Aerosol and Air Quality Research

An Overview: Organophosphate Flame Retardants in the Atmosphere

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ABSTRACT

Organophosphate flame retardants (OPFRs) have been adopted as safer alternatives to polybrominated biphenyl ether flame retardants. However, because of their ubiquitous presence in the environment and the growing evidence of health risks, there has been growing research interest in understanding the fate and effects of these compounds in the environment. This review focuses on the current knowledge of OPFRs in the atmosphere. There is no consensus on the target OPFR for analysis, making comparisons challenging. However, we can still conclude that OPFRs partition mainly in the particulate phase, and chlorinated-OPFRs are the main compounds in the atmosphere. The general concentration trends from the literature were: $PM_{2.5} > TSP > air$. However, the gas-phase OPFRs in the published studies might be significantly underestimated because of sampling artifacts. OPFRs were also found in remote environments in Antarctica, the Arctic, and high mountains, suggesting long-range transport potential. For example, concentrations up to 92.3 ± 13.8 pg m^{-3} in the air have been measured in the Antarctic. Lastly, atmospheric transformations of some OPFRs have been reported as more toxic and persistent than parent compounds, indicating additional risk. However, they are currently not measured or included during risk assessment.

Keywords: Atmospheric particle-bound contaminants, Emerging contaminants, Organophosphate esters, $PM_{2.5}$, Long-range transport

1 INTRODUCTION

Fire retardants are essential in meeting fire safety requirements by reducing the risk of fire breakouts. They are added to numerous materials, including wood products, textiles, and plastics used in construction, electrical equipment, furniture, and vehicles. Fire retardants work by either abstracting the reactive ·H and ·OH radicals, endothermically reacting, or forming a barrier between the fire and the material (DeArmitt, 2011; Salmeia et al., 2015). These compounds are ubiquitous in the environment and are of great interest to environmentalists.

Organophosphate ester flame retardants (OPFRs) have become widely used as alternatives to
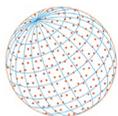
polybrominated diphenyl ethers (PBDEs). Penta-, octa-, and deca-brominated diphenyl ethers (penta-BDEs, octa-BDEs, and deca-BDEs) were once widely used halogenated organic flame retardants and are now listed in Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs) because of their environmental persistency and toxicity (Blum *et al.*, 2019; Sharkey *et al.*, 2020). Furthermore, PBDE flame retardants also contain dioxin and furan contaminants, and they are also precursors for the formation of brominated dioxins and furans during combustion (Altarawneh and Dlugogorski, 2013; Yang *et al.*, 2022). OPFRs replaced PBDE largely on the presumption that they were less persistent (Blum *et al.*, 2019). However, Zhang *et al.* (2016a) estimated that some OPFRs have medium to high persistency. In addition, the environmental safety of OPFRs has come under question since there is increasing evidence of their negative impact on human and ecological health (Kojima *et al.*, 2013; Du *et al.*, 2015; Blum *et al.*, 2019; Li *et al.*, 2019a).

Organophosphate ester flame retardants consist of straight (alkyl) or aromatic (aryl) chains attached to a phosphate moiety. Some OPFRs, e.g., Tris(1-chloro-2-propyl) phosphate (TCPP), are also chlorinated. OPFRs are mainly used as flame retardant plasticizers in engineering plastics (Brandsma *et al.*, 2013). Non-chlorinated OPFRs retard flames through reaction in the solid phase, where they build up a char layer providing a barrier between the flame and the material (Mihajlović, 2015). In addition to this action, chlorinated-OPFRs also retard flames via the gas phase, whereby the chlorine abstracts the reactive ·H and ·OH radicals (Mihajlović, 2015). Chlorinated-OPFRs also have longer lifetimes in the end product because of the stronger binding of chlorine to the polymer. OPFRs are incorporated into materials physically and thus could easily be released into the environment through abrasion or during hot conditions (Brandsma *et al.*, 2013). Blum *et al.* (2019) argued that the current information on the toxicity and ubiquity of organophosphate ester flame retardants indicates that they might not be a risk-free alternative to PBDE flame retardants, and safer alternatives should be developed since it will still take longer for sufficient scientific evidence to guide regulations.

Several useful reviews, perspective papers, and letters have been published on OPFRs: in microenvironments (Chupeau *et al.*, 2020; Hou *et al.*, 2021), soil (Zhang *et al.*, 2022b), biota (Pantelaki and Voutsa, 2020), oceans (Xie *et al.*, 2022), exposure and health risk assessment (Blum *et al.*, 2019), and industrial production (Huang *et al.*, 2022). Wang *et al.* (2020c) ambitiously covered the presence of OPFRs in air, water, sediment, and sludge and included human exposure and human and ecological risk assessment. However, what is missing in these reviews is the presence of OPFRs in atmospheric particles. This is an essential aspect that has not been given adequate attention. According to Li *et al.* (2019b), the median OPFR concentration in the particulate phase in the air accounted for ~90% of the total concentrations, with the rest partitioning in the gas phase. Particle-bound OPFRs would be more persistent and would be able to be transported to pristine environments (Shi *et al.*, 2021). Atmospheric $PM_{2.5}$-bound OPFRs would also present additional health risks.

Therefore, this review paper aims to collate and discuss recently published articles on organophosphate flame retardants in atmospheric air and particles. The manuscript will also include the production, consumption, physicochemical properties, and environmental effects of OPFRs. The sampling and analysis methods used by various studies and the challenges and potential solutions during these procedures. This review would be a valuable resource to researchers on emerging organic contaminants and air pollution interested in understanding the current literature on organophosphate ester flame retardants.

2 METHODS (LITERATURE ACQUISITION PROCESS)

Recently published articles were sourced from the Web of Science database using "organophosphate flame retardants", "$PM_{2.5}$", atmospheric particle-bound", "air", and "atmosphere" as search words. The results were further screened to include only Science Citation Index Expanded (SCI-E) original and review publications in the past fifteen years. The cumulative number of publications during the period is shown in Fig. 1. For the past 15 years, 390 research articles and research papers on organophosphate flame retardants in the air were published, as shown in Fig. 1. The data was accessed on May 26th, 2022. It is clear that the research interest in OPFRs has been increasing over the years. The majority of the published articles have been on OPFRs in indoor air.
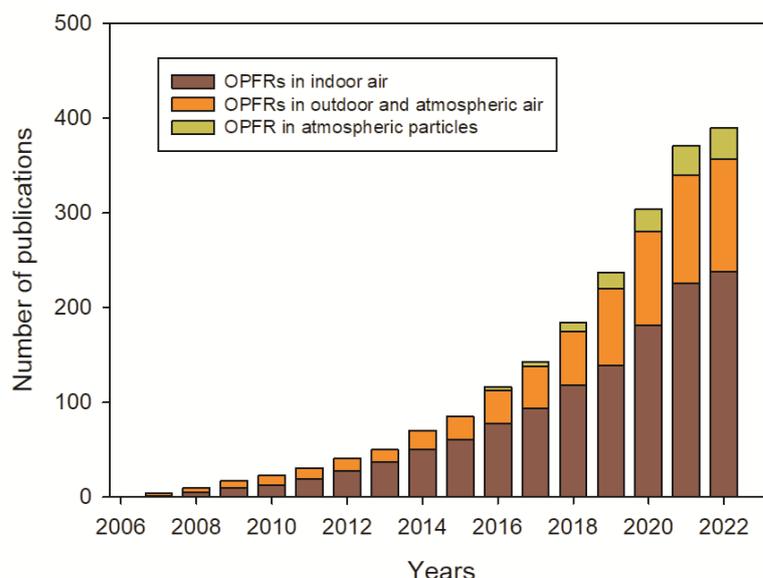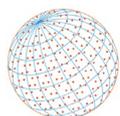
Fig. 1. The cumulative number of publications on organophosphate flame retardants published in the past 15 years. The publications are all in the Science Citation Index Expanded and consist of research articles and review papers. The data was sourced from the Web of Science. Accessed on May 26th, 2022.

However, research on outdoor air and particle-bound OPFR has been steadily growing over the years. A total of 119 articles were used in this review, with OPFR concentrations from 24 articles extracted and interpreted.

3 ORGANOPHOSPHATE FLAME RETARDANT PRODUCTION AND USE

The production and consumption information of organophosphate flame retardants (OPFRs) would be useful in understanding their presence in the environment. Several OPFRs are listed as High Production Volume Chemicals, defined by Organization of Economic Co-operation and Development (OECD) countries as chemicals produced or imported at > 1,000 metric tons year^{-1}. However, there is inadequate information about the production and uses of these compounds. Some outdated information include Van der Veen and de Boer (2012) that reported OPFR consumption in Europe in 2006 was 93,000 metric tons. The marketing research company, ResearchInChina, puts the global market volume of OPFR in 2013 at 690,000 metric tons (ResearchInChina, 2014). Blum et al. (2019) included the US production volume estimations of a few OPFRs in 2015 retrieved from the NIH PubChem database and showed that TCPP and TDCPP were produced at a volume of 22,600–45,000 and 4,500–22,600 metric tons, respectively, and TPhP, TCP, and TnBP at 450–4,500 metric tons each (converted from pounds).

The most recent and detailed publication on OPFR production is Huang et al. (2022), which reported 367 factories globally manufacture OPFRs as of 2020, 201 of which are in China. A little over 431,000 metric tons of these flame retardants were produced from the 201 factories, 84.2% being organophosphate esters. Fig. 2 shows the most produced OPFRs in 2020, with the top five OPFRs being TEP (~18%), TCPP (12%), and TiBP, BADP, and TCEP with 9% each. However, whether the production of these compounds reflects consumption in the flame retardant application cannot yet be drawn since some of these compounds have other industrial applications, as shown in Table 1. For example, TnBP is also used as a dielectric fluid in motor oils and lubricants (Gao et al., 2021); TBEP as an antifoaming agent (Mihajlović, 2015); and TPhP as a lubricant and hydraulic fluid (Wang et al., 2017; Li et al., 2019b). In addition, since the information comes from only one region and represents 55% of global OPFR-manufacturing factories, it is not certain that the same conclusions can be drawn from the other regions where the factories are located.
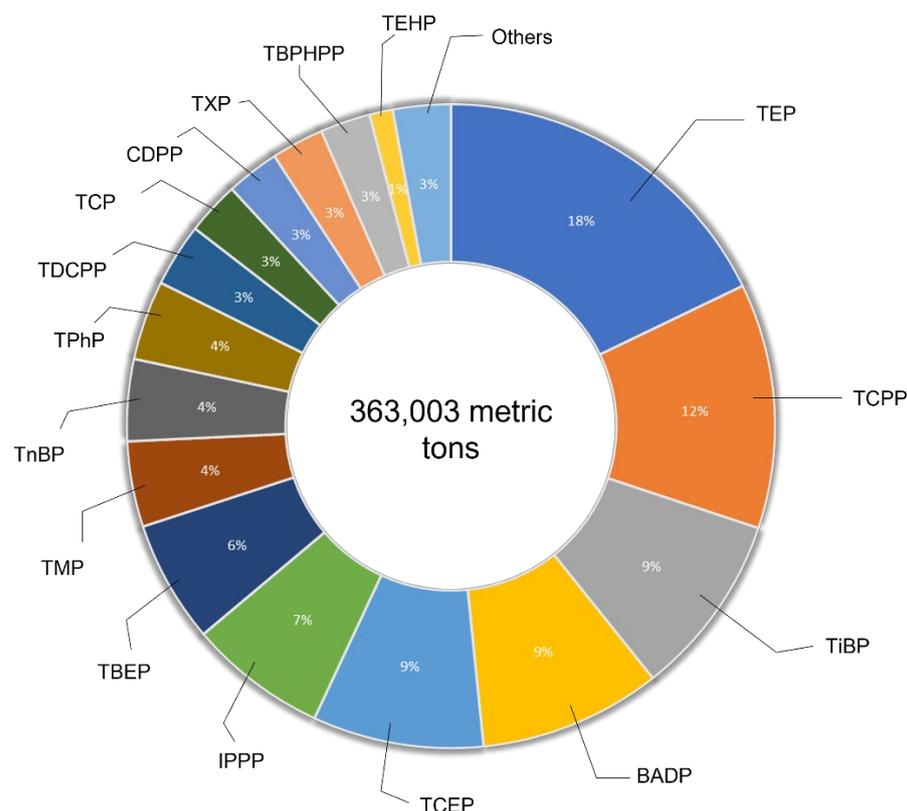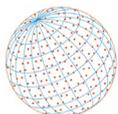
Fig. 2. Production of organophosphate ester flame retardants in 2020. The data is retrieved from Huang *et al.* (2022). The production data is from Mainland China which houses 55% of global OPFR factories. The others category consists of thirteen compounds with < 0.8% of the total production. TEP: Triethyl phosphate; TCPP: Tris(1-chloro-2-propyl) phosphate; TiBP: Tri-iso-butyl phosphate; BADP: Bisphenol-A bis(diphenyl phosphate); TCEP: Tris (2-chloroethyl) phosphate; IPPP: Isopropylated triphenyl phosphate; TBEP: Tris(2-butoxyethyl) phosphate; TMP: Trimethyl phosphate; TnBP: Tri-n-butyl phosphate; TPhP: Triphenyl phosphate; TDCPP: Tris (1,3-dichloro-2-propyl) phosphate; TCP: Tricresyl phosphate, CDPP: Cresyl diphenyl phosphate, TXP: Trixylenyl phosphate, TBPHPP: Tris(p-tert-butylphenyl) phosphate, TEHP: Tris(2-ethylhexyl) phosphate.

In the market, commercial OPFR products come as single OPFR compounds, e.g., Reofos® 50 which only consists of IPPP, or as a mixture of organophosphate ester compounds, e.g., ANTIBLAZE® V-500, which has chloroalkyl, aryl, and triaryl phosphates. In addition, some commercial OPFR products consist of proprietary OPFR compounds, e.g., SAYTEX® RZ-243, which contains proprietary aryl-OPFRs, and as mixtures of OPFRs and other flame retardants, e.g., Firemaster 550®, which is a formulation of aryl-OPFRs and brominated flame retardants. These formulations further complicate associating OPFR levels in the environment with production and consumption.

4 CHARACTERISTICS AND HEALTH EFFECTS OF ORGANOPHOSPHATE FLAME RETARDANTS

Organophosphate flame retardants consist of organic moieties attached to the phosphate molecule, as shown in Table 1. These organic moieties can be alkyl or aryl, and some alkyl-OPFRs are also halogenated. Therefore, because of the significant variation in the chemical structures, there is no general trend in the physicochemical properties of this class of compounds, unlike PBDEs which only vary in the number of bromines attached to the parent diphenyl ether molecule.

The physicochemical properties of OPFRs, shown in Table 1, can help us predict the occurrence and presence of these compounds in the environment. For example, Li *et al.* (2019b) found that OPFRs with low vapor pressure and high Log K_{OA} (aryl-OPFRs, TBEP, TEHP) were frequently present
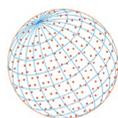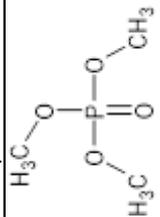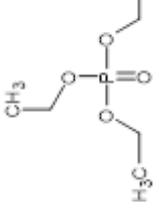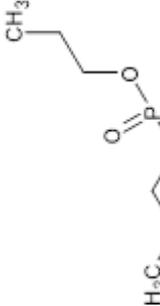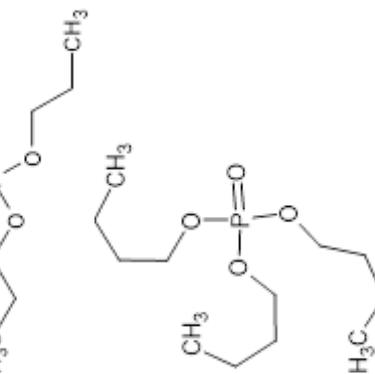
Table 1. The chemical structure, physicochemical properties, and application of commonly studied organophosphate ester flame retardants.

Compound structure and name	CAS No.	M.W.	S[c]	V.P	H	Log K_{OW}	Log K_{OC}	Log K_{OA}	Application
Trimethyl phosphate (TMP)	512-56-1	140.07	5.00E5	0.85[c]	2.49E-7[c]	−0.60[a]	0.88[c]	5.88[c]	Plasticizer and flame retardant for thermosetting resins
Triethyl phosphate (TEP)	78-40-0	182.15	5.00E5	0.165[c]	5.83E-7[c]	0.87[a]	1.68	6.63[b]	Plasticizer and flame retardant for thermosetting resins
Tripropyl phosphate (TPP)	513-08-6	224.24	6.45E3	2.31E-2[c]	1.36E-6[c]	2.35[a]	2.47[c]	6.43[b]	Plasticizer
Tri-n-butyl phosphate (TnBP)	126-73-8	266.31	7.35	3.49E-3[c]	3.19E-6[c]	4.00[a]	3.27[c]	8.24[b]	Flame retardant, plasticizer, dielectric, solvent, anti-foam agent

S: solubilities in water (mg L^{-1} at 25°C); V.P: Vapor pressures (mm Hg at 25°C); H: Henry's law constants (atm m^{-3} mol^{-1}); Log K_{OW}: n-octanol-water partitioning coefficients; Log K_{OC}: organic carbon-water partitioning coefficients; Log K_{OA}: n-octanol-air partitioning coefficients; Data from [a] Pubchem; [b] Wang et al. (2018b); and [c] Li et al. (2019b).

Table 1. (*continued*).

Compound structure and name	CAS No.	M.W.	S[c]	V.P	H	Log K_{OW}	Log K_{OC}	Log K_{OA}	Application
Tri-iso-butyl phosphate (TiBP)	126-71-6	266.31	16.2	1.28E-2[c]	3.19E-6[c]	3.60[a]	3.04[c]	7.48[c]	Pharmaceutical intermediate, polymerization catalyst, solvent flame retardant,
Tris(2-ethylhexyl) phosphate (TEHP)	78-42-2	434.6	0.6	6.07E-7[c]	9.56E-5[c]	9.49[a]	6.35[c]	15.0[b]	Plasticizer, fire retardant, solvent
Tris(2-butoxyethyl) phosphate (TBEP)	78-51-3	398.47	1.10E3	1.23E-6[c]	1.20E-11[c]	3.75[a]	5.66[c]	13.1[b]	Plasticizer, flame retardant, anti-foam agent

S: solubilities in water (mg L^{-1} at 25°C); V.P: Vapor pressures (mm Hg at 25°C); H: Henry's law constants (atm m^{-3} mol^{-1}); Log K_{OW}: n-octanol-water partitioning coefficients; Log K_{OC}: organic carbon-water partitioning coefficients; Log K_{OA}: n-octanol-air partitioning coefficients; Data from [a] Pubchem; [b] Wang *et al.* (2018b); and [c] Li *et al.* (2019b).
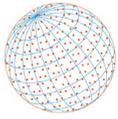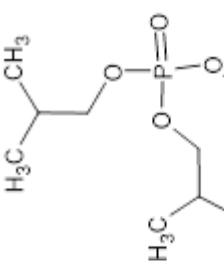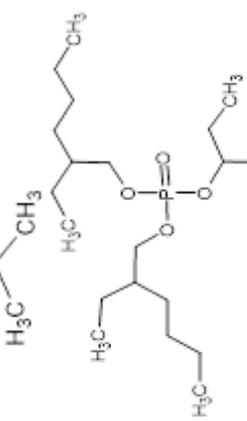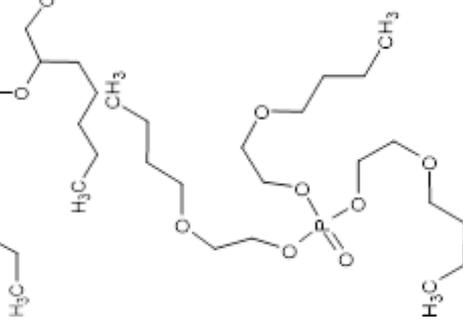
Table 1. (*continued*).

Compound structure and name	CAS No.	M.W.	S[c]	V.P	H	Log K_{OW}	Log K_{OC}	Log K_{OA}	Application
2-ethylhexyl diphenyl phosphate (EHDP)	1241-94-7	362.4	1.90	3.34E-5[c]	2.48E-7[c]	5.73[a]	4.20[c]	8.38[b]	Flame retardant, intermediate, plasticizer
Triphenyl phosphate (TPhP)	115-86-6	326.3	1.90	4.27E-7[c]	3.98E-8[c]	4.59[a]	3.71[c]	8.46[b]	Flame retardant for phenolic, epoxy resins, acetate plastics, and synthetic rubber, plasticizer
Tricresyl phosphate (TCP)	1330-78-5	368.36	0.30	1.04E-7[c]	4.39E-8[c]	6.34[a]	4.34[c]	12.0[b]	Flame retardant for PVC film, epoxy, and phenol resins, plasticizer, and lubricant oil additive
Resorcinol bis(diphenyl phosphate) (RDP)	57583-54-7	574.5	1.10E4	2.10E-8[c]	2.90E-13[c]	7.41[a]	4.63[c]	15.0[c]	Flame retardant
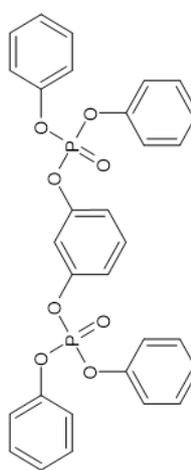
S: solubilities in water (mg L^{-1} at 25°C); V.P: Vapor pressures (mm Hg at 25°C); H: Henry's law constants (atm m^{-3} mol^{-1}); Log K_{OW}: n-octanol-water partitioning coefficients; Log K_{OC}: organic carbon-water partitioning coefficients; Log K_{OA}: n-octanol-air partitioning coefficients; Data from [a] Pubchem; [b] Wang *et al.* (2018b); and [c] Li *et al.* (2019b).
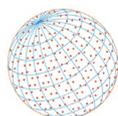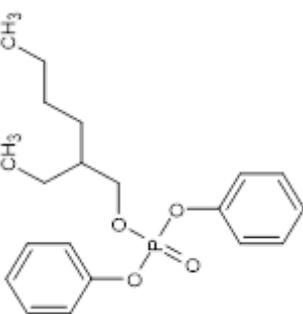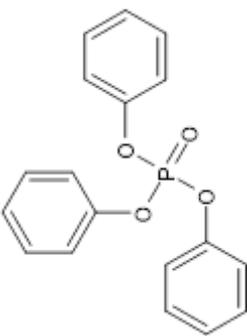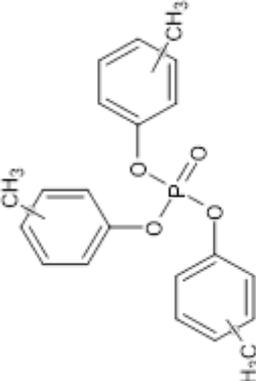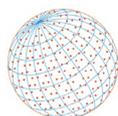
Table 1. (*continued*).

Compound structure and name	CAS No.	M.W.	S[c]	V.P	H	Log K$_{OW}$	Log K$_{OC}$	Log K$_{OA}$	Application
Bisphenol-A bis(diphenyl phosphate) (BADP)	5945-33-5	692.63	0.42	9.00E-6[c]	-	4.5[a]	4.53[c]	13.0[c]	Flame retardant
Tris (2-chloroethyl) phosphate (TCEP)	115-96-8	285.49	7.00E3	3.91E-4[c]	2.55E-8[c]	1.78[a]	2.48	5.31[b]	Flame retardant, plasticizer
Tris(1-chloro-2-propyl) phosphate (TCPP)	13674-84-5	327.57	1.20E3	5.64E-5[c]	5.96E-8[c]	2.59[a]	2.71	8.20[b]	Flame retardant, dielectric
Tris (1,3-dichloro-2-propyl) phosphate (TDCPP)	13674-87-8	430.89	7.00	2.86E-7[c]	2.61E-9[c]	3.65[a]	-	10.6[b]	Flame retardant
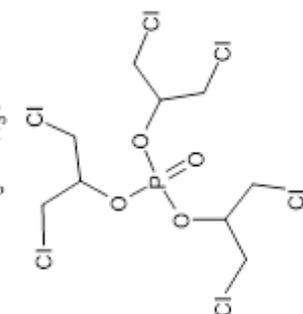
S: solubilities in water (mg L^{-1} at 25°C); V.P: Vapor pressures (mm Hg at 25°C); H: Henry's law constants (atm m^{-3} mol^{-1}); Log K$_{OW}$: n-octanol-water partitioning coefficients; Log K$_{OC}$: organic carbon-water partitioning coefficients; Log K$_{OA}$: n-octanol-air partitioning coefficients; Data from [a] Pubchem; [b] Wang et al. (2018b); and [c] Li et al. (2019b).
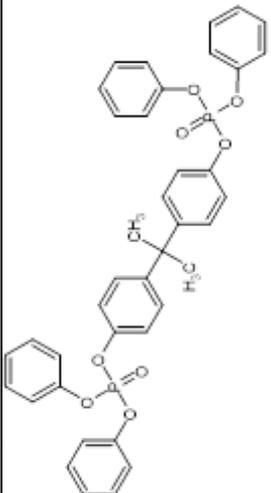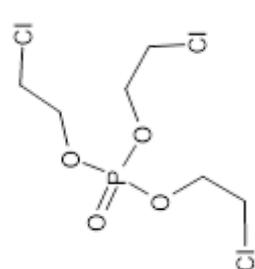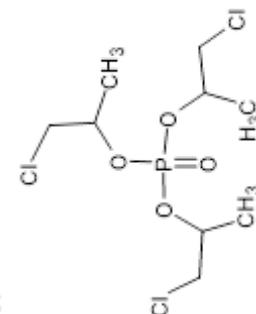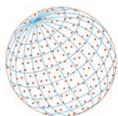
in the soil (> 75% of the samples), while straight-chain alkyl-OPFRs were often in the air. In the atmosphere, aryl-OPFRs, TBEP, and TEHP are more in the particulate phase than the gas phase, while non-chlorinated alkyl-OPFRs are more in the gas phase (Ma *et al.*, 2022). Okeme *et al.* (2018) concluded that > 50% of OPFRs, such as TCP and TEHP, with log $K_{OA} \geq 10.53$ and Log $P°_L$ (sub-cooled liquid vapor pressure) ≤ -3.73, are expected to partition in the particle phase, while more volatile compounds, e.g., TCEP and TCPP, are expected to be primarily in the gas phase. Furthermore, high molecular mass OPFRs with high K_{OW} (> 5), such as EHDP and TCP, can biomagnify in the aquatic food chain (Bekele *et al.*, 2019; Wang *et al.*, 2019b). Suhring *et al.* (2016) used the physical properties estimated by the EPI Suite and the OECD P_{OV} and long-range transport potential (LRTP) screening tool to predict the persistence and characteristic travel distance of OPFRs in air and water. In the air, the characteristic travel distance, a predictor of long-range transport potential, was in the order: aryl-OFRs and high molecular weight alkyl-OFRs > chloroalkyl-OPFRs > alkyl-OFRs. The same trend was observed for P_{OV}, an estimator of persistency, with the exception of TDCPP and TBEP, which had higher values than members of their respective groups. In conclusion, the physicochemical properties, together with the production and consumption information of OPFRs, can be useful in explaining their presence in the environment.

The wide application of OPFRs has resulted in their prevalence in the environment, including alarming concentrations in biota (Yao *et al.*, 2021). Greaves and Letcher (2014) found that OPFRs ($\sum_{16}$) mainly accumulated in the fat and muscle tissues of birds. OPFRs and their metabolites have been detected in human urine, hair, breast milk, placenta, and blood and seminal plasma (Zhang *et al.*, 2016b; Wang *et al.*, 2020a). This has raised further health risk concerns about these groups of compounds.

The effects of most of the OPFRs on humans and the environment have been studied using model organisms, e.g., zebrafish, Japanese medaka, and *Caenorhabditis elegans,* and *in vitro* investigations. Sun *et al.* (2016) found that TPhP, TnBP, TBEP, and TCEP caused embryotoxicity to Japanese medaka, decreasing hatchability, delaying hatching, and causing developmental problems. Although there are few studies on the health impact of these compounds on human beings, there has been a growing list of *in vitro* publications that show some OPFRs (TCPP, TCEP, and TPhP) have immunotoxicity (Butt *et al.*, 2014; Canbaz *et al.*, 2017; Li *et al.*, 2020a), developmental impairment (Noyes *et al.*, 2015; Sun *et al.*, 2016; Li *et al.*, 2019a; Hu *et al.*, 2021), endocrine disruption (Kojima *et al.*, 2013; Zhang *et al.*, 2017), and cardiotoxicity (Du *et al.*, 2015) potential. Blum *et al.* (2019) concluded from *in vitro* studies that OPFRs had similar developmental and neurodevelopment toxicity potential as PBDEs. Because of the differences among OPFRs, a presentation of physicochemical characteristics and effects of selected individual OPFRs was included in this review as follows:

4. 1 Alkyl-OPFRs

4.1.1 Triethyl phosphate (TEP)

TEP has high vapor pressure, Henry's law constant, low partition coefficients, and high solubility in water, as shown in Table 1. Therefore, TEP is expected to partition mostly in the gas phase and water bodies. Although it is produced at a much higher volume compared to other OPFRs, as shown in Fig. 2, TEP is primarily used as an intermediate in manufacturing (Liu *et al.*, 2021c). TEP is also considered to be less toxic than other OPFRs. Based on the current evidence (no-observed-affect level of 1000 mg kg^{-1} $_{bw}$ day^{-1} for subacute toxicity), the OECD Screening Information Data Set (SIDS) regards TEP as of low concern for risk to human beings or the environment.

4.1.2 Tri-n-butyl phosphate (TnBP)

As shown in Table 1, TnBP has low solubility in water and moderately low volatility. TnBP has additional applications including as an anti-foam agent and plasticizer (Wei *et al.*, 2015). Zhang *et al.* (2021) reported that TnBP damaged the reproductive capacity of gonad development, and induced DNA damage and oxidative stress in *C. elegans*. After 24 h exposure, TnBP inhibited acetylcholinesterase, a marker of neuronal damage, in rat adrenal pheochromocytoma cells, implying that it is likely to be neurotoxic (Chang *et al.*, 2020).

4.1.3 Tris(2-ethylhexyl) phosphate (TEHP)

Apart from being a fire retardant, TEHP is also used as a plasticizer and solvent (Wei *et al.*, 2015).
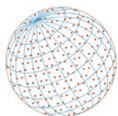
It has high partitioning coefficients and low volatility similar to aryl-OPFRs and is therefore expected to partition in the particulate phase in the atmosphere. Pelletier *et al.* (2020) reported that TEHP at high concentrations of 3000 mg kg_{bw}^{-1} day^{-1} for 28 days impaired body and organ weights and caused testicular toxicity in male rats. The study estimated that the no-observed-affect level for TEHP was 1000 mg kg_{bw}^{-1} day^{-1}.

4.1.4 Tris(2-butoxyethyl) phosphate (TBEP)

With low volatility, high partitioning coefficients, and moderate water solubility. TBEP is expected to partition in particulates. TBEP is also used as a plasticizer and an anti-foam agent in paints and floor finishes (Wei *et al.*, 2015). Several studies on TBEP on model organisms and cells have shown that it causes neurotoxicity and developmental problems (Kwon *et al.*, 2016; Ma *et al.*, 2016; Huang *et al.*, 2019). For example, TBEP decreased body length, heart rate, survival rate, and hatching rate (Xiong *et al.*, 2021) and altered motor behavior, and caused oxidative stress in zebrafish (Jiang *et al.*, 2018).

4.2 Aryl-OPFRs
4.2.1 2-ethylhexyl diphenyl phosphate (EHDP)

EHDP has low solubility in water, low volatility, and high partition coefficients, as shown in Table 1. In the atmosphere, it is expected to partition mostly in the particulate phase. EHDP is neurotoxic and hepatotoxic in zebrafish (Jarema *et al.*, 2015), and also causes reproductive toxicity in Japanese medaka fish (Li *et al.*, 2020b). Liu *et al.* (2021d) found that EHDP concentration in the plasma of women diagnosed with four female-specific tumors (benign breast cancer, breast cancer, benign cancer of the uterus, and cervical cancer) was associated with an elevated risk of breast and cervical cancers ($P < 0.05$).

4.2.2 Triphenyl phosphate (TPhP)

TPhP has low vapor pressure, Henry's law constants, and high partition coefficients and is expected to partition in the particulate phase. It is used as a fire retardant in a wide range of plastics, as shown in Table 1. Behl *et al.* (2016) found TPhP had comparable reproductive effects on *C. elegans* to commercial PBDE, DE-71 mixture (mostly comprising of penta-BDEs: BDE-47 and BDE-99). Sun *et al.* (2016) found that TPhP caused embryotoxicity to Japanese medaka, decreasing hatchability, delaying hatching, and causing developmental problems. Low concentrations of TPhP were shown to disturb the natural metabolism and DNA repair system in zebrafish (Du *et al.*, 2016). Toxicity in mice has also been shown, with Chen *et al.* (2015) reporting that TPhP and TCEP induced oxidative stress and endocrine disruption in mice at high concentrations of 300 mg kg_{bw}^{-1} for 35 days. Based on the effects on human nicotinic acetylcholine receptors, Hendriks *et al.* (2012) classified TPhP as a highly potent neurotoxic compound.

4.2.3 Tricresyl phosphate (TCP)

TCP comprises ten isomers with differing methyl group positioning. Apart from its use as a flame retardant and a plasticizer, it is widely used in aviation as an anti-wear lubricant additive (Guan *et al.*, 2016). TCP is highly hydrophobic and has a high bioaccumulation factor of 8.56×10^3 (Liu *et al.*, 2020). Because of its low volatility, TCP in the atmosphere is expected to partition mostly in the particulate phase. Tri-*ortho*-CP (ToCP) is thought to be more toxic than the meta and para isomers. The neurotoxicity of ToCP in humans has been long known since it was a common cooking oil adulterant (Craig and Barth, 1999; Paul, 2019). For example, the consumption of adulterated rape seed oil by ToCP leads to motor paralysis and permanent disability in victims in Kolkata, India (Paul, 2019). TCP in jet fuel has also been linked to aerotoxic syndrome observed in pilots and cabin crew (de Boer *et al.*, 2015).

4.3 Chloroalkyl-OPFRs

The EU region and parts of the United States have already responded to the growing evidence of the health risks associated with OPFRs by restricting the use of TCEP and TDCPP (Negev *et al.*, 2018). The EU placed TCEP on the Annex XVI authorization list, effectively banning its application
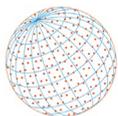
in the region. Some states, including New York and Vermont, prohibited using the two chemicals in children's toys and furniture (Negev *et al.,* 2018). It is expected for more countries to adopt similar measures.

4.3.1 Tris(2-chloroethyl) phosphate (TCEP)

TCEP has been used as a fire retardant and plasticizer in different types of plastics including polyurethanes and resins. According to Table 1, TCEP is volatile and highly soluble in water, and therefore it is expected to be found in water bodies and in the gas phase in the atmosphere. TCEP is toxic to aquatic life (Wu *et al.,* 2017), mammals (Chen *et al.,* 2015), and the EU considers TCEP a potential carcinogen to humans. As a result, it is restricted in the EU and also some parts of the US, as previously mentioned (Negev *et al.,* 2018).

4.3.2 Tris(1-chloro-2-propyl) phosphate (TCPP)

Similar to TCEP, TCPP is volatile and soluble in water, and therefore it is expected to behave in a similar manner to TCEP in the environment. TCPP has been shown to affect hormone synthesis, development, and gene transcription in zebrafish (Liu *et al.,* 2012; Yan *et al.,* 2022) and chicken embryos (Farhat *et al.,* 2013). TCPP caused oxidative stress and mitochondrial dysfunction in human umbilical vein endothelial cells (Saquib *et al.,* 2021).

4.3.3 Tris(1,3-dichloro-2-propyl) phosphate (TDCPP)

Unlike TCEP and TCPP, TDCPP has lower water solubility and a higher Log K_{OW}, as shown in Table 1. Because it has high volatility, TDCPP in the atmosphere is also expected to partition mostly in the gas phase. TDCPP replaced penta-BDE and is commonly used as a fire retardant in polyurethane foam plastics. Dishaw *et al.* (2014) found that developmental exposure to TDCPP elicited teratogenic and neurobehavioral effects on zebrafish. Urinary TDCPP metabolite, bis(1,3-dichloro-s-propyl) phosphate, measured in pregnant women's urine during their second and third trimesters was associated with decreased thyroid hormones, T3 and T4, levels, and increased thyroid-stimulating hormone levels in infants (Percy *et al.,* 2021). TDCPP is listed as a known carcinogen by the US Consumer Product Safety Commission (Babich, 2006).

4.4 Transformation products

In biota, OPFRs are quickly metabolized primarily as organophosphate diesters and hydroxylated products (Su *et al.,* 2014; Greaves *et al.,* 2016; Greaves and Letcher, 2017; Fu *et al.,* 2020). OPFRs also undergo atmospheric transformations, including photodegradation and oxidation. These transformation products might exhibit different properties and can cause additional risk. For instance, Su *et al.* (2014) found evidence to support that the diester metabolite of TPhP was more toxic than TPhP since it altered more toxicologically relevant genes. Zhang *et al.* (2020a) came to the same conclusion after investigating the endocrine disruption of TCPP, TDCPP, and TPhP metabolites. However, OPFR metabolites are currently not monitored and considered in health risk assessments.

Liu *et al.* (2021a) found 10 atmospheric transformation products (from 6 chlorinated- and 4 non-chlorinated-OPFRs), with a 94–100% detection frequency in 18 megacities globally, which uncovers a previously unrecognized exposure risk. In addition, they showed that the overall persistency of the transformation products of chlorinated OPFRs was on average 2.5 times higher than the parent compounds in all environmental media. On the other hand, non-chlorinated OPFRs were on average 25% less persistent than the parent compounds. Therefore, including the monitoring of atmospheric transformation products would present a more informed risk to the exposure of OPFR.

5 SAMPLING AND ANALYSIS OF OPFRS IN THE ATMOSPHERE

The section presents the sampling, extraction, purification, and analysis of OPFRs in the atmosphere that have been used in recent publications. The merits and disadvantages of the procedures are also included to guide researchers in selecting appropriate procedures.
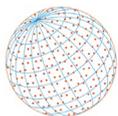
5.1 Sampling and Extraction

The simultaneous sampling of atmospheric air and particles (TSP or PM$_{2.5}$) has been carried out by equipping the samplers with quartz or glass fiber filter for particle-bound OPFRs and adsorbent, e.g., polyurethane foam (PUF), sorbent-infused PUF and styrene divinylbenzene copolymer (XAD) resin, for the gas-phase OPFRs. Medium and high-volume active air samplers have been used to continuously collect air samples, as shown in Table 2. The design flow rate is usually provided by the sampler manufacturer, but it appears most studies used similar flow rates to the one recommended (1.1–1.7 m^3 min^{-1}) by the U.S. EPA Compendium Method IO-2.1 on the sampling of particulate matter in the air using high-volume samplers. The flow rate is dependent on the analyte and the expected concentration in the air.

Active air samplers can give information about concentrations in both gas and particle phases; however, they need a power supply (Ahrens et al., 2013; Liu et al., 2016b). Passive air samplers have also been used to sample OPFRs in the air (Rauert et al., 2018; Wang et al., 2020e; Zhang et al., 2020c). Passive air samplers are low cost, do not require a power supply, and are suitable for spatial and long-term temporal investigations (Ahrens et al., 2013; Okeme et al., 2016; Huang et al., 2018). However, passive samplers cannot capture the distribution of OPFRs in the gas and particle phase and are prone to considerable human error and uncertainty in interpretation. These challenges are often associated with determining sampling rates and effective sampling volumes (Herkert and Hornbuckle, 2018).

Because OPFRs are ubiquitous in the environment and at very low concentrations, background contamination during the sampling, transport, storage, and treatment is quite common (Wang et al., 2020c). Therefore, blank tests are vital during the investigation of OPFRs in the environment. Also, all sampling materials should be pretreated and appropriately stored before and after sampling.

The extraction methods commonly used in studies are ultrasonic, Soxhlet, and accelerated solvent extractions, as shown in Table 2. Accelerated solvent extraction is the more modern extraction technique and reduces the extraction time and solvent consumption compared to Soxhlet and ultrasonic extractions (Clark et al., 2015). Microwave-assisted solvent extraction (MASE) is also a fast and cost-effective extraction technique that uses less solvent than Soxhlet and ultrasonic extraction. It is also easy to operate compared to ASE which requires tedious sample preparation and the assembly of complex sample holders. Naccarato et al. (2018) successfully used MASE to extract OPFRs from atmospheric particulate matter (PM$_{10}$) with a water and ethanol solution. OPFRs have been extracted using a single or combination of polar and non-polar solvents. Clark et al. (2015) investigated fifteen different solvent compositions (dichloromethane, methanol, and acetone) to determine the optimal solvent ratio and temperature for extracting OPFRs using accelerated solvent extraction. The optimal parameters were based on the analyte and surrogate recoveries. They found that a 2:1 ratio of dichloromethane to acetone and 100°C had the best average recoveries (77 ± 15%). Extracts undergo cleanup to remove impurities before analysis.

5.1.1 Sampling artifacts

Sampling artifacts are common in filter-sorbent samplers of SVOCs, and occur when particles are blown off the filter, gas-phase compounds sorb to the filter, particle-sorbed compounds are stripped off the filter and onto the sorbent, and breakthrough occurs in the sorbent (Arp et al., 2007; Melymuk et al., 2016; Okeme et al., 2018). The artifacts are affected by the operation of samplers (flow rate and air volume), meteorological conditions (temperature and relative humidity), and filter characteristics (Lohmann and Lammel, 2004; Cheruiyot et al., 2015; Okeme et al., 2018). Therefore, sampling artifacts influence the measurement of gas-particle partitioning, which is a crucial factor in determining the fate of a compound in the environment, including phase distribution, transportation, and deposition. However, the sampling artifacts during the sampling of OPFRs are still understudied. Studies have suggested that because of their polarity, gas-phase OPFRs will be sorbed on quartz and glass fiber filters which are also polar (Okeme et al., 2018). At high relative humidity, water films can also form on the fiber filters resulting in the absorption of OPFRs. These occurrences would lead to an underestimation of gas-phase OPFRs. Okeme et al. (2018) concluded glass fiber filter is better than a quartz fiber filter in sampling OPFRs because it has a lower predisposition to gas-phase sorption.
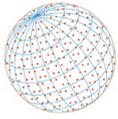
Table 2. The sampling and extraction techniques used in collecting organophosphate flame retardants in the atmosphere.

Sampling	Extraction technique	Clean up	Ref.
High-volume active air sampler (constant flow rate of 0.3 m³ min⁻¹ for 24 h)	Soxhlet extractor with dichloromethane DCM and n-hexane (1:1. v/v) for 24 h	Deactivated alumina and silica gel, anhydrous sulfuric acid–silica gel, and anhydrous sodium sulfate	(Yang et al., 2019)
High-volume active air sampler (0.3 m³ min⁻¹ for 48 h).	ASE with ethyl acetate for 2 cycles at 100°C and 1500 psi for 5 min	Silica gel and anhydrous sodium sulfate	(Wang et al., 2020d)
High-volume active air sampler (1.05 m³ min⁻¹ for 24 h)	ASE with DCM and n-hexane (1:1. v/v)	Florisil	(Zhang et al., 2020b)
High-volume active air sampler (1.13 m³ min⁻¹ for 24 h)	Soxhlet extractor with acetone and n-hexane (1:1. v/v) for 48 h	Florisil	(Wang et al., 2018a)
Medium-volume flow sampler (constant flow rate of 0.10 m³ min⁻¹ for 24 h)	Ultrasonic extraction with DCM	Deactivated Florisil and anhydrous sodium sulfate	(Chen et al., 2019)
High-volume active air sampler (0.20–0.23 m³ min⁻¹ for 24 h)	Soxhlet extractor with DCM and acetone (2:1. v/v)		(Clark et al., 2017)
High-volume active air sampler (1.05 m³ min⁻¹ for 24 h)	Ultrasonic extraction with acetonitrile		(Liu et al., 2021b)
High-volume active air sampler (1.13 m³ min⁻¹ for 24 h)	Soxhlet extractor with hexane and acetone (1:1. v/v)	Florisil	(Wang et al., 2018b)
High-volume active air sampler (1 m³ min⁻¹ for 24 h)	Soxhlet extractor with DCM	Silica gel	(Zhao et al., 2021)

DCM: dichloromethane; ASE: Accelerated solvent extractor.
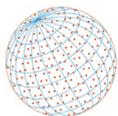
5.2 Instrumental Analysis

As shown in Table 3, gas chromatography-mass spectrometry (GC-MS), gas chromatography-tandem mass spectrometry (GC-MS/MS), and ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) have been used by different research groups in analyzing OPFR from atmospheric samples. All these analytical instruments have distinctive merits. GC has good separation capacity for most OPFRs except higher molecular ones where UPLC is more suitable.

After the compounds are separated and eluted from the GC column, they are subjected to ionization. The resulting fragmentations are used to identify the compounds by the MS or MS/MS. These mass detectors have replaced nitrogen and phosphorus nitrogen detectors in OPFR analysis due to their higher selectivity (Pantelaki and Voutsa, 2019). The MS uses the primary and secondary ions and the retention time to identify OPFRs. In contrast, MS/MS uses the transitions of the primary and secondary ions and retention times for identification. Therefore, MS/MS is more sensitive than MS and can be used to detect complex sample matrices (Wolschke *et al.*, 2016). Currently, a triple quadrupole MS detector with the multiple reaction monitoring mode provides the highest sensitivity for the structural identification of the compounds (Ma *et al.*, 2022).

Electron impact ionization (EI) has been used for GC-MS and GC-MS/MS for the fragmentation of OPFRs. However, the high energies of EI might lead to undesirable fragmentation. This is because OPFR yields low-mass fragments under high energies. Chemical ionization techniques such as electron spray ionization, used alongside UPLC, provide a more controllable fragmentation of OPFRs (Björklund *et al.*, 2004).

Helium gas, at a flow rate of 1.0–1.5 mL min^{-1}, has been used as a carrier gas in GC-MS and GC-MS/MS instruments. Nonpolar polyphenylmethylsiloxane capillary columns of 30 m × 0.25 mm × 0.25 μm dimensions have been used to separate the compounds. The nonpolar stationary phase coatings are preferred over polar ones because polarity reduces the thermal stability of columns (Patnaik, 2017).

The efficiency of the column to separate compounds is determined by the stationary phase and the polarity of the target compounds. The more polar OPFRs such as TEP will have shorter retention times in the nonpolar columns compared to less polar OPFRs. The ion source temperature for the GC ranged from 230–290°C, and the temperature program started at 60–90°C and ramped up to 300–320°C (Salamova *et al.*, 2014b; Clark *et al.*, 2015; Castro-Jiménez and Sempéré, 2018; Wang *et al.*, 2018a; Chen *et al.*, 2020; Wang *et al.*, 2020b; Wang *et al.*, 2020d; Zeng *et al.*, 2020; Prats *et al.*, 2022).

6 OCCURRENCE OF ORGANOPHOSPHATE FLAME RETARDANTS IN THE ATMOSPHERE

OPFR concentrations in atmospheric air, total suspended solids, and PM$_{2.5}$ published in recent articles are presented in Table 4. The main challenge in comparing the concentrations published in previous papers is that there are differences in the number of targeted OPFRs. For example, Li *et al.* (2021) targeted only 7 OPFRs while Zeng *et al.* (2021) studied 13 OPFRs and Li *et al.* (2019b) targeted 20 OPFRs. However, comparing the studies can still provide insights into how these compounds behave in the atmosphere.

From Table 4, we can deduce that OPFR concentrations in PM$_{2.5}$ are higher than in TSP and air. This observation is supported by Cao *et al.* (2022) that reported fine particles (< 3.3 μm) had the highest OPFRs ($\sum_9$) at 42 ± 6%, followed by coarse particles (> 3.3 μm) then gas phase at 37 ± 9% and 16 ± 12%, respectively. The highest median concentration in PM$_{2.5}$, 19,400 pg m^{-3} ($\sum_{11}$), was measured in an urban area in China by Chen *et al.* (2020), while the highest concentration in TSP, with almost the same number of analyzed OPFR, was measured at an integrated atmospheric deposition network sampling site in Chicago, US, at 1,390 pg m^{-3} ($\sum_{12}$). The higher concentrations in PM$_{2.5}$ than in TSP could be related to the larger surface area of PM$_{2.5}$. The highest median concentration in air was measured in Dalian, China, at 1,316 pg m^{-3} ($\sum_{10}$); however, higher concentrations have been reported in outdoor air outside buildings in Rhine, Germany and Stockholm, Sweden, as shown in the table.

Li *et al.* (2021) studied the concentration of OPFR in coarse (1.8 < Dp ≤ 10 μm), fine (0.10 < Dp < 1.8 μm), and ultrafine (Dp < 0.10 μm) atmospheric particles and found that the highest
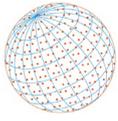
Table 3. The instrumental analysis techniques and QA/QC parameters were used to analyze organophosphate flame retardants.

Detection	Carrier gas/Mobile phase	Column	Method LOD	MDL	MQL	IDL	Recovery standard (recovery)	Internal standard (recovery)	Ref.
GC-MS/MS		HP-5MS column (30 m × 0.25 mm × 0.25 µm)		0.4–40.7 pg m⁻³				d_{12}-TCEP (87 ± 13%), d_{27}-TnBP (90 ± 9%), and d_{15}-TPhP (92 ± 12%)	(Li et al., 2021)
GC-MSD	Helium (1.5 mL min⁻¹)	DB-5MS (30 m × 0.25 mm × 0.25 µm)		0.78–63.2 pg m⁻³				d_{12}-TCEP (79.0 ± 8.2%), d_{18}-TCPP (86.8 ± 13.2%), and d_{15}-TPhP (89.8 ± 8.9%)	(Wang et al., 2020d)
GC-EI-MS	Helium (1.2 mL min⁻¹)	DB-5MS (30 m × 0.25 mm × 0.25 µm)	0.01–1.58 pg m⁻³					d_{27}-TBP (50–120%) and 10 ng TPP-d_{15} (81–114%)	(Zhang et al., 2020b)
GC-EI-MS	Helium (1.0 mL min⁻¹)	DB-5MS (30 m × 0.25 mm × 0.25 µm)		0.04–1.10 pg m⁻³			TPhP-d_{21}, (125 ± 23.7%), TnBP-d_{27}, (80.8 ± 10.4%) and d_{18}-TCPP (98.7 ± 9.4%)	d_{12}-TCEP and d_{15}-TDCPP	(Wang et al., 2018a)
GC-EI-MS/MS	Helium (1.5 mL min⁻¹)	TG-5MS (30 m × 0.25 mm × 0.25 µm)			0.07–5.41 pg m⁻³	0.003–0.23 pg	d_{15}-TPhP, d_{27}-TnBP, and d_{12}-TCEP 70–130%		(Chen et al., 2019)
GC-EI-MS	Helium (1.0 mL min⁻¹)	TG-5MS (30 m × 0.25 mm × 0.25 µm)		6.36–26.5 ppb			d_{15}-TPhP (50.0 ± 10.2%) and d_{12}-TCEP (50.0 ± 5.2%)		(Clark et al., 2017)
UPLC-ESI-MS/MS	Mobile phase: Water (A) and methanol (B), both spiked with formic acid (300 µm min⁻¹)	Kinetex® 5 µm EVO C18 100 Å (100 mm × 2.1 mm, 5 µm particle size)							(Liu et al., 2021b)
GC-EI-MS	Helium (1.5 mL min⁻¹)	DB-5MS (30 m × 0.25 mm × 0.25 µm)		0.25–10 pg m⁻³			d_{21}-TnPP (91.4 ± 15.4%), d_{27}-TnBP (92.2 ± 14.4%), d_{18}-TCPP (87.9 ± 15.5%) and d_{15}-TPhP (91.8 ± 15.8%)		(Wang et al., 2018b)

GC: gas chromatography; MS: mass spectrometry; MS/MS: tandem mass spectrometry; EI: electron impact ionization; UPLC: ultra-performance liquid chromatography; ESI: electronspray ionization.
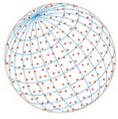
Table 4. Organophosphate flame retardant concentrations in the atmosphere published in recent studies.

Media	Region	Site type	Sampling year	n	No. OPFRs	Total concentration (pg m^{-3})		References
						Mean ± SD	Median	
Atmospheric PM$_{2.5}$	Dalian, China	Urban area	Nov 2016–Nov 2017	53	$\sum_9$	1,200 ± 674	1,080	(Wang et al., 2020d)
	Beijing, China	Urban area	Apr 2016–Mar 2017	22	$\sum_8$	930 ± 707	705	(Zhang et al., 2020b)
		Urban area		26		1,730 ± 1,477	1,067	
	Tianjin, China	Urban area		21		1,203 ± 1,652	746	
	Shijiazhuang, China	Urban area		21		949 ± 733	724	
	Beijing, China	Rural area		10		420 ± 331	355	
	Guangzhou, China	Industrial park	Jan 2015–Apr 2016	20	$\sum_{12}$	5,815 ± 10,044	2,854	(Wang et al., 2018a)
	Qingyuan, China	e-waste recycling park		4		4,350 ± 2,859	3,321	
	Guangzhou, China	Industrial park	Mar 2013–Feb 2014	72	$\sum_{12}$	2,504	2,346	(Zeng et al., 2020)
	Qingyuan, China	e-waste recycling park		72		12,625	10,955	
	Dinghushan Nature reserve, China	Nature reserve, background		72		7,838	2,170	
	Guangzhou, China	Rural area	May 2017–Apr 2018	24	$\sum_{11}$	15,900	15,200	(Chen et al., 2020)
	Guangzhou, China	Urban area		24		13,500	14,000	
	Taiyuan, China	Urban area		24		19,500	19,400	
Atmospheric TSP	Bizerte City, Tunisia	Urban area	Mar 2015–Jan 2016	60	$\sum_9$	510 ± 250	469	(Castro-Jiménez and Sempéré, 2018)
	South China Sea	Marine atmosphere	Oct 2013	10	$\sum_8$	94.4 ± 38.6	-	(Lai et al., 2015)
	New York, US	International airport	May 2018	24	$\sum_{20}$		3,210	(Li et al., 2019b)
	Zhengzhou, China	Urban	Jun–Nov 2018	30	$\sum_6$	1,040 ± 1,000	1,360	(Pang et al., 2019)
	Lingang New Area, Shanghai	Coastal areas	Jul 2016–Jun 2017	38	$\sum_{13}$	300 ± 410	150	(Ma et al., 2022)
	Jinshan Area, Shanghai			42		700 ± 730	430	
	Antarctic	Remote area	2018	24	$\sum_8$	73.9 ± 20.2	-	(Wang et al., 2020b)
	Chicago, US	Integrated Atmospheric Deposition Network sampling site	Mar–Dec 2012	27	$\sum_{12}$	1,500 ± 170	1,390	(Salamova et al., 2014b)
	Cleveland, US			22		2,100 ± 400	1,306	
	Sturgeon Point, US			16		340 ± 85	207	
	Sleeping Bear Dunes, US			16		120 ± 18	109	
	Eagle Harbor, US			26		170 ± 52	100	
	NE Atlantic and Arctic Oceans	Marine atmosphere	Jun 2014	9	$\sum_8$	58	48	(Li et al., 2017)
	Yongxing Island, South China Sea	Small island	May 2018–Jul 2019	100	$\sum_{10}$	306 ± 319	214	(Zhang et al., 2022a)
	Xinxiang City, China	Shopping area	Jul 2017–Oct 2018	74	$\sum_7$	17,700 ± 11,300	-	(Li et al., 2021)

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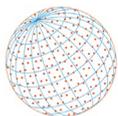
Table 4. (*continued*).

Media	Region	Site type	Sampling year	n	No. OPFRs	Total concentration (pg m^{-3}) Mean ± SD	Median	References
Atmospheric air	Rhine, Germany	Outdoor of buildings	Jan–Jul 2015	9	$\sum_9$	7,950 ± 6,550	5,130	(Zhou et al., 2017)
	Toronto, Canada	Urban area	Aug 2016–Sep 2017	39	$\sum_{16}$	1,790	-	(Saini et al., 2019)
	Lingang New Area, Shanghai	Coastal areas	Jul 2016–Jun 2017	38	$\sum_{13}$	650 ± 710	390	(Ma et al., 2022)
	Jinshan Area, Shanghai			42		133 ± 800	1,300	
	Dalian China	Urban area	Nov 2016–Nov 2017	53	$\sum_9$	829 ± 1,250	296	(Wang et al., 2020d)
	New York, US	International airport	May 2018	24	$\sum_{20}$	333	333	(Li et al., 2019b)
	Ny-Ålesund and Ny-London, Svalbard	Remote Arctic areas	Aug 2014–Aug 2015	5	$\sum_8$	576 ± 221	-	(Han et al., 2020)
	Stockholm, Sweden	The balcony of a laboratory	Apr 2014–May 2015	24	$\sum_{10}$	3,900 ± 2,500	3,100	(Wong et al., 2018)
	Antarctic	Remote area	2018	24	$\sum_8$	92.3 ± 13.8	-	(Wang et al., 2020b)
	Dalian, China	Urban, suburban, and rural areas	Jul–Sep 2017	20	$\sum_{10}$	1,632 ± 1,330	1,316	(Wang et al., 2020e)
	Nanning, China	Urban and rural area	May–Jul and Sep–Nov 2017	12	$\sum_{11}$	424 ± 335	-	(Zhang et al., 2020c)
	Yongxing Island, South China Sea	Small island	May 2018–Jul 2019	100	$\sum_{10}$	378 ± 217	327	(Zhang et al., 2022a)
	La Selva and Las Cruces, Costa Rica	Biological research stations	Jan–Jul 2017	23	$\sum_{19}$	-	1,193	(Wang et al., 2019a)
	Kibale National Park, Uganda	Biological research stations	May–Oct 2017	25	$\sum_{19}$	-	477	
	Bursa, Turkey	Industrial city	Feb–Dec 2014	40	$\sum_7$	7,435 ± 5,045	6,455	(Kurt-Karakus et al., 2018)
	NE Atlantic and Arctic Oceans	Marine atmosphere	Jun 2014	9	$\sum_8$	40	17	(Li et al., 2017)

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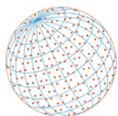
concentration was in fine particles with a mean concentration of 4,730 ± 2,520 pg m^{-3} followed by concentrations in coarse (2850 ± 1510 pg m^{-3}) and then ultrafine (2360 ± 1040 pg m^{-3}) particles. This was because OPFRs with higher concentrations, e.g., TCPP and TBEP, were predominantly adsorbed on fine particles and TCEP on coarse particles.

OPFR concentrations correlated well with proximity to pollution sources. Highly populated and industrial areas generally have higher OPFR concentrations in the atmosphere. For instance, the median concentration in rural Beijing (355 pg m^{-3}) was two to three times lower than in urban Beijing (Zhang *et al.*, 2020b). OPFRs have also been detected in remote locations in Antarctic and Arctic regions (Möller *et al.*, 2011; Salamova *et al.*, 2014a; Suhring *et al.*, 2016; Li *et al.*, 2017; Han *et al.*, 2020; Wang *et al.*, 2020b) and high mountains (Prats *et al.*, 2022). The presence of these compounds in remote regions with limited potential sources suggests the long-range transport and persistency of these compounds (Liu *et al.*, 2016a; Fu *et al.*, 2021).

Based on the total mean and median concentrations (Table 4), OPFRs tend to partition mainly in the particulate phase (Salamova *et al.*, 2014b; Shoeib *et al.*, 2014; Lai *et al.*, 2015; Ren *et al.*, 2016). Contrarily, Wolschke *et al.* (2016), Wang *et al.* (2020b), Ma *et al.* (2022), and Zhang *et al.* (2022a) concluded that OPFRs are mainly partitioned in the gas than particulate (TSP) phases. The contradictory conclusions would require further investigation. However, it appears the conclusion is dependent on which OPFRs were analyzed and their concentrations. Therefore, using the total mean concentration to draw a conclusion might not be suitable, and researchers should instead compare the gas-particle partitioning based on chemical structure: alkyl-, chloroalkyl-, and aryl-OPFRs. Another critical point is the underestimated gas-phase OPFRs due to sampling artifacts. Okeme *et al.* (2018) suggested that gas-phase OPFRs are sorbed on quartz and glass fiber filters because of high polarity.

Fig. 3 shows the stacked median concentrations of individual OPFRs published in recent publications. A comprehensive comparison is also limited because the publications did not analyze the same OPFRs. However, chloroalkyl-OPFRs, TCPP and TCEP, appear to be the dominant OPFRs in the atmosphere. Aryl-OPFRs, TPhP, and TCP, were mainly in atmospheric PM$_{2.5}$ (Fig. 3(a)), and alkyl-OPFRs, TiBP, and TnBP were in the air (Fig. 3(c)). Higher molecular weight alkyl-OPFRs, e.g., TEHP, were also in high concentrations in particulate matter. The gas-particle partition of individual OPFRs is dependent on their physicochemical properties, e.g., vapor pressure and Log K$_{OA}$, and environmental factors such as temperature and relative humidity. The partitioning of OPFRs will also affect the fate of the compounds in the atmosphere. Particle-bound OPFRs are more susceptible to wet and dry deposition than OPFRs in the gas phase, however, they are more

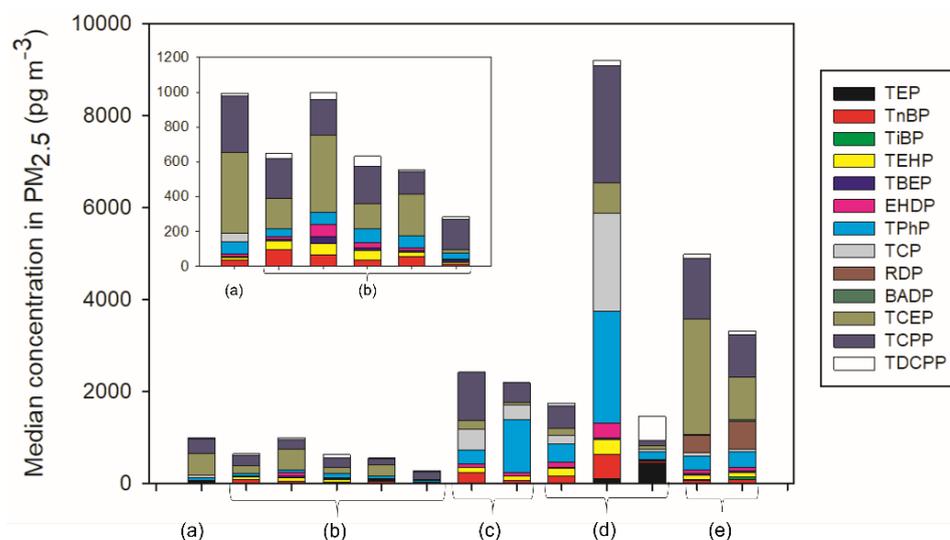**Fig. 3(a).** The median concentrations of atmospheric PM$_{2.5}$-bound organophosphate flame retardants from recent publications: (a) Wang *et al.* (2020d); (b) Zhang *et al.* (2020b); (c) Wang *et al.* (2018a); (d) Zeng *et al.* (2020); and (e) Zeng *et al.* (2021). The publications analyzed 8, 12, 12, and 13 OPFRs, respectively. The details are presented in Excel Table S1.
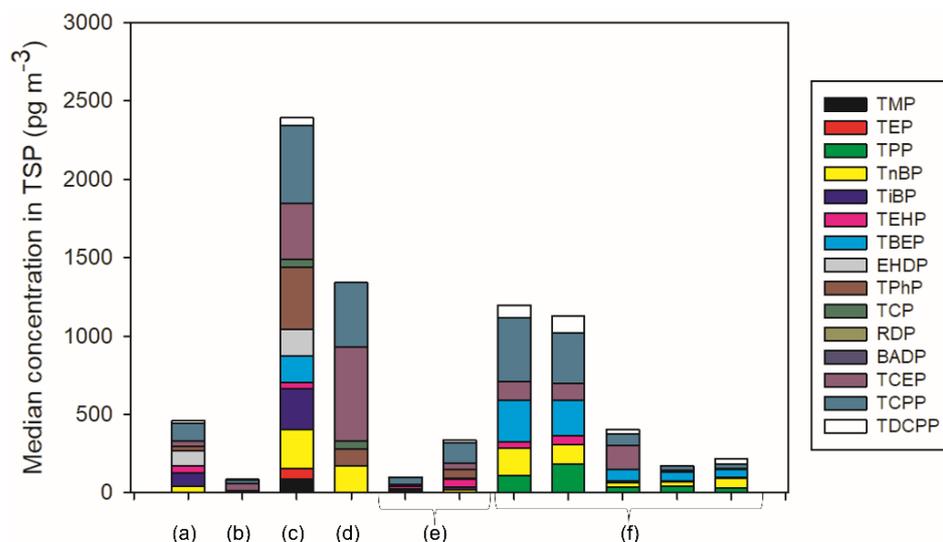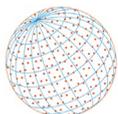
Fig. 3(b). Median concentrations of atmospheric total suspended solids- (TSP-)bound OPFRs from recent publications: (a) Castro-Jiménez and Sempéré (2018); (b) Lai *et al.* (2015); (c) Li *et al.* (2019b); (d) Pang *et al.* (2019); (e) Ma *et al.* (2022); (f) Salamova *et al.* (2014b). The publications analyzed 9, 8, 20, 6, 13, and 12 OPFRs, respectively. The details are presented in Excel Table S2.

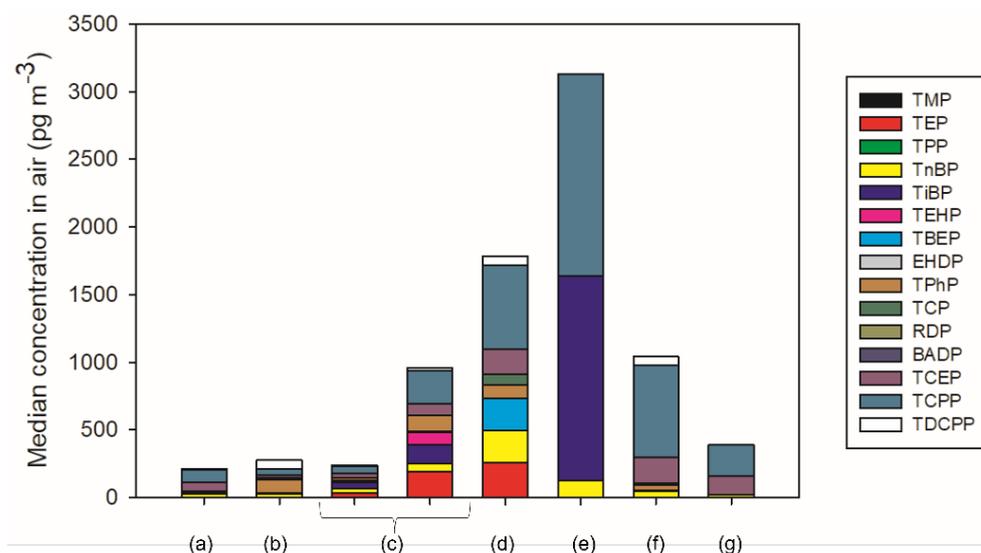**Fig. 3(c).** Concentrations of organophosphate flame retardants in atmospheric air from recent publications: (a) Wang *et al.* (2020d); (b) Li *et al.* (2019b); (c) Ma *et al.* (2022); (d) Saini *et al.* (2019); (e) Zhou *et al.* (2017); (f) Wang *et al.* (2020e); and (g) Zhang *et al.* (2020c). The publications analyzed 9, 20, 13, 16, 9, 10, and 11 OPFRs, respectively. The mean concentrations from Saini *et al.* (2019) were used. Zhou *et al.* (2017) sampled outside buildings explaining the high concentrations. The details are presented in Excel Table S3.

resistant to atmospheric transformation, e.g., oxidation by atmospheric radicals (Liu *et al.*, 2014). Therefore, particle-bound OPFRs persist more in the environment.

In summary, the presence of OPFRs in the atmosphere could be viewed as a combination of production and consumption of the OPFRs, physicochemical properties of the OPFR, and meteorological conditions. Atmospheric processes including photodegradation, photocatalysis, gas-particle partitioning, transportation, and deposition are influenced by meteorological conditions including temperature, relative humidity, wind, atmospheric pressure, and solar radiation (Bu *et al.*, 2021; Tian *et al.*, 2021; Yu *et al.*, 2021; Salvador *et al.*, 2022). Temperature would influence
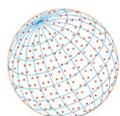
OPFR volatilization into the atmosphere and the partitioning of OPFRs into the gas phase. Atmospheric pressure and wind influence dispersion, dilution, and transportation of OPFRs. Solar radiation influences the transformation of OPFRs in the atmosphere. Wang et al. (2018a) studied the influence of temperature, humidity, solar radiation, atmospheric pressure, and wind speed on PM$_{2.5}$-bound and gas-phase OPFRs. They found that temperature (0.789, $p < 0.01$), humidity (0.525, $p < 0.01$), and solar radiation (0.429, $p < 0.01$) were positively correlated with the overall gas-phase OPFRs, especially TCEP, TCPP, and TPhP, while wind speed (–0.456, $p < 0.01$), and atmospheric pressure (–0.634, $p < 0.01$) were negatively correlated. Generally, the correlations between the overall PM$_{2.5}$-bound OPFR and the meteorological parameters were weak and statistically insignificant.

7 CONCLUSIONS AND FUTURE PERSPECTIVES

Organophosphate flame retardants (OPFRs) are a group of diverse compounds of interest to environmental science researchers due to their high-volume production, use, and ubiquitous presence in the environment. This review collated and assessed the current knowledge on OPFRs in the atmosphere. In the atmosphere, OPFRs tend to partition more in the particulate phase, and the concentrations correlated well with proximity to pollution sources. Chloroalkyl-OPFRs, TCPP and TCEP, appear to be the dominant OPFRs in the atmosphere. Aryl-OPFRs, TPhP and TCP, were mainly in atmospheric PM$_{2.5}$, and Alkyl-OPFRs, TiBP and TnBP, were in the air. Higher molecular weight alkyl-OPFRs, e.g., TEHP, are partitioned mostly in particulate matter. The gas-particle partition of individual OPFR depends on physicochemical properties, e.g., vapor pressure and Log K$_{OA}$, and environmental factors such as temperature and humidity. The gas-phase OPFRs, especially chloroalkyl-OPFR and low molecular alkyl-OPFR, might be underestimated because of sampling artifacts. Transformation products of OPFR should be measured and considered in risk assessment because they represent additional exposure risks. For example, some diester metabolites of TPhP, TCPP, and TDCPP are reported to be more toxic than the parent compounds. Chloroalkyl-OPFR atmospheric transformation products were also more toxic and persistent in the atmosphere. There should be a consensus on the target compounds for analysis in the future to make comparisons between studies easier. Adequate information about the production and use of OPFRs would make it easier to link the concentration levels with use. In addition, researchers could also include the effect of meteorological parameters on the fate of these compounds in the atmosphere.

ABBREVIATIONS

|	
BADP	Bisphenol-A bis(diphenyl phosphate)
CDPP	cresyl diphenyl phosphate
*D*p	Aerodynamic diameter
EHDP	2-ethylhexyl diphenyl phosphate
IPPP	isopropylated triphenyl phosphate
OPFRs	Organophosphate flame retardants
PBDEs	Polybrominated diphenyl ethers
RDP	Resorcinol bis(diphenyl phosphate)
TBEP	Tris(2-butoxyethyl) phosphate
TBPHPP	Tris(p-tert-butylphenyl) phosphate
TCEP	Tris (2-chloroethyl) phosphate
TCP	Tricresyl phosphate
TCPP	Tris(1-chloro-2-propyl) phosphate
TDCPP	Tris (1,3-dichloro-2-propyl) phosphate
TEHP	Tris(2-ethylhexyl) phosphate
TEP	Triethyl phosphate
TiBP	Tri-iso-butyl phosphate
TMP	Trimethyl phosphate
TnBP	Tri-n-butyl phosphate
TPhP	Triphenyl phosphate
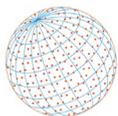
| TPP | Tripropyl phosphate |
| TXP | Trixylenyl phosphate |

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.220148

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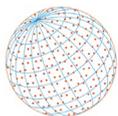
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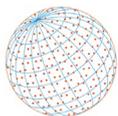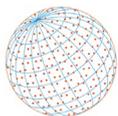
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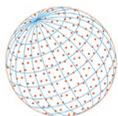
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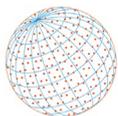
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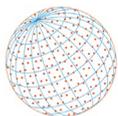
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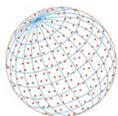
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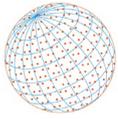
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