



Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma



Influence of natural organic matter on the extraction efficiency of flame retardants from surface waters

Jakob Gustavsson^{a,*}, Lutz Ahrens^a, Minh A. Nguyen^a, Sarah Josefsson^{a,b},
Dan Berggren Kleja^c, Karin Wiberg^a

^a Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Box 7050, SE-75007, Uppsala, Sweden

^b Geological Survey of Sweden, Box 670, 75128 Uppsala, Sweden

^c Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7050, SE-75007, Uppsala, Sweden

ARTICLE INFO

Article history:

Received 21 June 2017
Received in revised form
26 September 2017
Accepted 2 October 2017
Available online xxx

Keywords:

Flame retardant
Solid-phase extraction
Natural organic matter
Gas chromatography
Mass spectrometry

ABSTRACT

The influence of natural organic matter (NOM) on the solid-phase extraction (SPE) efficiency was investigated for legacy and emerging flame retardants (FRs; $n = 26$) in surface water. Three different groups of FRs were analyzed: polybrominated diphenyl ethers (PBDEs), halogenated flame retardants (HFRs), and organophosphorus flame retardants (OPFRs). In addition, five sorbents (Amberlite XAD-2, Amberlite IRA-743, Oasis HLB, Chromabond HR-P, and Chromabond HR-X) were evaluated for the extraction of FRs ($n = 33$) in water, of which Oasis HLB eluted with dichloromethane and acetone:*n*-hexane (1:1, v/v) provided the highest overall recoveries. In subsequent NOM experiments, where FRs were extracted from water containing different NOM concentrations, both increased and decreased extraction efficiency with increasing NOM level were observed. Physicochemical and semi-empirical quantum chemistry properties were calculated for the FRs and used for analyzing relations between FRs. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) showed that the FRs separated into four different groups based on their properties. The FRs within each group responded similarly to increasing NOM, while differences in behavior were observed between the groups. This suggests that the structural properties of micropollutants highly influence NOM-FR interaction mechanisms. For instance, at high NOM levels, recoveries decreased substantially for FRs containing a moiety that can form strong hydrogen bonds (such as the double-bonded oxygen in e.g., OPFRs). Many of the compounds showed maximum extraction efficiency at higher levels of NOM. This suggests that binding of NOM to the sorbent and subsequent interaction between sorbent-bound NOM and FRs is an important mechanism for extraction of micropollutants from surface waters.

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1. Introduction

Flame retardants (FRs) are widely used to provide fire protection [1–4] in daily life and industrial products, such as carpets, furniture, electronics, and building insulation. As a result, they are ubiquitously spread in the environment [2,5]. In the past, polybrominated diphenyl ethers (PBDEs) were used extensively as FRs. Nowadays, their use is restricted and banned as a consequence of concerns about their persistence, bioaccumulation, and potential health effects [6–8]. This has led to an increase in the use and environmental occurrence of alternative FRs [3–5,9–14], many of which possess similar physicochemical properties and environ-

mental persistence as the banned FRs [15,16]. Current analytical methods employ different isolation strategies (e.g., liquid-liquid extraction (LLE) [17–29] and solid-phase extraction (SPE)) and are typically developed for one, or more rarely, two classes of FRs using SPE sorbents such as XAD-2 [20], IRA-743 [30,31], and HLB [32]. Thus, there is a lack of trace analytical methods covering several classes of FRs. Only two studies have reported on a method covering several classes of FRs (PBDEs, halogenated FRs (HFRs), and organophosphorus FRs (OPFRs)) [12,32], and only one of these involved water samples.

Natural organic matter (NOM), conventionally measured as dissolved organic carbon (DOC), is a major constituent in natural waters around the world. Typical DOC concentrations in freshwaters range from 1.0 to 25 mg L⁻¹ [33,34], although DOC concentrations of more than 100 mg L⁻¹ have been reported [34,35]. The DOC concentrations in natural waters thus vary substantially

* Corresponding author.

E-mail address: jakob.gustavsson@slu.se (J. Gustavsson).

between different waters, but also within the same water body within and between years [33,36] as a result of e.g., seasonal hydrological events such as spring flood or heavy rainfall [37,38]. The NOM in soils is commonly fractionated into three groups, humin, humic acids, and fulvic acids, based on their solubility in strong acid and base [39]. Fulvic acids are more polar and water soluble than humic acids and humin [40], and therefore dominate the organic content of natural waters together with smaller, more hydrophilic molecules [35,41]. Organic micropollutants, especially those with high hydrophobicity (i.e., high K_{OW} values), have a favorable partitioning towards the organic microenvironments that are formed within NOM molecules in natural waters [42]. This may drastically alter the fate of micropollutants such as organic FRs in the environment [43] by making them more mobile. The interaction with NOM might also render FRs less bioavailable and therefore less degradable by biological and chemical processes [44].

Levels of FRs in pristine aqueous environments are low and require sensitive analytical methods and high enrichment factors; for example, sampling volumes of up to 1000 L have been reported for analysis of FRs (e.g., [21]). This also results in high enrichment factors for matrix components, which may have adverse effects on instrumental analysis [45–47] and on the recovery of target compounds when using e.g., SPE for water samples. This has previously been demonstrated for polycyclic aromatic hydrocarbons (PAHs) [48,49], pesticides [50,51], and polychlorinated biphenyls (PCBs) [52]. However, despite NOM being a major component in natural waters, little is known about its influence on the extraction efficiency of FRs and other POPs. Thus, there is a need to investigate the influence of NOM on the extraction efficiency of SPE. This is of particular importance for alternative FRs, since corresponding isotopically labeled standards used to correct for sample treatment losses are often not commercially available.

The main aim of this work was to investigate the influence of dissolved NOM on the extraction efficiency of legacy and alternative FRs in natural waters. Three classes of organic FRs were used as model substances: PBDEs, HFRs (containing bromine/chlorine), and OPFRs (containing phosphate), together covering a wide range of physicochemical properties. Specific objectives were to: (i) evaluate five sorbents (viz. Amberlite XAD-2, Amberlite IRA-743, Chromabond HR-P, Chromabond HR-X, and Oasis HLB) for the extraction of legacy and emerging FRs ($n=33$) in natural water, (ii) investigate the influence of dissolved NOM (fulvic acids) on the extraction efficiency of selected FRs ($n=26$), and (iii) increase understanding of how different physicochemical properties of the FRs affect the relative influence of dissolved NOM on extraction efficiency (recovery) and of the mechanisms behind the observed effects. To the best of our knowledge, the impact of NOM on SPE extraction has not been explored previously for FRs, which is also the case for other POPs using HLB as a sorbent, despite HLB being a commonly employed sorbent in the analysis of micropollutants in natural waters (e.g., [28,32,53]).

2. Experimental

The method development involved two experiments: Experiment 1a, where elution solvents were evaluated by spiking FRs directly onto sorbents, and Experiment 1b, where the performance of selected sorbents was studied by direct spiking of FRs (as in 1a) and using natural water. In a subsequent experiment (Experiment 2, Section 2.3), the behavior of FRs in the presence of NOM at different levels was studied using artificial fresh water (OECD guideline 201 [54]). The FRs included in the three experiments are listed in Table S1 in the Supporting Information (SI). Experiment 2 focused on alternative FRs and included fewer PBDEs, but more HFRs and OPFRs.

2.1. Chemicals and equipment

In total, 50 legacy and alternative FRs were studied, including 24 PBDEs, 19 HFRs, and seven OPFRs. One OPFR included in this study (TDCIPP) also contains chlorine, but for simplicity was classified solely as an OPFR. When available, abbreviations suggested by Bergman et al. [55] are used. PBDEs, TBP-AE, BATE, BTBPE, DBE-DBCH, DBS, DDC-CO, EH-TBB, HBB, PBB-Acr, PBBB, PBCH, PBEB, PBPAE, PBT, TBP-DBPE, TBCO, TBCT, TBNPA, TBX, EHDPP, *o*-TMPP, *m*-TMPP, *p*-TMPP, TBPP, TDCIPP, and TiPPP were obtained from Sigma-Aldrich (St. Louis, MO, USA), Wellington Laboratories (Guelph, ON, Canada), Accustandard (New Haven, CT, USA), BOC Sciences (Shirley, NY, USA), Chemos (Regenstauf, Germany), Carbone Scientific (London, UK), and MolMall Sarl (Lonay, Switzerland). Mirex (Cambridge Isotope Laboratories, Inc., Andover, MA, USA) and $^{13}\text{C}_{12}$ -BDE77 (Wellington Laboratories) were used as recovery standards (RS). The systematic name, CAS no., and structure of all FRs included are presented in Table 1. Detailed information about use and purity of reference compounds and isotopically labelled RS can be found in Table S2 in the SI.

The solvents toluene, dichloromethane, isooctane, and acetone (SupraSolv[®]) were purchased from Merck (Darmstadt, Germany), and cyclohexane (pesticide residue grade) was purchased from Fisher Scientific (Stockholm, Sweden). Solid chemicals included ammonium chloride, magnesium chloride (pro analysis), calcium chloride, magnesium sulfate, potassium dihydrogen phosphate (Emsure[®], Merck, Darmstadt, Germany), sodium bicarbonate (99%, Fisher Scientific, Stockholm, Sweden), and anhydrous sodium sulfate (AnalaR Normapur[®], VWR, Radnor, PA, USA). The five tested sorbents were purchased from Sigma-Aldrich (Amberlite XAD-2 and Amberlite IRA-743), Waters (Oasis HLB; Milford, MA, USA), and Macherey-Nagel (Chromabond HR-X and Chromabond HR-P; Düren, Germany). Fulvic acid (Nordic Aquatic Fulvic Acid Reference) was purchased from the International Humic Substances Society (IHSS; St. Paul, MA, USA). Glass beads (\varnothing 5 mm), glass wool, and glass-fiber filters (Whatman[®] GF/F, diameter 293 mm, 0.7 μm pore size) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Glass columns (i.d. 18 mm, length 250 mm) with stopcocks were custom-made by Saveen and Werner AB (Limhamn, Sweden) and 15 mL SPE cartridges were purchased from Macherey-Nagel. The pumps used were of type Masterflex L/S (Cole-Parmer, Vernon Hills, IL, USA) with Masterflex Norprene tubing. Sample containers (3 US gallons/ ~11 L) made of stainless steel were purchased from Sharpsville container/NSF Component[®] (Sharpsville, PA, USA). Extracts were dried with a DryDisk[®] separation membrane (Horizon Technology, Salem, NH, USA) and concentrated using a Biotage TurboVap II system (Uppsala, Sweden) and an Organomation N-EVAP Nitrogen Evaporator (Berlin, MA, USA). Milli-Q water (Millipore) was produced in-house by filtration through a MilliPak[®] 0.22 μm filter.

2.2. Method development for analysis of FRs in water (Experiment 1)

2.2.1. SPE column preparation

For XAD-2 and IRA-743 (pre-cleaned by Soxhlet extraction, 24 h toluene, 24 h acetone), glass columns were packed from the bottom and up with: 0.5 g glass wool (pre-cleaned by Soxhlet, 24 h toluene, 24 h acetone), 25 g sorbent, 1 g glass wool, and finally ~30 g glass beads (pre-cleaned by heating at 400 °C for four hours) to keep the sorbent in place. For HR-P, HR-X, and HLB, 4 g portions of sorbent were packed into 15 mL SPE cartridges with one frit on top and one at the bottom.

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