



Review

Organophosphate flame retardants (OPFRs): A review on analytical methods and occurrence in wastewater and aquatic environment



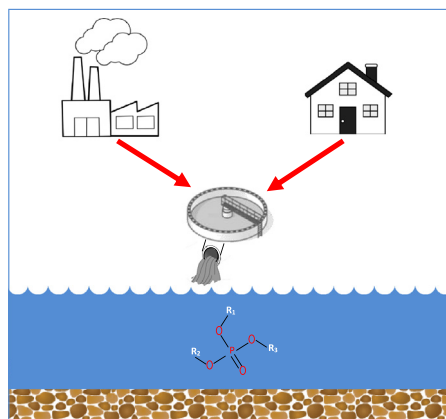
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HIGHLIGHTS

- This paper is an overview of OPFRs in waters.
- OPFRs are among the most frequently detected compounds in waters.
- Wastewater is a significant source of OPFRs in surface water.
- Occurrence and profile in aquatic environment reflects differences in production and use.

GRAPHICAL ABSTRACT



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ABSTRACT

Nowadays, there is an increasing concern for organophosphate flame retardants (OPFRs) due to high production and use following the phase out and stringent regulation in the use of brominated flame retardants. OPFRs represent a group of compounds with a wide range in their polarity, solubility and persistence. OPFRs are widely used as flame retardants in various consumer products such as textiles, electronics, industrial materials and furniture to prevent the risk of fire. They are also utilized as plasticizers, antifoaming or anti-wear agents in lacquers, hydraulic fluids and floor polishing agents. The present review outlines the current state of knowledge regarding the analytical methodology applied for their determination in wastewater and aquatic environment as well as their occurrence in water, wastewater, sediments and sludge. Knowledge gaps and future perspectives have been identified, which include the elucidation of sources, pathways and fate of OPFRs in aquatic environment and possible risks.

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Contents

1. Introduction	248
2. Searching methodology	248

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3.	Overview of characteristics and production	249
4.	Analytical methodologies	249
4.1.	Sampling/sample preparation	249
4.1.1.	Water and wastewater	249
4.1.2.	Sediments and sludge	249
4.2.	Extraction and clean-up	250
4.2.1.	Water and wastewater	250
4.2.2.	Sediments and sludge	251
4.2.3.	Clean-up	251
4.3.	Instrumental analysis	251
5.	Occurrence and fate of OPFRs in waters	256
5.1.	Wastewater and sludge	256
5.2.	Waters and sediments	259
5.2.1.	River water	259
5.2.2.	Seawater	260
5.2.3.	Drinking water	260
5.2.4.	Sediments	260
6.	Conclusions and future perspectives	261
	References	261

1. Introduction

Flame retardants (FRs) are chemical additives incorporated into combustible materials to prevent a fire or to delay its start and propagation by interrupting or hindering the combustion process. The use of these substances has proved to be lifesaving and also a key factor preventing injuries and property losses (EFRA, 2007). FRs are divided into 3 major categories depending on their chemical composition: a) inorganic FRs, b) halogenated FRs, with brominated and chlorinated FRs, c) organophosphorus-containing FRs (Van der Veen and De Boer, 2012). Despite their benefits, Environmental Protection Agency (EPA) is concerned about FRs, because they are widely used in products, such as electronics, vehicles, polyurethane foams or textiles and many of them could persist in the environment and be hazardous to people and animals (US EPA, 2016).

For many decades, brominated FRs, such as polybrominated diphenyl ethers (PBDEs) were highly used. However, due to their persistence, bioaccumulation in aquatic and terrestrial food chains and toxicity they were considered persistent organic pollutants (POPs) by the Stockholm Convention (2008). Due to these findings, PBDEs were banned for production and use in the European Union and have been voluntarily phased out of the US market (European Commission, 2017; US EPA, 2015a). Consequently, the use of emerging compounds, such as novel brominated FRs and organophosphate FRs (OPFRs) have been introduced in the market (Iqbal et al., 2017).

According to the European Flame Retardants Association (EFRA), the total consumption of FRs in Europe was estimated at 465,000 t in 2006, of which 10% were brominated FRs and 20% were OPFRs (EFRA, 2007). Most OPFRs have been regarded as high production volume chemicals, exceeding 1000 t per year in Europe (ECB, 2008). They are not chemically bound to materials and are easily released into the environment by volatilization, abrasion, and dissolution (Lai et al., 2015; Marklund et al., 2005a). Therefore there is interest regarding their environmental occurrence, fate and effects. Recent studies report their presence in aquatic, terrestrial, and atmospheric environment (He et al., 2017; Lee et al., 2018; Shi et al., 2016; Wolschke et al., 2015).

The effects of exposure to organophosphate flame retardants have not been studied to the same extent as for the phased-out brominated compounds, and are therefore less well-known. Recent studies focus on the assessment of the toxicity of OPFRs and their possible negative effects (Behl et al., 2016; Cristale et al., 2013; Gao et al., 2016; Shi et al., 2016). People are exposed to OPFRs in their everyday life through skin contact, ingestion of dust, inhalation and dietary intake, and may have potential adverse health effects (US EPA, 2015b). Particularly

there is concern on chlorinated phosphate ester cluster of flame retardants (Tris (chloroethyl) phosphate or TCEP, Tris (2-chloroisopropyl) phosphate or TCIPP and Tris (1,3-dichloro-2-propyl) phosphate or TDCIPP). According to the Danish Environmental Protection Agency there is anxiety on the presence of these OPFRs in children's products (Lassen et al., 2016). The European Commission has adopted specific limit values for their presence in toys, reaching at 5 mg kg⁻¹ (European Commission, 2014). Recently, various environmental organizations have submitted a Petition to the US EPA requiring further tests to assess if TCEP, TCIPP, and TDCIPP present an important risk to health or environment due to possible toxicity and persistence (US EPA, 2017).

This article provides a synthesis and critical evaluation of the state of knowledge about OPFRs occurring in wastewater treatment plants and aquatic environment based on updated information after an extended bibliographic survey for the period 2008–2018. Particularly, the analytical methodologies (extraction, clean up and detection) for the determination of OPFRs in water, sediment, wastewater and sludge were presented. The occurrence, distribution and fate of OPFRs in wastewater treatment plants and surface waters have been reviewed. Research gaps were identified to define the directions and the primary emphasis of future studies.

2. Searching methodology

This review aims to incorporate the majority of the studies that have been carried out and are available in the scientific literature regarding the occurrence and analysis of OPFRs. The following inclusion criteria were considered: 1) the studies must be published in a scientific journal, 2) they must refer the occurrence of OPFRs in water, wastewater, sediment and sludge samples, 3) different pretreatment techniques (extraction) and chromatographic techniques should be detailed.

The data used in this study were based on the online database of Science Direct covering studies published from 2008 to 2018 using the following keywords (and their combinations): “OPFRs”, “organophosphate flame retardants”, “water”, “wastewater”, “drinking water”, “surface water”, “sediments”, “occurrence”. The last search was conducted on June 2018.

A total of 1084 articles (keyword; organophosphate flame retardants) in the past 10 years from the online database of the Science Direct were found. Articles in this area increased exponentially from 2008 to 2018 (Fig. 1). Comparison of data from different sources worldwide needs attention because of the differences in the number of congeners used for the sum of OPFRs, different analytical protocols, sampling,

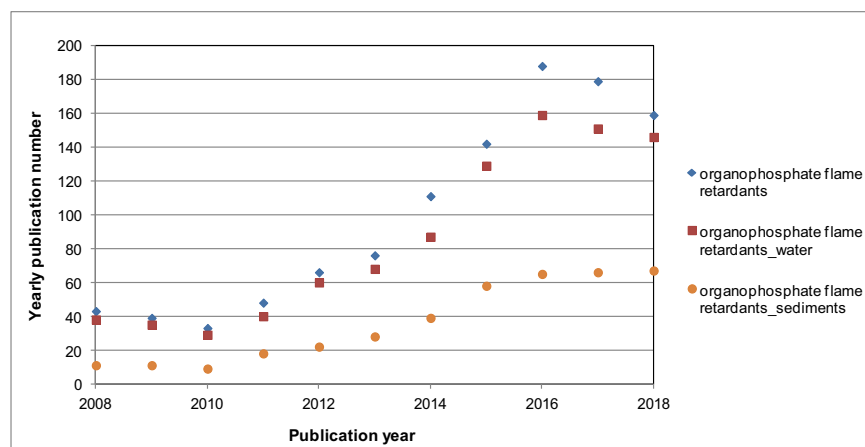


Fig. 1. A 10-year summary of publications in the field of OPFRs.

as well as treatment of concentrations below the limit of quantification and detection.

3. Overview of characteristics and production

In general, phosphorus-containing flame retardants are referred as esters of phosphoric acid along with phosphonates, phosphinates, red phosphorus and ammonium polyphosphate. Esters of phosphoric acid are mostly referred to triesters, and less often to diesters and monoesters. This study focus on triesters containing either aromatic or aliphatic groups. Table 1 presents the names, abbreviations and chemical properties of most common OPFRs covered in this review. Different abbreviations for the same chemical have been used so far. To avoid confusions Bergman et al. (2012) proposed practical abbreviations for OPFRs that were adopted in this article (Table 1).

Non chlorinated alkyl/aryl phosphates, such as TBOEP, TEHP, TNBP and TPHP are mainly employed as plasticizers, lubricants, antifoaming agents, additives to lacquers, in hydraulic fluids or floor polishing. Several chloroalkyl phosphates, such as TCEP, TCIPP and TDCIPP are additive flame retardants applied to polyurethane and other polymers for use in furniture, construction, textile industry and electronic equipment (EURAR, 2009a; EURAR, 2009b; WHO, 2000). According to a US EPA survey, TBOEP, TNBP and TCEP were listed as high production volume chemicals with individual production volumes from 1 to 10 million pounds annually (US EPA, 2010). In 2016, organophosphate compounds represented the second most produced flame retardant group reaching 18% of the total market worldwide. Global consumption of OPFRs increased from 186,000 t in 2001 to 680,000 t in 2015 (Van der Veen and de Boer, 2012; Wang et al., 2015).

Due to the varying nature of substituents, OPFRs have a wide range of physical and chemical properties, ranging from very polar to highly hydrophobic (Table 1). Certain compounds with high K_{ow} may present relatively high bioaccumulative potential. The presence of OPFRs in remote/polar regions implying possible long-range atmospheric transport (LRAT). Möller et al. (2012) determined OPFRs in airborne particles over oceans suggesting that these compounds can undergo medium to long range atmospheric transport over the global oceans towards Arctic and Antarctic areas. OPFRs have been also determined in ocean sediments (Ma et al., 2017) in Arctic area implying that these compounds are transported to long distances similarly to traditional POPs. The presence of OPFRs in northern Swedish rivers, in absence of a specific point source, has been reported by Gustavsson et al. (2018) who suggested LRAT as major source pathway. OPEs are not considered persistent organic pollutants as defined by the Stockholm Convention because they easily degrade in sunlight, particularly through OH radical processes and have a short half-life. According to Liagkouridis et al. (2015) OPFRs indicate low hazard for the environment with regard to LRAT

criteria. But nonetheless their presence in remote arctic areas suggest a POP-like behavior. It seems that, besides the properties of pure chemical compound, other ways of transport such as particle phase heterogeneous processes should account for the evaluation of environmental persistence and long range transport. The results from Liu et al. (2014) demonstrated an enhancement of atmospheric persistence for OPFRs that are associated to particles with regard to OH radical oxidation. The lifetimes of particle phase OPFRs were substantial higher than those of gas phase OPFRs (3.5–14 d vs <2 d); this is consistent with the assumption that OPFRs can undergo medium or long-range transport, as previously proposed on the basis of field measurements.

4. Analytical methodologies

4.1. Sampling/sample preparation

4.1.1. Water and wastewater

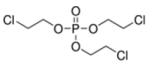
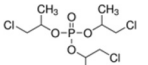
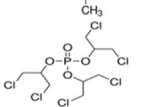
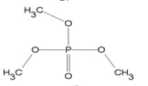
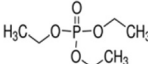
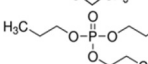
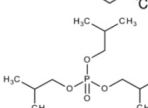
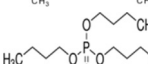
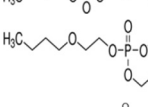
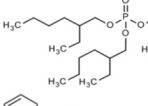
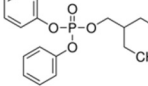
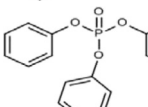
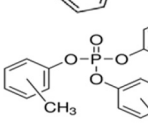
Conventional methods of screening for OPFRs rely on water analysis of grab samples from aquatic environment. Sampling of aqueous samples were collected in a stainless steel bucket (Gustavsson et al., 2018) or in a polypropylene or polyethylene bottle Hu et al., 2014; Lee et al., 2018; Wolschke et al., 2015). All sampling equipment was pre-rinsed with ethanol, Milli-Q water, and acetone before use in a clean lab and then rinsed three times with water sample prior to collection (Gustavsson et al., 2018; Wang et al., 2015). To avoid dust from fingers contaminating the samples, single-use gloves were used during the sampling. Collected samples were stored in tightly sealed stainless steel containers or glass bottles with no light permeability, at 4 °C until extraction and analysis within 1 month. Usually a filtration through glass fiber filters was employed upon transportation to the laboratory to remove suspended particles.

Recently, a passive sampling method for monitoring of OPFRs in aquatic environment has been studied and validated by Yang et al. (2017). Modified polar organic integrative samplers with OASIS HLB as sorbent were employed for passive sampling of OPFRs. Sampling rates were found under different conditions in the laboratory and field exposure experiments. The aqueous concentrations of OPFRs as time weighted average concentrations (TWA) were determined after two weeks of exposure in Yangtze river, China.

4.1.2. Sediments and sludge

Various investigators studied the presence of OPFRs in solid samples such as sediments and sludge. Sediment samples were usually collected using a box core sampler or stainless steel shovels. Samples were stored in amber glass bottles instead of plastic containers to avoid the interference of OPFRs. Aluminum-foil or polyethylene bags have been also used. Upon transportation to the laboratory, samples freeze-dried. After that,

Table 1
OPFRs reviewed in this paper and their physicochemical properties.

Compound	Abbr.	CAS no.	Chemical structure	Molecular formula	Henry's law constant (atm m ³ mol ⁻¹ , 25 °C)	Water solubility (mg L ⁻¹ , 25 °C)	Vapour pressure (mm Hg, 25 °C)	LogK _{ow}	BCF
Tris (chloroethyl) phosphate	TCEP	115-96-8		C ₆ H ₁₂ Cl ₃ O ₄ P	1.67×10^{-7}	7000	0.061	1.63	0.425
Tris (2-chloroisopropyl) phosphate	TCIPP	13674-84-5		C ₉ H ₁₈ Cl ₃ O ₄ P	4.69×10^{-7}	1200	5.64×10^{-5}	2.89	3.27
Tris (1,3-dichloro-2-propyl) phosphate	TDCIPP	13674-87-8		C ₉ H ₁₅ Cl ₆ O ₄ P	1.08×10^{-7}	7	2.98×10^{-7}	3.65	21.4
Trimethyl phosphate	TMP	512-56-1		C ₃ H ₉ O ₄ P	2.57×10^{-7}	50,000	0.85	-0.60	3.16
Triethyl phosphate	TEP	78-40-0		C ₆ H ₁₅ O ₄ P	3.55×10^{-6}	50,000	0.39	0.87	3.16
Tripropyl phosphate	TPP	513-08-06		C ₉ H ₂₁ O ₄ P	8.25×10^{-6}	6450	0.024	2.35	0.912
Tris (isobutyl) phosphate	TIBP	126-71-6		C ₁₂ H ₂₇ O ₄ P	2.76×10^{-4}	475.6	0.013	3.60	19.51
Tri-n-butyl phosphate	TNBP	126-73-8		C ₁₂ H ₂₇ O ₄ P	1.66×10^{-4}	280	1.13×10^{-3}	3.82	39.81
Tris (2-butoxyethyl) phosphate	TBOEP	78-51-3		C ₁₈ H ₃₉ O ₇ P	3.28×10^{-7}	1100	1.23×10^{-6}	3.00	25.56
Tris (2-ethylhexyl) phosphate	TEHP	78-42-2		C ₂₄ H ₅₁ O ₄ P	2.38×10^{-2}	0.6	8.25×10^{-8}	9.49	3.162
2-Ethylhexyl diphenyl phosphate	EHDPP	1241-94-7		C ₂₀ H ₂₇ O ₄ P	2.39×10^{-4}	1.9	5×10^{-5}	6.30	855.3
Tris (phenyl) phosphate	TPHP	115-86-6		C ₁₈ H ₁₅ O ₄ P	1.96×10^{-7}	1.9	1.12×10^{-5}	4.70	113.3
Tris (methylphenyl) phosphate (or Tricresyl phosphate)	TMPP	1330-78-5		C ₂₁ H ₂₁ O ₄ P	9.21×10^{-7}	0.3	1.1×10^{-7}	6.34	2534

Abbr: abbreviation; CAS no.: chemical abstract service number; log K_{ow}: octanol-water partition coefficient; BCF: bioaccumulation factor. The data are compiled from US EPA EPISuite™ (2018, version 4.11, USA), Chemspider (2018) and Sigma-Aldrich (2018).

samples were sieved by stainless-steel sieves (usually <400 µm) and stored at -20 °C until further treatment (Gao et al., 2016; Hu et al., 2017; Pang et al., 2016; Wang et al., 2018).

4.2. Extraction and clean-up

4.2.1. Water and wastewater

Liquid-liquid extraction (LLE) and solid phase extraction (SPE) are the most frequently used techniques for the recovery of OPFRs from water/wastewater samples (Table 2). OPFRs are effectively extracted by LLE with dichloromethane (Martínez-Carballo et al., 2007; Wang et al., 2015; Wolschke et al., 2015). LLE has low equipment cost, however it demands large amounts of solvents and is associated with emulsion formation, contamination from glassware and analyte losses

(Pawliszyn and Lord, 2010). SPE is a popular technique, because it doesn't consume large volumes of toxic organic solvents, analysis time is shorter, and on-line or automated procedures can be easily designed (Pawliszyn and Lord, 2010). Various SPE have been used for the extraction of OPFRs from waters and wastewaters (Table 2); Oasis HLB and ENVI-18 are the most commonly used for this purpose. Several extractive solvents have been used for the elution of the OPFRs; acetonitrile, ethyl acetate, dichloromethane/hexane or methanol. In general, SPE and LLE work well and give efficient recoveries for most OPFRs (Table 2). However, poor recoveries have been reported for TMP (the most polar and volatile compound) (Wang et al., 2011), as well as EHDPP and TEHP (Li et al., 2014). In addition, the presence of natural organic matter in water samples could adversely affect the efficiency of the extraction (Gustavsson et al., 2017a).

Microextraction techniques that use minor amounts of solvents or solvent-free extraction techniques have been applied for the recovery of OPFRs. García-López et al. (2007) proposed dispersive liquid–liquid microextraction (DLLME) for the extraction of 10 OPFRs by adding 1 mL acetone containing 2% of 1,1,1-trichloroethane to 10 mL of sample with 20% sodium chloride. Solid-phase microextraction (SPME), a relatively simple and solvent-free procedure, has also been used for the extraction of OPFRs (Rodríguez et al., 2006; Tsao et al., 2011; Gao et al., 2013; Jin et al., 2016). The efficiency of different SPME fibers (PDMS, CAR-PDMS, PDMS-DVB, PDMS-CAR-DVB, and CW-DVB) was tested for the recovery of OPFRs from water (Rodríguez et al., 2006). PDMS-DVB, at room temperature, in the direct-sampling (DS) mode, with the addition of NaCl to increase the yield of extraction for the most polar OPFRs, was found as the best choice for OPFRs with a broad range of volatility and polarity. To avoid matrix effects and improve the extraction efficiency, Tsao et al. (2011) employed microwave-assisted head-space SPME technique (MA-HS-SPME). PDMS-DVB fiber reached maximum extraction within 5 min at 140 W. Lately, new SPME fibers have been developed. Stainless steel fibers coated with an ionic liquid-based sol-gel (Gao et al., 2013) or a graphene oxide based sol-gel (Jin et al., 2016) in a headspace solid-phase microextraction showed high extraction capabilities.

4.2.2. Sediments and sludge

Soxhlet extraction and ultrasonic extraction have been used for the recovery of OPFRs from sediments (Table 3). Target compounds were extracted with solvents, such as dichloromethane/hexane, acetone/hexane or ethyl acetate/hexane. (Lee et al., 2018; Hu et al., 2017; Cristale and Lacorte, 2013). Soxhlet extraction is time consuming; usually the duration of extraction is 16–24 h and uses high volumes of solvents (Hu et al., 2017; Lee et al., 2018; Woudneh et al., 2015). On the other hand, ultrasonic extraction demands lower volumes of solvents and shorter times (10–30 min) usually in 2–3 repeated cycles (Cristale and Lacorte, 2013; Wang et al., 2018). Moreover, microwave assisted extraction (MAE) and pressurized liquid extraction (PLE) have been also used (García-López et al., 2009; Giulivo et al., 2017). These techniques employed higher temperatures and pressures that allow better penetration of solvent in the sample, resulting in efficient extraction of OPFRs in shorter times with less volume of solvents. García-López et al. (2009) used MAE for extraction of OPFRs from sediment at 150 °C in two sequential steps of 15 min duration, using 5 mL of solvent (acetone and acetonitrile) for 0.5 g of sample. Pressurized liquid extraction (PLE) was employed for the recovery of OPFRs from sediments by Giulivo et al. (2017) using hexane: acetone (1:1) at 1500 psi and 100 °C. Moreover, these techniques are automated and permit the extraction of many samples simultaneously.

Lately, there is a concern on the bioavailable fraction of organic compounds in sediments, besides total concentration, since it reflects better the actual risk (You et al., 2011). He et al. (2017) used SPME and Tenax extraction to assess the bioavailable fraction of TCIPP and TDCIPP in sediments. The SPME fiber measured the chemical activity in sediments to estimate the freely dissolved pore water concentrations. In this case, target compounds were absorbed in a PDMS SPME fiber, when sediments were mixed with calcium chloride (0.01 M) and sodium azide (50 mg L⁻¹). Afterwards, target compounds were desorbed from SPME fibers in ethyl acetate for 36 h at 4 °C. Tenax was used to estimate the amount of chemicals desorbed from the sediments. In this case Tenax was added in a mixture of sediment, calcium chloride (0.01 M) and sodium azide. After this, Tenax was placed in a vial and sonicated sequentially with acetone and acetone: hexane (1:1 v/v) for 10 min. The extracts were combined, concentrated and analysed for desorbed OPFRs.

4.2.3. Clean-up

A clean-up step through column chromatography usually follows extraction process of environmental samples to minimize matrix

effects. Clean up should only remove matrix components that may affect the performance of analytical methods and not the target analytes. Most studies in water samples did not include a clean up step. However, recently Gustavsson et al. (2017b) reported the necessity for a clean up step for surface waters. He tested the efficiency of three sorbents, florisil (10% deactivation), alumina (6% deactivation) and acidified silica (40% H₂SO₄ w/w) in river water sample; alumina showed better efficiency for most OPFRs.

A clean-up is usually employed in solid samples as necessary step to remove matrix interferences. Oasis HLB, florisil and silica cartridges have been used for this purpose in sediments and sludge samples (Table 3) (Aznar-Aleman et al., 2018; Cristale et al., 2013; Liang et al., 2018; Martínez-Carballo et al., 2007; Pang et al., 2016; Wang et al., 2018). Elemental sulfur, often encountered in sediments, is considered as serious interference in analysis of organic micropollutants since is responsible for masking effects in chromatograms. For this purpose activated copper granules are added to avoid this interference on GC–MS performance.

After the recovery of OPFRs from clean-up step, eluents dried with a gentle flow of nitrogen and reconstituted with suitable solvents for chromatographic analysis (i.e. acetonitrile/water for LC-MS/MS or iso-octane for GC–MS). Samples can be usually spiked with internal standards such as deuterated OPFRs; TNBP-d27 and TPHP-d15 (Cristale and Lacorte, 2013; He et al., 2017; Wang et al., 2018) to check for the efficiency of clean up step.

4.3. Instrumental analysis

There is a growing need to develop reliable analytical methods, which enable a rapid, sensitive and selective determination of these emerging pollutants in environmental samples (Rodil et al., 2009). Due to the varying nature of substituents, OPFRs have a wide range of physical and chemical properties, ranging from very polar to very hydrophobic. Method development should focus on exploiting all features to enhance sensitivity and to obtain accurate quantification. Several instrumental methodologies are already available in the literature for the determination of OPFRs in surface water, wastewater and sediments. The OPFRs determined in most studies are triesters of OPFRs, mainly aryl phosphates, alkyl phosphates and chlorinated alkyl phosphates. These compounds are detected by using gas or liquid chromatography (GC or LC), in combination with mass spectrometry or selective detectors, after a previous extraction/clean up step (Hao et al., 2018; Pang et al., 2016; Rodríguez et al., 2006; Wolschke et al., 2015) (Tables 2 and 3).

GC has been used for determination for non-polar compounds, using non-polar stationary phases, mostly 5% phenyl methyl-polysiloxane, such as HP5, DB-5MS. The column lengths vary from 15 m to 30 m; most common are columns of 30 m × 0.25 mm of internal diameter and 0.25 µm of film thickness (Cristale et al., 2013; Jin et al., 2016). There are difficulties in separation and detection of certain OPFRs components depending on the material of stationary phase. Rodríguez et al. (2006) tested the efficiency of two capillary columns with the same dimensions (30 m × 0.25 mm i.d., 0.25 µm film thickness) but different coated phases: a DB-5 ((5%-phenyl)-methylpolysiloxane) and a SPB-1701 ((14%-cyanopropyl-phenyl)-methyl-polysiloxane). He reported good results for most OPFRs, but poor separation of TCEP and an isomer of TCIPP in SPB-1701 column and temperature dependent selectivity of TBOEP and TPHP in DB-5 column. Finally a DB-5 column was proposed as most suitable for his study.

Nitrogen phosphorous detector (NPD) has been used for determination of OPFRs in waters (Jin et al., 2016; Rodríguez et al., 2006). As an alternative to NPD, flame photometric detector (FPD), which can provide sensitivity and selectivity similar to NPD has been employed (Gao et al., 2013). However, the use of mass spectrometry offers certain advantages in identification of these compounds. Consequently, GC–MS or GC–MS/MS is the technique mostly used under electron impact ionization in

Table 2

Extraction conditions and analytical methods for the determination of OPFRs in water and wastewater samples.

Type of matrix	Extraction technique/conditions		Instrumental system	LOD ^a (ng L ⁻¹)	Recovery (%)	References
River water	SPE	Sample volume 500 mL Elution Solvent DCM, Hex, Ac Cartridges: Oasis HLB	GC–MS/MS, EI Column: DB-5MS Internal standard: TBP-D27, TPhP-D15	8–44	–	Cristale et al. (2013)
River water and wastewater	SPE	Sample volume 100–500 mL Elution solvent: MeOH Cartridges: OASIS MAX	LC–MS/MS ESI ⁺ or ESI [–] Column: C18 Eluents: Water/MeOH	0.1–1 (ng mL ⁻¹ , LOQ)	–	Garcia-Lopez et al. (2010)
River water	SPE	Sample volume 12,000 mL Elution solvent: DCM Cartridges: Amberlite XAD-2	GC–MS/MS EI, MRM Column: DB-5MS Internal standard: ¹³ C ₁₂ -BDE28, ¹³ C ₁₂ -BDE99, ¹³ C ₁₂ -BDE153	0.082–8.6 (MDL)	–	Gustavsson et al. (2018)
River and drinking water	SPME	Sample volume 10 mL Fiber: graphene-oxide based sol-gel coated fiber	GC–MS/MS Column HP5–MS	1.4–135.6	–	Jin et al. (2016)
River water	LLE	Sample volume 600 mL Elution solvent: DCM	GC–MS/MS EI, MRM Column: DB5–MS Internal standards: TCEP-D12, TCPP-D18, TDCPP-D15, TPhP-D15 as surrogate	0.13–9.6 (LOQ)	67–121	Lee et al. (2018)
River water	SPE	Sample volume: 1000 mL Elution Solvent: ethyl acetate Cartridges: OASIS HLB	GC–MS EI, SIM Column: RXI-17SIL MS Internal standards: TnPP-d ₂₁ , TnBP-d ₂₇ , TPhP-d ₁₅ , MGTBEP, TDCPP-d ₁₅ , T35DMPP-d ₉ , TCEP-d ₁₂ as surrogate	0.084–1.51	–	Loos et al. (2017)
River water and wastewater	SPE	Sample volume 1 L Elution solvent: MeOH/DCM Cartridges: Phenomenex Strata-X 33u	UHPLC–MS/MS ESI ⁺ , SRM Column: C18 Eluents: Water/MeOH Internal standards: TDCPP-D15, TPP-D15, TCEP-D12, TCIPP-D18	0.03–0.1 (ng mL ⁻¹)	94–106	Lorenzo et al. (2016)
River water and wastewater	LLE	Sample volume 500 or 800 mL Elution Solvent DCM	LC–MS/MS ESI ⁺ , MRM Column: Luna C8 Mobile phase: Water/MeOH Internal standards: TBP-D27	2.6–13 (MQL)	80–94 (TEP: 63, TCEP: 70)	Martínez-Carballo et al. (2007)
River water and wastewater	SPME	Sample volume 100–500 mL Fiber: PDMS-DVB	GC–NPD Column: DB-5MS, SPB-1701	0.005–0.01 (ng mL ⁻¹ , LOQ)	86.1–119.2 (TEHP: 26.7)	Rodriguez et al. (2006)
River water	SPE	Sample volume 500 mL Elution Solvent ACN Cartridges: Oasis HLB, C18, ODS-C18, WAX, MAX	LC–MS/MS Column: BEH C8 Eluents: Water/ACN (0.1% FA) gradient Internal standard: TBP-D27	2–6 (LOQ)	73–110 (TMP: <10, TEHP: 40–76)	Wang et al. (2011)
River water and wastewater	SPE	Sample volume < 2 L Elution solvent: ethyl acetate Cartridges: OASIS HLB	GC–NPD Column: DB-5MS, SPB-1701	–	82.8–109.7 (TEHP: 24)	Rodriguez et al. (2006)
River water	LLE	Sample volume 800 mL Elution solvent: DCM	GC–MS EI, SIM Column: HP-5MS Internal standards: 13C6-PCB 208 (TBP-D27 and TPP-D15 as surrogate)	0.02–0.54 (MDL)	67–95	Wang et al. (2015)
River water	SPE LLE	Sample volume: 500 mL Elution Solvent: DCM Sorbent: SERDOLITH PAD III (particle size 0.1–0.2 mm)	GC–MS/MS EI, MRM Column: HP5–MS Internal standards: TEP-D15, TCEP-D12, TBP-D27, TPhP-D15	2.7–26.6	43–78 (SPE) 45–77 (LLE)	Wolschke et al. (2015)
Fish farming water	SPE	Sample volume 700 mL Elution Solvent ethyl acetate & DCM Cartridges OASIS HLB	GC–MS EI, SIM Column: DB5–MS Internal standards: TDCPP-D15, TBP-D27, TCEP-D12, ¹³ C ₂ -TBEP, TPHP-D15	0.13–20.7	28–165	Aznar-Alemany et al. (2018)
Aqueous samples	SBSE	PDMS coated stir bar	GC–MS, EI Column: CP5860 Internal standards: d-TnBP, d-HDBP, and d-H ₂ MnBP	–	93–102	Bridoux et al. (2015)

Surface water	SPE	Sample volume 1 L Elution solvent: DCM Cartridges: n.m.	GC–MS EI, SIM Column: HP5–MS Internal standard: ¹³ C-hexachlorobenzene	0.1–3.9	30–105	Bollman et al. (2012)
Surface water and wastewater	SPME	Sample volume 10 mL Fiber: [AMIM][BF4)]-based sol–gel fibers	GC–FPD Column: HP-5MS	0.7–12 (MDL)	75.2–101.8	Gao et al. (2013)
Surface water	SPE	Sample volume 1–2.5 L Elution solvent: MeOH/ACN Cartridges: Bond Elute PPL	GC–MS SIM Column: n.m. Internal standard: squalane	3–30 (LOQ)	72–99	Regnery and Püttmann (2010)
Surface water, wastewater, rainwater, road run-offs	SPE	Sample volume 200 mL Elution solvent: DCM in ACN Cartridges: ENVI-18	LC–MS/MS ESI ⁺ , MRM Column: Mixed Mode HILIC-1 Eluents: Water/ACN Internal standards: TMP-D9, TEP-D15, TPrP-D21, TnBP-D27, TPhP-D15, TCPP-D18	0.3–16	64.8–103.9	Shi et al. (2016)
Surface water	SPE	Sample volume 500 mL Elution Solvent MeOH:MTBE 1:1 Cartridges OASIS HLB	GC–MS/MS EI, MRM Column: HP5–MS Internal standards: TCPP-D18, TDCPP-D15, TPP-D15, TBP-D27, TCEP-D12	0.5–14	85–132	Teo et al. (2015)
Surface water	SPE	Sample volume 1 L Elution solvent: MeOH/ACN Cartridges: Poly-Sery PSD	GC–MS EI, SIM Column: DB-5MS Internal standard: TnBP-D27	0.015–2	70.4–114.3 (TEHP: 34.3–69.3)	Yan et al. (2012)
Surface water and wastewater	MAE SPME	Sample volume 20 mL Fiber: PDMS–DVB	GC–MS, EI, SIM Column: DB-5MS	0.2–1.5	86–106	Tsao et al. (2011)
Drinking, surface, ground water, wastewater	Direct injection		LC–MS/MS ESI ⁺ , MRM Column: C18 Eluents: Water/MeOH or ACN Internal standards: TEP-D15, TPrP-D21, TBP-D27, TCEP-D12, TDCPP-D15, ¹³ C18-TPP, BDCP-D10 and ¹³ C2-TBEP	1.5–30 (IDL)	86–111	Hao et al. (2018)
Drinking water	SPE	Sample volume 1 L Elution solvent: Hex/DCM Cartridges: ENVI-18	GC–MS/MS EI, SIM Column: DB5–MS Internal standards: ¹³ C-PCB 141	0.027–0.3	77.38 (standard TCEP-d ₁₂)	Khan et al. (2016)
Drinking water	LLE	Sample volume 600 mL Elution solvent: DCM	GC–MS EI, SIM Column: DB5–MS Internal standards: TCEP-D12, TCPP-D18, TDCPP-D15, TPP-D15	0.7–2.96	67–125	Lee et al. (2016)
Drinking water	SPE	Sample volume 1 L Elution solvent: ACN Cartridges: ENVI-18	LC–MS/MS ESI ⁺ , MRM Column: BEH phenyl Eluents: Water/MeOH (0.1% FA) Internal standard: TBP-D27 as surrogate	0.5–1 (MDL)	70–99 (EHDPP: 19.3, TEHP: 38.4)	Li et al. (2014)
Tap water, surface water, wastewater	SPE	Sample volume 200–500 mL Elution Solvent MeOH Cartridges: Oasis HLB	LC–MS/MS, ESI ⁺ or ESI [−] , MRM Column: RP18 (+) or Phenyl-Hexyl (−) Eluents: Water/MeOH Internal standard: TEP-D15, TBP-D27, TPhP-D15	0.2–14	56–116	Rodil et al. (2009)
Seawater	SPE	Sample volume 500 mL Elution Solvent ACN Cartridges ENVI-18	LC–MS/MS ESI ⁺ , MRM Column: BEH phenyl Mobile phase: Water/ACN (0.1% FA) Internal standard: TBP-D27	0.5–1 (MQL)	66.7–104	Hu et al. (2014)
Seawater	SPE	Sample volume 1 L Elution solvent: ethyl acetate Cartridges: Oasis HLB	GC–MS EI, SIM Column: DB5–MS Internal standards: TnBP-D27, TCEP-D12, TPhP-D15	30–529 (MDL, pg L ^{−1})	80–101	Zhong et al. (2017)
Wastewater	SPE	Sample volume: 100 mL Elution Solvent: ACN	UPLC–MS/MS ESI ⁺	0.3–6.0	51.5–129 effl 42.7–125 infl	Liang et al. (2018)

(continued on next page)

Table 2 (continued)

Type of matrix	Extraction technique/conditions		Instrumental system	LOD ^a (ng L ⁻¹)	Recovery (%)	References
Wastewater	SPE	Cartridges: OASIS HLB	Column: BEH C18 Eluents: Water/ACN (0.1% FA) Internal standard: TBP-D27	30–3000	70–112 (TiBP: 50, TnBP: 53)	O'Brien et al. (2015)
		Sample volume 200 mL Elution solvent: MeOH, toluene Cartridges: OASIS MCX	GC–MS EI, SIM Column: BPX5 Internal standards: TPHP-D15, TNBP-D27, TCEP-D12, TDICPP-D15			
Influent and effluent wastewater	SPE	Sample volume 500 mL Elution solvent: DCM Cartridges: n.m.	LC–MS/MS ESI ⁺ , MRM Column: C18 Eluents: Water/MeOH Internal standards: TPP-D15, TCEP-D12, TCPP-D18, TnBP-D27, TDBPP-D15, TnPrP-D21	0.1–5	80–123	Woudneh et al. (2015)

LC: liquid chromatography; GC: gas chromatography; MS: mass spectrometry; UHPLC: ultra high pressure liquid chromatography; I.S.: internal standard; EI: electron ionization; ESI: electrospray ionization; MRM: multiple reaction monitoring; SIM: selective ion monitoring; ECNI: electron capture negative ionization; SRM: selective reaction monitoring; NPD: nitrogen phosphorus detector; FPD: flame photometric detector.

^a LOD: limit of detection; LOQ: limit of quantification; MDL: method detection limit; MQI: method quantification limit; IDL: instrumental detection limit.

Table 3

Extraction and clean-up conditions for the determination of OPFRs in sediment and sludge samples.

Extraction technique/solvent		Clean-up	Instrumental system	LOD ^a ($\mu\text{g kg}^{-1}$ dw)	Recoveries (%)	References
Sediments						
Soxhlet	Dichloromethane in hexane, 1:4	SPE Florisil cartridge Elution: ethyl acetate	GC–MS/MS Column DB-5MS MRM I.S. TCEP-Dd12, TCPP-D18, TDCPP-D15, TPHP-D15 as surrogate standard	0.02–1.44 (LOQ)	67–125	Lee et al. (2018)
Soxhlet	Hexane: acetone, 1:1	SPE Oasis HLB cartridge Elution: ethyl acetate	GC–MS Column DB-5MS ECNI, SIM I.S. TPHP-D15	0.0054–0.098 (MDL)	79.5–123.3	Hu et al. (2017)
Soxhlet	Acetone	SPE 50 mg silica cartridges Elution: ethyl acetate	GC–ICP–MS Column HP-5 I.S. Triphenyl phosphate (TPeP)		78–105	García-López et al. (2009)
MAE	Acetone and acetonitrile	SPE 50 mg silica cartridges Elution: ethyl acetate	GC–ICP–MS Column HP-5 I.S. Triphenyl phosphate (TPeP)		78–105	García-López et al. (2009)
PLE	Hexane: acetone, 1:1		LC–MS/MS Columns: Purosphere Star RP-18 ESI, SRM I.S. TCEP-D12, TDCPP-D15, TBP-D27, TPHP-D15, and ¹³ C2-TBEP	0.05–1.25	67–103 (TCEP: 51)	Giulivo et al. (2017)
SPME (bioavailable fraction-freely dissolved)	SPME fiber: PDMS CaCl ₂ + NaN ₃ Desorption: Ethyl acetate	–	GC–MS Column DB-5MS EI, SIM I.S. TNBP-D27	–	–	He et al. (2017)
Tenax (bioavailable fraction-absorbed)	Tenax + CaCl ₂ + NaN ₃ Acetone:hexane, 1:1	–	GC–MS Column DB-5MS EI, SIM I.S. TNBP-D27	–	–	He et al. (2017)
Sonication	Hexane: acetone, 1:1	SPE Florisil cartridge Elution: ethyl acetate	GC–MS Column DB-5MS EI I.S. TBP-D27, TPHP-D15	0.02–4.10	56.9–98.0	Wang et al. (2018)
Sonication	Ethyl acetate: cyclohexane, 5:2	SPE Florisil cartridge Elution: ethyl acetate:cyclohexane	GC–MS/MS Column DB-5MS EI, SRM I.S. TBP-D27, TPHP-D15	1.9–60	67–107 (TBEP: 48)	Cristale and Lacorte (2013)
Sludge						
Soxhlet	DCM:EtOAc acetate, 1:1	SPE Agilent Bond elute-NH ₂ cartridge Elution EtOAc:DCM, 1:9	LC–MS/MS Column C18 MS ESI ⁺ , MRM Mobile phase H ₂ O (0.1% FA + 0.1% AF)/MeOH (0.1% FA) I.S. TPP-D15, TCEP-D12, TCPP-D18, TnBP-D27, TDBPP-D15, TEP-D15, TnPrP-D21	0.01–0.5	83–124	Woudneh et al. (2015)
Sonication	Acetonitrile/H ₂ O (25/75 v/v)	SPE Oasis HLB cartridges Elution: ACN	HPLC–MS/MS Column BEH C18 ESI Gradient mobile phase: Water/ACN (0.1% FA) I.S. TnBP-D27	2–3 ng L ⁻¹	52.9–128	Pang et al. (2016)
Shaking	Acetonitrile	SPE ENVI-18 cartridges Elution: 25% DCM in ACN	LC–MS/MS Column Mixed-Mode HILIC-1 Mobile phase H ₂ O/ACN ESI ⁺ Gradient I.S. TMP-D9, TEP-D15, TPRP-D21, TNBP-D27, TPHP-D15	0.41–24.7	59.4–113.9	Gao et al. (2016)

LC: liquid chromatography; GC: gas chromatography; MS: mass spectrometry; I.S.: internal standard; EI: electron ionization; ESI: electrospray ionization; MRM: multiple reaction monitoring; SIM: selective ion monitoring; ECNI: electron capture negative ionization; SRM: selective reaction monitoring.

^a LOD: limit of detection; LOQ: limit of quantification; MDL: method detection limit;

selected ion monitoring (SIM) mode (Tables 5–6). According to Gustavsson et al. (2017b) both techniques showed similar detectability for most OPFRs, whereas other studies reported improvement of detection limits in GC–MS/MS due to better selectivity (Wolschke et al., 2015; Cristale et al., 2012). GC–MS under chemical ionization was less effective for most OPFRs, except for TCIPP that showed higher detectability (Cristale et al., 2012; Gustavsson et al., 2017b). García-López et al. (2009) proposed gas chromatography connected through a heated

interface with inductively coupled plasma mass spectrometry (GC–ICP–MS) for determination of ten OPFRs. This method provides good sensitivity and selectivity for determination of P-containing molecules in environmental matrices due to the combination of pulsed splitless injection with low radio frequency power and hard extraction conditions.

Liquid chromatography coupled with mass spectrometry is also suitable for the determination of OPFRs, which are not volatile enough for GC analysis, such as TEHP, EHDPP, TPHP, TMPP, and TNBP (Lorenzo

et al., 2016). As shown in Tables 2–3, liquid chromatography (LC) or ultra-high performance liquid chromatography (UPLC) were carried out in the reversed-phase mode, mainly using C18 or C8 stationary phases (UPLC BEH C18, Luna C8, Waters Xterra C18) or a combination of reversed phase with hydrophilic interactions column (HILIC-1). Generally, for the reversed-phase separation of OPFRs, mixtures of water (acidified with formic acid) with methanol or acetonitrile in gradient elution were used as mobile phases. LC-MS/MS or UHPLC-MS/MS methods using triple quadrupole (QqQ) mass analyzers were most frequently used to determine OPFRs in environmental samples because of their high sensitivity and selectivity. Analysis was undertaken using electrospray ionization (ESI) in positive or negative ionization mode depending on the compound and in the multiple selected reaction monitoring (MRM) acquisition mode.

In general, chromatographic methods coupled with mass spectrometry are characterized by accurate identification and quantification. However, matrix effects result to enhancement or suppression of the signal (Gustavsson et al., 2017b). To avoid this, isotopically labeled internal standard and isotopic dilution quantification methods were used (Tables 2–3). The limited availability of commercial standards and the relatively high cost could lead to alternative approaches such as matrix-matched calibration or standard addition method.

Chromatographic methods offered good recoveries and relative low quantification limits ($0.02\text{--}30\text{ ng L}^{-1}$) for most OPFRs. However, care must be taken on possible contamination due to the ubiquitous presence of OPFRs in laboratory air, dust and laboratory equipment (van der Veen and de Boer, 2012). In an interlaboratory study, evaluating the quality of the results of OPFRs in various matrices, blank problems for different OPFRs, mainly TNBP, TIBP, TBOEP and TCIPP, were found (Brandsma et al., 2013). Plastic containers were thought to be the main source of interferences of OPFRs. The use of glassware was proposed instead of plastic containers to avoid this contamination (Pang et al., 2016). Wang et al. (2011) reported TBOEP and TEHP as possible interference in the plastic/glass SPE cartridges, which could be eliminated with careful prewash with acetonitrile. Moreover, Rodriguez et al. (2006) showed that Teflon-layered silicone septum used to close the extraction vial was responsible for TBOEP.

Overall, to avoid contamination, all laboratory equipment (glass, stainless steel, or Teflon) must be controlled to be OPFRs-free. Glassware should be carefully cleaned, heated under high temperature ($100\text{--}400\text{ }^{\circ}\text{C}$ for 4–6 h) rinsed with polar and non-polar organic solvents and covered with aluminum foil until use (Brandsma et al., 2013; Giulivo et al., 2016; Gustavsson et al., 2018; Regnery and Püttmann, 2010).

5. Occurrence and fate of OPFRs in waters

As shown in Fig. 1 there is a growing concern regarding the occurrence and fate of OPFRs in aquatic environment. The levels of OPFRs usually measured in wastewaters, waters, sediments and sludge are shown in Tables 4–6. A direct comparison is difficult due to many and different species of OPFRs determined. Treated and untreated wastewater discharges were presumed to be a major entry pathway for OPFRs to surface water and affected groundwater through infiltration.

5.1. Wastewater and sludge

The research of OPFRs has been focused on wastewater treatment plants (WWTPs) lately. Few data is available regarding the fate of OPFRs during wastewater treatment. The occurrence of OPFRs in WWTPs either influent or effluent sewage sample and sewage sludge is shown in Table 4.

The most frequent and abundant OPFRs reported in wastewater (influent or effluent) are TBOEP, TCIPP, TCEP, and TNBP (Fig. 2). The presence of OPFRs in wastewaters could be due to their wide use in

Table 4
Concentrations^a of OPFRs in wastewater samples (ng L^{-1}) and sludge ($\mu\text{g kg}^{-1}$).

Type of matrix	Location	Period	n	TCEP	TCIPP	TDClPP	TNBP	TPP	TBOEP	TPHP	TEP	Ref.
Sludge (8 STPs)	China	2008–2010, 2014	43	<LOD–208	<LOD–378		1.2–286		6.3–281	4.4–66.8	<LOD–366	Gao et al. (2016)
Raw & treated WW (STPs)	Spain	09/2009	2	70 ^R 210 ^T	540 ^R 680 ^T	100 ^R 140 ^T	47 ^R 230 ^T		3100 ^R 3400 ^T			García-López et al. (2010)
Effluents (WWTP)	Canada	2014–2015	90	140–340	1250–2390	210–400	120–310	5760	290–10,200		80–290	Hao et al. (2018)
Effluent (WWTPs)	Europe	2010	16	130.9	1231.2	176.2	259.8	35.6	2220.3			Loos et al. (2012)
Effluents (16 WWTPs)	Austria	Summer 2005	16	<MQL–1600	270–1400	19–1400	<MQL–810		13–5400	<MQL–170	22–210	Martínez-Carballo et al. (2007)
Influent (11 STPs)	Australia	08/2011	24	200–600	500–4100	50–300	4.4–197 25.4		400–6600	4.4–46.4		O'Brien et al. (2015)
Sewage sludges (WWTPs)	China	–	24	5–203	7–161				1.60–383			Pang et al. (2016)
				43	33.6				36	15		
Raw & treated WW (WWTP)	Spain	11/2007	4	127–359 ^R	616–630 ^R		784–1246 ^R		1004–1285 ^R		59–92 ^R	Rodil et al. (2009)
				57–90 ^T	344–2612 ^T		141–317 ^T		693–3705 ^T		49–76 ^T	
Influent & effluent (7 STPs)	China	10/2013	14	150 ^T	465 ^T		120 ^T		398 ^T	15 ^T	47 ^T	Shi et al. (2016)
				254 ^E	605 ^E		93 ^E		103 ^E	6 ^E	64 ^E	
Aqueous: Influent & effluent	Canada	09/2014	12	598 ^T	380 ^T	227 ^T	747 ^T	89.7 ^T	3293 ^T		299 ^T	Woudneh et al. (2015)
Solid: sludge				133 ^E	440 ^E	227 ^E	581 ^E	27.2 ^E	547 ^E		344 ^E	
(WWTP)				21.5 ^S	196 ^S	106 ^S	174 ^S	168 ^S	1069 ^S		139 ^S	

R: Raw; T: Treated; I: Influent; E: Effluent; S: Sludge; LOD: limit of detection; MQL: method quantification limit.

^a Mean values or range (min–max) are shown.

Table 5Concentrations^a of selected OPFRs in surface water samples (surface water, seawater, drinking water; ng L⁻¹).

Type of matrix	Location	Period	n	TCEP	TCIPP	TDCIPP	TNBP	TPP	TBOEP	TPHP	EHDPP	ΣOPFRs	Ref.
Rivers (Nalón, Arga and Besòs)	Spain	Spring 2012	32	1.5–330	7.2–1800	5.3–35	1.2–370	–	45–4600	1.6–35	11–46	7.6–7200	Cristale et al. (2013)
Rivers (Ebro, Llobregat, Júcar and Guadalquivir)	Spain	2010 & 2011	77	<LOD-232	<LOD-6377	–	–	–	5.3–569	–	–	–	Gorga et al. (2015)
Rivers	Sweden	Oct 2013	23	0.68–6.6	4.6–30	0.11–48 (sum of TDCIPP/TEHP)	2.9–24	–	–	–	5.4–9.2	<MDL-130	Gustavsson et al. (2018)
Surface water	Canada	2014 & 2015	n. m.	100–190	290–2010	130	140–1230	<200	100–10,300	–	–	–	Hao et al. (2018)
Lake Shihwa	Korea	May 2015	43	255	211	15.6	24.8	–	164	8.3	6.62	28.3–16,000	Lee et al. (2018)
Danube River	Europe	Aug–Sept 2013	71	2.4–41 (mean: 11)	28–603 (mean: 115)	<LOQ-28 (mean: 11)	0.4–70 (mean: 5.6)	<LOQ-2.1 (mean: 0.42)	<LOQ-93 (mean: 13)	<LOQ-7.6 (mean: 1.5)	<LOQ-5.9 (mean: 0.6)	–	Loos et al. (2017)
Urban & rural lentic surface waters (lakes, ponds, drinking water reservoirs)	Germany	June 2007–October 2009	151	3–61	7–126	–	4–32	–	<LOQ-53	–	–	–	Regnery and Püttmann (2010)
Urban surface water (river & lake)	China	2013–2014	340	<LOD-5698 (mean; 219)	<LOD-1742 (mean; 291)	<LOD-855 (mean; 46.3)	<LOD-256 (mean; 19.6)	–	<LOD-3617 (mean; 116)	<LOD-96.3 (mean; 4.49)	<LOD-40.3 (mean; 0.38)	3.24–10,945 (mean; 954)	Shi et al. (2016)
Surface water from a pond	Australia	–	1	116	891	26	21	6	–	–	–	–	Teo et al. (2015)
Songhua River	China	–	51	38–3700	5.3–190	2.4–46	–	2.3–5.3	4.5–310	4.5–65	4.3–67	265.4–4777.2	Wang et al. (2011)
Rivers (around Bohai and Yellow sea)	China	Aug 2013	40	1–268	5–921	<LOD-44	<LOD-81	<LOD-16	<LOD-47	–	–	–	Wang et al. (2015)
Taihu Lake	China	–	5	259.2–2406	7.7–19.1	7.4–42.1	2.2–13	–	–	1.6–1.8	–	–	Yan et al. (2012)
Surface water (from fish & shellfish farms)	Europe	Summer 2016	27	–	–	–	–	–	–	–	–	0.43–867	Aznar-Alemany et al. (2018)
Seawater (Bohai and Yellow seas)	China	Aug–Sept 2015	106	2.35–29.24	2.83–31.4	<MDL-3.24	–	–	–	<MDL-0.75	–	8.12–98.04	Zhong et al. (2017)
Seawater (Yellow sea and East China sea)	China	n.m.	13	21.01–105.4	15.77–170.2	24–353.3	–	–	–	–	–	91.87–506.7	Hu et al. (2014)
Swimming pool water	Australia	–	1	190	1653	259	6	15	–	–	–	–	Teo et al. (2015)
Rain water	Australia	Summer 2013	10	3560	366	–	19.4	–	758	2.59	–	–	Teo et al. (2015)
Road runoff water	Australia	Summer 2013	43	941	1578	242	86.2	–	186	50	–	–	Teo et al. (2015)
Drinking water	Pakistan	Nov 2014	39	<BDL-31.23	<MDL-85.57	–	<MDL-1.59	<MDL-11.9	–	–	–	–	Khan et al. (2016)
Drinking water (tap, purified, bottled)	Korea	Aug–Sept 2014	127	38.8	67	–	3.4	2.12	26.1	–	–	<MDL-1660	Lee et al. (2016)
Tap and bottled water	China	2012	47	12.5	14.4–83.2 (mean; 33.4)	–	7.48	19.8–84.1 (mean; 40)	24.1–151 (mean; 70.1)	–	–	85.1–325	Li et al. (2014)

LOD: limit of detection; MDL; method detection limit.

^a Mean values or range (min–max) are shown.

Table 6
Concentrations^a of selected OPFRs in sediment ($\mu\text{g kg}^{-1}$).

Type of matrix	Location	Period	n	TCEP	TCIPP	TDCIPP	TNBP	TBOEP	TPHP	TEHP	Σ OPFRs	Ref.
Sediments (from fish farms)	Europe	Summer 2016	24	–	–	–	–	–	–	–	0.04–92.8	Aznar-Alemany et al. (2018)
River sediments (from Arga, Nalón and Besós)	Spain	Spring 2012	21	<LOD–9.7	<LOD–365	<LOD–12	<LOD–13	–	<LOD–23	<LOD–290	–	Cristale et al. (2013)
River sediments (Adige, Evrotas, Sava)	Italy	2014–2015	52	–	–	–	–	–	–	–	11.5–549	Giulivo et al. (2017)
	Greece										0.31–31	
	Slovenia										10.5–248	
River sediments (from Ebro, Llobregat, Júcar and Guadalquivir)	Spain	2010–2011	77	<LOD–54	<LOD–459	–	–	<LOD–66	–	–	–	Gorga et al. (2015)
River Sediments (from Pearl river)	China	Nov 2015	48	1–26.5	2.27–186.3	<LOD–6.05	1.29–12.8	<LOD–19.7	0.42–316.5	–	13.2–377.1	Hu et al. (2017)
Sediment from lake Shihwa	Korea	May 2015	43	<LOQ–290	<LOQ–2500	<LOQ–405	<LOQ–33.3	<LOQ–2755	<LOQ–257	<LOQ–99.7	2.99–3800	Lee et al. (2018)
River sediments	Austria	Summer 2005	4	<MDL–160	<MDL–1300	–	<MDL–50	2.4–130	<MDL–160	4.4–140	–	Martínez-Carballo et al. (2007)
Soils (from waste-recycling areas)	China	–	36	<MDL–548	<MDL–1370	–	<MDL–4.68	21.1–306	0.53–303	0.54–45.7	37.7–2100	Wang et al. (2018)
Sediment (from 8 estuaries and delta)	Europe	2013–2015	29	0–39.7	0–141.6	0.097–3.8	0–4.1	0–12.6	0.063–9.3	–	2.5–181	Wolschke et al. (2018)

LOD: limit of detection; MDL: method detection limit; LOQ: limit of quantification; MQI: method quantification limit.

^a Range (mix-max) is shown.

various products and their persistence during treatment processes. Especially in Europe, limited studies are focused on the determination of OPFRs in wastewater, particularly in Spain and Austria. In a first Austrian study in 2005, 7 OPFRs were detected in effluent of municipal wastewater treatment plants, reaching the maximum concentration of 5400 ng L^{-1} for TBOEP (Martínez-Carballo et al., 2007). Similarly, Spanish studies showed that TCIPP and TBOEP were also the analytes detected in higher concentrations in raw and treated wastewater from WWTPs (Rodil et al., 2009; García-López et al., 2010). Nowadays, TCIPP is more prominent in effluents than TCEP, reflecting the phasing out of the latter. Chlorinated OPFRs are hardly removed in WWTPs. Of a series of 29 polar trace pollutants, TCIPP was among the 10 with no significant elimination in WWTPs, whereas TCEP showed slight removal (only 20%) (Reemtsma et al., 2006). This European WWTP survey by Reemtsma et al. (2006) confirmed that TCEP and TCIPP are routinely detected in WWTP effluents, with mean concentrations of 200 and 600 ng L^{-1} , respectively. These values are in good agreement to the pan-European survey on the occurrence of micropollutants in 90 WWTP effluents, where the examined OPFRs (TIBP, TNBP, TCEP, TCIPP, TDCIPP, TBOEP, TPP, EHDPP, TEHP, and TMPP) were detected in all samples. These compounds were among the most abundant and frequently detected micropollutants studied. A wide range in maximum concentrations was observed from 610 ng L^{-1} for TPP to $43,000 \text{ ng L}^{-1}$ for TBOEP and the median levels were: TCIPP 620 ng L^{-1} , TCEP 71 ng L^{-1} , and TBOEP 190 ng L^{-1} (Loos et al., 2012).

O'Brien et al. (2015) studied OPFRs in influents from eleven WWTPs for a week in Australia. TBOEP, TCIPP, TCEP and TDCIPP were found at all sites, with the first two compounds at high concentrations (median concentrations; 4400 , 2500 , 300 and 100 ng L^{-1} , respectively). TIBP and EHDPP were found in half of cases. Teo et al. (2015) revealed OPFRs (total concentration; 9 – 1139 ng L^{-1}) in secondary effluent from water recycling plant in Australia, with TCIPP as dominant compound. A recent study investigating 14 OPFRs in sewage samples in China, confirmed this picture, as, TCIPP was again the most abundant compound in both influent and effluent samples (Shi et al., 2016). TCIPP was also the dominant compound in municipal landfill leachate accounted for 80% of the sum of OPFRs in the influent and 50% in the treated effluent (Deng et al., 2018).

In a survey of effluent wastewater in Canada, TBOEP, TPP and TCIPP showed the highest concentrations, with TBOEP up to $10,000 \text{ ng L}^{-1}$, which may indicate high usage of this compound in comparison to other OPFRs (Hao et al., 2018). Woudneh et al. (2015) reported the fate of OPFRs along WWTP in a 2-day sampling in Canada. In raw wastewater, the OPFRs, in descending occurrence, were TBOEP (3292 ng L^{-1}), TNBP (747 ng L^{-1}), TCEP (598 ng L^{-1}), TCIPP (380 ng L^{-1}), TEHP (299 ng L^{-1}) and TDCIPP (227 ng L^{-1}). The same compounds were found in treated effluent at lower concentrations, except from TDCIPP.

Wastewater treatment reduces the concentrations of OPFRs through biological or chemical degradation and aqueous/solid partition processes. According to Woudneh et al. (2015) TBOEP, the dominant OPFR, reduced along WWTP from influent (3292 ng L^{-1}) to effluent (581 ng L^{-1}), whereas it increased in solid waste stream (from $1069 \mu\text{g kg}^{-1}$ dw in primary sludge to $1420 \mu\text{g kg}^{-1}$ in activated sludge, to $2236 \mu\text{g kg}^{-1}$ dw in biosolids), suggesting affinity of this compound to sludge. EHDPP also showed a similar trend. The other OPFRs (TPP, TNBP, TCEP and TCIPP) declined in both aqueous and solid streams, suggesting biological or chemical degradation during treatment. However, TDCIPP was not removed. The chlorinated OPFRs (TCEP, TDCIPP, TCIPP) are considered as very persistent and were not degraded during wastewater treatment according to Marklund et al. (2005b) and Reemtsma et al. (2006). As a result, they are often detected in effluents. O'Brien et al. (2015) estimated that TCIPP represent 69% of annual load of OPFRs discharged to the environment from all WWTP in Australia. Consequently, chlorinated OPFRs may be an environmental issue for the receiving reservoirs.

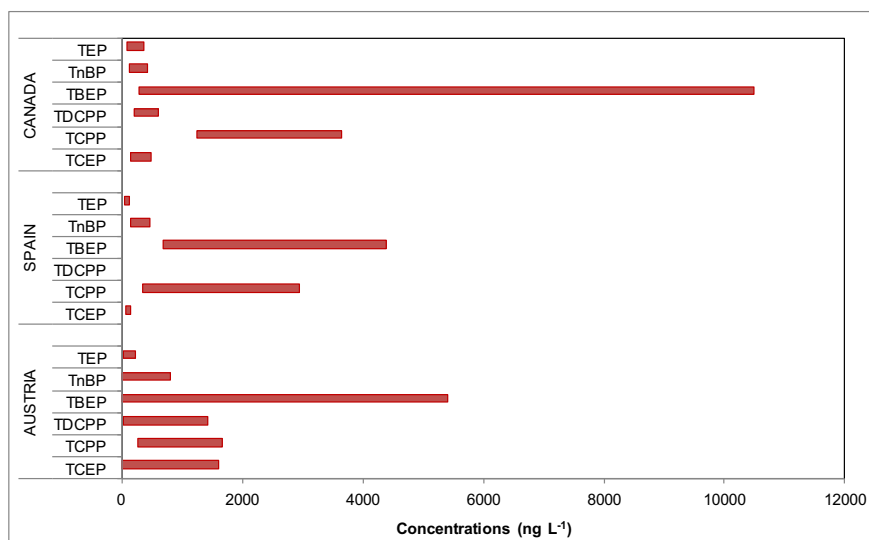


Fig. 2. Range of OPFRs concentrations in effluent wastewaters reported in literature. Data is compiled from Table 4.

For sludge samples (Table 4) Gao et al. (2016) determined 18 OPFRs in samples collected from 8 WWTPs in China, with total concentration ranged from 204 to 4101 $\mu\text{g kg}^{-1}$ (dw). TEHP (46.0–1200 $\mu\text{g kg}^{-1}$), TMPP (3.7–3550 $\mu\text{g kg}^{-1}$) and TBOEP (6.3–281.4 $\mu\text{g kg}^{-1}$) were the dominant compounds, detected in all samples. TCEP, TCIPP, TNBP, TBOEP and TPHP followed at maximum levels of 208, 378, 286, 383 and 67 $\mu\text{g kg}^{-1}$, respectively. Especially for TEHP and TMPP, they were not ubiquitous in wastewater samples (Martínez-Carballo et al., 2007), so their presence in sludge may be due to their strong absorption tendency, resulting from their high values of LogK_{ow} (9.49 and 6.34, respectively). Similar results for TBOEP, TCEP, TNBP, TPHP and TCIPP were found by Pang et al. (2016) in WWTPs, Central China; they detected in all samples during the period of January to March 2015.

Diffuse sources such as emissions from industrial production of OPFRs, usage of products containing OPFRs in private households and in industry, and road run-offs are considered as possible sources of OPFRs in wastewater (Wei et al., 2015). Previous studies from Marklund et al. (2005b) and Schreder and La Guardia (2014) suggested that 1–5% of the OPFRs that are in use enter the wastewater stream, annually. Schreder and La Guardia (2014) determined that laundry wastewater may be the primary source for OPFRs entering STPs, possibly as a result of household dust accumulating on clothing and transferring to the laundry wastewater. Shi et al. (2016) revealed high TCIPP and TCEP concentrations in road runoff water. Traffic has been also reported as possible source of OPFRs in previous studies (Marklund et al., 2005a; Meland and Roseth, 2011).

The occurrence of OPFRs in wastewater has been used for assessment of per capita input of OPFRs in wastewater (O'Brien et al., 2015; Kim et al., 2017). In Australia 2.1 mg person/day of OPFRs were reported during campaign on Census day in eleven WWTPs (O'Brien et al., 2015). In New York, USA, a mass load range of 0.02 mg/person/day for TPP to 28.7 mg/person/day for TBOEP was estimated (Kim et al., 2017). Moreover, the presence of metabolites of OPFRs in urine samples and in wastewater could serve as biomarkers of exposure to OPFRs in a wastewater epidemiology approach (Been et al., 2017; Choi et al., 2018).

5.2. Waters and sediments

Even though the indoor environment may be the main source for OPFRs, these compounds will eventually reach aquatic environment via wastewater treatment plants (WWTPs) (Loos et al., 2012; Reemtsma et al., 2006), traffic (Marklund et al., 2005a), road run-off (Meland and Roseth, 2011; Shi et al., 2016) or road dust (Li et al.,

2018) and LRAT (Gustavsson et al., 2018; Ma et al., 2017). Table 5 compiles most relevant studies of OPFRs in surface water (river water, lakes, seawater) and drinking water. The concentration and profile of OPFRs found in surface waters strongly depend upon the local emissions and dilution factors.

5.2.1. River water

A wide range in OPFRs concentrations was observed in surface water, depending on the urban and industrial activities in their catchment area. The most frequent and abundant OPFRs in surface water were TCIPP, TCEP, TBOEP and TNBP (Fig. 3).

An extended 2-year survey was conducted by Regnery and Püttmann (2010) in urban and rural lentic surface waters in Germany for the presence of five non-chlorinated and chlorinated OPFRs (TCEP, TCIPP, TBOEP, TIBP, TNBP). Relatively low concentrations were reported in urban lakes; chlorinated OPFRs exhibited the highest 5 and 95 percentile concentration values ranged from 9 to 184 ng L^{-1} for TCEP, 27–379 ng L^{-1} for TCIPP, <LOQ–652 ng L^{-1} for TBOEP, <LOQ–82 ng L^{-1} for TIBP and <LOQ–122 ng L^{-1} for TNBP. In rural lentic lakes lower concentrations of chlorinated and non chlorinated OPFRs were reported. Overall, the presence of persistent chlorinated compounds in surface water could be due to atmospheric transport and wash out pathways.

Two studies reported OPFRs concentrations in various rivers in Spain. The concentrations of the dominant compounds TCIPP and TBOEP in rivers close to industrial areas (Nalon, Argá and Besos) ranged from 7.2–1800 ng L^{-1} and 45–4600 ng L^{-1} , respectively (Cristale et al., 2013). Similarly, these two compounds were also the most abundant species in rivers Llobregat, Ebro, Júcar and Guadalquivir with levels <LOD–6300 ng L^{-1} for TCIPP and 5.3–569 ng L^{-1} for TBOEP (Gorga et al., 2015).

The occurrence of OPFRs was reported along Danube River and its major tributaries from Western to Eastern European capitals (Loos et al., 2017). Among OPFRs examined, median concentrations of TCIPP (92 ng L^{-1}), TIBP (18 ng L^{-1}), TBOEP (16 ng L^{-1}), TCEP (10 ng L^{-1}) and TDCIPP (11 ng L^{-1}) were found at highest levels. Higher concentrations were observed in three tributaries of the main river. In an extended survey in Sweden, 19 OPFRs were studied in water samples from rivers along the whole country. TDCIPP and TEHP were the most frequently detected compounds in all 23 rivers at concentrations up to 48 ng L^{-1} . Especially in the northern Swedish rivers, TDCIPP and TEHP were the only compounds detected, without any significant point source, which suggested that a major source pathway for OPFRs to

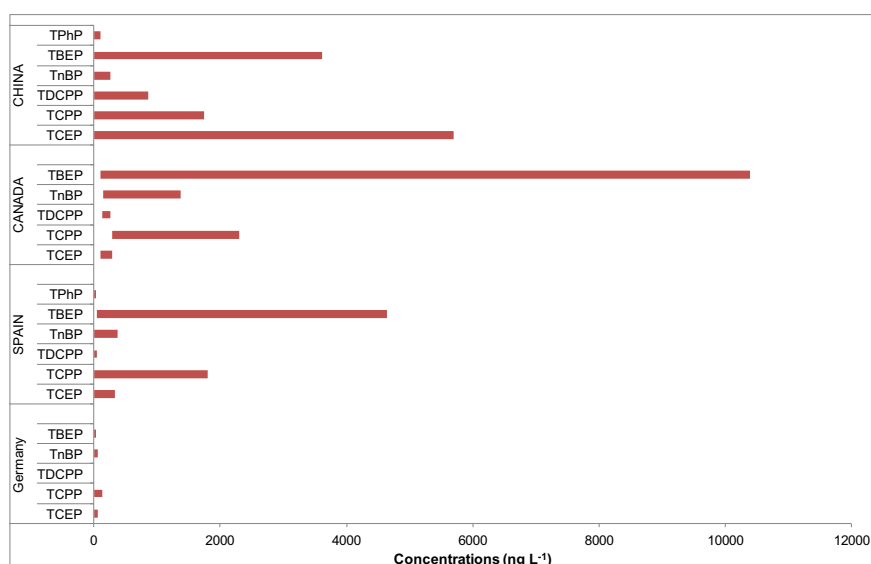


Fig. 3. Range of OPFRs concentrations in surface waters reported in literature. Data is compiled from Table 5.

northern rivers might be through LRAT, atmospheric deposition and mobilization to stream water (Gustavsson et al., 2018).

In a recent study investigating 18 OPFRs in the artificial lake Shihwa in Korea, TBOEP, TCIPP and TDCIPP were the most frequently detected compounds, with detection rates 100%, 93%, and 81%, respectively. The concentrations of sum and individual OPFRs varied. The sum of 18 OPFRs for all the sampling sites ranged from 28.3 to 16,000 ng L⁻¹ and the most abundant OPFRs were TCEP, TCIPP, TEP and TBOEP with mean values of 255, 211, 182, and 164 ng L⁻¹, respectively (Lee et al., 2018). The highest OPFRs concentrations were found for water samples collected from creeks, indicating the primary contamination route associated with intensive industrial activities. According to Shi et al. (2016) relatively high concentrations of OPFRs have been found in rivers in Beijing. The sum of 14 OPFRs ranged from 3.24 to 10,945 ng L⁻¹, with mean value of 954 ng L⁻¹ reflecting anthropogenic impacts from densely populated city. TCIPP and TCEP were the dominant OPFRs with mean concentrations of 291 and 219 ng L⁻¹, respectively. In addition, TCIPP, TCEP, TMP, TEP and TBOEP were the most frequently detected (frequency rate; 80–99%) in the river and lake water in Beijing (Shi et al., 2016).

5.2.2. Seawater

Few studies reported OPFRs concentrations in seawater. In a survey conducted by Aznar-Alemay et al. (2018) in coastal areas of seven European countries, OPFRs in fish farms and shellfish farms were studied in different matrices (water, sediments, mussels). The sum of OPFRs (TBOEP, TCEP, TCIPP, EHDPP, TNBP, TPHP, and TDCIPP) was found in concentrations of 0.43–867 ng L⁻¹ in transitional/coastal water. Since flame retardants have no application in fish farming and most samples were collected near urban shores, the occurrence of OPFRs reflects the impact of human activity on the farm locations. Overall, TCEP and TPHP were the most frequently detected compounds.

A recent study conducted in coastal seas of China (Bohai Sea and Yellow Sea) to determine TCEP, TCIPP, TDCIPP, TIBP, TNBP, and TPHP in seawater samples. The study revealed a total range of OPFRs from 8.12 to 98.04 ng L⁻¹. All compounds were highly detected except from TIBP and TNBP. TCIPP and TCEP were the dominant pollutants with mean values of 9.49 and 6.51 ng L⁻¹, respectively. Overall, the presence of OPFRs indicated major land-based sources, caused by the riverine discharge and input from sewage outfalls (Zhong et al., 2017). In a previous study, much higher total concentrations of 4 OPFRs were measured in coastal cities from Yellow Sea and East China Sea, ranging from 91.87 to 1392 ng L⁻¹. The recorded mean values of TCEP, TCIPP, TDCIPP and

TDBPP were 134.44, 84.12, 109.28, and 96.70 ng L⁻¹, respectively and TCEP was the dominant compound. According to the authors the main sources of halogenated OPFRs were the municipal and industrial effluents of wastewater treatment plants in the nearby economic and industrial zones (Hu et al., 2014).

5.2.3. Drinking water

Only three studies are available on the OPFRs concentrations in the drinking water, thus their significance for the health of exposed populations is also inadequately highlighted in the existing literature. Khan et al. (2016) determined 7 OPFRs in potable water from 3 different sampling sites in order to present the concentrations levels, distribution and risks to human health connected to contaminated drinking water. Potable water samples from the industrial zones (<LOD–71.05 ng L⁻¹) contained the highest concentration of OPFRs, followed by the rural (<LOD–12.06 ng L⁻¹) and background zones (<LOD–0.08 ng L⁻¹). TCIPP, TCEP and TDCIPP were the dominant compounds. These results were lower than those recorded in drinking water in China (85.1–325 ng L⁻¹) (Li et al., 2014) and Korea (up to 1660 ng L⁻¹) (Lee et al., 2016). Both determined the levels of OPFRs in bottled and tap water and found that TCIPP, TPP, and TBOEP were the most frequently detected compounds in all samples. Li et al. (2014) reported that the contamination levels were much higher in tap water than in bottled water, in contrast to the results from Lee et al. (2016).

In general, the OPFRs contamination in drinking water may be due to the fact that the conventional water treatment processes is not often capable of removing these compounds adequately, or the use of products containing these compounds. In addition, their presence in bottled water may be related to bottle closure processes, the use of recycled polyethylene terephthalate (PET) bottles or water contamination before bottling (Lee et al., 2016; Li et al., 2014).

5.2.4. Sediments

Various studies showed the occurrence of OPFRs in sediments with concentrations varied in a wide range (Table 6). The most frequent and abundant OPFRs in sediments were TCIPP, TCEP, TBOEP and TPHP (Fig. 4). In an extended survey in 29 surface sediment samples of 8 large river basin estuaries and deltas across Europe (Scheldt, Elbe, Rhine, Thames, Po, Gironde, Danube and Tiber) OPFRs were detected in all samples. The total concentrations for the European river sediments ranged from 2.5 µg kg⁻¹ dry weight (dw) in the river Gironde (France) to 181 µg kg⁻¹ dw in the Belgian river Scheldt (Wolschke et al., 2018). In general, individual concentrations varied from not detected to 141.55

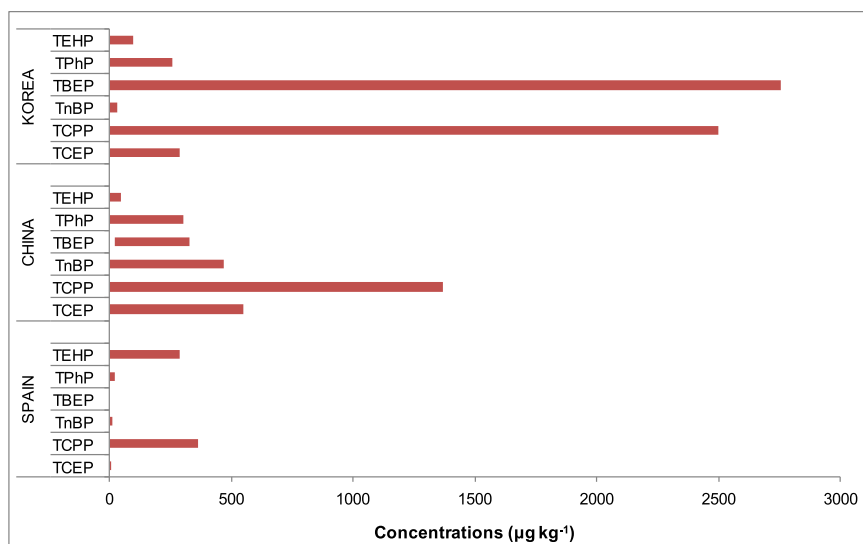


Fig. 4. Range of OPFRs concentrations in sediments reported in literature. Data is compiled from Table 6.

$\mu\text{g kg}^{-1}$, with TCIPP and TBOEP being the most abundant and prevalent compounds. Similarly, [Giulivo et al. \(2017\)](#) studied the OPFRs contamination in sediment samples from three different European river basins: the Sava River (flows through Slovenia, Croatia, Bosnia and Herzegovina and Serbia), the Evrotas River (Greece) and the Adige River (Italy). OPFRs were detected in all sediment samples and total levels ranged from 0.31–31.0, 11.5–549 and 10.5–248 $\mu\text{g kg}^{-1}$ dw for the Evrotas, Adige and Sava, respectively. Another study conducted in sediments from fish farms in 7 European countries showed lower total levels of OPFRs (0.04–92.8 $\mu\text{g kg}^{-1}$), in comparison to previous studies. TPHP, EHDPP and TCIPP were the most frequently detected OPFRs, in 92%, 83% and 54% of the samples, due to their higher hydrophobicity ($\log K_{ow}$ of 4.70, 6.30 and 2.89, respectively) ([Aznar-Alemany et al., 2018](#)).

Comparable OPFRs concentrations were found by [Hu et al. \(2017\)](#) who studied the occurrence of 11 OPFRs in sediment samples from Pearl River estuary. They were found in all sediment samples with concentrations ranging from 13.2 to 377.1 $\mu\text{g kg}^{-1}$ dw. Varied results ascribed to completely different sampling sites, indicated that the presence of OPFRs was linked to industrialization and urbanization. TCIPP and TCEP were the most abundant species found in all samples. In general, TCIPP was the most abundant and frequently detected compound in all studies described in Table 6, reaching at maximum concentration of 2500 $\mu\text{g kg}^{-1}$ in lake Shihwa in Korea ([Lee et al., 2018](#)) and 1300 $\mu\text{g kg}^{-1}$ in a river in Austria ([Martínez-Carballo et al., 2007](#)).

6. Conclusions and future perspectives

The review article was focused on the occurrence of organophosphate flame retardants (OPFRs) in aquatic environment. OPFRs are widely used not only as flame retardants, in replacement of persistent brominated FRs, but also as plasticizers and antifoaming agents. There is a large number of compounds in this group with different properties regarding their polarity, solubility, volatility and persistence. The analytical methodology, including extraction, clean up and analytical methods for determination of OPFRs was reviewed. The concentrations and profiles of OPFRs in surface water, seawater, sediments as well as in wastewater and sludge are presented. OPFRs are among the most frequently detected compounds with relatively significant contribution regarding the examined emerging micropollutants in surface waters. Chlorinated analogues are usually the most prominent. Their occurrence and profile in aquatic environment worldwide reflects the differences between production and usage areas, as well as the differences in legislations.

Due to increasing volumes produced and extensive use, the presence of OPFRs in the aquatic environment needs further research. There are significant knowledge gaps that merit future attention to complete our understanding of the fate of OPFRs. First of all, there is a need for a robust, sensitive and valuable method for the determination of a number of representative OPFRs compounds that need to be monitored, based on their properties, production volumes, environmental behavior and possible impact in the environment. This will lead to directly comparable results among various countries/areas. More studies are needed to elucidate the contribution of point and diffuse sources of OPFRs in aquatic environment. There are limited studies that examine the fate of OPFRs during conventional wastewater treatment processes or possible impact of advanced treatment processes. The magnitude and significance of long range transport remains unclear and studies on this are needed to understand regional or global distribution. The fate of OPFRs in aquatic environment regarding their distribution between water, suspended solids and sediments, their accumulation in aquatic life, possible transformation process warrant more research. Since the knowledge of detrimental effects is incomplete, the increasing production and eventually the increasing release of OPFRs may pose a risk to the aquatic environment.

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