



Bioavailability of classical and novel flame retardants: Effect of fullerene presence



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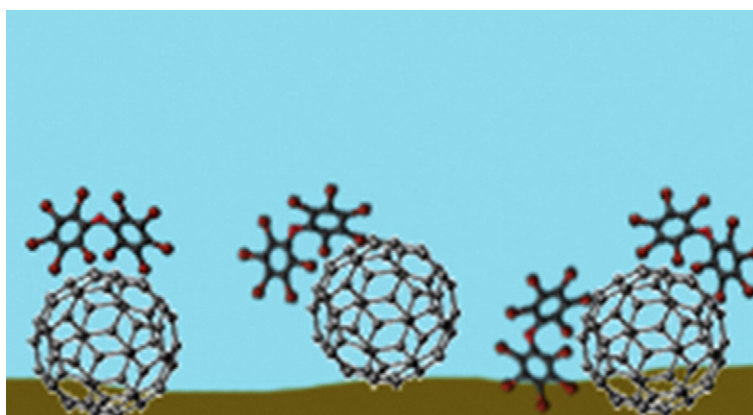
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HIGHLIGHTS

- PBDE, MeO-PBDE and novel FR bioavailability was determined using Tenax extractions.
- Emerging FRs have similar bioavailability to PBDEs, then similar risk to organisms.
- Decrease of bioavailability with TOC and time aged increases were observed.
- Pollutant retention in sediment is favoured by NMs, reducing impact on organisms.

GRAPHICAL ABSTRACT



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ABSTRACT

To understand the behavior of some emerging flame retardants (FRs) in the environment, a nonexhaustive extraction using Tenax was applied to study their behavior in aquatic ecosystems. Desorption of 8 polybrominated diphenyl ethers (PBDEs), 8 methoxylated PBDEs, 3 emerging brominated FRs and 6 halogenated norbornenes from sediments spiked in the laboratory was studied. Results showed that emerging FRs have a similar bioavailability than that of legacy FRs, already banned. In addition, some parameters such as sediment total organic carbon (TOC), aging or nanomaterial (NMs) presence in the sediment were modified in order to study their effects on the bioavailability of FRs. Bioavailability increases with a diminution of sediment TOC, while diminishes with an increase of aging. The study of effect of NM presence was performed at three different pH (acidic, neutral and basic), and for the three scenarios, FR bioavailability decreased with NM presence. The retention of pollutants in the sediment seems to be favoured by NM presence, minimizing their impact on living organisms.

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1. Introduction

Studies related to halogenated flame retardants (HFRs) are mostly confined to the analysis of sediments and biota. However, even if these studies are important because they give us information about

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the occurrence of HFRs, they do not explain the behavior of these contaminants once they are in the environment. When HFRs end up in the rivers, they tend to be adsorbed in the sediment. Nevertheless, not all the HFRs present in the sediment are available for the uptake or transformation by living organisms. Depending on their physical and chemical properties the contaminants can be more or less reticent to stay in the sediment. The properties of the sediment also play an important role to understand their behavior. Properties such as total organic carbon (TOC) or the presence of other substances in the sediment can decrease or increase the bioavailability of the contaminants present in there.

Recent advances in nanotechnology and the corresponding increase in the use of nanomaterials (NMs) in products in every sector of society have resulted in uncertainties regarding their environmental impact. NMs are shown to be taken up in the gastro intestinal tract of several aquatic and terrestrial organisms and may act as a carrier for traditional toxic chemicals, a mechanism referred to as Trojan horse effect (Cho et al., 2008). Recent studies have shown that the presence of NMs can alter the behavior of halogenated organic contaminants (HOCs). For instance, (Gao et al., 2008) suggested that Hg sorbed onto SiO₂-TiO₂ nanocomposites could become more bioavailable and toxic if introduced in natural systems. Carbon nanotubes can also affect the microbial degradation of polycyclic aromatic hydrocarbons (PAHs) in sediments (Cui et al., 2011), inhibiting the degradation up to 60% or absorb HOCs on their surface, due to the NMs surface and HOCs apolar nature (Cui et al., 2011; Deng et al., 2012). Different C₆₀-derivatives have been also investigated as potential vectors. Bioaccumulation studies with phenanthrene in *Daphnia magna* showed that the uptake of phenanthrene was faster when C₆₀ was present in suspension (Baun et al., 2008). An in vitro study by Ribas Ferreira et al. (2014) showed that C₆₀ increased cellular intake of benzo[a]pyrene in a *Danio rerio* (zebrafish). Recently, Sanchís et al. (2016) assessed synergistic and antagonistic effects of mixtures composed of one carbon nanomaterial (fullerene-soot, multiwall carbon nanotubes or graphene) and one organic contaminant (malathion, glyphosate, diuron, triclosan or nonylphenol) on the aquatic toxicology. Toxicity to *D. magna* was as higher with the fullerene presence, followed by multiwall carbon nanotubes and finally graphene.

To better understand the HFR behavior it is necessary to use nonexhaustive extraction techniques, which are based on the fact that contaminants in a freely dissolved or weakly adsorbed state are more available to aquatic organisms than those strongly attached to particles (Voie et al., 2002). One of these techniques is the extraction with a polymeric adsorbent, where contaminated sediment is placed in water together with a polymer, which has a great affinity for HFRs. The concentration of the contaminants in the water during the experiment is virtually zero, so this method is considered a solid-solid extraction between the sediment and the polymer. There are different types of polymers that can be used, one of them are the Tenax beads. A simple method using Tenax extractions was developed and validated by (Cornelissen et al., 1997). The method was based on using Tenax, a polymeric sorbent synthesized from 2,6-diphenyl-*p*-phenylene oxide, as solid-phase extraction for measuring the rate of mass transfer from sediment to the Tenax. Determination of the rapidly desorbing fraction by Tenax extraction has been proven several times to correlate well with the fraction that a living organism can take up or degrade from sediment (Cornelissen et al., 1998a; Kraaij et al., 2002; Kukkonen et al., 2004). Different studies have been carried out applying Tenax extraction to study the desorption of different HOCs such as PAHs, polychlorinated biphenyls (PCBs) (Kukkonen et al., 2004), dichlorodiphenyltrichloroethane (DDT) and polybrominated diphenyl ethers (PBDEs) (de la Cal et al., 2008).

FRs are widely used to increase the fire resistance of some materials. Among them, halogenated FRs are one of the most widely used. The most studied are PBDEs, which were added in 2009 to the Annex A of the Stockholm Convention. Thus, their production and use are expected to end eventually, leading to the introduction of new compounds as

substitutes. Industries are producing and using emerging FRs such as pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), decabromodiphenyl ethane (DBDPE) and halogenated norbornenes (HNs) as PBDE substitutes. These compounds have some similarities to PBDEs, such as toxicity and high hydrophobicity. Besides these compounds, there is a family of naturally produced compounds, methoxylated PBDEs (MeO-PBDEs), which are produced by marine organism (Vetter et al., 2002; Malmvärn et al., 2005). This family has similar properties as PBDEs, and can be also bioaccumulated through the trophic chain (Weijs et al., 2009).

The aim of this study was to evaluate the bioavailability of classical PBDEs, their naturally-produced methoxylated homologues MeO-PBDEs and novel FRs, using Tenax extractions. The effect of some sediment properties will be also tested, including TOC, aging (time of residence of the contaminants in the sediment) and the presence of other organics such as fullerenes.

2. Materials and methods

2.1. Chemicals

PBDEs and MeO-PBDEs were obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). PBEB, HBB, DBDPE, *syn*-Decchlorane Plus (*syn*-DP), *anti*-Decchlorane Plus (*anti*-DP) and Decchlorane Plus monoadduct (DPMA) were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Decchlorane 602 (Dec 602), Decchlorane 603 (Dec 603) and Decchlorane (Dec 604) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). Fullerenes C₆₀ and C₇₀ were purchased from Sigma Aldrich (St. Louis, MO, USA). Tenax-TA (20/35 mesh) was acquired from Buchem (Apeldoorn, The Netherlands). Copper (<63 μm) was purchased from Merck (Darmstadt, Germany). Acetone, dichloromethane (DCM), hexane, toluene and water solvents for organic trace analysis were obtained from Avantor Performance Materials (Center Valley, PA, USA).

2.2. Sediment spiking

A sediment sample from the Llobregat River (northeastern Spain), far away from potential sources of contamination, was used for the experiments. Sediment was homogenized and 2-mm mesh sieved and stored at 4 °C. Exhaustive extraction of this sediment showed the absence of target chemicals, with the exception of a minimum amount of BDE-47 and BDE-209, which was negligible in comparison to amounts spiked to perform the experiments. TOC was determined after removal of carbonates with HCl to be 2.99% of dry weight (dw). The pH of the sediment was also determined, being 7.7. Wet weight equivalent to 2 g dw of sediment was spiked on its surface with a solution of PBDEs, MeO-PBDEs, emerging BFRs and HNs to reach individual concentrations of 15 ng/g dw for BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, 6-MeO-BDE-47, 2-MeO-BDE-68, 5-MeO-BDE-47, 4-MeO-BDE-49, 5-MeO-BDE-100, 4-MeO-BDE-103, 5-MeO-BDE-99, 4-MeO-BDE-101, HBB and PBEB, 150 ng/g dw for BDE-209 and 250 ng/g dw for DBDPE, Dec 602, Dec 603, Dec 604, *syn*-DP, *anti*-DP and DPMA. After allowing the solvent evaporation briefly under a nitrogen stream, the spiked sediment was shaken vigorously using a rolling wheel for 10 min. Then it was kept at 4 °C for 12 h.

In order to test the effect of some sediment properties on the bioavailability of selected pollutants, some characteristics of the sediment were modified. To test the effect of NM presence, the sediment was spiked to reach a concentration of 25 μg/g dw of both fullerene C₆₀ and C₇₀. This spike was made three hours after FR addition, to let the contaminant be in contact with the sediment. In order to assure the homogenous distribution of fullerenes into the sediment, a spike in toluene was added drop by drop distributing it throughout the available sediment surface. Then, the spiked sediment was shaken during four hours in the dark at 4 °C. It is expected that some aggregation of nano-

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