JOURNAL OF WATER AND LAND DEVELOPMENT
e-ISSN 2083-4535
Polish Academy of Sciences (PAN) Institute of Technology and Life Sciences – National Research Institute (ITP – PIB)

JOURNAL OF WATER AND LAND DEVELOPMENT
DOI: 10.24425/jwld.2023.147227
2023, No. 59 (X–XII): 44–49

An overview of the (eco)toxicological effects of flame retardants emerging in water and sediment

Adriana M. Dowbysz[1)], Mariola Samsonowicz[1)], Bożena Kukfisz[2)]

[1)] Bialystok University of Technology, Department of Chemistry, Biology and Biotechnology, 45E Wiejska St, 15-351, Bialystok, Poland
[2)] Fire University, Institute of Safety Engineering, Warsaw, Poland

RECEIVED 31.05.2023 ACCEPTED 17.08.2023 AVAILABLE ONLINE 31.12.2023

Abstract: Flame retardants (FRs) that have an adverse effect on human and the environment have been subject to regulation since 1972. However, FRs emerging as a replacement, are not proving to be fully environmentally safe. Water and sediment contamination by FRs, including organophosphorus (OPFRs) and novel brominated (NBFRs) ones, is a matter of major concern. Due to their common usage, many release sources, and relatively high mobility, they pose a threat to aquatic organisms and ecosystems. This review summarises studies on the OPFRs', and NBFRs' simultaneous occurrence in water and corresponding sediment. The main sources of occurrence and routes of entry of FRs into the environment are presented. The newest reports on the ecotoxicity of selected FRs had been summarised in order to bring the matter to attention. The research revealed that although great efforts had been made to study the occurrence of OPFRs and NBFRs in water and sediment separately, there is a lack of research on their occurrence in both media in the same area. Although major efforts have been made to study the ecotoxicity of OPFRs, there are some deficiencies for the NBFRs. Considering their relatively high ecotoxicity, further studies should be conducted on joint ecotoxicity, which may cause synergistic or antagonistic effects.

Keywords: organophosphorus flame retardants, novel brominated flame retardants, ecotoxicity, water, sediment

INTRODUCTION

For many years much attention had been paid to extending life and maintaining the integrity of materials present in people's lives. Since the 18th century flame retardants (FRs) were used in order to reduce fire hazard and later to achieve suitable levels of fire protection for several materials, including furnishings, electronics, building, and construction materials.

FRs are a group of various compounds that reduce the adverse effect of thermal degradation and combustion of materials on people and the environment. They extend the time to ignition, inhibit flame spreading and restrain the pyrolysis process. FRs may be divided according to several criteria, e.g. contained elements or structures, mode of action, or bonding method. The most common FRs over the years were halogenated FRs (HFRs), inorganic hydroxides (including $Al(OH)_3$ and $Mg(OH)_2$), phosphorus, nitrogen, boron, tin, and zinc compounds, nanoclays, polyhedral oligomeric silsesquioxanes, as well as its mixtures, and intumescent coatings. However, not all FRs are environmentally safe. Many of them have an adverse effect on human health and the environment. This applies mainly to the HFRs (chlorinated and brominated) and organophosphorus FRs (OPFRs) which give serious cause for concern for scientists and the government (Dowbysz, Samsonowicz and Kukfisz, 2021).

Regulation of usage and production of HFRs started in 1972 by banning polychlorinated biphenyls (PCBs) being persistent organic pollutants (POPs) (Miranda *et al.*, 2022), that have an adverse effect on the ecosystem and human health. Seeking satisfactory alternatives led to growing interest in brominated FRs (BFRs), which exhibit a similar mode of action. However, the toxicity and ecotoxicity of their representatives such as polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), and tetrabromobisphenol A (TBBPA) turned out unacceptable and resulted in further restrictions of their usage in European Union and North America. At that time OPFRs became the focus of attention. However, BFRs and OPFRs are nowadays found as "regrettable substitutions" (Lippold *et al.*, 2022).

Nowadays, although national regulations and fire safety standards vary for different industry sectors in Europe, the European Commission strives for harmonisation by imposing more stringent regulations concerning general product safety and the usage of certain hazardous substances. However, fire safety standards themselves, do not forbid specific FRs. At the same time, the awareness of the importance of ecolabels and voluntary product assessments increases; the requirements to meet the standard often limit the usage of specific compounds, such as HFRs for the Blue Angel (ECHA, 2023).

Although non-toxic alternatives are commercially available in the market, still, despite of high toxicity and ecotoxicity of HFRs, a new class of FRs known as new brominated FRs (NBFRs) has emerged (Montano *et al.*, 2022).

Recent studies on the occurrence of these toxic FRs revealed that organophosphate esters, including tris(butoxyethyl) phosphate (TBOEP), tris(2-chloroethyl) phosphate (TCEP), tris (2-chloroisopropyl) phosphate (TCIPP), triethyl phosphate (TEP), tris(1,3-dichloro-2-propyl)phosphate (TDCPP), triphenyl phosphate (TPP), and NBFRs including decabromodiphenyl ethane (DBDPE), bis(2,4,6-tribromophenoxy) ethane (BTBPE), hexabromobenzene (HBB), bis(2-ethylhexyl) tetrabromophtalate (TBPH), were found in water and sediment across the globe.

The objective of this review is to summarise the recent knowledge of the occurrence of FRs in water and sediment and evaluate the risk posed by these compounds in terms of their toxicity, bioaccumulation properties, and eco(toxicity). Sources and distribution of OPFRs and NBFRs, as well as their ecotoxicological effects are analysed.

SOURCES OF FLAME RETARDANTS

FRs may enter aquatic ecosystems via point, line, or volume sources. They may undergo several processes including partitioning and degradation followed by sinking in sediments (Hou *et al.*, 2021). The pathways encompass atmospheric deposition, surface run-off, and precipitation (Wang *et al.*, 2023). PBDEs, NBFRs, and OPFRs production, their leaching from the materials, and improper discharge are major sources of environmental contamination. Reuse and recycling of materials containing these FRs, including electronic waste, upholstery, and furniture, may also have a limited impact on the environment (Miranda *et al.*, 2022). The occurrence of FRs in the environment is shown in Figure S1.

FLAME RETARDANTS INCLUDING ORGANOPHOSPHORUS (OPFRs) OCCURRING IN WATER AND SEDIMENT

OPFRs contain a phosphate group with organic compounds attached (Kung *et al.*, 2022). They are a group of mainly additive FRs, which can easily enter the environment via volatilisation, leaching, or abrasion. They may be divided into three subgroups: Cl-alkyl (containing chlorine atoms), non-Cl alkyl, and aryl compounds. The Cl-alkyl subgroup contains e.g. tris(2-chloropropyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tris(2-chloroethyl) phosphate (TCEP) (Liu, Y. *et al.*, 2022), bis(1,3-dichloro-2-propyl) phosphate (BDCPP) (Kim, Oh and Kannan, 2017). Non-Cl alkyl compounds include e.g. triisopropyl phosphate (TiPrP), tris(2-butoxyethyl) phosphate (TBOEP), trimethyl phosphate (TMP), tri-n-butyl phosphate (TnBP), tri-iso-butyl phosphate (TIBP), triethyl phosphate (TEP), tris(2-ethylhexyl) phosphate (TEHP) (Liu, Y. *et al.*, 2022), tripropyl phosphate (TPrP) (Shi, Y. *et al.* 2016). Triphenyl phosphate (TPHP), triphenylphosphine oxide (TPPO), tetraphenyl m-phenylene bis(phosphate) (RDP) (Liu, Y. *et al.*, 2022), cresyl diphenyl phosphate (CDPP) (Shi, Y. *et al.*, 2016), tris (methylphenyl) phosphate (TMPP), diphenyl phosphate (DPhP) (Kim, Oh and Kannan, 2017) are ones of aryl compound representatives.

Present in water, OPFRs may degrade to potentially toxic organophosphate diesters (Di-OPs) by the wastewater treatment processes or photolysis. Examples of Di-OPs are bis(2-butoxyethyl)2-hydroxyethyl phosphate triester (BBOEHP) and bis (2-butoxyethyl)2-(3-hydroxybutoxy)ethyl phosphate triester (3-OH-TBOEP) (Liu, Y. *et al.*, 2022).

NOVEL BROMINATED FLAME RETARDANTS (NBFRs) OCCURRING IN WATER AND SEDIMENT

NBFRs are a group of additive or reactive FRs, marketed to replace the traditional BFRs. Additive NBFRs may be divided into three subgroups: polyaromatic, monoaromatic, and other. Polyaromatic subgroup contains e.g. decabromodiphenylethane (DBDPE), and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE). Hexabromobenzene (HBB) (Lee *et al.*, 2020; Dong *et al.*, 2021), pentabromotoluene (PBT), and 2,3,4,5,6-pentabromoethylbenzene (PBEB) (Carlsson *et al.*, 2018; Dong *et al.*, 2021) are examples of monoaromatic additive NBFRs. Other additive types are 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) (Lee *et al.*, 2020, Dong *et al.*, 2021), bis-(2-ethylhexyl) tetrabromophthalate, 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (DBE-DBCH), tris(2,3-dibromopropyl) isocyanurate (TBC) (Dong *et al.*, 2021). NBFRs are a wide group of compounds; other representatives are HBCD (Chokwe *et al.*, 2015), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE) (Lee *et al.*, 2020), 2,4,6-tribromophenol (TBP), pentabromophenol (PBP) (Xiong *et al.*, 2016), pentabromobenzene (PBBz), 2,3,5,6-tetrabromo-p-xylene (TBX), and 1,2,5,6-tetrabromocyclooctane (α-TBCO) (Carlsson *et al.*, 2018). All mentioned NBFRs are present in water. Although they can be efficiently removed during treatment processes, they may be still disposed into sewage sludge and sediments.

PHYSICOCHEMICAL PROPERTIES OF FLAME RETARDANTS INCLUDING ORGANOPHOSPHORUS (OPFRs) AND NOVEL BROMINATED FLAME RETARDANTS (NBFRs)

Due to the variety of OPFRs and NBFRs structures, there is no overall pattern of changes in their physicochemical properties. However, that knowledge allows us to predict and explain their occurrence in different ecosystems. Chemical structure, molecular mass, solubility in water, vapour pressure, or sub-cooled liquid vapour pressure are important properties in terms of a profound understanding of their occurrence and concentration in water, soil, and atmosphere (Bika *et al.*, 2022; Kung *et al.*, 2022). However, one of the most important characteristics is the octanol-water partition coefficient (K_{OW}) value. Table S1 presents selected physicochemical properties of various OPFRs and NFBRs.

Most of the OPFRs exhibit greater than zero log K_{OW} values, indicating their lipophilic properties and higher tendency to bioaccumulation. On the other hand, chlorine-containing OPFRs are hydrophilic and stand as a threat to aquatic organisms – Table S1 (Bika *et al.*, 2022). Additionally, the bioconcentration factor (BCF), which is the coefficient for the equilibrium partitioning process between water and aquatic organisms, may be simplistically predicted and estimated based on the log K_{OW} values (Dimitrov *et al.*, 2002).

Differences in the physicochemical properties of FRs affect the considerable variety in the presence and concentration of these groups of FRs in water and sediment. Lipophilic, hydrophobic, and low vapour pressure properties of PBDEs influence their appearance in sediments, eatables, and particles and droplets in the air (Miranda *et al.*, 2022). Lipophilic properties of NBFRs influence their high accumulation levels in aquatic organisms, and further spread through the food chain; thus their concentration in water is lower, such as for DBDPE or BTBPE – Table S2 (Hou *et al.*, 2021). At the same time, more hydrophilic FRs, such as some OPFRs containing chlorine, are found in water in higher concentrations compared to sediments, e.g. TCEP (Tab. S2). Lower solubility OPFRs, e.g. TEHP, 2-ethylhexyl diphenyl phosphate (EHDPP) – Table S2, have a higher tendency to absorb in sediments. Interestingly, OPFRs distribution and concentration may constantly change, due to their complicated migration and transformation processes occurring under the influence of internal water forces (Wang *et al.*, 2023). FRs exhibiting higher vapour pressure, are more likely to volatilise into the atmosphere. For NFBRs, the decrease in molecular weight results in an increase in the vapour pressure (Al-Omran, 2018).

CONCENTRATIONS OF FLAME RETARDANTS INCLUDING ORGANOPHOSPHORUS (OPFRs) AND NOVEL BROMINATED FLAME RETARDANTS (NBFRs) IN WATER AND SEDIMENT

The mean values or concentrations of selected OPFRs and NFBRs in water and sediment collected recently from various locations (Chokwe *et al.*, 2015; Xiong *et al.*, 2016; Carlsson *et al.*, 2018; Lee *et al.*, 2018; Zha *et al.*, 2018; Lee *et al.*, 2020; Zhang *et al.*, 2021; Liu, Y. *et al.*, 2022) are presented in Table S2. Based on that research, the most frequently detected OPFRs in water are alkyl not containing Cl atoms (e.g. TnBP, TPrP, TEP), and alkyl containing Cl atoms (TCPP, TDCPP, TCEP). Among these groups, the highest concentrations in waters were observed for the TCEP (4776.73 ng·dm^{-3}) and TEP (459 ng·dm^{-3}) respectively. The highest concentration of aryl-OPFRs was achieved for TPPO (190.81 ng·dm^{-3}).

High concentrations of selected FRs may be attributed to the existence of several sources of contamination. The fact that some FRs, such as TCEP, may also be used as plasticisers is not out of significance. A high concentration of TPPO was observed; again, it could be due to its usage in the pharmaceutical and metal industries. That leads to the conclusion that the sampling area has a real meaning in the proper interpretation of results (Liu, Y. *et al.*, 2022).

The differences in the concentration of FRs in water and sediment are directly related to their physicochemical properties, including hydrophilicity. FRs exhibiting limited ability to degrade in water (e.g. TCEP, TCPP, and TDCPP) are present in lower concentrations in sediments compared to water. At the same time some of the FRs soluble in water can also be found in sediments, by their combination with plankton, and then fall free (Wang *et al.*, 2023). OPFRs exhibiting lower molecular weight are more likely to be found in water than in sediment. Generally, they are more soluble in water than NFBRs, although the log K_{OW} values indicate the lipophilic properties of several OPFRs (Miranda *et al.*, 2022).

Although separate research on the occurrence of NBFRs in water and sediment has been conducted, the issue of their occurrence in both environments is still not studied in detail. The results of the research on the occurrence of NBFRs (Tab. S2) demonstrate that among studied compounds, the HBCD have the highest concentration in water (1770 ng·dm^{-3}). Very low concentrations of TBP, PBP, PBBz, PBEB, TBX, PBT, α-TBCO, and DBE-DBCH had been found in Archipelago Svalbard. Among these TBP and PBP exhibited the highest concentrations in water of 0.18 ng·dm^{-3} and 0.16 ng·dm^{-3} respectively. Textile and electronic industries also commonly use TBP and PBP. In addition, TBP is also formed as a by-product of the tetrabromo-bisphenol A (TBBPA) biodegradation processes occurring in water and sediment (Xiong *et al.*, 2016).

THE ECOTOXICOLOGICAL EFFECTS OF FLAME RETARDANTS INCLUDING ORGANOPHOSPHORUS (OPFRs)

Bioaccumulation and biomagnification of OPFRs may occur in the tissues of rodents, fish, or birds. Although the ability to bioaccumulate is lower compared to halogen HFRs, OPFRs still may pose a significant threat to human and the environment. They may cause endocrine disruption and are related to a high risk for reproduction and systemic toxicity (Miranda *et al.*, 2022).

Cristale *et al.* (2013) studied the acute toxicity of the TnBP, TCEP, TCPP, TPHP, EHDPP, TBOEP, TEHP, and TCP (tricresyl phosphate), being the most common contaminants in the three Spanish rivers, on *Daphnia magna*. Among these OPFRs, the highest acute toxicity was observed for TCP and EHDPP, with the half maximal effective concentration (EC_{50}) values of 0.31 mg·dm^{-3}. The lowest was achieved for the TCPP and TCEP, exhibiting significantly higher EC_{50} values of 38 and 81 mg·dm^{-3} respectively.

The results demonstrate a strong correlation between toxicity and lipophilicity. The OPFRs with the lowest log K_{OW} values, such as TCPP (2.59), and TCEP (1.78), remain less toxic than those with higher octanol-water coefficients, such as TCP and EHDP. Moreover, the research included also the joint toxicity assessment of nine OPFRs at their EC_{50} concentration. The results showed that the joint toxicity of these compounds is mainly additive.

Due to the possible interactions between different contaminants, testing more than one substance is important in order to study the existence of synergistic or antagonistic effects. Lin (2008) studied the acute toxicity of the TnBP and TPHP mixtures using *D. magna*. Individual median lethal concentration (LC_{50}) values of TnBP vary from 5.48 mg·dm^{-3} (after 24 h) to 1.17 mg·dm^{-3} (after 48 h). Significantly higher toxicity exhibits TPHP, with the LC_{50} values of 0.51 mg·dm^{-3} (after 24 h) to 0.09 mg·dm^{-3} (after 48 h). The toxic units of mixtures, defined as the ratio of the compound measured concentration in a mixture to the corresponding effect concentration of a compound in the same medium, of the varying toxic unit ratios of these two FRs were nearly equal 1, suggesting the additive toxicity of TnBP and TPHP. This may be ascribed to the fact that both compounds are bound chemically with the *D. magna* enzyme – acetylcholinesterase.

It is reported that some of the OPFRs may biomagnify in organisms. The waterborne and dietary accumulation of TCEP, TDCPP, TBOEP, and TPHP in *D. manga* were investigated by Liu, W. *et al.* (2022). The results of the waterborne exposure tests revealed that accumulation and depuration of OPFRs in *D. magna* occur the fastest at the first 6 hours of exposure regardless of whether the initial OPFRs concentration is high or low. The highest uptake rate constant was observed for TPHP (138.80 dm^3·kg^{-1}·h^{-1}), which was nearly an order of magnitude higher compared to the other studied FRs. The lowest was observed for TBOEP (0.57 dm^3·kg^{-1}·h^{-1}). The half-life times ranged between 4.13 h (TCEP) and 7.88 h (TPHP). Again, it is attributed to the highest lipophilicity of TPHP among studied OPFRs, which makes its transfer to the solution more difficult. The bioaccumulation factors were the lowest for TBOEP and TCEP, and the highest was obtained for TPHP. Interestingly, they were higher in *D. magna* than in invertebrates and fish, which confirms that total OPFRs concentration is the lowest for plankton. The uptake rate constants for the dietary exposure were significantly lower compared to waterborne exposure, and the highest was achieved for the TCEP (5.82 h^{-1}). On the other hand, the depuration of *D. magna* was occurring significantly faster, which may be ascribed to the different metabolic pathways of OPFRs via waterborne and dietary routes. The biomagnification factors were rising with the increase of the concentration of OPFRs for all FRs excluding TBOEP. This may be ascribed to the easier accumulation in algae and degradation into BBOEHP and 3-OH-TBOEP.

The bioaccumulation and trophic transfer of OPFRs in the marine food webs of Laizhou Bay were studied by (Bekele *et al.*, 2019). The highest detection frequencies among biota samples were achieved for TCPP (85%), TIBP (80%), and TBOEP (77%), which is in agreement with other studies on freshwater and marine species. The concentration of OPFRs in fish and invertebrates has shown no significant difference. However, the concentrations of alkyl-, Cl-containing, and aryl-OPFRs in benthic fishes (1450–2550 ng·g^{-1} lipid weight lw) were considerably higher than in pelagic (642–1890 ng·g^{-1} lw), showing their greatest accumulation ability. The bioaccumulation potential depends on the lipid content – the higher concentrations were observed for invertebrates and fish, which exhibited higher lipid contents. The trophic magnification factors analysis revealed an increasing trend in the concentration of OPFRs with the increasing trophic level, which indicates the biomagnification potential of e.g. TBEP, TEP, TEHP, TCPP, or TCPP in a marine food web.

Interesting findings on the growth, reproduction, and survival of *D. magna* after exposure to TCEP have been reported by Li *et al.* (2020). The growth was accelerated compared to unexposed organisms, and the body length increase was observed on the 22nd day of exposure to TCEP. However, the changes disappeared on the 32nd day, concluding that accurate experiments should be conducted for a longer period. Again, in terms of survival measurements, in the longer period (78–82 days) there was an increase in the survival rate, which was not observed until 32 days. Moreover, after the 83rd day, the effect disappeared, which denies ensuring longevity by TCEP, and suggests the hormesis effect. Although TCEP does not significantly affect neonatal production, the overall offspring production was increased. To summarise, TCEP might not have an adverse effect on the reproduction of *D. magna*. Again, in terms of survival measurements, in the longer period (78–82 days) there was an increase in the survival rate, which was not observed until 32 days.

THE ECOTOXICOLOGICAL EFFECTS OF NOVEL BROMINATED FLAME RETARDANTS (NBFRs)

Studies on the ecotoxicity of NBFRs are limited, but their amount increases due to the widespread occurrence of these novel FRs in environmental sources and biota. NBFRs may undergo bioaccumulation and biomagnification, which depends on the individual metabolic rates in the organisms. Some of them, e.g. DBDPE, exhibit hepatotoxic properties and disrupt the endocrine system. Due to the similarity of NBFRs and BFRs structures, it is assumed that they may also pose a considerable threat to human and the environment (Miranda *et al.*, 2022).

Scanlan *et al.* (2015) studied the toxicity of TPHP and bis(2-ethylhexyl) phthalate (BEHP), and two formulations; the first, consisting of bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP) (8%), EHTBB (30%), TPHP (17%) and isopropylated triaryl phosphates (ITP) (45%), and the second, consisting of 30% of BEH-TEBP and 70% of EHTBB. The highest acute toxicity in *D. magna* was observed for the FM550 (0.486 mg·dm^{-3}), and the BZ54 and TPHP LC_{50} values were similar. BEH-TEBP was found to be the least toxic (0.91 mg·dm^{-3}). However, all of the studied FRs are toxic and pose a threat to freshwater ecosystems. The increase of the glycosphingolipid biosynthesis pathway is a molecular effect of the BEH-TEBP. Glycosphingolipids may influence cell proliferation, senescence, or differentiation. Transduction of the Wnt signal was observed for the second formulation, which is related to changes in embryonic patterning and morphogenesis, and may affect the whole population. In addition, exposure to the first formulation may cause nutritional dysregulations in *D. magna*.

Although DBDPE shows low acute toxicity to chicken embryos and is not toxic to fish, algae, or *D. magna* up to 110 mg·dm^{-3}, recent studies revealed that exposure to sediment containing DBDPE causes low-level developmental neurotoxicity in zebrafish larvae. What is more important, the existence of other organic pollutants may result in underestimating or overestimating the risk. Interesting research on the influence of the TiO_2 nanoparticles on the existence, uptake, metabolism, and toxicity of DBDPE in zebrafish larvae had been conducted by Wang *et al.* (2022). The DBDPE concentration in larvae has raised almost twice when the mixture contained nano TiO_2. The changes in metabolites included the increase in concentrations of the nona-BDPE and nona-brominated compounds, and the decrease in the concentrations of octa-BDPE, hepta-BDPE, and other brominated products. Although the hatching, survival, and malformation rates, as well as body weight, were not significantly different, the increase in the heart rates and changes in the locomotor behaviour had been observed. Despite that the presence of nano TiO_2 did not cause obvious toxicity to zebrafish at this time, changes observed at high concentrations of TiO_2 suggest that it may pose a potential risk in the future.

HBCD is known for its toxicity to vertebrates and invertebrates, it slows the growth of *D. magna* at 5.6 $\mu g \cdot dm^{-3}$ and induces malformation. It induces oxidative stress by the transcription of responsive genes and has a high bioaccumulation potential. The research by Shi, D. *et al.* (2016) indicates its toxicity to *Tigriopus japonicus*, resulting in the growth delay. Moreover, the next generation of organisms was more sensitive to HBCD, which shows the significance of long-term exposure tests.

CONCLUSIONS

Although extensive research on the organophosphorus flame retardants (OPFRs) and novel brominated flame retardants (NBFRs) emerging in water and sediment separately is carried out, a matter requiring more attention is their occurrence and distribution in both media in the same area. Sampling areas considerably influence the occurrence of FRs in water and sediment; the greatest concentrations had been found in industrialised areas. However, several compounds are not only used as FRs but may also serve as e.g. plasticisers, antifoaming or hydraulic agents, which affects their final concentration.

Due to the fact that groups of OPFRs and NBFRs have enlarged over the years, there is still a need to further investigate the occurrence, distribution, and ecotoxicity of these compounds. The ecotoxicity of novel FRs, their bioaccumulation and biomagnification potentials in organisms indicate that not all of these new compounds may serve as environmentally friendly FRs. Further studies are needed in order to update existing requirements and regulations.

Moreover, joint effects – synergistic, additive, or antagonistic – of the OPFRs and NBFRs should be the subject of future studies because of the common occurrence of several compounds in studied areas.

SUPPLEMENTARY MATERIAL

Supplementary material to this article can be found online at https://www.jwld.pl/files/Supplementary_material_Dowbysz.pdf.

FUNDING

The research was carried out as part of work No. WI/WB-IIŚ/8/2022 at the Bialystok University of Technology and was funded by a research subvention provided by the Ministry of Education and Science.

REFERENCES

Al-Omran, L.S. (2018) "Physicochemical properties and environmental levels of legacy and novel brominated flame retardants," in F. Zafar and E. Sharmin (eds.) *Flame retardants*. Available at: https://doi.org/10.5772/intechopen.79823 (Accessed: April 5, 2023).

Bekele, T.G. *et al.* (2019) "Bioaccumulation and trophic transfer of emerging organophosphate flame retardants in the marine food webs of Laizhou Bay, North China," *Environmental Science & Technology*, 53, pp. 13417–13426. Available at: https://doi.org/10.1021/acs.est.9b03687.

Bika, S.H. *et al.* (2022) "Spatiotemporal distribution and analysis of organophosphate flame retardants in the environmental systems: A review," *Molecules*, 27, pp. 4–18. Available at: https://doi.org/10.3390/molecules27020573.

Carlsson, P. *et al.* (2018) "New brominated flame retardants and dechlorane plus in the Arctic: Local sources and bioaccumulation potential in marine benthos," *Chemosphere*, 211, pp. 1193–1202. Available at: https://doi.org/10.1016/j.chemosphere.2018.07.158.

Chokwe, T.B. *et al.* (2015) "Alkyphenol ethoxylates and brominated flame retardants in water, fish (carp) and sediment samples from the Vaal River, South Africa," *Environmental Science and Pollution Research*, 22, pp. 11922–11929. Available at: https://doi.org/10.1007/s11356-015-4430-x.

Cristale, J. *et al.* (2013) "Priority and emerging flame retardants in rivers: Occurrence in water and sediment, *Daphnia magna* toxicity and risk assessment," *Environment International*, 59, pp. 232–243. Available at: https://doi.org/10.1016/j.envint.2013.06.011.

Cristale, J. *et al.* (2016) "Can activated sludge treatments and advanced oxidation processes remove organophosphorus flame retardants?," *Environmental Research*, 144, pp. 11–18. Available at: https://doi.org/10.1016/j.envres.2015.10.008.

Cristale, J. and Lacorte, S. (2015) "PBDEs versus NBFR in wastewater treatment plants: occurrence and partitioning in water and sludge," *Environmental Science*, 2, pp. 533–546. Available at: https://doi.org/10.3934/environsci.2015.3.533.

Dimitrov, S. *et al.* (2002) "Predicting bioconcentration factors of highly hydrophobic chemicals. Effects of molecular size," *Pure and Applied Chemistry*, 74, pp. 1823–1830. Available at: https://doi.org/10.1351/pac200274101823.

Dong, L. *et al.* (2021) "New understanding of novel brominated flame retardants (NFBRs): Neuro(endocrine) toxicity," *Ecotoxicology and Environmental Safety*, 208, 111570. Available at: https://doi.org/10.1016/j.ecoenv.2020.111570.

Dowbysz, A., Samsonowicz, M. and Kukfisz B. (2021) "Modification of glass/polyester laminates with flame retardants," *Materials*, 14(24), 7901. Available at: https://doi.org/10.3390/ma14247901.

ECHA (2023) *Regulatory strategy for flame retardants*. Helsinki: European Chemicals Agency. Available at: https://doi.org/10.2823/854233.

Giulivo, M. *et al.* (2017) "Occurrence of halogenated and organophosphate flame retardants in sediment and fish samples from three European river basins," *Science of The Total Environment*, 586, pp. 782–791. Available at: https://doi.org/10.1016/j.scitotenv.2017.02.056.

Hou, R. *et al.* (2021) "Occurrence, bioaccumulation, fate, and risk assessment of novel brominated flame retardants (NBFRs) in aquatic environments – A critical review," *Water Research*, 198, 117168. Available at: https://doi.org/10.1016/j.watres.2021.117168.

Kim, U., Oh, J.K. and Kannan, K. (2017) "Occurrence, removal and environmental emission of organophosphate flame retardants/

plasticizers in a wastewater treatment plant in New York State, USA," *Environmental Science & Technology*, 51, pp. 7872–7880. Available at: https://doi.org/10.1021/acs.est.7b02035.

Kung, H. *et al.* (2022) "An overview: Organophosphate flame retardants in the atmosphere," *Aerosol and Air Quality Research*, 22, 220148. Available at: https://doi.org/10.4209/aaqr.220148.

Lee, H. *et al.* (2020) "Legacy and novel flame retardants in water and sediment from highly industrialized bays of Korea: Occurrence, source tracking, decadal time trend, and ecological risks," *Marine Pollution Bulletin*, 160, 111639. Available at: https://doi.org/10.1016/j.marpolbul.2020.111639.

Lee, S. *et al.* (2018) "Organophosphate flame retardants (OPFRs) in water and sediment: Occurrence, distribution, and hotspots of contamination of Lake Shihwa, Korea," *Marine Pollution Bulletin*, 130, pp. 105–112. Available at: https://doi.org/10.1016/j.marpolbul.2018.03.009.

Li, W. *et al.* (2020) "Toxicity of tris(2-chlorethyl) phosphate in *Daphnia magna* after lifetime exposure: Changes in growth, reproduction, survival and gene transcription," *Ecotoxicology and Environmental Safety*, 200, 110769. Available at: https://doi.org/10.1016/j.ecoenv.2020.110769.

Lin, K. (2008) "Joint acute toxicity of tributyl phosphate and triphenyl phosphate to *Daphnia magna*," *Environmental Chemistry Letters*, 7, pp. 309–312. Available at: https://doi.org/10.1007/s10311-008-0170-1.

Lippold, A. *et al.* (2022) "Occurrence of emerging brominated flame retardants and organophosphate esters in marine wildlife from the Norwegian Arctic," *Environmental Pollution*, 315, 120395. Available at: https://doi.org/10.1016/j.envpol.2022.120395.

Liu, W. *et al.* (2022) "Waterborne and dietary bioaccumulation of organophosphate esters in zooplankton *Daphnia magna*," *International Journal of Environmental Research and Public Health*, 19, 9382. Available at: https://doi.org/10.3390/ijerph19159382.

Liu, Y. *et al.* (2022) "Occurrence, distribution, and ecological risk of organophosphorus flame retardants and their degradation products in water and upper sediment of two urban rivers in Shenzhen, China," *Environmental Pollution*, 30, pp. 14932–14942. Available at: https://doi.org/10.1007/s11356-022-23088-4.

Miranda, R.G. *et al.* (2022) "Flame retardants: New and old environmental contaminants," in D. Junqueira Dorta, D. Palma de Oliveira (eds.) *The toxicity of environmental pollutants*. IntechOpen. Available at: https://doi.org/10.5772/intechopen.104886.

Montano, L. *et al.* (2022) "Polychlorinated biphenyls (PCBs) in the environment: Occupational and exposure events, effects on human health and fertility," *Toxics*, 10(7), 365. Available at: https://doi.org/10.3390/toxics10070365.

Scanlan, L.D. *et al.* (2015) "Gene transcription, metabolite and lipid profiling in eco-indicator *Daphnia magna* indicate diverse mechanisms of toxicity by legacy and emerging flame-retardants," *Environmental Science & Technology*, 49, pp. 7400–7410. Available at: https://doi.org/10.1021/acs.est.5b00977.

Shi, D. *et al.* (2016) "Accumulation and developmental toxicity of hexabromocyclododecanes (HBCDs) on the marine copedod *Tigriopus japonicus*," *Chemosphere*, 167, pp. 155–162. Available at: https://doi.org/10.1016/j.chemosphere.2016.09.160.

Shi, Y. *et al.* (2016) "Occurrence, distribution and seasonal variation of organophosphate flame retardants and plasticizers in urban surface water in Beijing, China," *Environmental Pollution*, 209, pp. 1–10. Available at: https://doi.org/10.1016/j.envpol.2015.11.008.

Wang, X. *et al.* (2022) "Nano-TiO_2 absorbed decabromodiphenyl ethane and changed its bioavailability, biotransformation and biotoxicity in zebrafish embryos/larvae," *Frontiers in Environmental Science*, 10, 860786. Available at: https://doi.org/10.3389/fenvs.2022.860786.

Wang, Y. *et al.* (2023) "A review of organophosphate esters in aquatic environments: levels, distribution, and human exposure," *Water*, 15, 1790. Available at: https://doi.org/10.3390/w15091790.

Xiong, J. *et al.* (2016) "Emission patterns and risk assessment of polybrominated diphenyl ethers and bromophenols in water and sediments from the Beijiang River, South China," *Environmental Pollution*, 219, pp. 596–603. Available at: https://doi.org/10.1016/j.envpol.2016.06.021.

Xiong, P. *et al.* (2019) "A review of environmental occurrence, fate, and toxicity of novel brominated flame retardants," *Environmental Science & Technology*, 53, pp. 13551–13569. Available at: https://doi.org/10.1021/acs.est.9b03159.

Zha, D. *et al.* (2018) "Assessment of organophosphate flame retardants in surface water and sediment from freshwater environment (Yangtze River, China)," *Environmental Monitoring and Assessment*, 190, 222. Available at: https://doi.org/10.1007/s10661-018-6587-5.

Zhang, L. *et al.* (2021) "Organophosphorus flame retardants (OPFRs) in the seawater and sediments of the Qinzhou Bay, Northern Beibu Gulf: Occurrence, distribution, and ecological risks," *Marine Pollution Bulletin*, 168, 112368. Available at: https://doi.org/10.1016/j.marpolbul.2021.112368.