Concentrations of Organochlorine Pesticides and Polychlorinated Biphenyls in Surface Water of the Dnieper River

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The article analyzes the levels of organic ecotoxicants, specifically organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), in the surface waters of the Dnieper River and other global water systems, highlighting trends over recent decades. The levels of OCPs and PCBs in the Dnieper River remained stable, with slight increases observed between 1994 and 2021. The average total concentrations during this period were 12.19±4.73 ng/dm³ (OCPs) and 23.13±20.64 ng/dm³ (PCBs). In other regions, average OCP concentrations (ng/dm³) were: 5.74±1.82 (Italy), 1.77±0.56 (Tyrrhenian Sea), 317.85 (Ganga River), 21.27 (Yangtze River), 34.37 (Huai River), and 69.93 (Pearl River Delta). For PCBs, the respective concentrations (ng/dm³) were: 27.90±8.70 (Italy), 11.67±1.48 (Tyrrhenian Sea), 8.47±6.36 (Yangtze River), and 3.50 (Pearl River Delta). Relative standard deviations ranged from 31.6% to 140.3% for OCPs and 12.7% to 94.3% for PCBs, reflecting variability in data collection over time and across studies. In China and India, PCB levels showed a declining trend, remaining below 50 ng/dm³. Correlation analysis between individual OCPs and PCBs helped estimate emission timing into aquatic systems. Overall, while some regions show downward trends in ecotoxicant levels, PCB concentrations in natural waters remain relatively stable globally.

Keywords: concentration, organic ecotoxicants, organochlorine pesticides, polychlorinated biphenyls, Dnieper River

Концентрації хлорорганічних пестицидів і поліхлорованих біфенілів у поверхневій воді р. Дніпро

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У статті проаналізовано рівні органічних екотоксикантів, а саме органохлорних пестицидів (ОХП) та поліхлорованих біфенілів (ПХБ), у поверхневих водах Дніпра та інших світових водних систем, з урахуванням тенденцій останніх десятиліть. Рівні ОХП та ПХБ у водах Дніпра залишалися стабільними, з незначним зростанням у період з 1994 до 2021 років. Середні концентрації становили 12.19±4.73 нг/дм³ (ОХП) та 23.13±20.64 нг/дм³ (ПХБ). В інших регіонах середні концентрації ОХП (нг/дм³) були такими: 5.74±1.82 (Італія), 1.77±0.56 (Тірренське море), 317.85 (Ганг), 21.27 (Янцзи), 34.37 (Хуайхе), 69.93 (дельта Перлинної річки). Концентрації ПХБ (нг/дм³): 27.90±8.70 (Італія), 11.67±1.48 (Тірренське море), 8,47±6,36 (Янцзи), 3,50 (дельта Перлинної річки). Відносні стандартні відхилення становили 31.6–140.3% для ОХП і 12.7–94.3% для ПХБ, що пов’язано з різнорідністю даних, отриманих у різні роки та різними авторами. У водних системах Китаю та Індії спостерігається зниження рівня ПХБ, який залишається нижчим за 50 нг/дм³. Кореляційний аналіз між окремими ОХП та ПХБ дозволив визначити часові рамки викидів екотоксикантів у водні системи. Загалом, попри зниження концентрацій у деяких регіонах, рівні ПХБ у природних водах залишаються відносно стабільними.

Ключові слова: концентрація, органічні екотоксиканти, хлорорганічні пестициди, поліхлоровані біфеніли, р. Дніпро

Introduction

After the Second World War, thousands of types of synthetic chemicals became widely used in various spheres of human activity. Some of these substances are organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). OCPs (dich lorodiphenyltrichloromethylmethane (DDT), hexachlorocyclohexane (HCH), aldrin, dieldrin, endrin, chlordane, mirex, toxaphene, heptachlor, hexachlorobenzene (HCB) and others) are broadspectrum contact insecticides [1]. Due to their ease of production and high efficiency, DDT and other OCPs have been widely used to control insect-borne infections (malaria, typhus) and in agriculture. At the beginning of the 60s of the last century, about $4.0{\cdot}10^5$ tons of DDT were used annually throughout the world, while 70–80 % of them were used in agriculture [2].

PCBs belong to a class of aromatic compounds consisting of two benzene rings connected by an internuclear C-C bond and substituted by one to ten chlorine atoms in the *o*-, *m*-, or *p*-positions. Their unique physical and chemical properties (exceptional thermal and physical characteristics, low electrical conductivity, heat resistance, inertness to acids and alkalis, fire resistance, good solubility in lipids, oils and organic solvents, high compatibility with resins, excellent adhesive ability) led to the wide application of PCBs as dielectrics in transformers and capacitors, coolants, fluids for hydraulic systems, plasticizers, topographic paints. PCBs are also used as additives to the composition of paints to ensure anti-corrosion resistance of the coating of ships and warships. According to estimates for the period 1930–1993, more than $1.3{\cdot}10^6$ tons of PCBs were produced. The leaders in their production were the USA, Germany, the former USSR and France [3].

In the 60–80s of the 20th century, it was discovered that OCPs, PCBs and some other compounds are characterized by extremly high toxicity, resistance to destruction, and even in small concentrations have a negative impact on human health and the environment. It has been established that these compounds are dangerous for the reproductive, nervous, endocrine and immune systems of human, his development and behavior. They accumulate along the food chain as a result of dissolution in the lipid tissue of living organisms, and an increase of concentration is observed in each new link of the trophic chain. Subsequently, this group of substances was named persistent organic pollutants (POPs) [1].

In order to protect the health of the population and the environment, the Stockholm Convention on POPs was approved at the UN conference on May 22, 2001. The parties to the convention undertook to stop or limit the production of POPs, safe disposal of their waste, and monitoring of these compounds in natural objects [4].

Despite the decisions made, a number of POPs continue to be used to this day. For instance, DDT is used to fight malaria and leishmaniasis. During the period 2001–2014, the global use of this pesticide decreased from 5388 to 3772 tons per year. At the same time, the largest producer and consumer of DDT was India [5].

In Ukraine, DDT and other pesticides were widely used in agriculture in the second half of the XX century, which led to global environmental pollution, including of aquatic ecosystems. According to official data, there are more than $2{\cdot}10^4$ tonnes of obsolete, unusable, and banned plant protection chemicals in Ukraine, a significant portion of which belongs to OCPs. These pesticides are stored in 4271 warehouses that have long been out of compliance with the requirements. As a result, pesticides are released from these warehouses into the water environment of Ukraine [6]. The main sources of PCBs entering the environment are: leaks from transformers, capacitors, hydraulic systems; vapours from varnishes, paints, plastics containing PCBs; emissions from the incineration of industrial and municipal waste; pesticides with PCBs. In addition, the entry of PCBs and OCPs into Ukrainian water systems may be associated with transboundary transfer [1].

The danger of POPs for the health of living organisms and humans is that they are powerful factors of immune suppression. Intoxication of OCPs and PCBs leads to damage to the nervous system, kidneys, liver, provokes the development of cancer, wasting syndrome, reproductive disorders, and teratogenesis [7].

The concentrations of organic ecotoxicants in natural and drinking waters are quite low (at the level of $1{\cdot}10^{-12}$ – $1{\cdot}10^{-6}$ g/dm^3). Therefore, there is a need for their preliminary selection, concentration, fractionation and purification of the obtained extracts in order to achieve the necessary enrichment factor to ensure the sensitivity of the detectors in the physicochemical methods of analysis of the target components. This testifies to the complexity, labor-intensiveness and high cost of the procedure of determination of these compounds in the objects of water systems. As a result, a few scientists deals with the problem of determination of OCPs and PCBs, information about the concentrations of these compounds in the natural waters of the world is quite limited.

The results of the determination of organic ecotoxicants OCPs and PCBs in natural waters of Ukraine are given in the monograph [1], as well as in articles [8–19].

As a result of their physical and chemical properties, OCPs and PCBs exist in different physical forms in natural water systems, namely: in a soluble state; in a bound state with suspended particles; in solubilized and sorbed states with organic compounds of natural and anthropogenic origin. The results of determination of the dispersed-phase distribution of these ecotoxicants are given and summarized in the articles [20, 21].

The aim of this study is to summarize data on the concentrations of OCPs and PCBs in surface water of the Dnieper River, to compare them with the results for other water systems, to establish trends in changes of the concentrations of these compounds, as well as to assess the degree of danger posed by organic ectoxicants to the world's water ecosystem.

Experimental part

Methods of extraction, concentration, fractionation and purification of organic ecotoxicants OCPs, PCBs

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and methods of their quantitative determination by gas chromatography/mass spectrometry (GC/MS), gas chromatography/electron capture detection (GC/ECD), which were used to study the surface waters of the Dnieper River, are described in detail in the monograph [1] and the articles [18–20].

Results and discussion

Concentration of OCPs in surface waters

During 1994–2021, a several studies were carried out with the aim of monitoring of a number of OCPs (α-, β-, γ-HCH, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT, heptachlor, aldrin, HCB) in the surface water of the Dnieper River [1, 8–11, 14, 15, 17–19]. The results of these studies were summarized and presented in fig. 1a. The total concentration of OCPs was in the range from 6.1 to 20.8 ng/dm^3. The average concentration was 12.19±4.73 ng/dm^3. During the study period, a slight increase of the pesticide content in the water was observed. This situation is due to the fact that OCPs are highly resistant to biodegradation. In particular, the half-life of DDT in water reaches 10 years. In addition to the classical sources of pollution, there are new inflows of OCPs that may be associated with various factors, one of which is transboundary transfer. This causes the accumulation of pesticides in the aquatic environment and a gradual increase of their concentration.

Information on the concentrations of 17 OCPs (α-, β-, γ-, σ-HCH, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT, aldrin, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, methoxychlor) in the water of the rivers of Southern and Central Italy, the Tyrrhenian Sea is given in the articles [22–25] and presented in fig. 1b and fig. 1c, respectively. The average total concentrations in river and sea water accuanted 5.74±1.82 and 1.77±0.56 ng/dm^3, respectively. As in the case of the Dnieper River, some increase of the OCPs content in the water was observed.

For the water systems of Asia, in particular the Ganga River [26–30], the Huai River [31–34], the Yangtze River [31, 35–38], the Pearl River Delta [39–43], on the contrary, there is a tendency to decrease of the total concentration of OCPs in water (fig. 1d, fig. 1e, fig. 1f, fig. 1g). The average values of the sum of OCPs in these water systems consist of 17.85 (22.5–908.3); 34.37 (14.3–82.4); 21.27 (3.7–56.8); 69.93 (2.6–300.0) ng/dm^3, respectively. It should be noted that in these cases the sum of OCPs consists only of the content of compounds of the DDT and HCH groups.

Let's consider the data on the ratio of individual OCPs in the water systems. It is known that DDT is converted over time to DDE in aerobic conditions and to DDD in anaerobic conditions. It follows from this that the ratio (DDE+DDD)/DDT can be used to estimate the interval of the pesticide emission in the natural environment. The value of this ratio > 0.5 indicates longtime DDT contamination; a value < 0.5, on the contrary, is a sign of recent DDT emission. For most water samples from the Dnieper River, the ratio (DDE+DDD)/DDT > 0.5, which indicates that sufficient time has passed since the pesticide entered the water.

It should also be noted that a high value of the α-HCH/γ-HCH ratio indicates the use of technical HCH, a low value – the use of lindane. High concentrations of γ-HCH compared to α-HCH were determined in the water of the Dnieper River, which may indicate the recent emission of lindane in this water system.

In the rivers of Southern and Central Italy, namely the Sarno River, the Tiber River, the Volturno River, the Sele River, and the Tyrrhenian Sea, the concentrations of metabolites DDE and DDD significantly exceed the concentrations of DDT. For example, the average values of the ratio (DDE+DDD)/DDT in the water phase, suspended particulate matter (SPM) and bottom sediments of the Volturno River were 13.8; 14.8 and 16.8, respectively [24]. These results indicate a longtime emission of DDT into the water systems of this region. Until 1987, when the use of DDT was banned, Italy was one of the largest consumers of the pesticide in the world. During the period 1948–1987, 4.6·10^4 tonnes of DDT were used in the agricultural sector of Italy [44].

Among the isomers of HCH in water systems of Italy, β-HCH prevailed. This isomer is the most stable among the others due to its high resistance to biodegradation and the fact that α-HCH and γ-HCH can be transformed to β-HCH in the environment. It follows that the use of HCH in Italy took place in a fairly distant past.

For some water samples from the Ganga River (India), the ratio (DDE+DDD)/DDT < 0.5, which is related to the recent use of DDT in India. According to the data of the study [26] in 1991, α-isomer prevailed among HCH isomers, which indicates the use of technical HCH in those years. However, later the situation changed. According to paper [30], γ-HCH predominated in 2015, which is associated with the active use of lindane in this region.

For samples from the Huai River, the Yangtze River, the Pearl River Delta (all – China), sufficiently low values of the ratio (DDE+DDD)/DDT are characteristic, which in some cases are lower than 0.5. For example, according to the article [42] in 2005 for the Pearl River Delta this ratio was on average 0.27. From this, we can make an assumption about the probable existence of new sources of DDT entering these water systems. It should be noted that high concentrations of γ-HCH were determined in the water of the Huai River compared to other isomers, and α-HCH prevailed in the water of the Yangtze River, the Pearl River Delta. In the case of the Huai River, a recent emission of lindane can be pruved. In the case of the Yangtze River and the Pearl River Delta, pollution is associated with the use of technical HCH.

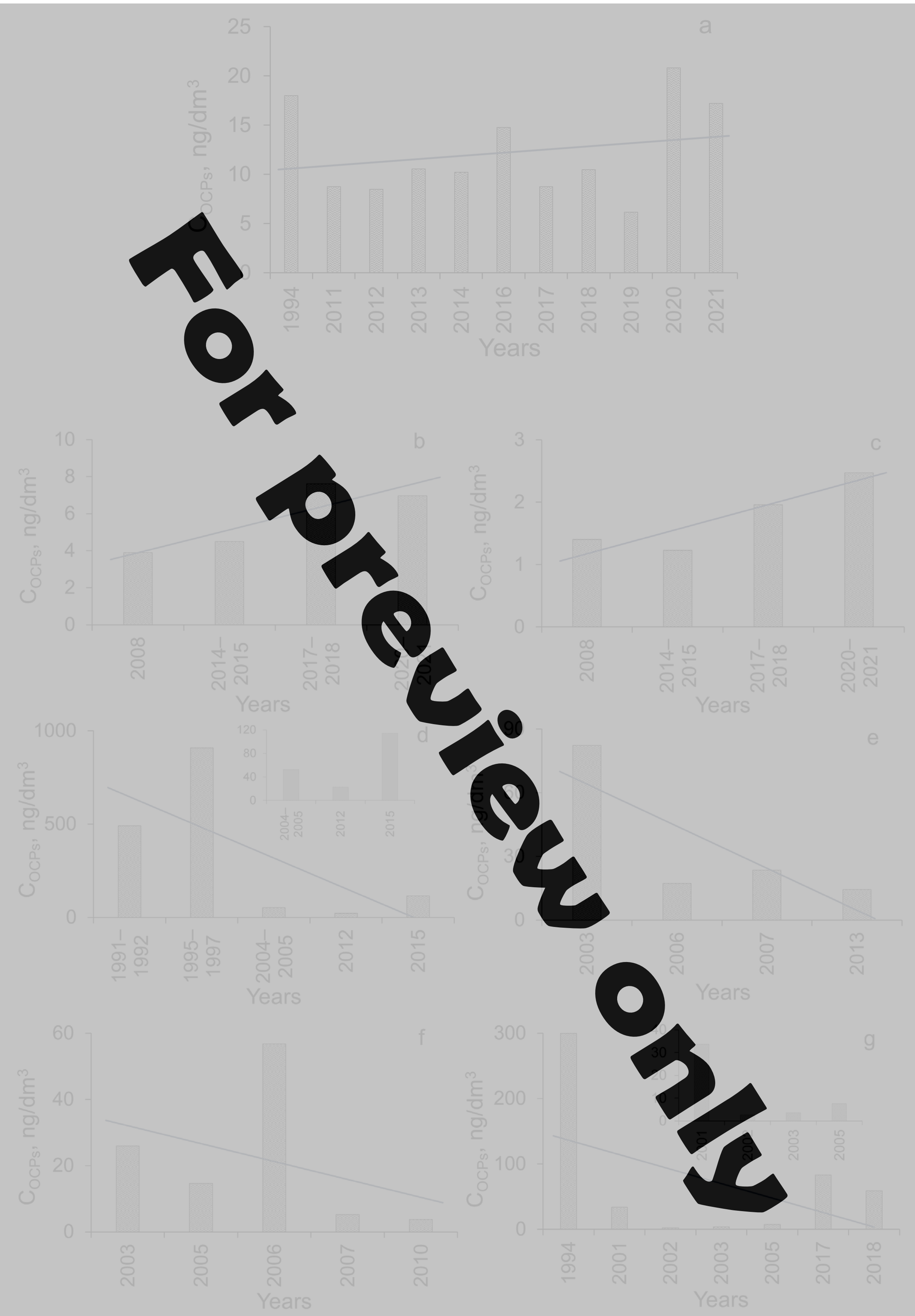

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Fig. 1. Average total concentrations of OCPs in surface water of the Dnieper River (a), the rivers of Southern and Central Italy (b), the Tyrrhenian Sea (c), the Ganga River (d), the Huai River (e), the Yangtze River (f), the Pearl River Delta (g). A trend line is a graph of an approximating function that can be used for predictions based on statistical data.

In general, the concentrations of OCPs in the Dnieper River are relatively stable and average compared to the water systems of other countries. Lower levels of pollution are determined in the water of the rivers of Southern and Central Italy and the Tyrrhenian Sea. Most samples from Asian water systems have significantly higher concentrations of OCPs. However, for these water systems, there is a noticeable tendency to decrease of the total concentration of pesticides, which is associated with a reduction of their use in various spheres of human activity.

Concentration of PCBs in surface waters

According to the results of research carried out during 1991–2021, the total PCB content in the surface water of the Dnieper River ranged from 4.8 to 49.6 ng/dm^3 [1, 8, 9, 11–14, 16–19]. The average concentration was 23.13±20.64 ng/dm^3. Fig. 2a shows the trend in the change of PCB concentrations in the water of the Dnieper River. The increase of the levels of PCBs can be explained by their emission into the environment together with transformer and capacitor fluids and transboundary transfer. As is well known, in the former USSR there was mass production of transformers and capacitors filled with sovol (PCB) and sovtol (a mixture of PCB and 1,2,4-trichlorobenzene). About 1.8·10^5 tonnes of PCBs were used for these purposes. Nowadays, the use of PCBs in electrical equipment is a significant source of environmental pollution in Ukraine. According to the results [45], the amount of PCBs entering the environment from the use of electrical equipment only in the Odesa industrial-urban agglomeration is 136 kg per year. The emission of PCBs occurs throughout Ukraine and causes an increase of their concentration in water systems.

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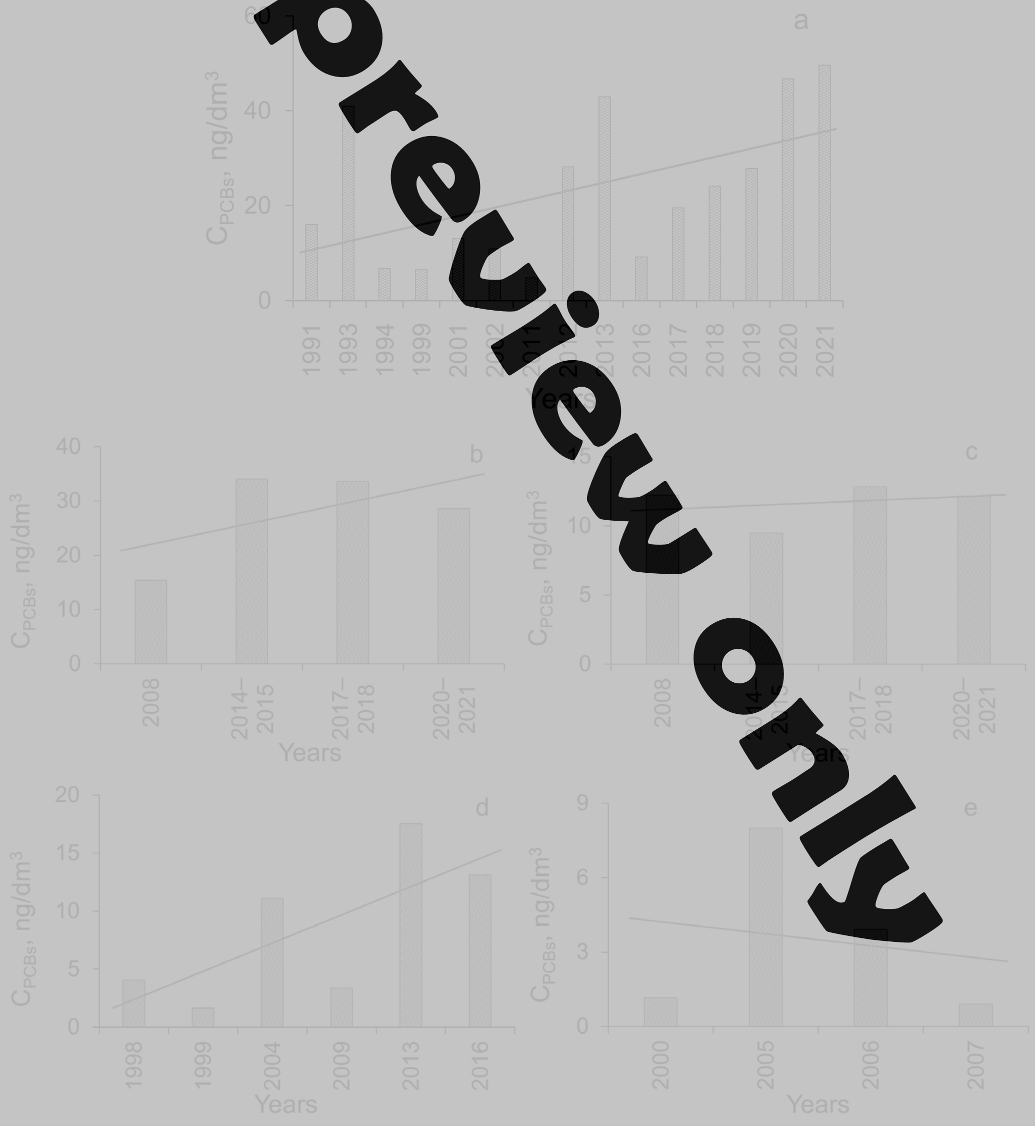

Fig. 2. Average total concentrations of PCBs in surface water of the Dnieper River (a) the rivers of Southern and Central Italy (b), the Tyrrhenian Sea (c), the Yangtze River (d), the Pearl River Delta (e). A trend line is a graph of an approximating function that can be used for predictions based on statistical data.

According to the results presented in the articles [22–25], a certain increase of the concentration of PCBs is characteristic for the water of the rivers of Southern and Central Italy for the period 2008–2021 (fig. 2b). In the water of the Tyrrhenian Sea, the PCB concentrations remained approximately at the same level (fig. 2c). The average total concentrations in river and sea water were 27.90±8.70 and 11.67±1.48 ng/dm³, respectively.

The total PCB concentrations in the water of the Yangtze River [46–50] and the Pearl River Delta [42, 51–53] were slightly less lower and averaged 8.47±6.36 and 3.50 (0.9–8.0) ng/dm³, respectively. As can be seen from fig. 2d, for the Yangtze River there was a trend of increasing PCB concentration in water. It is difficult to establish a certain regularity for the Pearl River Delta (fig. 2e). Sufficiently high total levels of PCB, namely 8.0 ng/dm³, were determined in 2005. During the other periods of the study, the sum of PCBs did not exceed 4.0 ng/dm³.

Analysis of the isomer-specific composition of PCBs showed that the surface water of the Dnieper River was dominated by congeners with the number of chlorine atoms from 4 to 6. Their part accounted for more than 80% of the total concentration. Parts of di-, tri-, and hepta-PCBs were insignificant [8, 9, 11–14, 16].

A similar isomer-specific distribution of PCBs is also characteristic for water systems in Italy. Thus, according to the results [22, 25], the total parts of tetra-, penta-, and hexa-PCBs in the water phase from the Tiber River and the Sele River were 84 and 82%, respectively. The predominance of these congeners in water can be explained by their high concentration in industrial oils and relatively high hydrophilicity compared to highly chlorinated congeners. Congeners of PCBs with a higher number of atoms are less hydrophilic and, as a result, have a tendency to bind with SPM and end up in bottom sediments.

In the water of the Yangtze River and the Pearl River Delta, congeners of PCBs with the number of chlorine atoms 3 and 4 prevailed. According to paper [42], in the water of the Pearl River Delta, the PCB concentrations decrease in the row of tri- > tetra- > penta- > hexa- > hepta-. Tri-PCBs accounted for more than half of the total amount. Probably, this isomer-specific distribution of PCBs is related to the composition of industrial fluids used in this region.

From the fulfilled analysis, it can be concluded that the considered water systems are characterized by relatively low total concentrations of PCBs, not exceeding 50 ng/dm³. However, it should be noted that the concentrations of PCB in some water systems, in particular the Dnieper River, have increased slightly during the past decades. Therefore, it is an actual task to continue monitoring studies to determine the concentrations of PCBs in surface waters and control their emission to the environment. These compounds are bioavailable, so they can pose a significant threat to all animal and plant life, including humans.

Conclusions

The paper discusses and analyzes the results of several studies on the determination of the concentrations of organic ecotoxicants (OCPs and PCBs) in the surface waters of the Dnieper River, conducted over the past few decades (1991–2021). The calculated average concentrations of OCPs and PCBs during the study period were 12.19±4.73 and 23.13±20.64 ng/dm³, respectively.

Trends in changes in the concentrations of organic ecotoxicants in the water of the Dnieper River were studied. A slight increase in the concentrations of OCPs and PCBs was observed over the past decades. In water samples collected in 2020 and 2021, the total concentrations of OCPs and PCBs reached 21 and 50 ng/dm³, respectively.

For comparison, similar trends in changes in the concentrations of OCPs and PCBs have been observed in other water systems around the world. In particular, data are presented for the rivers of Southern and Central Italy, the Tyrrhenian Sea, the Ganga River (India), and the Yangtze River, the Huai River, and the Pearl River Delta (all in China).

It was shown that the concentrations of organic ecotoxicants in the waters of the rivers of Southern and Central Italy and the Tyrrhenian Sea were approximately at the same level. The total average concentrations of OCPs and PCBs in the waters of the rivers of Southern and Central Italy were 5.74±1.82 and 27.90±8.70 ng/dm³, respectively. For seawater from the Tyrrhenian Sea, the following values were established: 1.77±0.56 and 11.67±1.48 ng/dm³. It follows that these water systems are characterized by relatively low concentrations of OCPs and PCBs.

The water systems of China and India are characterized by a decrease in the concentrations of OCPs in recent years. Despite this, the observed concentrations of these ecotoxicants remain quite high. For example, the average values of the sum of OCPs in the waters of the Ganga River, the Huai River, the Yangtze River, and the Pearl River Delta were 317.85 (22.5–908.3), 21.27 (3.7–56.8), 34.37 (14.3–82.4), and 69.93 (2.6–300.0) ng/dm³, respectively.

The total PCB concentrations in Chinese water systems, such as the Yangtze River and the Pearl River Delta, were low compared to other water systems, averaging 8.47±6.36 and 3.50 (0.9–8.0) ng/dm³, respectively. For the Yangtze River, there was an increasing trend in PCB concentrations in water. For the Pearl River Delta, there was a slight downward trend in PCB concentrations, but no clear pattern was identified.

Justification of self-citations

It should be noted that the significant number of self-citations in this work is due to the fact that the current study builds upon our previous research, which provided the foundation for the methods, approaches, and analyses employed in this investigation.

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