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A new application of passive samplers as indicators of *in-situ* biodegradation processes

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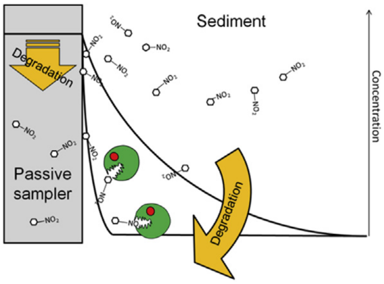
HIGHLIGHTS

- Passive samplers were used with tracer compounds to analyze degradation processes.
- Degradation increases the dissipation of labeled nitro-PAH from passive samplers.
- In-situ nitro-PAH degradation was demonstrated in field sediments.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a method for evaluating the *in-situ* degradation of nitro polycyclic aromatic hydrocarbons (nitro-PAH) in sediments is presented. The methodology is adapted from the passive sampler technique, which commonly uses the dissipation rate of labeled compounds loaded in passive sampler devices to sense the environmental conditions of exposure. In the present study, polymeric passive samplers (made of polyethylene strips) loaded with a set of labeled polycyclic aromatic hydrocarbons (PAH) and nitro-PAH were immersed in sediments (in field and laboratory conditions) to track the degradation processes. This approach is theoretically based on the fact that a degradation process induces a steeper concentration gradient of the labeled compounds in the surrounding sediment, thereby increasing their compound dissipation rates compared with their dissipation in abiotic conditions. Postulating that the degradation magnitude is the same for the labeled compounds loaded in polyethylene strips and for their native homologs that are potentially present in the sediment, the field degradation of 3 nitro-PAH (2-nitro-fluorene, 1-nitro-pyrene, 6-nitro-chrysene) was semi-quantitatively analyzed using the developed method.

1. Introduction

Regulated PAH (16 compounds according to the USEPA) are among the main compound classes responsible for sediment pollution. They produce numerous degradation products, and their occurrence, persistence and fate in the aquatic environment have been studied extensively. Conversely, the occurrence and persistence of nitro polycyclic aromatic hydrocarbons (nitro-PAH), are rarely reported in the literature, although they have stronger carcinogenic and mutagenic activities than do the parent PAH (Yaffe

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et al., 2001). Nitro-PAH are mostly released or formed in the atmosphere, associated with particulate matters and are then deposited on land or water surfaces, which makes them likely to end up in sediments (Huang et al., 2014). It appears that due to their hydrophobic properties and health risks, the simultaneous assessment of the nitro-PAH and PAH is of great interest (Yaffe et al., 2001). However, although sediment is the site of numerous processes essential to understanding the fate of pollutants, a substantial lack of knowledge remains about the biodegradation processes of nitro-PAH and other anthropogenic pollutants.

In this context, the present study attempts to use a passive sampling methodology to assess degradation processes directly in field sediments with a minimum alteration of environmental conditions. Passive samplers were first used in a hydro-system research to define the dissolved concentration of pollutants in the water column (Adams et al., 2007; Belles et al., 2014; Fernandez et al., 2014) and the sediment compartment (Apell and Gschwend, 2014; Charrasse et al., 2014). Nowadays, they are increasingly used for other applications than dissolved concentration determination, such as determining the readily available fraction of compounds sorbed to the sediment particles (Smedes et al., 2013; Yates et al., 2013; Belles et al., 2016a). Among numerous other benefits, passive samplers also allow *in-situ* measurements to be obtained, which is essential for many situations in which grab sampling is not adequate because it could disturb several parameters, including those driving degradation processes. This is of particular value for developing new passive sampler applications aiming to assess *in-situ* degradation processes. In the present study, the degradation of compounds in the sediment in contact with the devices is expected to accelerate the dissipation of some labeled compounds that are spiked in the passive samplers because of the steeper concentration gradient in the surrounding sediment generated by the degradation processes. Ultimately, the dissipation rate of the labeled compounds could be used to evaluate the *in-situ* degradation of the corresponding unlabeled compounds in the sediment bed.

To implement the approach, the polyethylene (PE) to water distribution coefficients (K_{PE}) of the targeted PAH and nitro-PAH were measured to assess the affinity of both compound classes for the PE material. Next, the dissipation rates of 24 labeled PAH and nitro-PAH in consolidated sediments in biotic and abiotic conditions were determined. Finally, the *in-situ* dissipation rates of a selection of 8 PAH and nitro-PAH from devices exposed in bedded sediment were analyzed in the field.

2. Materials and methods

2.1. Chemicals and passive sampler preparation

PAH (naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, dibenz[a,h]anthracene and indeno[1,2,3-c,d]pyrene) and the nitro-PAH (1-nitro-naphthalene, 2-nitro-naphthalene, 5-nitro-acenaphthene, 2-nitro-fluorene, 3-nitro-fluoranthene-d9, 9-nitro-anthracene, 9-nitro-phenanthrene, 1-nitro-pyrene and 6-nitro-chrysene) were all purchased as native and ^{2}H-labeled compounds (excepted nitro-naphthalene and 9-nitro-phenanthrene) from LGC standards. Additionally, ^{13}C-labeled PCB 28/52/138/180, which are used as internal standards for some experiments, were purchased from Sigma-Aldrich. A list of the PAH and nitro-PAH screened in the study and their abbreviations is given in Table 1. All of the solvents, NaN_3 and PE sheets (100 μm thickness) were from Fischer Scientific. The temperature data logger used in the field and laboratory experiments was from Hobo.

2.2. Determination of the PE-to-water distribution coefficients

The distribution coefficients of the selected PAH and nitro-PAH between water and the PE (K_{PE}) were determined at 20 °C using 6 different concentration levels to examine the linear sorption isotherm (spanning almost 2 orders of magnitude). For this purpose, 6 amber glass bottles with 3 polyethylene pieces (approximately 5 mg each) were stored (under stirring) for 90 d in 1 L of water spiked with various amounts of unlabeled PAH and nitro-PAH. After equilibration, the resulting concentrations in the aqueous phase ranged between 3 and 5028 ng L^{-1}, depending on the compound and the spiking treatment. The bottle spiked with 640 ng of PAH and nitro-PAH was replicated at 4 °C to examine the temperature dependency of K_{PE}. The same experiments were replicated for a period of 124 d to confirm the equilibrium achievement. After the selected time period, all of the polymer pieces and water samples were extracted and analyzed separately as described in Section 2.6.

2.3. Characterization of the selected site

The study site is an urban water pond (Heron Lake) that collects the runoff water of the city of Villeneuve d'Ascq (France). The pond is 33 ha and has an average depth of 1.5 m and a volume of 634 000 m^3. A preliminary study conducted on 40 subsamples of a 60-cm sediment core showed a low but significant contamination by PAH and nitro-PAH derivatives (average $\sum_{16}$PAH = 1086 ng g^{-1}; average $\sum_{8}$nitro-PAH = 0.5 ng g^{-1}) (Table 1). Similarly, Huang et al. (2014) estimated the nitro-PAH concentration, including 1-N-Nap, 2-N-Flo, 1-N-Pyr and 6-N-Chr, to be 2.9–18.6 ng g^{-1} in Lake Michigan sediment. Moreover, in Europe, nitro-PAH including 1-N-Nap, 1-N-Pyr and 6-N-Chr have been found at ng g^{-1} levels in sediments from the Elbe River (Lübcke-von Varel et al., 2011, 2012). Although our nitro-PAH concentrations are lower than those reported in the literature, they are consistent with previous studies that reported nitro-PAH levels between 100 and 1000 times lower than the parent PAH (Lübcke-von Varel et al., 2011).

2.4. Laboratory study of PAH and nitro-PAH degradation

Fourteen kilograms of sediment were collected at the output area of the pond and were homogenized using a 1000-W mixer (Metland MP-Mix). The sediment was divided into 2 pools (3.23 kg each): the first was mixed with 35 g of NaN_3 to inhibit bacterial activity and was left to consolidate under an 8-cm-diameter glass column, whereas the second was mixed with 35 g of NaCl to correct the experimental conditions for an identical ionic strength and was left to consolidate in an identical glass column. The resulting sediment columns were capped by 5 cm of water that was left in contact with the laboratory air. Three PE sheets (26 cm × 5 cm × 100 μm; 1.2 g) were spiked with all of the available ^{2}H-labeled PAH and nitro-PAH by soaking for 1 month in 1 L of methanol-water mixture (50/50:v/v) fortified with 7.2 μg of each compound (Booij et al., 2002; Belles et al.,2016b). Labeled compounds were used to spike the PE sheets to measure their dissipation without interfering with the native PAH and nitro-PAH that were originally present in the sediment. One of the 3 sheets was conserved to assess the initial amounts of loaded compounds, and the remaining sheets were vertically exposed in the NaN_3 poisoned and un-poisoned sediment columns. The volume of the sediment and its expected affinity for the studied compounds are assumed to be sufficiently large to allow the free decay of PAH and nitro-PAH spiked in the PE sheets (infinite sink assumption). After 18 days