PERSISTENT ORGANIC POLLUTANTS: SOURCES, MIGRATION IN ECOSYSTEMS, REMOVAL METHODS IN WASTEWATER TREATMENT AND REMEDIATION OF SOILS AND NATURAL WATER

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DOI: https://doi.org/10.20535/2218-930032023309558

Persistent organic pollutants are among the most dangerous pollutants due to their resistance to destruction in natural conditions, the ability to migrate in ecosystems, bioaccumulation, biomagnification and significant harmful effects on health. Persistent organic pollutants include organochlorine pesticides, polychlorinated naphthalenes, polychlorinated biphenyls, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons, etc. Even in small amounts, these compounds can cause endocrine disorders and have a carcinogenic effect. Most of these compounds are exclusively of anthropogenic origin. Although the Stockholm Convention has severely restricted the production and use of persistent organic pollutants, many soils and water bodies are already contaminated with these compounds, and some banned substances continue to be produced as byproducts of industrial processes. Also, although the lists of substances prohibited for production are periodically updated, a large number of compounds, which by their properties are persistent organic pollutants, have not yet entered these lists. There are many methods for removing persistent organic pollutants from water, but most of them are insufficiently effective or lead to the generation of large quantities of contaminated waste that need to be disposed of. Photocatalysis is the most promising method of wastewater treatment that contains persistent organic pollutants. Unlike coagulation, adsorption, biological treatment and nanofiltration/reverse osmosis, this method avoids the generation of solid and liquid waste contaminated with these pollutants. In the case of remediation of polluted waters and soils, the main methods are bioremediation and adsorption, since these methods can immobilize persistent organic pollutants directly in the ecosystem without taking soil or water for treatment.

Keywords: *aquatic environment, bioaccumulation, persistent organic pollutants, soil pollution, water pollution*

Received: 20 March 2024 Revised: 28 March 2024 Accepted: 1 April 2024

1. Introduction

Persistent organic pollutants are one of the significant environmental problems of today. Mankind faced this problem relatively recently as a result of significant industrialization and development of chemical industries. Persistent organic pollutants are among the most dangerous pollutants due to their resistance to destruction in natural conditions, the ability to migrate in ecosystems, significant harmful effects on health, bioaccumulation and biomagnification (Pariatamby & Kee, 2016).

Persistent organic pollutants (POPs) include organochlorine pesticides, polychlorinated naphthalenes, polychlorinated biphenyls, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons, etc. (Akhtar et al., 2021). Most of these compounds are exclusively of anthropogenic origin (Jones, 2021).

Even in small amounts, these compounds can cause endocrine disorders and have a carcinogenic effect (Pariatamby & Kee, 2016).

For a long time, only environmental activists and scientists paid attention to the problem of persistent organic pollutants, but in 2002 the Stockholm Convention on Persistent Organic Pollutants was held, which marked the beginning of a legal ban on the production and use of some persistent organic pollutants (Torres et al., 2022). The initial list consisted of only 12 compounds and included aldrin, chlordane, dieldrin, endrin, mirex, toxaphene, hexachlorobenzene (HCB), heptachlor, polychlorinated biphenyls (PCBs), dioxins, dichlorodiphenyltrichloroethane (DDT) and polychlorinated dibenzofurans (Lallas, 2001). The list of the Stockholm Convention is regularly updated. The following compounds are currently being considered for listing:

- chlorinated paraffins with carbon chain lengths in the range C_{14-17} and weight content of chlorine at least 45 %;
- long-chain perfluorocarboxylic acids (PFCAs), their salts and related compounds;
- chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate) (Stockholm Convention, 2019).

Although the production and use of a number of such compounds is prohibited in most countries of the world, there are a large number of compounds that are persistent organic pollutants by their properties, but are not included either in the list of the Stockholm Convention of 2001 or in the lists amended in following years (Sheriff et al., 2022).

However the Stockholm Convention has severely restricted the production and use of persistent organic pollutants, many soils and water bodies are already contaminated with these compounds, and some banned substances continue to be produced as byproducts of industrial processes.

2. Sources of Persistent Organic Pollutants

Persistent organic pollutants can originate from natural processes like volcanic eruptions and wildfires, as well as from human activities, including industrial and agricultural practices (Akhtar et al., 2021). But most persistent organic pollutants are compounds of exclusively artificial origin. Common examples of POPs include organic dyes, pesticides, synthetic chemicals, personal care products and many others (Akhtar et al., 2021).

In general, sources of anthropogenic persistent organic pollutants can be divided into three types:

- pesticides;
- industrial chemicals;
- unintentional production (Fig. 1).

But some substances can have several types of sources. These include hexachlorobenzene, hexachlorobutadiene, pentachlorobenzene, polychlorinated biphenyls, polychlorinated naphthalenes, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (Stockholm Convention, 2019).

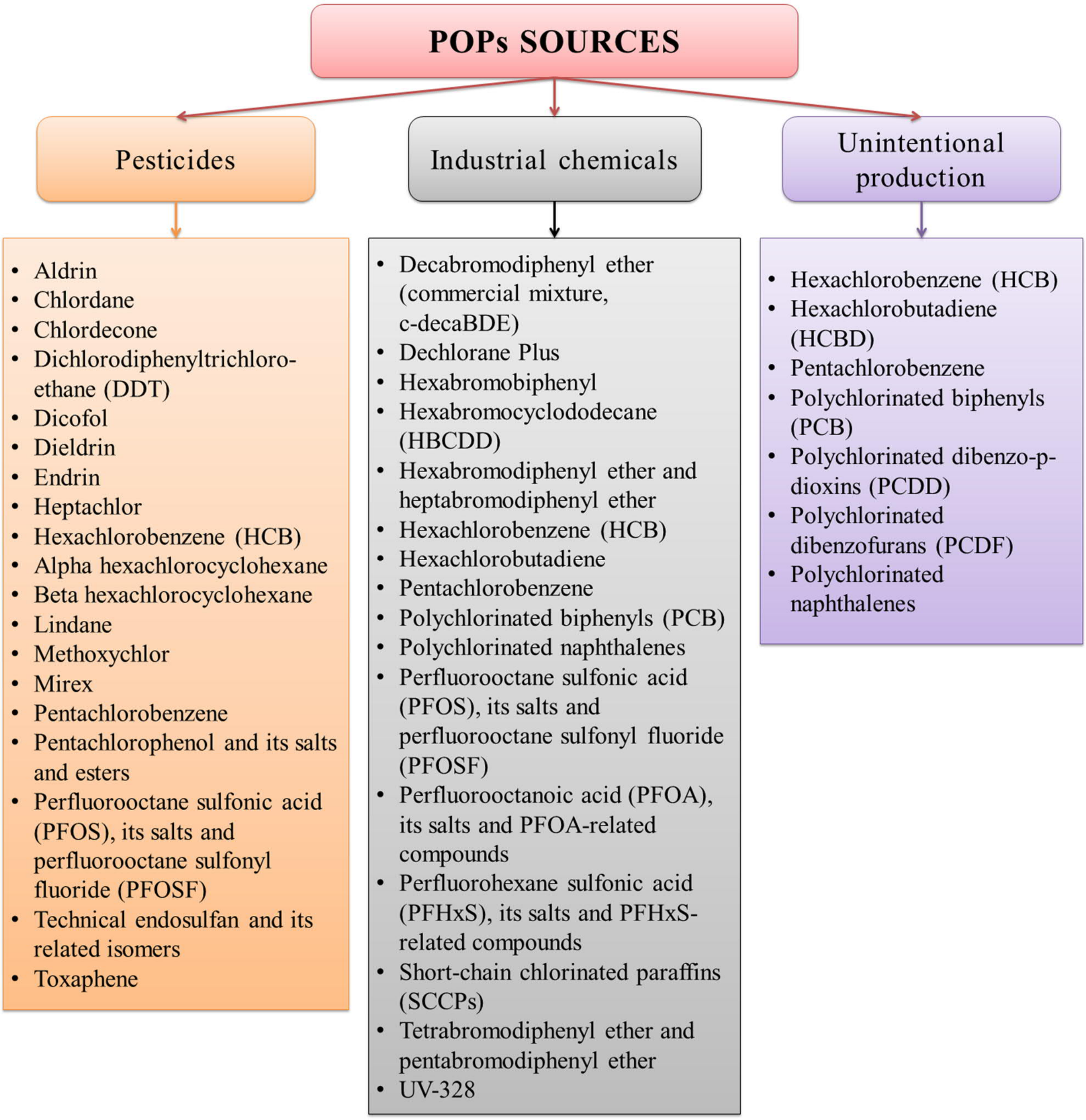

Fig 1. *Anthropogenic persistent organic pollutants and their sources*

In this way, anthropogenic persistent organic polutants can enter the environment intentionally (pesticides, flame retardants) or in case of poor organization of the technological process (leaks of chemicals, insufficiently purified industrial wastewater, unutilized waste, impurities in chemicals, etc.). Different types of persistent organic pollutants are produced for various purposes. Organochlorine pesticides used in agriculture to control pests, polybrominated diphenyl ethers and dechlorane plus are flame retardants, polychlorinated biphenyls are used in transformers and capacitors, polychlorinated naphthalenes are used as dielectrics, plasticizers and preservatives for paper and fabric, etc. (Akhtar et al., 2021).

The pollution of the area with persistent organic pollutants differs significantly depending on whether the area is urban or agricultural. Some chemicals or categories of chemicals, such as polychlorinated biphenyls and flame retardants, exhibit a distinct urban signature, while hexachlorocyclohexanes and certain other substances display a clear agricultural signature (Venier et al., 2019).

A large amount of equipment containing persistent organic pollutants is still in use and may become an additional source of pollution in the future. In Ukraine the number of transformers and capacitors containing PCBs has decreased substantially in most areas between 2003 and 2018. The exception is the Dnipropetrovsk region, where the number of such capacitors, on the contrary, increased from 7,322 to 21,577 (Chetverykov et al., 2021). But in the territories of the regions most affected by hostilities, there is still a large amount of such equipment, including 15 transformers and 1,016 capacitors in the Kharkiv region (Chetverykov et al., 2021).

In Ukraine, ferrous and non-ferrous metal production, heat and power generation, waste incineration are the main sources of POPs emissions (Chetverykov et al., 2021). But the main sources can differ significantly in individual cities due to the uneven distribution of industrial capacities. For example, in the case of the Odesa urban agglomeration, the most persistent organic compounds enter the atmosphere as a result of cement production. In 2017 the formation of POPs during clinker burning was PCB – 56.56 g, HCB – 2.53 g and PCDD/F – 2.75 g (Mykhailenko & Safranov, 2021).

At March 31, 2006 21,615 tons of unusable or prohibited pesticides were accumulated in Ukraine, including 2,019 tons of POPs, among which majority is DDT (1,744 tons) and hexachlorocyclohexane (273 tons) (Chetverykov et al., 2021). The soils around such storehouses are heavily contaminated with pesticides. In some cases, at a distance of 1 m from the warehouse, the observed content of DDT in the soil is 55.01 mg/kg, at a distance of 5 meters - 34.51 mg/kg, and at a distance of 100 m - 0.53 mg/kg, although the maximum permissible content is 0.1 mg/kg (Moklyachuk et al., 2014). Before 2019, 8 regions completely disposed of accumulated unusable pesticides, but in many cases, storehouses and surrounding areas were not cleaned of pesticide residues. The largest stocks of unsuitable pesticides are in Vinnytsia region (2,964.0 tons) and in Kherson region (1,921.8 tons). (Chetverykov et al., 2021). The situation is complicated by the fact that as a result of active hostilities in the territory of the Kherson region, warehouses may be destroyed and pesticides may be released into the atmosphere, soil, reservoirs, and underground water.

3. Persistent Organic Pollutants in Ecosystems

Persistent organic pollutants can interact with ecosystems via the disposal of industrial effluents, agricultural runoff, drainage leaks, urban runoff, leachate from landfills, significant atmospheric deposition, etc. (Kumar et al., 2022).

Persistent organic pollutants have very significant half-lives in soils, sediments, air, and living organisms. The carbon-chlorine bond is highly resistant to hydrolysis, and a greater number of chlorine substitutions and/or functional groups increase their resistance to biological and photolytic degradation (Ashraf, 2015). Thus, these compounds are not degraded by sunlight or microbial activity like most other organic compounds.

Due to the slow breakdown of persistent organic pollutants, they can remain in the environment for a prolonged period, even if all new sources are eliminated right away (Ashraf, 2015).

The residual contents of most organic insecticides in natural water or soils are usually significantly higher in agricultural areas than in non-agricultural regions (Kumar et al., 2022).

From water and soil, persistent organic pollutants enter plants, algae and plankton, and then into other links of food chains. Also, these compounds are lipophilic, that is, they are able to accumulate in the fatty tissue of animals, birds and fish (Pariatamby & Kee, 2016). Thus, persistent organic pollutants are able to accumulate in food chains. As a result, these compounds can be found in all parts of polluted ecosystems, including water, soil, bottom sediments, air, plants, animals, etc. (Fig.2).

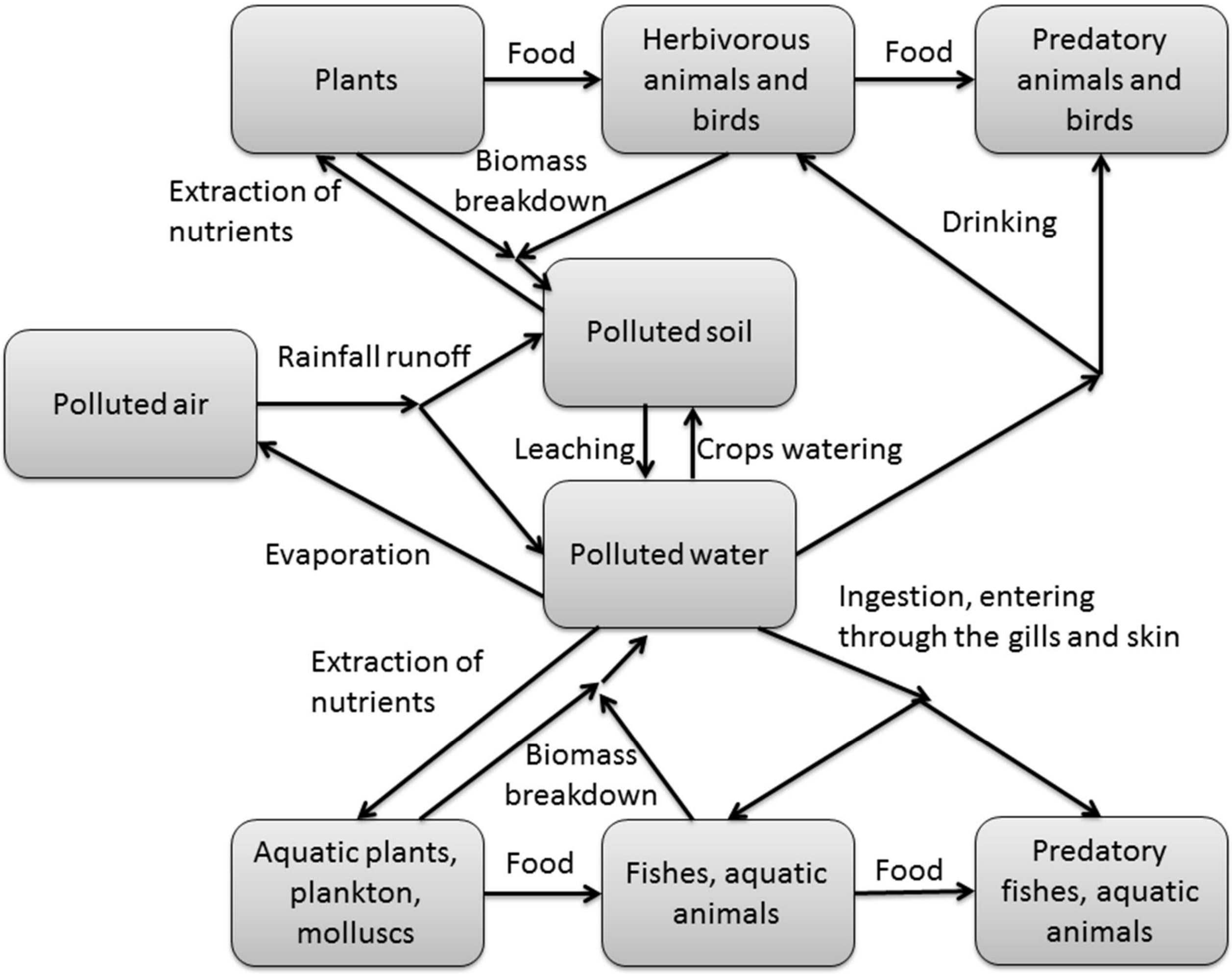

Fig 2. *Migration of persistent organic pollutants in the ecosystem*

The problem of pollution with persistent organic pollutants has already covered the whole world, including Arctic ecosystems, where the accumulation occurred due to the migration of these compounds. This problem did not escape Ukraine either. Both the territories of settlements and agricultural lands are polluted (Sukhorebra, 2009). In general, the pollution of Ukrainian water resources by persistent organic pollutants is similar to the situation in the EU. Persistent organic pollutants are present in almost all reservoirs of Ukraine. For example, 8 PAHs and 4 PCBs were found in a river near Kharkiv (Vystavna et al., 2018).

4. Removal Methods in Wastewater Treatment and Remediation of Soils and Natural Water

Contamination of ecosystems with persistent organic pollutants makes it necessary to remediate natural waters and soils in order to avoid the accumulation of these compounds in food chains and, as a result, in the human body. And thorough treatment of industrial wastewater will reduce re-pollution of ecosystems.

There are many methods of treatment/remediation water and soil from persistent organic pollutants, including the use of both chemical reagents and biological methods (Table 1). But most of these methods, including microbial degradation, coagulation and flocculation, show extremely low efficiency in relation to persistent organic pollutants. Phthalic acid esters were not effectively removed by coagulation/ flocculation (Pariatamby & Kee, 2016) and only 6.7 % of DEHP was removed using polyferric sulfate as coagulant (Zolfaghari et al., 2014). But some natural compounds, including guar gum or xantan gum, are quite effective. Xanthan gum is 5% more effective at removing pops than an aluminum-based coagulant at the same dosage, and is also significantly cheaper (Pariatamby & Kee, 2016).

Table 1. *Some most popular POPs removal/degradation methods*

Methods	Disadvantages	Reference
Microbial bioremediation	Limited microbial capabilities; reduced bioavailability of contaminants across temporal and spatial scales; microorganisms are very sensitive to environmental conditions; the absence of benchmark values for testing the efficacy of bioremediation.	Pariatamby & Kee, 2016
Coagulation and flocculation	The effectiveness of the process depends on a large number of conditions (pH, mixing speed, dosage of reagents, temperature, retention time, water turbidity, etc.); often coagulants, especially aluminum salts, are not environmentally friendly; the formation of a large amount of sludge with high humidity, which require disposal; low efficiency relative to many POPs.	Pariatamby & Kee, 2016 Zolfaghari et al., 2014
Adsorption	The effectiveness of the process depends on a large number of conditions (pH, dosage of adsorbents, type of adsorbents, temperature, retention time, etc.); often effective adsorbents are expensive.	Akhtar et al., 2021 Ighalo et al., 2022
Photocatalytic degradation	The effectiveness of the process depends on a large number of conditions (pH, dosage of photocatalysts, light wavelength, retention time, etc.); often photocatalysts, especially in suspended nano-sized form, are not environmentally friendly; high cost.	Nguyen et al., 2020 Gaur et al., 2022

Some methods, including the use of certain microorganisms, coagulation with metal-containing coagulants, baromembrane methods, can only be used ex situ, but phytoremediation or adsorption can be used both ex situ and in situ. Often, the use of adsorption to remove persistent organic pollutants is quite expensive, but there are also cheap and effective adsorbents, especially lignocellulosic materials, various adsorbents for carbonaceous waste, activated natural clays and others (Akhtar et al., 2021). Nanoadsorbents are particularly effective, but their use in suspended form for remediation is impractical due to the carcinogenic effect of nanoparticles (Ighalo et al., 2022).

Advanced oxidation processes have been extensively utilized for the complete mineralization of POPs, as they generate hydroxyl radicals in adequate concentrations at ambient temperature and pressure. Of all the advanced oxidation technologies, photocatalysis has shown to be highly effective for POPs removal in wastewater treatment, air purification, and disinfection due to its operating conditions, complete conversion of the pollutants into inorganic components, use of solar energy, cost-efficiency (Gaur et al., 2022). Immobilizing semiconductor photocatalysts on various supports can mitigate many of the disadvantages associated with suspension systems, such as retrieving suspended photocatalyst powders from the effluent stream and preparing for large-scale photoreactors, among others (Nguyen et al., 2020). The development of hybrid photocatalytic membranes that combine photocatalysis and membrane technology has demonstrated significant potential in treating wastewater contaminated with persistent organic pollutants, owing to their synergistic effects. This article offers a comprehensive review of the roles of both photocatalysis and membrane technology in hybrid photocatalytic membranes for the treatment of wastewater containing persistent organic pollutants (Subramaniam et al., 2021).

4. Conclusions

Persistent organic pollutants can originate from natural processes like volcanic eruptions and wildfires, as well as from human activities, including industrial and agricultural practices. But most persistent organic pollutants are compounds of exclusively artificial origin.

Persistent organic pollutants include organochlorine pesticides, polychlorinated naphthalenes, polychlorinated biphenyls, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons, etc. Even in small amounts with long-term consumption POPs can cause serious harm to health.

There are many methods of treatment/remediation water and soil from persistent organic pollutants, but most of these methods, including microbial degradation, coagulation and flocculation, show extremely low efficiency in relation to persistent organic pollutants.

Photocatalysis is the most promising method of wastewater treatment that contains persistent organic pollutants. Photocatalysis are highly effective for POPs removal during wastewater treatment due to its operating conditions, complete conversion of the pollutants into inorganic components, use of solar energy, cost-efficiency Unlike coagulation, adsorption, biological treatment and nanofiltration/reverse osmosis, this method avoids the generation of solid and liquid waste contaminated with these pollutants.

In the case of remediation of polluted waters and soils, the main methods are bioremediation and adsorption, since these methods can immobilize persistent organic pollutants directly in the ecosystem without taking soil or water for treatment.

References

1. Akhtar, A. B. T.; Naseem, S.; Yasar, A.; Naseem, Z. Persistent Organic pollutants (POPs): sources, types, impacts, and their remediation. In *Environmental and microbial biotechnology*; 2021; pp 213–246. https://doi.org/10.1007/978-981-15-5499-5_8.

2. Ashraf, M. A. Persistent organic pollutants (POPs): a global issue, a global challenge. *Environmental Science and Pollution Research* **2015**, *24* (5), 4223–4227. https://doi.org/10.1007/s11356-015-5225-9.

3. Chetverykov, V. V.; Holoubek, I.; Pianykh, K. K. The Current State of the Issue of Persistent Organic Pollutants in Ukraine and Approaches for its Resolution. *Energy Technologies & Resource Saving* **2021**, *2*, 80–88. https://doi.org/10.33070/etars.2.2021.07.

4. Gaur, N.; Dutta, D.; Singh, A.; Dubey, R.; Kamboj, D. V. Recent advances in the elimination of persistent organic pollutants by photocatalysis. *Frontiers in Environmental Science* **2022**, *10*. https://doi.org/10.3389/fenvs.2022.872514.

5. Ighalo, J. O.; Yap, P.-S.; Iwuozor, K. O.; Aniagor, C. O.; Liu, T.; Dulta, K.; Iwuchukwu, F. U.; Rangabhashiyam, S. Adsorption of persistent organic pollutants (POPs) from the aqueous environment by nano-adsorbents: A review. *Environmental Research* **2022**, *212*, 113123. https://doi.org/10.1016/j.envres.2022.113123.

6. Jones, K. C. Persistent organic pollutants (POPs) and related chemicals in the global environment: Some personal reflections. *Environmental Science & Technology* **2021**, *55* (14), 9400–9412. https://doi.org/10.1021/acs.est.0c08093

7. Kumar, J. A.; Krithiga, T.; Sathish, S.; Renita, A. A.; Prabu, D.; Lokesh, S.; Geetha, R.; Namasivayam, S. K. R.; Sillanpaa, M. Persistent organic pollutants in water resources: Fate, occurrence, characterization and risk analysis. *The Science of the Total Environment* **2022**, *831*, 154808. https://doi.org/10.1016/j.scitotenv.2022.154808.

8. Lallas, P. L. The Stockholm Convention on Persistent Organic Pollutants. *American Journal of International Law* **2001**, *95* (3), 692–708. https://doi.org/10.2307/2668517.

9. Moklyachuk, L.; Drebot, O.; Moklyachuk, O.; Moklyachuk, T.; Monarh, V. Ecological Risks from Contamination of Ukrainian Soils by Persistent Organic Pollutants. *Environment and Ecology Research* **2014**, *2* (1), 27–34. https://doi.org/10.13189/eer.2014.020105.

10. Mykhailenko, V.; Safranov, T. Estimation of Input of Unintentionally Produced Persistent Organic Pollutants into the Air Basin of the Odessa Industrial-and-Urban Agglomeration. *Journal of Ecological Engineering* **2021**, *22* (9), 21–31. https://doi.org/10.12911/22998993/141479.

11. Nguyen, V.-H.; Smith, S. M.; Wantala, K.; Kajitvichyanukul, P. Photocatalytic remediation of persistent organic pollutants (POPs): A review. *Arabian Journal of Chemistry* **2020**, *13* (11), 8309–8337. https://doi.org/10.1016/j.arabjc.2020.04.028.

12. Pariatamby, A.; Kee, Y. L. Persistent organic pollutants management and remediation. *Procedia Environmental Sciences* **2016**, *31*, 842–848. https://doi.org/10.1016/j.proenv.2016.02.093.

13. Sheriff, I.; Debela, S. A.; Mans-Davies, A. The listing of new persistent organic pollutants in the stockholm convention: Its burden on developing countries. *Environmental Science & Policy* **2022**, *130*, 9–15. https://doi.org/10.1016/j.envsci.2022.01.005.

14. Stockholm Convention. *Chemicals proposed for listing under the Convention*. Copyright 2019 by Stockholm Convention. https://www.pops.int/TheConvention/ThePOPs/ChemicalsProposedforListing/tabid/2510/Default.aspx.

15. Stockholm Convention. *Listing of POPs in the Stockholm Convention*. Copyright 2019 by Stockholm Convention. https://www.pops.int/TheConvention/ThePOPs/AllPOPs/tabid/2509/Default.aspx.

16. Subramaniam, M. N.; Goh, P. S.; Kanakaraju, D.; Lim, J. W.; Lau, W. J.; Ismail, A. F. Photocatalytic membranes: a new perspective for persistent organic pollutants removal. *Environmental Science and Pollution Research* **2021**, *29* (9), 12506–12530. https://doi.org/10.1007/s11356-021-14676-x.

17. Sukhorebra, S. Current state in the field of persistent organic pollutants management in Ukraine. In *NATO science for peace and security series. C,*

Environmental security; 2009; pp 47–54. https://doi.org/10.1007/978-90-481-2903-4_5.

18. Torres, F. B. M.; Guida, Y.; Weber, R.; Torres, J. P. M. Brazilian overview of per- and polyfluoroalkyl substances listed as persistent organic pollutants in the Stockholm Convention. *Chemosphere* **2022**, *291*, 132674. https://doi.org/10.1016/j.chemosphere.2021.132674.

19. Venier, M.; Salamova, A.; Hites, R. A. How to distinguish urban vs. agricultural sources of persistent organic pollutants? *Current Opinion in Environmental Science & Health* **2019**, *8*, 23–28. https://doi.org/10.1016/j.coesh.2019.01.005.

20. Vystavna, Y.; Frkova, Z.; Celle-Jeanton, H.; Diadin, D.; Huneau, F.; Steinmann, M.; Morin-Crini, N.; Loup, C. Priority substances and emerging pollutants in urban rivers in Ukraine: Occurrence, fluxes and loading to transboundary European Union watersheds. *The Science of the Total Environment* **2018**, *637–638*, 1358–1362. https://doi.org/10.1016/j.scitotenv.2018.05.095.

21. Zolfaghari, M.; Drogui, P.; Seyhi, B.; Brar, S. K.; Buelna, G.; Dubé, R. Occurrence, fate and effects of Di (2-ethylhexyl) phthalate in wastewater treatment plants: A review. *Environmental Pollution* **2014**, *194*, 281–293. https://doi.org/10.1016/j.envpol.2014.07.014.

СТІЙКІ ОРГАНІЧНІ ЗАБРУДНЮВАЧІ: ДЖЕРЕЛА, МІГРАЦІЯ В ЕКОСИСТЕМАХ, МЕТОДИ ВИДАЛЕННЯ ПРИ ОЧИЩЕННІ СТІЧНИХ ВОД ТА РЕМЕДІАЦІЇ ҐРУНТІВ ТА ПРИРОДНИХ ВОД

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Стійкі органічні забруднювачі є одними з найнебезпечніших полютантів внаслідок своєї стійкості до руйнування в природних умовах, властивості мігрувати у екосистемах, біоакумуляції, біомагніфікації та значного шкідливого впливу на здоров'я. До стійких органічних полютантів відносяться хлорорганічні пестициди, поліхлоровані нафталіни, поліхлоровані біфеніли, полібромовані дифенілові етери, поліциклічні ароматичні вуглеводні тощо. Навіть у незначних кількостях ці сполуки можуть призводити до ендокринних розладів та чинити канцерогенну дію. Для більшості цих сполук є характерним виключно антропогенне походження. Хоча Стокгольмська конвенція сильно обмежила виробництво та використання стійких органічних забруднювачів, але багато ґрунтів та водойм вже є забрудненими цими сполуками, а деякі заборонені речовини продовжують утворюватись як побічні продукти у промислових процесах. Також хоча списки заборонених для виробництва речовин періодично поповнюються, але велика кількість сполук, які по властивостям є стійкими органічними забруднювачами, ще не ввійшли до цих списків. Існує велика кількість методів видалення стійких органічних забруднювачів з води, але більшість з них мають недостатню ефективність чи призводять до утворення великої кількості забруднених відходів, які потребують утилізації. Фотокаталіз є найбільш перспективним методом очищення стічних вод, які містять стійкі органічні забруднювачі. На відміну від коагуляції, адсорбції, біологічного очищення та нанофільтрації/зворотного осмосу цей метод дозволяє уникнення утворення твердих та рідких відходів, забруднених цими полютантами. У випадку ремедіації забруднених вод та ґрунтів основними методами є біоремеціація та адсорбція, оскільки цими методами можна зв'язувати стійкі органічні забруднювачі безпосередньо у екосистемі без вилучення ґрунту чи води на очищення.

Ключові слова: *бінакопичення, водне середовище, забруднення ґрунту, забруднення води, стійкі органічні забруднювачі*