept that sediments are not only a sink for pollutants but also act as a source closely linked to the overlying water column is now well recognized (Eggleton and Thomas, 2004; Eek et al., 2010; Liu et al.,

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2013; Belles et al., 2016a). In this context, the management of contaminated sediments (Lampert et al., 2011; Xu et al., 2013) and the study of the fate of the sediment-accumulated pollutants have received considerable attention at an international level over the last decade (Fernandez et al., 2014; Belles et al., 2016d). Hence, to improve our knowledge of the risks associated with polluted sediments, the measurement of the transport of compounds within the sediment and across the sediment-water interface has become a priority. However, the study of the transport of pollutants in bedded sediments and between the sediment and water phases remains extremely difficult because it results from the mixing of various simultaneous processes, such as (1) laminar flux of pore water (Darcy flow), (2) molecular diffusion (Liu et al., 2013), (3) movement of the matrix (e.g., bioturbation) (Lampert et al., 2011), (4) co-transport by mobile microorganisms, (5) colloid-mediated transport (Johnson et al., 1998), (6) water intrusion from groundwater, (7) resuspension of sediment (Belles et al., 2016a), (8) gas ebullition (Brennwald et al., 2005; Flury et al., 2015), (9) tidal rush and wave pumping, and (10) the heterogeneity of the water-sediment interface. In the interests of simplification, most studies have focused on a single process, thereby neglecting the contributions of others. However, this approach is limited when confronted with the complexity of natural systems, where all these processes occur simultaneously. These studies nevertheless provide valuable baseline information for an initial estimate of the magnitude of the exchange of the compounds at the sediment-water interface. Among the most important processes driving the transport of dissolved compounds into the sediment across the sediment surface, molecular diffusion is of particular interest because it is constant and independent of environmental events, such as the remobilization of sediments or organism activities. (Here, the flux of pollutants associated with particulate matter, such as sedimentation and erosion, are not considered).

The most convenient method for determining the molecular diffusive fluxes is to use Fick's first law, which requires defining the diffusion coefficient of the pollutants into the media and the concentration gradient of the pollutants. Alternatively, if a precise concentration gradient is not available, the concentrations at 2 points on both sides of the diffusing layer and the thickness of the diffusing layer can be used (Achman et al., 1996; Liu et al., 2014). This approach, the so-called 2-points measurement technique, has often been conducted during active sampling to determine the dissolved concentrations of the pollutants. However, this process is laborious and requires a time-consuming extraction procedure. In this context, the ability of passive samplers to assess the dissolved concentration gradient of pollutants with a high spatial resolution and with the required detection limits in both compartments (i.e., water column and sediment bed) is highly valuable for quantifying the diffusive fluxes (Liu et al., 2013). As an example, the Solid Phase Micro Extraction (SPME) methodology has provided satisfactory performance for measuring such concentration gradients at a high resolution but with a poor suitability for field deployment due to the cost and fragility of the SPME fibre (Lampert et al., 2011). In contrast, the method involving polyethylene (PE) strips used as passive samplers and subsampled after field exposure at the required spatial resolution has been used by Fernandez et al. (2014) without the aforementioned limitations. Similar sampler designs were also used by Liu et al. (2013), who achieved μm-scale resolution for deducing the flux of DDT and its metabolites at the sediment-water interface. SPME and PE strips allow the determination of the concentration gradient with many concentration point measurements, which enhance the accuracy of the calculated diffusive flux. In this respect, the PE passive samplers appear to be a cost-effective and suitable tool for evaluating the concentration gradients of compounds on both sides of the sediment-water interface. A summary of the different techniques and their main benefits and drawbacks is presented in Table S1.

However, the field measurements of compound diffusion in sediment and across the sediment surface are impeded by the difficulty of measuring the compound mobility (diffusion coefficient) at the same time as the chemical gradients. Typically, the diffusive flux of compounds across the water-sediment interface is evaluated from the concentration gradient on the water side of the interface and the diffusion coefficient of the compounds in the water (Fernandez et al., 2014; Liu et al., 2013). This approach is easy to implement because the diffusion coefficients of many compounds in pure water are reported in the literature (Hayduk and Laudie, 1974; Schwarzenbach et al., 2003) but suffers from a lack of precision because the thickness of the concentration gradient on the water side is very small (on the order of μm; Fernandez et al., 2014) and the concentrations inside and/or at the boundary of the gradient are difficult to evaluate.

The motivation for this study is to quantify the diffusive flux exchange of 3 polycyclic aromatic hydrocarbons (PAH) inside the sediment bed (to a depth of 44 cm) and at the sediment-water interface in a complex natural system by measuring the concentration gradient of the pollutants and their in situ diffusivity in the sediment. Using this approach, the measurement of the diffusive flux is expected to be easier than in previous publications because it is based on the sediment side where several concentration point measurements could be performed (along the gradient). Contrary to the previous passive sampler-based studies that focus on the measurement of PAH flux across the water-sediment interface, the present work also attempts to investigate the characteristic time for PAH diffusion from the deep sediment towards the overlying water. For this purpose, 3 tasks were undertaken. (1) The desorption kinetics of 3 tracer compounds spiked in a set of passive samplers were used to evaluate site-specific diffusion coefficients of pollutants in the bedded sediments. (2) The concentration gradients of the PAH with depth were measured using passive samplers. (3) Finally, both measurements were used to calculate the fluxes of compounds in the sediment bed and across the sediment interface. This study presents a new approach that combines tracer compound techniques and the passive sampler methodology to investigate the movement of PAH in the deep sediment and in the vicinity of the water-sediment interface. The results can serve as an example that can be extended to other classes of compounds in the future.

## 2. Materials and methods

### 2.1. Chemicals and sampling strategy

The studied site is an urban storm water pond located in suburban Lille (Northern France). The pond has an area of 33 ha and receives water from 5 other connected ponds and the runoff from the surrounding area. Its estimated volume is 634,000 m³, and its average depth is of 1.5 m. At the base of the pond a compacted clay liner limits hydraulic exchange with the groundwater.

Passive samplers were exposed over the course of 21 days near the outlet of the lake in a muddy area to simplify deployment of the devices on the pond floor. Since part of the study focuses on the spatial variability of the results, two devices were exposed at the same location, while a second duplicate was exposed approximately 10 m away from the first pair (elsewhere referred as site A and site B, respectively). Each passive sampler device consists of two 50-μm-thick PE strips (5 × 70 cm) attached to a galvanized holder (following the setup described by Belles et al. (2016d)). In the field, the passive sampler devices were inserted into the muddy sediment by pushing them with a telescopic pole. In this way, the samplers provided information about the contamination of pore water between 0 and 44 cm below the interface and about the contamination in the water column between 0 and 13 cm above the interface (Fernandez et al., 2014). Before use, the PE strips were soaked twice in dichloromethane for a 1 week period and dried at 60 °C for 5 h. Subsequently, 3 labelled compounds (fluorene-d10, fluoranthene-d10 and pyrene-d10) were spiked in the polymer sheets following the procedure recommended by Booij et al. (2002). The amount of added compounds was selected in order to reach a compound concentration of approximately 6 μg/g in the polymer. After exposure, the passive