Trends in Analytical Chemistry 103 (2018) 137–155

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

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

Analytical challenges to determine emerging persistent organic pollutants in aquatic ecosystems

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ARTICLE INFO

Article history:
Available online 10 April 2018

Keywords:
Emerging persistent organic pollutants
Perfluoroalkyl substances
Novel brominated flame retardants
Organophosphorus flame retardants
Aquatic ecosystem
Sample treatment
Extraction
Analytical determination

ABSTRACT

Emerging persistent organic pollutants (ePOPs) include polybrominated diphenyl ethers (PBDEs) and perfluorooctane sulfonyl fluoride/perfluorooctane sulfonate (POSF/PFOS), which are newly listed in the Stockholm Convention. Other ePOPs, which have not been regulated, include organophosphate flame retardants (PFRs), novel brominated flame retardants (NBFRs) and other perfluoroalkyl substances (PFASs). Often ePOPs data related to occurrence, toxicity, impact or environmental behavior are insufficient or inadequate because of the lack of proper analytical methods to obtain them. Thus, a critical review of the analytical procedures proposed in the last six years (2011–2017) for determining ePOPs by chromatographic methods in the different compartments of the aquatic ecosystems is presented. The overall analytical procedure, from sampling to final determination, is emphasized presenting recent developments in the extraction, pre-concentration, and instrumental detection needed for the accurate quantification of ePOPs in environmental samples. Finally, this review examines the basic challenges we face in order to anticipate future directions and urgent needs of this field.

Abbreviations: μSIS, micro-selected ion storage mode; 1-MP, 1-methyl-piperidine; AA, ammonium acetate; ACE, acetone; ACN, acetonitrile; AcOH, acetic acid; AF, ammonium formate; APCI, atmospheric pressure chemical ionization; APPI, atmospheric pressure photoionization; BTBPE, 1,2-bis-(2,4,6-tribromophenoxy) ethane; CAR, carboxen; CI, chemical ionization; cLC, capillary liquid chromatography; DAD, diode array detection; DBDPE, Decabromodiphenyl ethane; DCM, dichloromethane; DDA, data dependent analysis; DI, direct injection; DIA, data independent analysis; DLLME, dispersive liquid-liquid microextraction; dSPE, dispersive solid-phase extraction; DVB, divinylbenzene; EI, electron ionization; ECNI, electron capture negative chemical ionization; ePOP, emerging persistent organic pollutant; ESI, electrospray ionization; EtAc, Ethyl acetate; FA, formic acid; FOSA, perfluoroalkyl sulfonamides; FOSE, perfluoroalkyl sulfonamide ethanol; FTOH, fluorotelomer alcohols; FUSLE, focused ultrasound solid-liquid extraction; GC, gas chromatography; GCB, graphitized carbon black; GCxGC, comprehensive two-dimensional gas chromatography; GPC, gel permeation chromatography; HBCD, hexabromocyclododecane; HEX, hexane; HPLC, high performance liquid chromatography; HRMS, high-resolution mass spectrometry; HRPS, high resolution product scan; HS, headspace; ICP, inductively coupled plasma; IDA, information dependent acquisition; ILL, immobilized ionic liquid; IMS, ion-mobility mass spectrometry; LC, liquid chromatography; LDTD, laser diode thermal desorption; LLE, liquid-liquid extraction; LLP, Liquid-liquid partition; LOD, limit of detection; LOQ, limit of quantification; MAE, microwave assisted extraction; MeOH, methanol; MS/MS, tandem mass spectrometry; MS, mass spectrometry; MSPD, matrix solid-phase dispersion; MTBE, methyl tert-butyl ether; N-EtFOSA, 2-ethylperfluoro-1-octanesulfonamide; N-EtFOSE, 2-(*N*-ethylperfluoro-1-octanesulfonamido)-ethanol; N-MeFOSA, *N*-methylperfluoro-1-octanesulfonamide; N-MeFOSE, 2-(*N*-methylperfluoro-1-octanesulfonamido)-ethanol; NBFR, novel brominated flame retardant; NCI, negative chemical ionization; nLC, nano liquid chromatography; PBDE, polybrominated diphenyl ether; PBT, pentabromotoluene; PDMS, polydimethylsiloxane; PFAS, perfluoroalkyl substance; PFBA, perfluorobutanoic acid; PFBS, perfluorobutane sulfonate; PFCA, perfluoroalkyl carboxylic acids; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonate; PFP, pentafluorophenyl; PFR, organophosphate flame retardant; PFSA, perfluoroalkyl sulfonic acids; PLE, pressurized liquid extraction; POP, persistent organic pollutant; POSF, perfluorooctane sulfonyl fluoride; PRM, parallel reaction monitoring; PSA, primary secondary amina; QqLIT, quadrupole linear ion trap; QqQ, triple quadrupole; QqTOF, quadrupole time-of-flight; QuEChERS, quick, easy, cheap, effective, rugged and safe extraction method; RP, reversed phase; SEC, size exclusion chromatography; SFC, supercritical fluid chromatography; SLE, solid-liquid extraction; SPE, solid-phase extraction; SPLE, selective pressurized liquid extraction; SPM, solid particulate matter; SPME, solid-phase microextraction; SRM, selected reaction monitoring; TBAS, tetrabutyl ammonium hydrogen sulphate; TBBPA, tetrabromobisphenol-A; TCEP, tris(2-chloroethyl) phosphate; TCIPP, tris(2-chloroisopropyl) phosphate; TDCPP, tris(1,3-dichloro-2-propyl) phosphate; TEHP, tris(2-ethylhexyl) phosphate; TFC, turbulent flow chromatography; TMPP, tricresyl phosphate; TPhP, triphenyl phosphate; TPP, tripropyl phosphate; t-SIM, targeted selected ion monitoring; UHPLC, ultra-high performance liquid chromatography; UPC^2, ultra-performance convergence chromatography; USE, ultrasound assisted extraction; WAX, weak anion exchange; WW, wastewater.

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https://doi.org/10.1016/j.trac.2018.04.003
0165-9936/

1. Introduction

According to the Stockholm Convention on persistent organic pollutants (POPs) [1], these compounds are resistant to chemical, biological, and photolytic environmental degradation. POPs are stable and persistent, long-distance transportable, bioaccumulative, biomagnifiable in the food chain, and could pose significant impact on human health and the environment [2–7]. Exposure to POPs can cause serious health problems including certain cancers, birth defects and dysfunctional immune and reproductive systems, among others. Tracing the occurrence, distribution and fate of POPs in the environment is challenging because they can occur in different phases [*e.g.*, as a gas, dissolved and attached either to airborne particles or to solid particulate matter (SPM)] and can be exchanged among environmental compartments. Sediments can be considered as a sink of many POPs. Once POPs are released into waterbodies, they may also come into contact with SPM or they can be bioaccumulated in aquatic organisms, producing side effects [8]. Initially, twelve POPs coined as the "dirty dozen" were recognized as causing adverse effects on humans and the ecosystem. These are legacy POPs, the behavior and toxicity of which are well-known and have been banned or strictly regulated under the United Nations Environment Program [1], the European Union [9], the United States Environmental Protection Agency and Environment Canada [10]. However, they are still found in the environment and used in some developing countries.

Currently, there is a rising concern about the presence of new organic synthetic compounds in the environment, the so-called new or emerging contaminants. In many cases, these compounds are present in the environment since long time ago but they have not been identified until the development of new and more sensitive analytical methods. Therefore, most of them are not regulated and their effects on the environment and human health are unknown. These emerging contaminants also included emerging POPs (ePOPs) that are either, very recently or not yet regulated. In 2009, polybrominated diphenyl ethers (PBDEs) and perfluorooctane sulfonyl fluoride/perfluorooctane sulfonate (POSF/PFOS) were added to the list of Stockholm Convention and hexabromocyclododecanes (HBCDs) listed as candidate. ePOPs include these substances as well as several others widely used in industrial processes and consumer products, such as perfluoroalkyl substances (PFASs), non-PBDEs or novel brominated flame retardants (NBFRs), organophosphate flame retardants (PFRs), Dechlorane plus and related compounds and sort-chain chlorinated paraffin that have been proposed as a replacement alternative for banned formulations [11,12]. The inclusion of some of these group as ePOPs is still controversial. PFRs are prone to be metabolized by liver in organisms [13]. The metabolites of PFRs, mainly diesters, have been found in numerous studies [14]. However, most of the studies considered them as ePOPs. Table 1 classifies ePOPs according to their chemical structure and physico-chemical properties. These compounds have a wide range of physical-chemical properties as water solubility, polarity, volatility, etc. As a whole ePOPs exhibit properties different from legacy POPs. These new POPs belong to several chemical classes with different origins and are often more polar, less volatile, even though some NBFRs, such as DP and DBDPE are lipophilic. This renders to an analytical determination much more demanding and difficult, particularly for the assessment of the aquatic ecosystems introducing a number of analytical matters that need to be solved. Moreover, ultra-trace analysis of these contaminants in aquatic environments is problematic due to the complexity and diversity of natural matrices, including biotic ones that are lipid-rich (the Achilles' heel within efficient extraction).

Due to the high number of ePOPs, this review focuses on NBFRs, PFRs and PFASs because of their widespread use. Previous reviews on analytical aspects of these ePOPs in several matrices can be found for NBFRs [11,15], PFRs [16] and PFASs [17–19]. These reviews are partial, need an update or are not focused on aquatic ecosystems. One book chapter by Guo and Kannan [20] presented an overview of the methodology to analyze traditional and new POPs in environmental matrices, but the wide coverage and the higher number of studies on the former had as a counterpart that methods related to the latter were scarce and less representative. Then, our critical review that provides a broader coverage on analytical challenges for ePOPs would be useful. In it, we outline the most recent extraction techniques, clean-up procedures and instrumental analyses of ePOPs in aquatic environment matrices published since 2011 offering a global overview of the analysis of ePOPs. The review also discusses the advantages and disadvantages of these techniques as well as future prospects related to the extraction and determination of ePOPs.

2. Sample extraction and clean-up

Current extraction and clean-up procedures for the analysis of ePOPs are summarized in Tables 2 and 3 for water and any other aquatic environmental matrices, respectively, and discussed in the following sections.

2.1. Understanding types and sources of sample contamination within QC/QA

Sampling procedures have a direct impact on the quality of analytical data. These topics were already detailed in deep in a previous review on legacy and new ePOPs and do not change since many years ago [18]. Relevant samples in the aquatic ecosystems are water and solid samples as sediment and/or biota. Aquatic biota (biofilm, macroinvertebrates, mollusc or fish) is sampled scrapping the rock surface, collected the species from water or using electric fishing and/or contacting to the local associations of fishermen, depending on the type of specimens [21–23]. The most common sediments samples reported to determine ePOPs are superficial samples taken with a grab sampler (dredgers, shovels, scoops, etc.) [23–25]. As these compounds are emerging POPs, deep sediment cores have not been reported yet. ePOPs are at low concentration in water samples, in addition to convention 1 or 2 L grab samples, both higher volume grab samples or passive samplers are commonly used. Even polar PFASs were sampled in Polar Organic Chemical Integrative Samplers (POCISs) filled as receiving phase materials with ionic liquids, HLB, Isolut ENV$^+$, carbonaceous materials, etc. [22,26,27]. To minimize the risks of sample contamination and to ensure sample integrity, basic precautions must be taken. Sample containers should be previously rinsed to eliminate any trace amount of ePOPs and after sampling, they must be sealed [28]. Furthermore, the quality control (QC) can play an important role to avoid contamination during sampling and transport, through the use of field blanks and field duplicate samples.

Once in laboratory, blank contamination is an important issue to take into account during the sample preparation process because of the ubiquity of ePOPs in laboratory material and equipment, and their presence in indoor air and dust. Some strategies to avoid or reduce blank contamination are: (i) rinse, heat and keep wrap in aluminum foil the non-volumetric material before use, (ii) minimize surface contact during sample handling, (iii) work in a cleanroom, (iv) reduce the use of plastic materials, or (v) perform a pre-extraction of materials that are used have been reported [16,23,29–35]. In the case of instrumental contamination, the replacement of some pieces by other fabricated with different