DOCTORAL SCHOOL OF BIOLOGICAL, GEONOMIC, CHEMICAL AND TECHNOLOGICAL SCIENCES WITHIN THE NATIONAL CONSORTIUM ADMINISTRATED BY MOLDOVA STATE UNIVERSITY

As manuscript

C.Z.U: 504.064:574.58(478)(043.3)

IVANOVA ANASTASIA

PERSISTENT ORGANIC POLLUTANTS IN AQUATIC ECOSYSTEMS OF THE REPUBLIC OF MOLDOVA

166.01. Ecology

Summary of the doctoral thesis in biological sciences

CHIȘINAU, 2022

The thesis has been developed in the Laboratory of Hydrobiology and Ecotoxicology, Hydrobiocenosis and Ecotoxicology Research Center of the Institute of Zoology

Doctoral supervisor:

Zubcov Elena, correspondent member of Academy of Sciences, professor, doctor habilitate of biological sciences

Doctoral Commission for public defense of the doctoral thesis:

UNGUREANU Laurenția	professor, doctor habilitate of biological sciences, Institute of Zoology – president;
ZUBCOV Elena	correspondent member of Academy of Sciences, professor, doctor habilitate of biological sciences, Institute of Zoology – doctoral supervisor;
BILEȚCHI Lucia	associate professor, doctor of biological sciences, Institute of Zoology – scientific secretary;
TODERAȘ Ion	academician, professor, doctor habilitate of biological sciences, Institute of Zoology – reviewer;
BOGDEVICI Oleg	associate professor, doctor of geology¸ Institute of Chemistry – reviewer;
BULIMAGA Constantin	associate professor, doctor habilitate of biological sciences, Institute of Ecology – reviewer;
GLADCHII Viorica	associate professor, doctor of chemical sciences, MSU – member;

The thesis defense will take place on **15th of April 2022** at **10:00** at the meeting of the Doctoral Commission within the Doctoral School of Biological, Geonomic, Chemical and Technological Sciences, _____

The doctoral thesis and summary can be consulted at the National Library of the Republic of Moldova, Central Scientific Library „Andrei Lupan", Moldova State University Library, and on the website of the National Agency for Quality Assurance in Education and Research (http://www.cnaa.md) and on the MSU website (http://usm.md/).

The summary was sent on _____2022

Doctoral supervisor Zubcov Elena, correspondent member of Academy of Sciences, professor, doctor habilitate of biological sciences

Author Ivanova Anastasia

Ivanova Anastasia, 2022

CONTENT

CONCEPTUAL FRAMEWORK OF THE RESEARCH

Actuality and importance of the research

Chemical pollution of the environment is recognized as a major global threat to human health. The UN documents, the SETAC resolution, together with the Water Framework Directive 60/2000/EC, provide for the need and timeliness of investigations into the understanding of ecosystem processes and the development of biotechnologies for the estimation and sustainable use of aquatic resources. The degradation of aquatic ecosystems is, in fact, the failure of society. Community programs contain 4 priority directions for research and innovation; one of which is the sustainable use of ocean resources and the degradation and depletion of freshwater resources. Thus, the importance and necessity of research on assessment of circuit, biomigration, bioaccumulation, bioamplification and biodegradation of persistent and toxic organic substances, impact of hazardous substances on aquatic organisms and functioning of ecosystems, is a key approach in solving aquatic management problems.

Persistent organic pollutants (POPs) pose a serious threat to both the living environment and human health, being severely degradable and toxic. Although most organochlorine compounds that are part of POPs have been banned since the 1970s, their harmful effects are still manifested today.

Monitoring of the migration, spread and accumulation of pesticides, especially organochlorine pesticides, in the aquatic environment is up-to-date worldwide. In the Republic of Moldova, organic pollution is considered one of serious environmental problems, and the migration and accumulation of POP in aquatic ecosystems is a scientific ecological and socioeconomic problem, and consequently a problem of maintaining human health.

The purpose of the research consists of the investigation of persistent organic pollutants and their accumulation processes in some components of the aquatic ecosystems of the Dniester and the Prut Rivers by implementing modern methods, laboratory techniques and high-performance analytical equipment.

To achieve this goal, the following **objectives** have been outlined:

- Studying, testing and implementation of modern analytical methods for the determination of persistent organic pollutants in the components of aquatic ecosystems, according to international standards and methods;
- Determination of the dynamic of the organochlorine pesticides and other POPs content in the waters of transboundary aquatic ecosystems within the borders of the Republic of Moldova;

- Determination of the accumulation level of organochlorine pesticides residues, polychlorinated biphenyls and polybrominated diphenyl ethers in the river sediments, assessment the ecological quality of the sediments according to the POP content;
- Specification of the methodological aspects regarding the determination of pesticides in fish tissues and their analysis in the muscles of the body, liver and gonads in 2 species with different types of nutrition (bentophages and predators).

The novelty and scientific originality consists of establishing the dynamics of the content of $\sum_4$HCH, $\sum_6$DDT, PAH in the waters, sediments and fish tissues from transboundary aquatic ecosystems, deciphering the migration of these substances under current conditions. For the first time, some legitimacy of accumulation in the underwater deposits of the compounds $\sum_{20}$BPC and $\sum_{29}$DEPB was established and the ecological status of the sediments is evaluated according to several evaluation systems on the POP content. By adjustment, specifying and implementing high-performance techniques and equipment, the results of the accumulation of organochlorine pesticides in the muscles of the body, liver and gonads of 2 species of fish were obtained. The investigations and the results obtained extend the knowledge regarding the complex monitoring of the functioning of the aquatic ecosystems.

The solved scientific problem consists of the scientific substantiation of the complex monitoring of the migration of persistent organic pollutants in the transboundary aquatic ecosystems of the Republic of Moldova, by implementing performant analytical techniques and equipment that highlight the residues of these pollutants in the aquatic environment, aspect that will contribute to the development of theoretical aspects of the functioning of aquatic ecosystems.

Theoretical significance: The tested methods, the advanced analytical techniques, approved in Sweden and the Republic of Moldova, allowed to obtain the results on the accumulation and migration of POPs and compounds formed in the process of transformation. The established laws regarding the dependence of the level of POP accumulation in underwater deposits on the total organic carbon content and other physico-chemical parameters, have a great theoretical importance in the development of ecological science of the functioning of aquatic ecosystems and the principles of their complex monitoring.

Applicative value: The results of the testing of POP analysis techniques in the components of aquatic ecosystems contribute to the development of the methodological basis of ecotoxicological studies. The results on the POP content are valuable for estimating surface water quality and the ecological status of underwater deposits. The research results are not only of scientific interest, but also

of public interest, regarding the state of the investigated aquatic ecosystems, e.g. for the Ministry and Environmental Agencies, for students, master students, doctoral students, young researchers and specialists in the field.

Implementation of scientific results. The results of research on the state of aquatic ecosystems are of interest to the Ministry of Environment and subordinate agencies. They are implemented at the "Dunărea de Jos" University of Galați. The results became part of 2 international projects (BSB27 MONITOX, BSB165 HydroEcoNex) and 1 national project under the State Program 2020-2023 (20.80009.7007.06 AQUABIO).

Approval of results. The main results presented in the thesis have been presented at 3 doctoral student conferences (2016, 2018, Galați; 2018, Chisinau) and at 3 international conferences (2016, Chisinau, 2019, SETAC Europe Helsinki, Finland; 2020, Kavala, Greece). On the topic of the thesis 13 scientific papers were published.

1 PERSISTENT ORGANIC POLLUTANTS IN THE AQUATIC ENVIRONMENT

Persistent organic pollutants, or POPs, are organic substances that have different origins, but at the same time, have important common properties, being toxic, persistent and bioaccumulative, prone to long-distance migration. The issue of pollution with xenobiotics is one of the most current environmental problems in the Republic of Moldova. The use of pesticides has decreased from 38 thousand tons of active ingredients in 1984 to 2.8 thousand tons in 2000. The Republic of Moldova signed the Stockholm POP Convention in 2001, but there are many pesticides and residues in the country (Cumanova, Gilca, Orlova 2008).

Based on the study of scientific publications (30 bibliographic sources), the physico-chemical characteristic of the following organic pollutants has been carried out: 1) pesticides dichlorodiphenyltrichloroethane (DDT) and its transformation compounds DDD and DDE, hexachlorocyclohexane (HCH) which have eight isomers (α, β, γ, δ, ζ, η and θ), hexachlorobenzene (HCB) 2) industrial compounds polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (DEPB). 16 polycyclic aromatic hydrocarbons (PAHs) are considered to be persistent and priority pollutants in monitoring the aquatic environment (Priority Pollutant List, EPA 2014).

The sources of POP pollution (45 bibliographic sources), global migration and the accumulation of POPs in the aquatic environment (90 bibliographic sources) are described. The bibliographic analysis identified the history of the use of pesticides and other persistent xenobiotics in the

environment, including the Republic of Moldova, and the importance of these investigations for the sustainable use of the environment (33 bibliographic sources);

The synthesis of scientific resources on the investigation of persistent xenobiotics proves the timeliness and importance of scientific monitoring of migration processes, their level of persistence and toxicity in the aquatic environment, including in the food chains, and the importance of testing and implementing efficient research methods using unified isotopic standards and high-performance equipment (high-resolution mass spectrometry).

2 AQUATIC ECOSYSTEMS INVESTIGATED

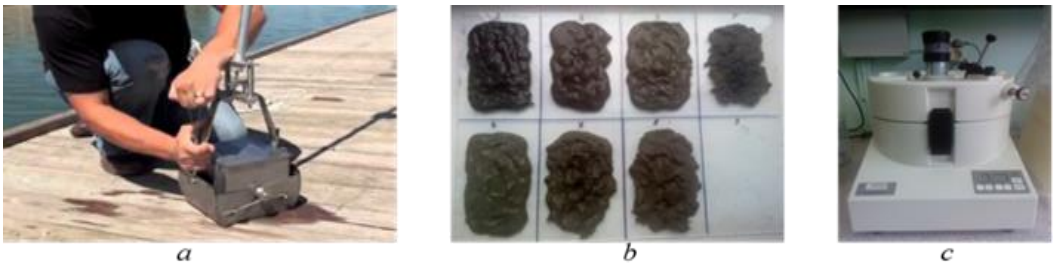
The ecosystems of the Dniester River were investigated, including the Dubasari Reservoir and the Răut and Bâc tributaries, and the Prut River ecosystem within the Republic of Moldova. The physical-geographical and hydrochemical characteristics of these ecosystems are partially presented. The influence of the construction and operation of hydropower plants is described, which was reflected on these two transboundary aquatic bodies – the Dniester and Prut Rivers.

The layout of the sampling stations is shown in Figure 2.1. Water and sediment samples were collected during the years 2016-2020 from the Dniester River and the Prut River. Samples from the Răut and Bâc rivers were collected in 2018.

Fig. 2.1 Scheme of water and sediments sampling points and underwater deposits.

The water samples were collected according to the ISO standard (SM EN ISO 5667-6: 2017) in a volume of 1 L in dark glass containers. The water samples were stored at 4 °C before the extraction process. A total of almost 200 water samples were collected.

Sediments samples were collected using the Ekman grab sampler according to the Hydrochemical and hydrobiological sampling guide (2015) (… Ivanova, et al., 2015, pp. 9-11, 40-42). A total number of 108 composite samples were collected (Figure 2.2). To determine the accumulation of POPs in biological material, 2 species of fish Abramis brama L. and Perca fluviatilis L. were collected.



a *b* *c*

Fig. 2.2. Sampling of sediments using the Ekman grab (a), drying of samples (b), processing of samples using the automated Pulverisette® grinding mill (c).

3 RESEARCH METHODOLOGY AND TECHNIQUES

One of the objectives of the doctoral thesis was the learning and implementation in the research process of new methods and high-performance analysis techniques for the determination of persistent organic substances in aquatic ecosystems. To accelerate this process, 2 doctoral grants have been awarded to author at the Laboratory of Persistent Organic Pollutants at the University of Agricultural Sciences in Uppsala, Sweden (Visby Program), which have resulted in a paper published in the journal Chemosphere (Ivanova et al., 2021).

3.1 Characteristics of the used analytical techniques

The gas chromatography method is the most efficient method of separating substances from volatile and semi-volatile multicomponent mixtures. This method has also been used in our investigations by specifying and implementing several laboratory techniques, in particular on the collection and preparation of material for analysis, and by the use of various sophisticated accessories and equipment. The methodological aspects have been published in 3 guides, which are implemented in the teaching and research process of the "Dunărea de Jos" University of Galați, the international interdisciplinary platform for investigating the environment INPOLDE and in research of the Institute of Zoology.

Instrumental measurement consists of injecting a sample into the chromatograph, where the mixture of compounds, together with the solvent, is converted to a gaseous state. The chromatographic column separates each compound that is subsequently detected. Mass spectrometry is the most sensitive method of structural analysis, being a microanalytical technique. The Hydrobiology and

Ecotoxicology Laboratory of the Institute of Zoology, in which its own investigations were carried out, is equipped with a gas chromatograph, model "Agilent 8860 GC System" coupled with 5977B MS Detector and separation column model Elite MS-5 with pre-column.

3.2 Analytical procedures

Analytical procedures used in the research process are presented in Figure 3.1. Extraction from water samples was performed according to the method SM SR EN ISO 6468: 2007 and EPA 3510C which is described in the Hydrochemical and hydrobiological sampling guide (2015) (…Ivanova et al., 2015, pp. 9-11, 40-42) and High performance analytical techniques for the monitoring of toxicants in Environment, methodological guide (2021) (… Ivanova et al., 2021, pp.57-64 and pp.142-149).

Water samples (500 ml) were extracted with dichloromethane by the liquid-liquid extraction method. The final volume of extracts (60 ml) was reduced to 1 ml and then purified on columns filled with activated silica gel according to EPA 3630C. The extracts after purification were reduced to 1 ml by exchanging the solvent for hexane in the concentration process using the IKA® RV10 digital rotary evaporator (Figure 3.2 b).

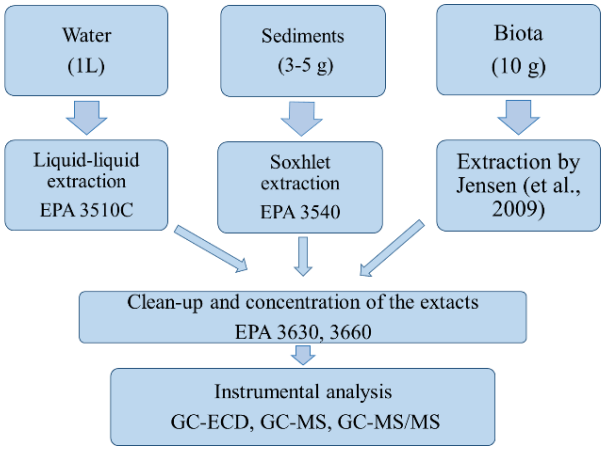
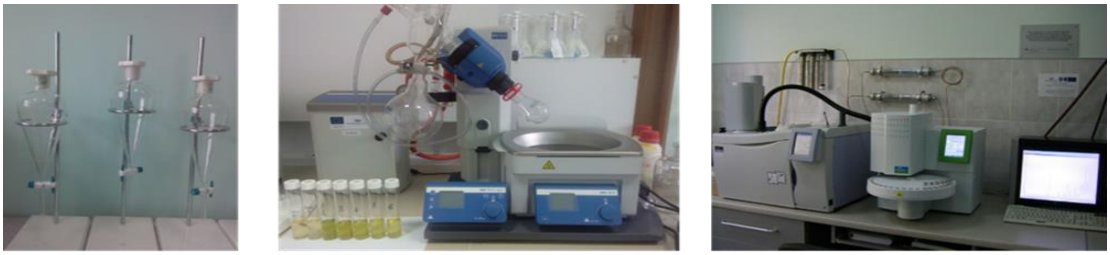


Fig. 3.1. Analytical scheme used in the research.



a *b* *c*

Fig. 3.2. Separation funnels (a), rotary evaporator (b) for concentration of extracts, chromatograph with electron capture detector (ECD) (c).

Quantitative analysis of water extracts was performed by gas chromatography using the Clarus 500 gas chromatograph (Perkin Elmer, USA), equipped with an electron capture detector (ECD) (Figure 3.2 c). Examples of the calibration curve and chromatograms obtained in the analysis process (Figure 3.3).

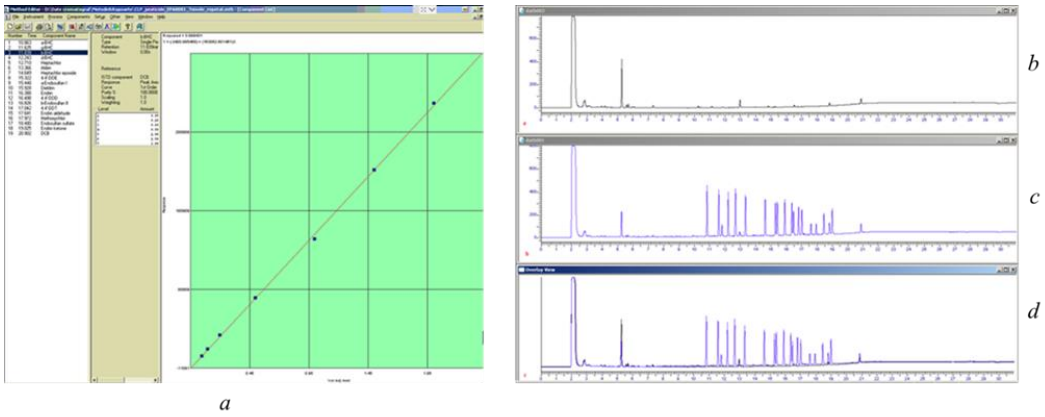


Fig. 3.3. Example of calibration curve of the analysed pesticide β-HCH (a), chromatogram of the water sample from the Prut River (b), chromatogram of the standard solution in hexane (c), chromatograms from b) and c) overplayed for comparison.

Sediments samples (3 g dry mass) were extracted by Soxhlet method for 16 hours in acetone:hexane (225 mL, 1:1, v/v), based on method 3540C, US EPA. After Soxhlet extraction, the extracts were evaporated with the Biotage TurboVap II® system to 1 ml in a water bath at 40 °C and under a gentle stream of nitrogen. Subsequently, 3 g of activated copper was added to remove sulphur compounds from the extract, according to EPA 3660 purification method. POP analysis in fish was performed according to the extraction method developed by (Jensen, Lindqvist, Asplund, 2009). Columns filled with acidified silica gel and anhydrous sodium sulphate were used to purify the extracts. Concentration to the final volume of 0.3 ml was performed under a slight stream of nitrogen. Sediments and biota extracts were analysed on a gas chromatograph (GC 7890A, Agilent Technologies) coupled with a quadruple mass spectrometer (7010 GC-MS/MS Triple Quad, Agilent Technologies). The total organic carbon content (TOC) was determined according to SS-ISO 10694, by dry burning at 1320 °C, using the TruMac instrument (Leco Corporation, St-Joseph, USA).

3.3 Quality assurance and control

Quality assurance and control were applied to all samples (… Ivanova et al., 2021, pp.57-64). A blank sample was prepared for each batch of 8 samples. Isotopic carbon-labeled recovery standard (^{13}C) was added to the sample prior to injection. The analysed compounds and chemical reagents are specified by SO, EPA (17 organochlorine pesticides: α-, β-, γ-, δ-HCH, HCB, o,p'-DDT, p,p'-DDT and

their transformation products: o,p'-DDD, o,p'-DDD, p,p'-DDD and p,p'-DDE, heptachlor, heptachlor epoxide, endosulfan I and II, endrin aldehyde, and endrin ketone The group of 20 PCB, 29 DEPB congeners and 16 PAH compounds have been analysed.

4 PERSISTENT ORGANIC POLLUTANTS IN THE AQUATIC ECOSYSTEMS OF THE REPUBLIC OF MOLDOVA

4.1 Organochlorine pesticides in the waters of the Dniester and Prut Rivers ecosystems

Among the organochlorine compounds analysed, using the standard of 17 pesticides, in most of the water samples investigated, four isomers of HCH (α-HCH, β-HCH, γ-HCH, δ-HCH) and three isomers of DDT (p, p'-DDT, p, p'-DDD, p, p'-DDE) were found.

It should be noted that the pesticide hexachlorocyclohexane (HCH) was in the attention of researchers of the Institute of Zoology in the years 1970-1980. Currently, the γ-HCH isomer has been detected in almost all water samples collected from the Dniester River, oscillating in the range 52 ng/L-114 ng/L (with maximum values at Naslavcea site) and Prut River, with the range between 10-168 ng/L (with maximum values at Giurgiulesti) (Figure 4.1). The current pesticides dynamics of concentrations along the river was ten times lower, comparing to 1977-1987 years.

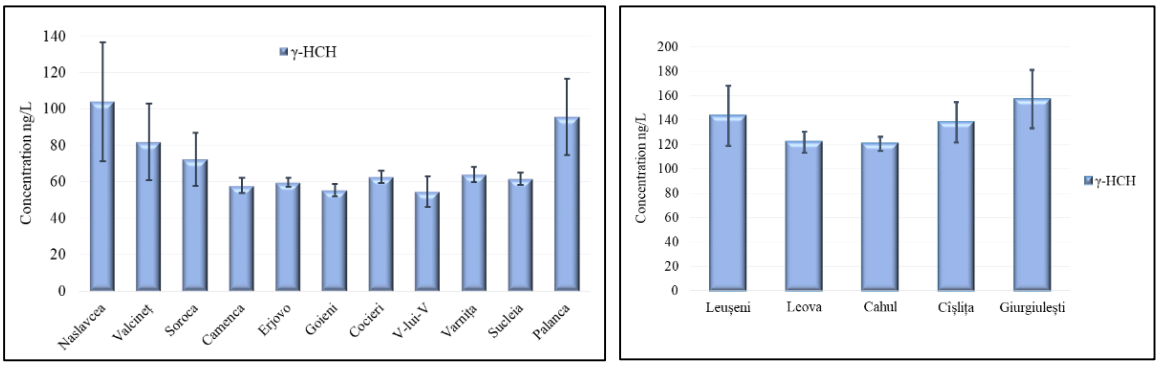


Fig. 4.1. γ-HCH concentration in the Dniester and Prut Rivers, ng/L, (2016-2020).

The α-HCH, β-HCH and δ-HCH isomers were not detected in all the investigated samples, only in 7-10% of the water samples from the Dniester River the α-HCH isomer was registered in the range of concentrations 20-70 ng/L, β-HCH – 16-22 ng/L, and δ-HCH – 3-11 ng/L. It has been established that in the waters of the Prut River the concentrations of the γ-HCH isomer are visibly higher than those in the Dniester River. On the Leușeni - Giurgiulești section, the average values of γ-HCH constituted 138±11 ng/L.

The increase of the γ-HCH content downstream of the confluence with the Jijia River was observed - the tributary on the right side of the Prut River, which brings with its waters an increased volume of suspensions (> 600 mg/L). It should be noted that increased concentrations of POPs were

recorded in the soils and deposits of the Jijia and Bahlui rivers basins (Dragan et al., 2006; Neamtu et al., 2009).

DDT pesticide and its transformation products were detected in over 70-80% of water samples collected from the Dniester River and in all the samples collected from the Prut River. The concentrations of these compounds (p,p'-DDT, p,p'-DDD, p,p'-DDE) ranged from 2 ng/L to 45 ng/L in the Dniester River and from 10 ng/L to 150 ng/L in the Prut River (Figure 4.2).

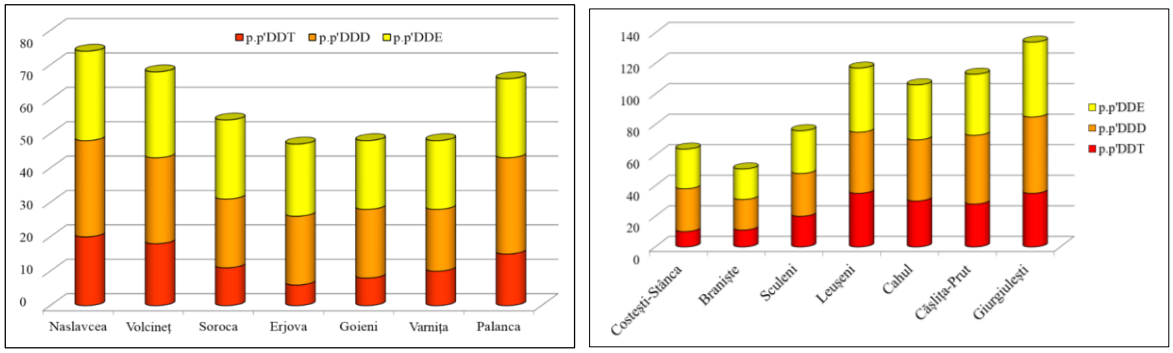


Fig. 4.2. DDT and its transformation products in the waters of the Dniester River and the Prut River ng/L, years 2016-2020.

The compound p,p'-DDD and the parent compound p,p'-DDT were detected throughout the river within the borders of the Republic of Moldova in concentrations not exceeding 50 ng/L, which indicates the existence of fresh pollution with this pesticide, despite the fact that its use has been banned for many years. DDT transformation products are subject to photolytic and hydrolytic degradation, but the presence of these compounds in running surface water is evidence of their recent penetration. The compound p,p'-DDE is the product of the decomposition of DDT under aerobic conditions, being very stable in the environment and having a high toxicity (Lin, Chang, 2007; Tcaciuc et al., 2018).

In 1977-1987 the concentration of these toxic substances was much higher - the sum p,p'-DDT + p,p'-DDD exceeded 3.0 µg/L, and p,p'-DDE - reached 3.3 µg/L, being maximum at Otaci-Camenca site and in the Turunciuc tributary (data from the archive of the Hydrobiology and Ecotoxicology Laboratory). The values registered in the years 2016-2020 exceeded the limit values for the quality requirements of surface water (Government Decision No. 890 of 12.11.2013). The highest concentrations were recorded at Giurgiulesti site, which is probably due to the influence of the Danube River, in whose waters the POP concentrations, in most cases, are higher (Vosniakos et al., 2012).

The increase in the concentration of the p,p'-DDT, p,p'-DDD, p,p'-DDE isomers on the Leușeni-Câșlița-Prut section is caused by the high amount of suspensions in the waters of the Prut river, which were not filtered during the sampling. The results of the analysis of filtered and non-filtered from

suspensions samples confirm this assumption. In order to monitor the migration of pesticides in waters with a high content of suspensions, we propose the analysis of suspended waters, in parallel to the analysis of filtered samples directly in the sampling process (*in situ*).

In addition to HCH and DDT, three highly toxic organochlorine pesticide compounds included in Annex III of the Rotterdam Convention and the Stockholm Convention regulations were detected in the water samples: endosulfan, and endrin transformation products: endrin aldehyde and endrin ketone. Endosulfan in the Dniester River was detected in 7% of the analysed samples in concentrations up to 57 ng/L (Naslavcea) and up to 35 ng/L (Palanca). The presence of only endosulfan sulphate compound in water samples indicates that the α- and β-endosulfan isomers have degraded significantly, so that they were not detected by the analytical instrument. The values of endrin aldehyde and endrin ketone concentrations were 61 and 57 ng/L.

4.2 Polycyclic aromatic hydrocarbons in the waters of the Dniester and Prut River ecosystems

The penetration of PAHs into the environment is caused by several human activities, such as the production of industrial and agricultural materials, the elimination of exhaust gases from motor vehicles and other transport, emissions from petroleum products, the combustion of coal and biomass (Soliman et al., 2019).

In the waters of the Prut River, the average values of ∑HAP concentrations varied between 61 and 264 ng/L, being maximum at Brânișteand Leușeni sampling sites. These concentrations are almost twice as high as those recorded in the Dniester River (37-109 ng/L). Out of 16 priority compounds analysed, 8 were detected: naphthalene (Np), acenaphthene (Ace), acenaphthylene (Acn), fluorine (F), phenanthrene (Ph), anthracene (An), fluoranthene (Fl) and pyrene (Py). It should be noted that the analysis of these compounds was possible thanks to the use of sophisticated equipment, namely the gas chromatograph equipped with a mass spectrometer. Fenanthrene was recorded in the highest concentrations in Brânișteste (162 ng/L) in the Prut River and at Naslavcea station (63 ng/L) - in the Dniester River (Figure 4.3).

The following ratios were used to determine the dominant sources of pollution: An/(An + Ph) < 0.1 indicates the presence of PAHs generated in the combustion process of petroleum products (gasoline, diesel, kerosene), while the value > 0.1 indicates the dominance of PAHs generated by the burning of heavy fuel.

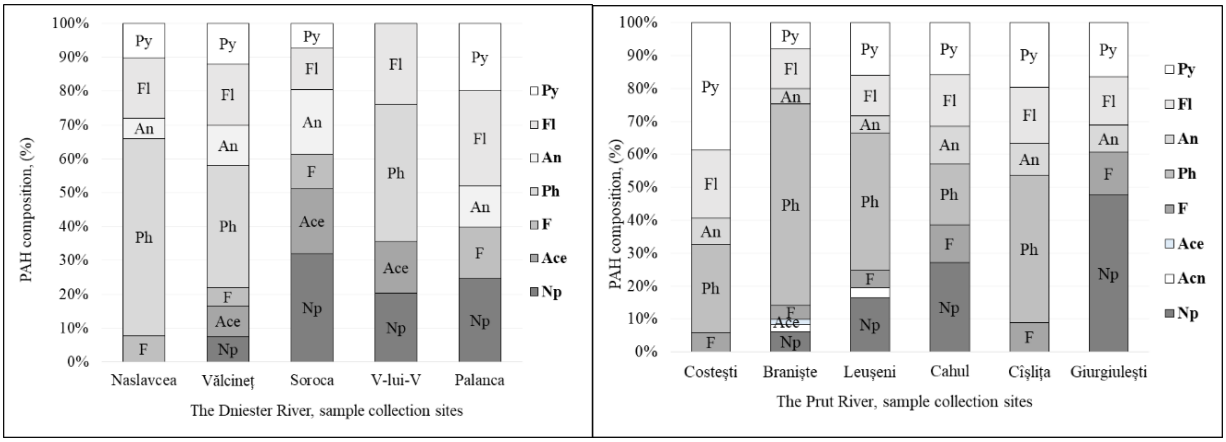


Fig. 4.3. The composition of polycyclic aromatic hydrocarbons detected in water samples of the Dniester and Prut Rivers: Np - naphthalene, Acn - acenaphthylene, Ace - acenaphthene, F - fluorine, Ph - phenanthrene, An - anthracene, Fl - fluoranthen, Py - pyrene.

The ratio Fl/(Fl + Py) being < 0.40 indicates the dominance of PAHs generated by the combustion of petroleum products, the interval between 0.40 and 0.50 can indicate the presence of PAHs formed by the combustion of liquid fuel, and the ratio > 0.50 - the processes of burning coal and plant matter (Yunker et al., 2002). Thus, the presence of PAHs in the investigated waters is related to pyrolytic sources (fuel burning).

4.3 Persistent organic pollutants in the sediments in the Dniester and Prut Rivers

Being the most stable components of aquatic ecosystems, sediments represent a reflection of the physico-chemical and biological processes that take place in aquatic ecosystems. Sediments are accumulators of pollutants and play a dominant role in the migration and circulation of chemicals in the aquatic environment. The sediments from the Dniester and Prut rivers refer to sandy muds, of the Dubăsari and Costești-Stânca reservoirs - to muddy and clayey muds, of the Răut and Bâc Rivers - to the muds (from the archive of the Laboratory of Hydrobiology and Ecotoxicology of the Institute of Zoology).

4.3.1 Organochlorine pesticides in the sediments

In the Dniester River sediments the concentrations of $\sum_4$HCH varied from 0.072 to 1.7 ng/g d.w. with maximum values at the Cocieri site, upstream of the Dubăsari dam, where the amount of organic substances and sediment fractions with a diameter <0.005 mm is the highest (Figure 4.4). The average concentration of $\sum_4$HCHs in the sediments in the reservoir was in the range 1.0 ± 0.55 ng/g d.w. and is visibly higher than in the lower Dniester (0.15 ± 0.10 ng/g d.w.) – the river segment from Vadul-lui-Vodă to Palanca sites. In the Prut River, the maximum concentration of HCH isomers was observed at Sculeni site (1.0 ng/g m.usc.).

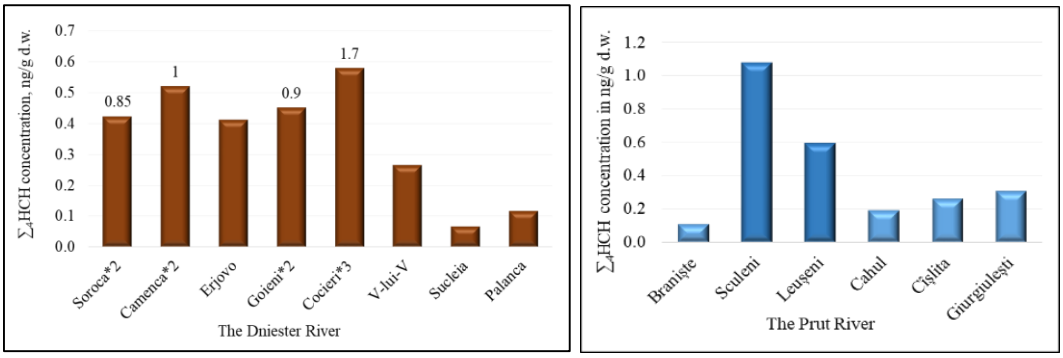
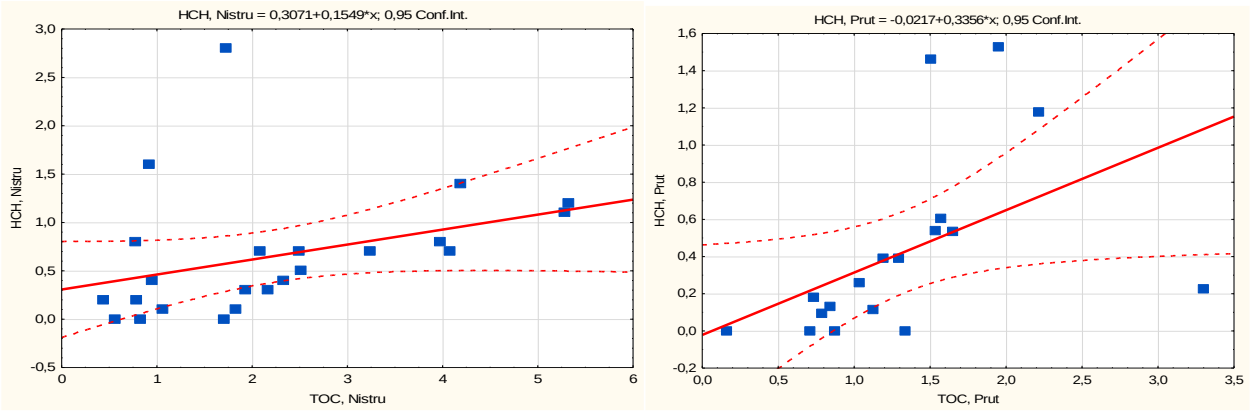


Fig. 4.4. The dynamics of ∑4HCH in the sediments of the Dniester and Prut Rivers, ng/g d.w.

The highest values of HCH concentrations were observed downstream of the Jijia tributary, being 2-3 times lower than those established for HCH dynamics in the Jijia River Basin (Neamtu et al., 2009) and 4 times lower than those established in 2006 (Dragan et al., 2006).

The dependence of the level of pesticide accumulation in the sediments on the concentration of organic substances also results from the ratio between the content of pesticides and that of the total organic carbon (TOC) in the sediments of the Dniester and Prut Rivers within the borders of the Republic of Moldova (Figure 4.5). No high correlation was found between ∑4HCH and TOC, as both ecosystems are under several natural and anthropogenic factors that are reflected in the content of these components. However, most data are included within the 0.95 confidence interval in an almost linear dependence.



(a) (b)

Fig. 4.5. The ratio between ∑4HCH concentrations and total organic carbon content (TOC) in the sediments of the Dniester (a) and Prut River (b).

In the rivers Răut and Bâc the average concentrations of ∑4HCH were 1.6±0.45 ng/g d.w. and 2.5±0.57 ng/g d.w. (Figure 4.6). Concentrations of HCH in the sediments of these tributaries were higher downstream of the crossed cities, being comparable to the data previously reported for the Black

Sea region (Covaci et al., 2006) and for other regions in Europe (Sazakli et al., 2016; Liber et al., 2019).

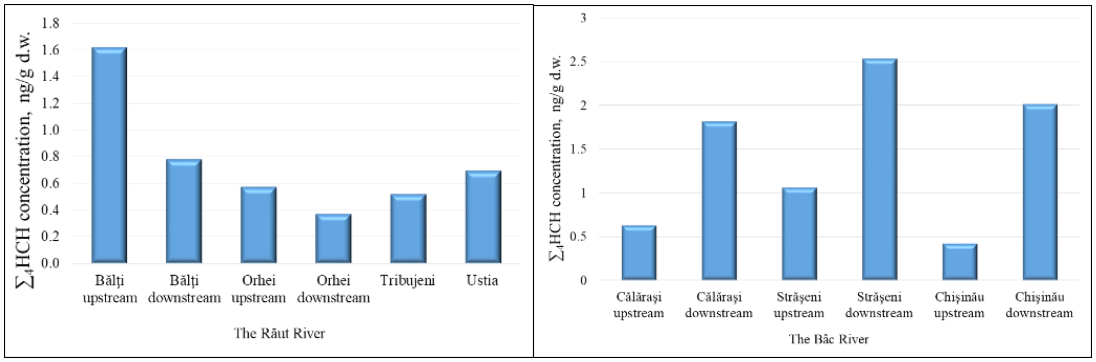


Fig. 4.6. Dynamics of ∑4HCH in the sediments of the Răut and Bâc Rivers, ng/g d.w.

It should be noted that, among the four isomers analysed, α-HCH and β-HCH were predominated compounds in the investigated sediments, while the γ-HCH and δ-HCH isomers were below the detection limit, or in very small quantities. Isomer γ-HCH was detected only in the sediments of the Prut River, at Giurgiulești site.

In the years 1977-1987 the concentrations of isomers in the sediments of the Dniester and Prut Rivers ecosystems were higher, and γ-HCH was detected in less than 5-10% of cases. The fact that currently only the β-HCH isomer predominates, proves that in the investigated aquatic ecosystems the HCH residues of previous long-term contamination predominate.

HCB residues were detected in all analysed samples, oscillating in the Dniester River between 0.057 ng/g d.w. (Vadul-lui-Vodă site) and 0.66 ng/g d.w. (Soroca site). In the sediments from the Prut River, the concentration of HCB residues ranged from 0.076 (Leușeni site) to 0.14 ng/g d.w. (Giurgiulești sampling site) (Figure 4.12).

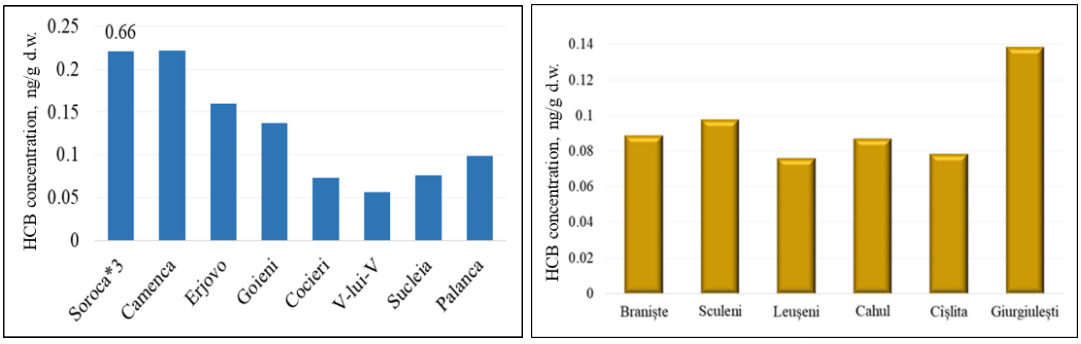


Fig. 4.12. HCB concentrations in the sediments of the Dniester and Prut Rivers.

A positive correlation (r = 0.81) was established between HCB and TOC in the sediments in the Dniester River. In the rivers Răut and Bâc, the maximum concentrations of HCB were registered in the

sediments in the area of the Bălți municipality (downstream, 1.8 ng/g d.w.) and, respectively, downstream of the Chișinău municipality (0.58 ng/g d.w.).

The dynamics of DDT compounds in sediments are, for the most part, similar to that of HCH compounds. Summary concentrations of ∑DDT (o,p′-DDT, p,p′-DDT, o,p′-DDD, o,p′-DDD, p,p′-DDD and p,p′-DDE) in the sediments of the Dniester and Prut Rivers are shown in Figure 4.7.

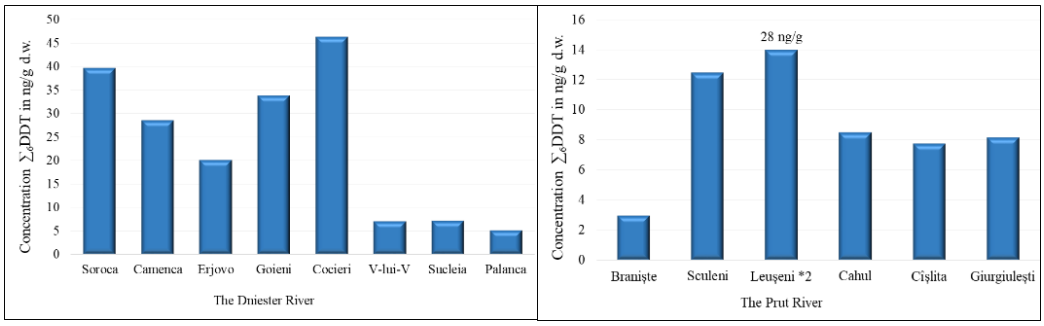


Fig. 4.7. The dynamics of Σ_6DDT in the sediments of the Dniester and Prut Rivers, ng/g d.w.

In the Dniester River the average values of $\sum_6$DDT (23±16 ng/g d.w.) were twice as high as those in the Prut River (11±8.7 ng/g d.w.). The maximum concentrations of $\sum_6$DDT were detected in the samples at the Dubăsari reservoir at Cocieri site in 2016 (71 ng/g d.w.) and at the downstream of Soroca site in 2018 (45 ng/g d.w.). There was a visible increase in $\sum_6$DDT content in the Dubăsari reservoir from the upper sector (Erjova) to the middle sector (Goieni) and then to the lower sector (Cocieri) (Figure 4.7), which corresponds to the dynamics of fine particles with a diameter <0.005 mm. Thus, the dynamics of $\sum_6$DDT is similar to that of ∑HCH. Downstream of the Dubăsari dam, the $\sum_6$DDT content was 7-9 times lower than upstream of the dam.

The concentrations of $\sum_6$DDT determined in the sediments of the Prut River were lower compared to the Dniester River (Figure 4.7) and demonstrated an opposite dynamics for the water samples of these ecosystems. In the water samples from the Dniester the concentrations of this pesticide were lower than in the waters of the Prut River. In 2017, in the Prut River, at the Leușeni site, the total Σ_6DDT concentration in sediments reached the value of 67 ng/g d.w. This high concentration can be explained by the position of the Leușeni site - downstream of the confluence with the Jijia River.

The ratio of DDT compounds to total organic carbon content (OCD) in the investigated sediments samples was analysed. It was observed that the dynamics of the accumulation level in the sediments of Σ_6DDT in the Dniester and Prut Rivers were in an obvious connection with the composition of sediments, more precisely with the TOC content in the sediments (Figure 4.8).

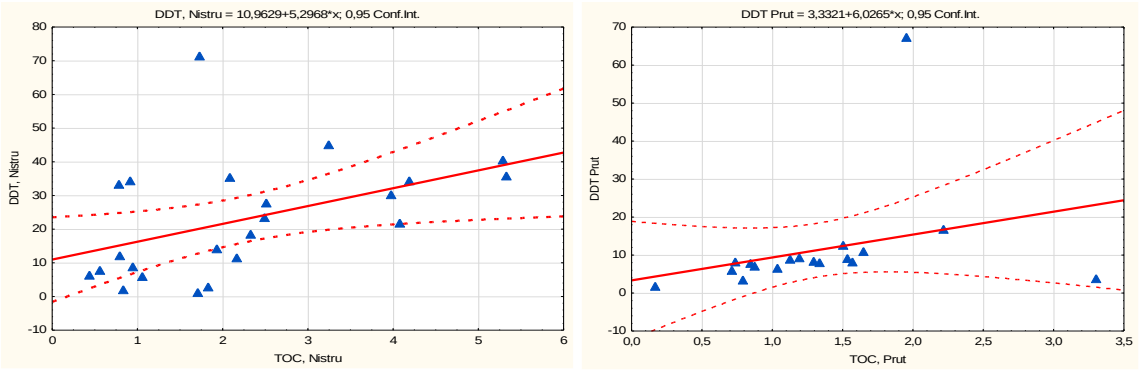


Fig. 4.8. The ratio of Σ_6DDT concentrations to total carbon content (TOC) in the sediments of the Dniester and Prut Rivers.

An analogous trend was observed for the ratio between $\sum_4$HCH, Σ_6DDT and TOC in the Dniester and Prut Rivers (Figures 4.5, 4.8). Taking into account the dynamics of $\sum_4$HCH and Σ_6DDT residues, similar in the Dniester and Prut Rivers, as well as the existence of relationship between these compounds and organic carbon content in the sediments, the correlation between these 2 groups of pesticides in sediments was established (Figure 4.9).

The concentrations of Σ_6DDT established in the sediments of the Răut and Bâc Rivers were higher than those in the River Dniester. Thus, in the sediments of the River Răut they varied in the limits of 7.4-137 ng/g d.w., and those of the River Bâc in the limits of 7-60.5 ng/g d.w. Downstream of the crossed cities (Bălți, Orhei, Călărasi, Strașeni and Chișinău), the Σ_6DDT concentrations were 2-3 times higher than those from upstream of the mentioned cities.

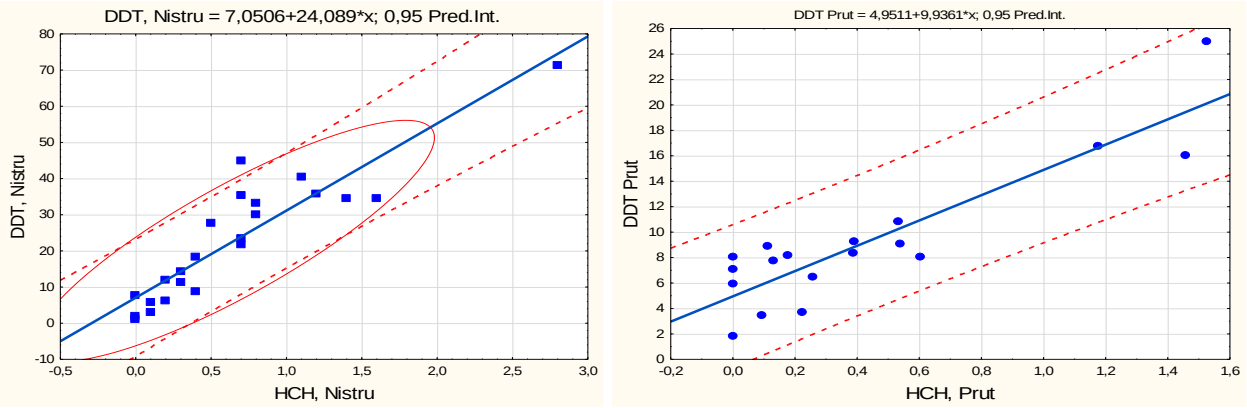


Fig. 4.9. The correlation between Σ_6DDT and $\sum_4$HCH concentrations in sediments of the Dniester (r = 0.91) and Prut Rivers (r = 0.89).

For the first time, the composition and the ratio of DDT compounds (p,p'-DDD, o,p'-DDD, p,p'-DDT, o,p'-DDT, p,p'-DDE and o,p'-DDE) were determined in the sediments of the Dniester and Prut Rivers (Figure 4.10).

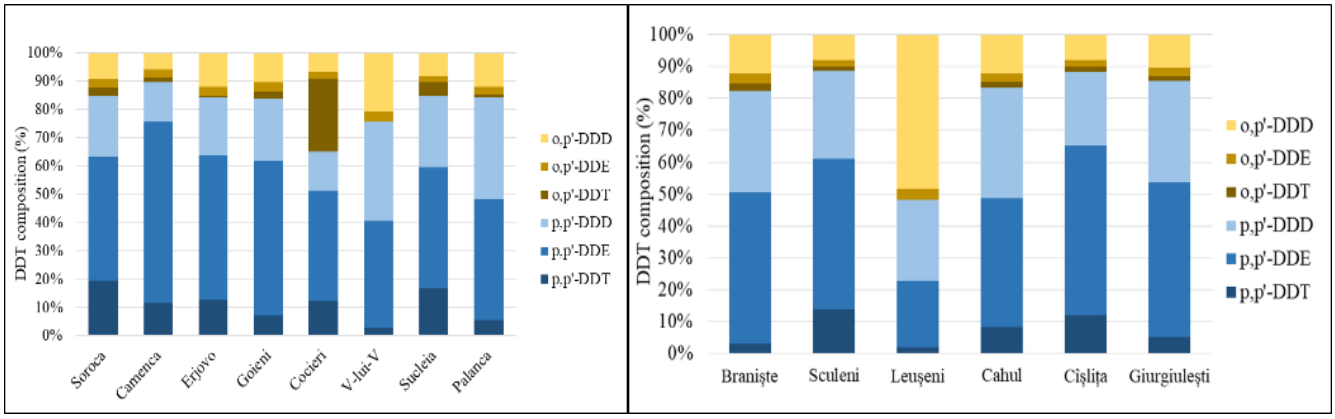


Fig. 4.10. DDT compounds composition in the sediments of the Dniester and Prut Rivers.

In the sediments of the Dniester and Prut Rivers p,p'-DDE compound was dominant, constituting on average 45±10% of 6 determined compounds, followed by p,p'-DDD (26±7%), o,p'-DDD (13±11%), p,p'-DDT (9±6%), o,p'-DDT (3±7%) and o,p'-DDE (3±0.5%).

Similar to the Dniester and Prut Rivers, p,p'-DDE and p,p'-DDD compounds were predominated in the sediments from the Răut and Bâc Rivers (Figure 4.11).

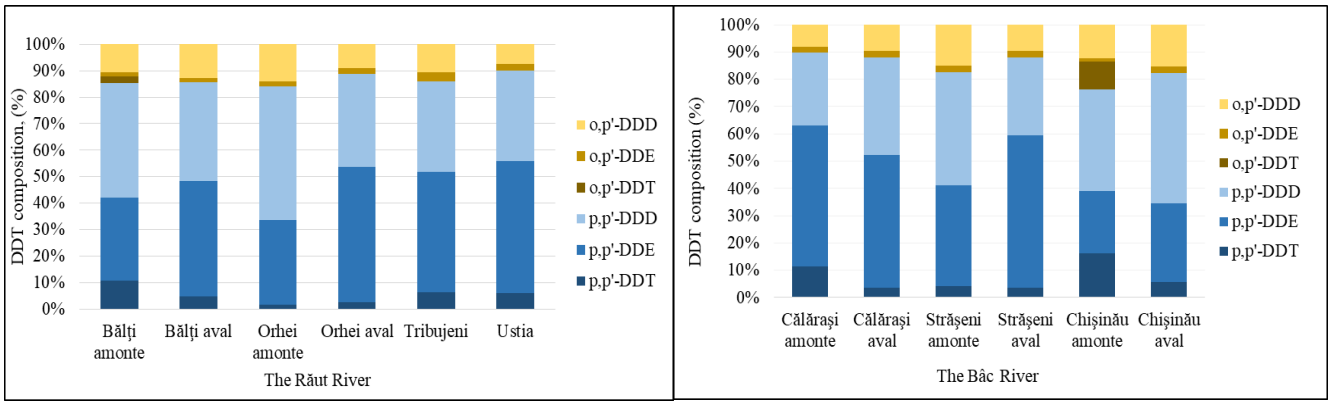


Fig. 4.11. DDT compounds composition in the sediments of the Răut and Bâc Rivers.

In the sediments from the upstream of Dubăsari dam o,p'-DDT compound made up 42% of all DDT compounds (Figure 4.10). This situation reveals the recent input of DDT in the waters of the Dubăsari reservoir (Ivanova, 2018). The ratio (DDE + DDD)/∑DDT) ranged from 0.77-0.98, indicating that parental DDT has suffered a long-term process of degradation, which is in accordance to data from the literature (Mansouri et al., 2017).

The process of degradation of DDT, as well as other organic substances, in aquatic ecosystems depends on redox conditions. The ratio DDD/DDE > 1 denotes the dominance of biodegradation processes under anaerobic conditions of DDT in DDD, while DDD/DDE <1 - biotransformation of DDT into DDE under aerobic conditions. Thus, in most of the investigated samples, the processes of

aerobic biodegradation of the parent compound DDT predominated, and in some areas of stagnation or of spillage of poorly treated wastewater, anaerobic conditions can be created, which was observed in the samples from the Răut and Bâc Rivers.

4.3.2 Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in the sediments

PCBs are quite inert chemicals in the aquatic environment due to their low solubility. The water solubility of PCBs decreases with increasing number of chlorine atoms in their structure (Pozo et al., 2014). Out of the group of 20 PCB compounds analysed in sediments, 16 congeners were detected. In the Dniester River the concentrations $\sum_{16}$BPC varied in the limits of 0.65-13 ng/g d.w., with maximum at Soroca site. In the Dubăsari reservoir $\sum_{16}$BPC have differed from one sector to another: 1.2 ng/g d.w. in the upper sector, and increase up to 7.1 ng/g d.w. in the medial sector and decreased slightly up to 2.8 ng/g d.w. in the lower sector (Figure 4.13).

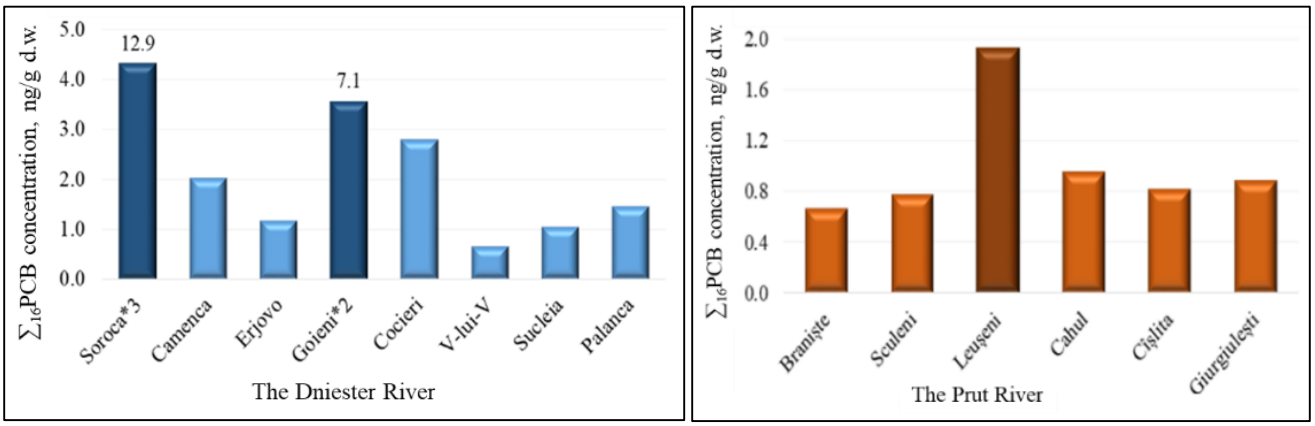


Fig. 4.13. Σ_{16}BPC concentrations in sediments of the Dniester and Prut Rivers.

PCB concentrations in the Prut River varied within the limits of 0.66-1.9 ng/g d.w., with maximum values at Leușeni site (Figure 4.13), as in the case of organochlorine pesticides. The Σ_{16}BPC concentrations established in the Prut River were 1.5-14 times lower than those recorded by M. Neamțu (2009) and 12-83 times lower than those established in eastern Romania by other authors (Dragan et al., 2006).

In the Răut and Bâc Rivers, the $\sum_{16}$BPC concentrations varied from 0.67 to 6.2 and from 0.93 to 28 ng/g d.w., respectively (Figure 4.14). Maximum $\sum_{16}$BPC concentrations were recorded in the sediments in the Răut River in the area of Bălți municipality. In the case of the Bâc River, an increase of PCB concentrations was detected downstream of the cities of Călărași, Strașeni and, especially, in the municipality of Chisinau, with the maximum concentration was recorded (28 ng/g d.w.).

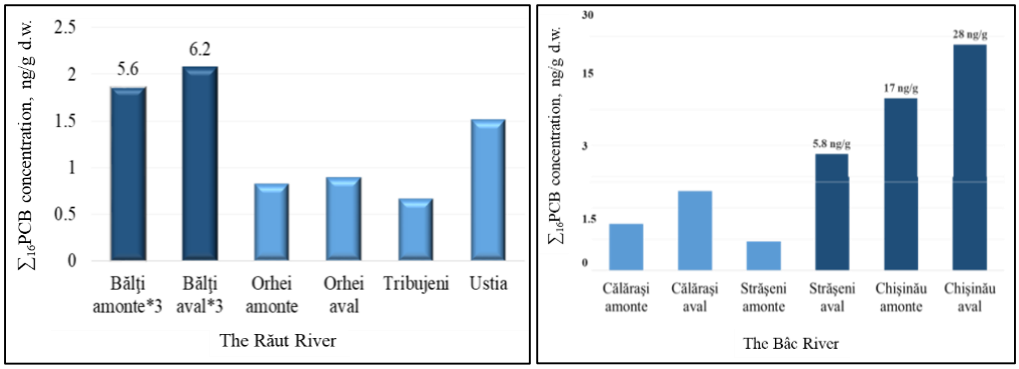


Fig. 4.14. Σ_{16}BPC concentrations in the sediments of the Răut and Bâc Rivers.

From the 20 PCB congeners analysed, 16 compounds were detected in almost every sediments sample, of which PCB-28, -52, -77, -101, -105, -118, -126, -138, - 156, -157, -167, 170, -180, -189, -209 in the range of concentrations 0.47-22.8 ng/g d.w. (Figures 4.15, 4.16). The ratio of noncoplanar or "non-dioxin-like" congeners made up 62-92% of the total content of determined PCB compounds. The coplanar PCB congeners with coplanar structure possess toxic properties close to dioxins. They were grouped into "dioxin-like" PCBs. The ratio of these compounds was 8-38% of the total PCB content.

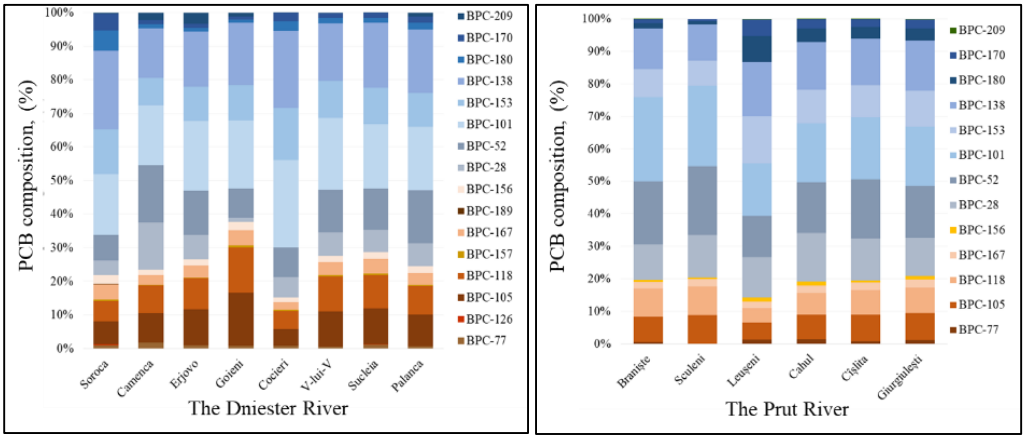


Fig. 4.15. PCB congeners composition in sediments of the Dniester and Prut Rivers.

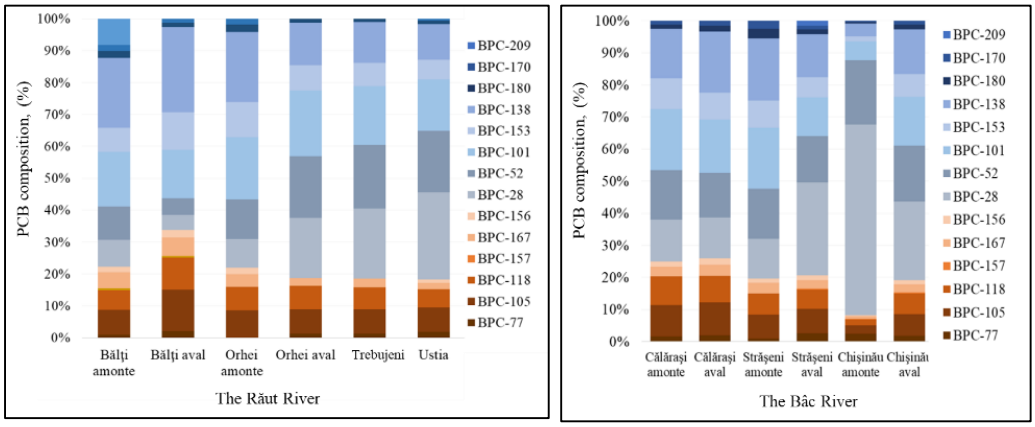


Fig. 4.16. PCB congeners composition in sediments of the Răut and Bâc Rivers.

Several coplanar or "dioxin-like" compounds (∑8BPC = -77, -126, -105, -118, -157, -167, -189, -156) were detected in the underwater deposits of the Dniester River (at Soroca site, with 2.8 ng/g d.w.), in the River Răut (2.1 ng/g d.w.) and Bâc River (5.5 ng/g d.w.). The content of the penta- and hexa-chlorinated congeners made up 33% and 28%, correspondingly, of all the detected congeners. Those of the tri- and tetra-chlorinated congeners made up 16% each, of the hepta-chlorinated congeners - 3% and of the deca- chlorinated - 1%.

A positive correlation (r = 0.81) was established between $\sum_{16}$BPC concentrations and total organic carbon content (TOC) in sediments the Dniester Rivers. A positive correlation was also established between the concentrations of individual PCB compounds and TOC (r = 0.45-0.63), between the concentration of penta- and hexa-chlorinated compounds (r = 0.64), such as hexa- and hepta -chlorinated (r = 0.55), and between the least chlorinated - tri- and tetra- (r = 0.51). Also, a strong negative correlation was established between the tri- and penta-chlorinated compounds (r =-0.828), tri- and hexa-chlorinated (r = -0.800).

Currently, polybrominated diphenyl ethers (PBDEs) are considered ubiquitous environmental pollutants (Van Ael et al., 2012). From the group of 34 congeners of PBDEs analysed, several compounds were detected in the sediment samples, namely PBDE-47, -99, -49/71, -28 and -209. In the Dniester River maximum values of PBDEs (sum of compounds PBDE-47, -99, -49/71, -28) were recorded at Soroca sampling site (0.32 ng/g d.w.). In the rivers Răut and Bâc the maximum values were recorded downstream of the Bălți city (0.27 ng/g d.w.) and downstream of Chișinău city (2.53 ng/g d.w.). The congeners BDE-47 and BDE-99 were the dominant compounds, the most common being BDE-47 which made up 52% of all congeners, being in the range from <LDD to 0.51 ng/g d.w. It was followed by BDE-99, which accounted for 37%, ranging from <LDD to 1.3 ng/g d.w. Compound BDE-209 was recorded in the Dniester River at Soroca site (12 ng/g d.w.) and downstream of Chișinău city in the Bâc River (6.6 ng/g d.w.) downstream of the discharge of wastewater.

In addition to the mentioned compounds, BDE-49/77 (downstream of Călărași and Chișinău) and BDE-28 (downstream of Chișinău) were found in the sediments of the Bâc River. Tetra- and penta-BDE were dominant in the analysed sediment samples of the investigated ecosystems, with the exception of BDE-209 which was detected at only two sampling sites. Although, decabromilated diphenyl ethers and, especially, BDE-209 account for almost 75% of the world's PBDEs production, research shows that slightly brominated compounds (BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154) which in some studied areas predominated over the fraction of the most strongly brominated.

4.4 Assessment of the ecological status of the sediments

Sediments monitoring has become a key component in the complex estimation of the status of freshwater bodies, in particular the level of pollution with persistent organic substances. Three guidelines developed in Russia, Norway and Canada, were used in the investigations. The normative elaborated in Russia involves 5 quality classes for most persistent pollutants: class 0 - clean, class I - lightly polluted, class II - moderately polluted, class III - polluted, class IV - extremely polluted (Региональный норматив, 1996). According to this guideline, based on temporary standards, on the $\sum_6$DDE content the sediments of the Dniester River from Soroca to Cocieri sites, of the Prut River - at Leușeni, of the Răut River at the Bălți-Orhei segment and of the Bâc River downstream from Călărași to downstream of Chisinau, refer to class IV - extremely polluted and correspond to disaster area, which requires prevention interventions.

Other sites: Prut Rievrs at Sculeni, Răut River upstream of Orhei and Ustie, Bâc River at Călărași sampling sites correspond to class III - polluted, crisis area, very unfavourable condition and require verification activities. Sediments from the lower Dniester (Vadu-lui-Vodă - Palanca), Prut River (Branište, Cahul - Giurgiulești), Răut River at Trebujeni correspond to class II - moderately polluted, risk area, unfavourable condition, activity at the limit level. It should be noted that the sediments in the river Bâc downstream of the municipality of Chișinău correspond to class III and II according to the total content of the 7 PCBs congeners.

Comparison of the results with the temporary sediments standards, included in the Canadian Environmental Quality Assessment Guide (Canadian environmental quality guidelines, 1999), showed that the concentrations of p,p'-DDD, p,p'-DDE and p,p'-DDT in the analysed sediments are higher than the values of the Canadian temporary standards (Interim sediment quality guideline standards, ISQGS - 3.54, 1.42 and 1.19 ng/g of d.w.) in many sampling areas.

In the Dniester and Prut Rivers p,p'-DDE concentrations exceeded the values of temporary standards in all samples analysed. p,p'-DDD and p,p'-DDT concentrations exceeded in 43% in the Dniester and in 50% in the Prut Rivers. In the rivers Răut and Bâc the concentrations p,p'-DDD exceeded the established limits in 65% of cases, p,p'-DDE - in 59% and p,p'-DDT - in 53% (Ivanova et al., 2021). Sediments in the Dniester River exceeded the level of probable adverse effects on aquatic organisms (PEL) for p,p'-DDE and p,p'-DDT concentrations at Soroca and Cocieri sampling sites which demonstrated a high potential for adverse effects on benthic and planktonic organisms. A larger number of sediment samples from the Răut and Bîc Rivers exceeded the PEL for both p,p'-DDE and

p,p'-DDT compounds, and for p,p'-DDD, especially, in the area of Călărași, Strășeni, Orhei, Balti and Chișinău. PCB compounds were within ISQG limits and have not exceeded PEL.

The Norwegian Environmental Quality Guideline (2018), which can also be used to estimate the toxicity of sediments, also provides 5 quality classes. According to the guide, the content of $\sum_4$DDT and $\sum_4$HCH in the Dniester River at Soroca, Camenca, Erjova, Goieni, Cocieri sites were within the limits of class III quality and correspond to sediments with chronic long-term effects, and for $\sum_4$HCH content upstream of the Dubăsari dam - within the limits of class IV, with extensive toxic effects on aquatic organisms (Ivanova et al., 2021).

4.5 Accumulation of the organochlorine pesticides in fish from the Dniester River

The processes of uptake and bioaccumulation of pesticides in fish depend not only on their content in sediment and water, but also on the composition of food, metabolic processes in fish, in particular, the intensity of generative processes (reproduction) and those of growth (Ecotoxicological methodological guide for environmental monitoring, 2021). Pesticides accumulation, especially in tissues with high fat deposits, and bioaccumulation also depends on the ecological status of ecosystems, and the direct properties of pesticides (Nollet, Rathore, 2019).

In the 1980s, the level of DDT and the isomers of this pesticide in the muscles of cyprinids and perches in the aquatic ecosystems of Moldova reached up to 500 ng/g of w.w, in the liver - up to 1200 ng/g and in the gonads - up to 700 ng/g of w.w, HCH isomers being in quantities almost 10-20 times lower (from the archive of the Laboratory of Hydrobiology and Ecotoxicology). It is not possible compare the present data with the materials of the past, when there was an extremely intense chemicalization process, and the laboratory methods and techniques were different from the contemporary ones, although, in general, these results give an image of pesticides accumulation levels in various tissues and organs of fish. It should be noted, that the tissues and all organs of freshwater fish contain lipids (fats) which during the process of sample treatment and extraction end up in the extract together with the investigated pesticides. In this case, the cleaning procedure of the extract from the lipids is necessary. Much work has been done on this process to reduce the impact of "cleaning" on pesticide content.

HCH (α-, and β-HCH), DDT and its transformation products DDE and DDD were present in the analysed fish samples of *Abramis brama* and *Perca fluviatilis*. The predominant isomer was β-HCH which, together with α-HCH, was detected in 70% of the samples analysed. Concentrations of ∑HCH in the muscles of the body, liver and gonads in *A. brama* were higher compared to the concentrations detected in *P. fluviatilis*. The content of ∑HCH in the muscles of the body *A. brama* was 0.87-3.2 ng/g

w.w., the maximum concentration being observed in individuals aged 6 years. ∑HCH concentrations in *A. brama* liver ranged from 3.4 to 6.6 ng/g w.w.; in the gonads - 2.8 and 5.1 ng/g w.w. In the body muscles of *P. fluviatilis* ∑HCH were in the range of 0.21 to 0.34 ng/g w.w., in the liver - 0.45-1.1 ng/g w.w. and in the gonads – 0.41-0.99 ng/g w.w.

DDT compounds were detected in 94% of the analysed samples. The content of metabolites decreases in the following order: p,p'-DDE> p,p'-DDD> o,p'-DDD> p,p'-DDT> o,p'-DDE> o,p'-DDT. In the muscles of the body *A. brama* the value of DDT was 15-27 ng/g, in the muscles of *P. fluviatilis* - 1.2-5.4 ng/g w.w. In the *A. brama* and *P. fluviatilis* liver the content was higher 21-41 ng/g, and 19-36 ng/g, respectively, in the gonads – 3.4-7.4 ng/g, and, respectively, 3.1-6.8 ng/g wet weight (Ivanova, 2020). The obtained results are similar to the concentrations found by Sapozhnikova, Zubcov (et al., 2005b) for fish from the Lower Dniester, for the Danube Delta and the Black Sea (Stancheva, Georgieva, Makedonski, 2013) and much lower than those reported by other authors (Сытник, Колесник, Берсан, 2012).

CONCLUSIONS

1. The assessment of persistent organic pollutants including pesticides (α-HCH, β-HCH, γ-HCH and δ-HCH, p, p'- DDT, o, p'-DDT and their transformation products p, p'-DDD, o, p'-DDD, p, p'-DDE and o, p'-DDE, endosulfan, endrin, HCB), 16 hydrocarbons polycyclic aromatics (PAHs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in water and sediment samples in the Dniester River, Dubăsari reservoir, tributaries Răut and Bâc rivers, and Prut River has been carried out by applying the adjusted methods and advanced analytical techniques.
2. The isomers of γ-HCH, p,p'-DDT, p,p'-DDD, p,p'-DDE were detected in almost all water samples, with maximum concentrations found in the Dniester River at Naslavcea site and in the waters of the Prut River at Leușeni and Giurgiulești sites.
3. The total concentrations of the 8 polycyclic aromatic hydrocarbons from the 16 priorities tested (PAHs: naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene and pyrene) were detected in the water samples of both water bodies and indicate the existence of permanent pollution of aquatic ecosystems with petroleum products.

4. The sediments of both ecosystems are accumulators of the investigated xenobiotics. A positive correlation was established between the content of residues $\sum_4$HCH, Σ_6DDT and the content of total organic carbon (TOC) in the investigated sediments; a strong correlation (r = 0.81) between HCB and TOC. The highest concentrations of pesticides are established in the sediments with the dominance of the particle size fractions <0.005 mm upstream of the Dubăsari dam and downstream of the cities, crossed by rivers.
5. The dynamics and migration of $\sum_4$HCH and Σ_6DDT is similar, and a very strong correlation between the total concentration of these pesticide residues in the sediments (r = 0.91 - for the Dniester River and r = 0.89 - for the Prut River) was established.
6. The dynamics of organochlorine pesticides in water and sediments along the Dniester River is similar to that of 1977-1987, but today concentrations are ten times lower. However, the quality of the investigated water samples was attributed to quality classes IV-V and of the sediment samples – to classes III-IV, according to the national regulations and temporary standards on bottom sediments.
7. For the first time, polychlorinated biphenyls ($\sum_{20}$BPC) and polybrominated diphenyl ethers ($\sum_{34}$DEPB) in the sediments of aquatic ecosystems were studied and the predominance of heavier compounds (penta- and hexa-chlorinated) and slightly brominated compounds was established, as an evidence of input of wastewater or surface runoff containing PCBs and DEPBs into aquatic ecosystems.
8. A positive correlation (r = 0.81) was established between the total $\sum_{16}$PCB content and TOC in the sediments in the Dniester River, as well as between the content of individual PCBs and TOC (r = 0.45-0.63). Also, a positive correlation was established between the individual PCB compounds (r = 0.60-0.98).
9. The tested methodology of biological sampling and processing was used for the organochlorine pesticides DDT and HCH accumulation level determination in the muscles of the body, liver and gonads of fish species *Abramis brama* and *Perca fluviatilis*, taking into account the biological properties of the fish and the content of pesticides in the aquatic environment.

RECOMMENDATIONS

1. The processes of bioaccumulation, biotransformation and bioredistribution of xenobiotics in the body of organisms and in the food web are very difficult and depend on age, sex, stage of development, intensity of metabolism of organisms, living environment and last but not least

the properties and composition of xenobiotics, their total effect, the processes of additism, synergism and antagonism, thus it is recommended to perform ecotoxicological research of xenobiotics depending on external factors and biological parameters.

2. Thus, the works initiated through the doctoral program will have a long in-depth continuity. Gaining new knowledge in monitoring, deciphering the processes of migration and biotransformation of xenobiotics in the aquatic environment, determining the level of tolerance and ways to minimize the adverse effects of these chemicals are the main approaches for estimating, preventing risks and sustainable use of aquatic resources.

BIBLIOGRAPHY

1. Canadian environmental quality guidelines. 1999. Canadian sediment quality guidelines for the protection of aquatic life: DDT, DDE, and DDD. Canadian Council of Ministers of the Environment, Winnipeg. Disponibil: https://ccme.ca/en/res/ddt-dde-and-ddd-canadian-sediment-quality-guidelines-for-the-protection-of-aquatic-life-en.pdf
2. COVACI, A., GHEORGHE, A., HULEA, O., SCHEPENS, P. 2006. Levels and distribution of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in sediments and biota from the Danube Delta, Romania. In: *Environmental Pollution*, vol. 140, nr. 1, pp. 136–149. ISNN 02697491.
3. CUMANOVA, A., GILCA, G., ORLOVA, N. 2008. The Fate of Persistent Organic Pollutants (POPs) in the Environment. In: The Fate of Persistent Organic Pollutants in the Environment NATO Science for Peace and Security Series. Springer, Dordrecht. pp. 161–171. e-ISBN 978-1-4020-6642-9.
4. DRAGAN, D., CUCU-MAN, S., DIRTU, A. C., MOCANU, R., VAECK, L. VAN, COVACI, A. 2006. Occurrence of organochlorine pesticides and polychlorinated biphenyls in soils and sediments from Eastern Romania. In: *International Journal of Environmental Analytical Chemistry*, vol. 86, nr. 11, pp. 833–842. ISNN 10290397.
5. Ghid de prelevare a problelor hidrochimice şi hidrobiologice = Hydrochimical and hydrobiological sampling guidance. 2015, ed.: Toderaş Ion, Zubcov Elena, Bileţchi Lucia, Chişinău, 64 p., JURMINSKAIA, O., BAGRIN, N., ZUBCOV, N., BORODIN N., **IVANOVA, A**. 2015. Prelevarea suspensiilor şi sedimentelor, pp. 40-42. ISBN 978-9975-128-28-5. Disponibil: https://www.eco-tiras.org/docs/berg/book%20eng%20ro.pdf
6. Ghid metodologic ecotoxicologic de monitorizare a mediului: problematică, tehnici de laborator și investigarea riscului asupra sănătății. 2021. BSB27-MONITOX, Programul Operațional Comun Bazinul Mării Negre, Institute of Zoology, Center of Research of Hidrobiocenoses and Ecotoxicology; editori: Elena Zubcov, Antoaneta Ene. Chișinău, 112 p.,
7. ISBN 978-9975-157-79-7. Disponibil: https://zoology.md/sites/default/files/2021-10/Ghid%20metodologic%20ecotoxicologic%202021.pdf.
8. Ghidul Norvegian de calitate a mediului. 2018. Direcția Grupa Directiva Apei 02:2018. 222 p.
9. Klassifiseringsveileder 02:2018 Klassifisering av miljøtilstand i vann. Økologisk og kjemisk klassifiseringssystem for kystvann, grunnvann, innsjøer og elver. Disponibil: https://www.vannportalen.no/veiledere/klassifiseringsveileder/
10. Hotărârea Guvernului Nr. 890 din 12.11.2013 pentru aprobarea Regulamentului cu privire la cerinţele de calitate a mediului pentru apele de suprafaţă. 2013. În: *Monitorul Oficial Nr*. 262-267 art. Nr:1006, 12 p.

11. **IVANOVA, A**. 2018. Long-term residue of DDT compounds in surface sediments from the Dniester River. În: *Tendințe contemporane ale dezvoltării științei: viziuni ale tinerilor cercetători*. Ediția 7, Vol.1, 15 iunie 2018, Chișinău. Chișinău, Republica Moldova: Tipogr. „Biotehdesign", 2018, pp. 154-159. ISBN 978-9975-108-45-4.
12. **IVANOVA, A**. 2020. Conținutul unor pesticide organoclorurate în Abramis brama L. (Cyprinidae) din fluviul Nistru. În: Buletinul AȘM. Științele vieții. Nr. 3(342), pp. 136-142. ISSN 1857-064X
13. **IVANOVA, A**., WIBERG, K., AHRENS, L., ZUBCOV, E., DAHLBERG, A-K. 2021. Spatial distribution of legacy pesticides in river sediment from the Republic of Moldova. In: *Chemosphere*, vol. 279, 130923. ISSN 0045-6535. Disponibil: https://www.sciencedirect.com/science/article/pii/S0045653521013941
14. JENSEN, S., LINDQVIST, D., ASPLUND, L. 2009. Lipid extraction and determination of halogenated phenols and alkylphenols as their pentafluorobenzoyl derivatives in marine organisms. In: *Journal of Agricultural and Food Chemistry*, vol. 57, nr. 13, pp. 5872–5877. ISNN 00218561.
15. LIBER, Y., MOURIER, B., MARCHAND, P., BICHON, E., PERRODIN, Y., BEDELL, J. P. 2019. Past and recent state of sediment contamination by persistent organic pollutants (POPs) in the Rhône River: Overview of ecotoxicological implications. In: *Science of the Total Environment,* vol. 646, pp. 1037–1046. ISNN 18791026.
16. LIN, C., CHANG, T. C. 2007. Photosensitized reduction of DDT using visible light: the intermediates and pathways of dechlorination. In: *Chemosphere*, vol. 66, nr. 6, pp. 1003-1011. ISNN 00456535.
17. MANSOURI, A., CREGUT, M., ABBES, C., DURAND, M. J., LANDOULSI, A., THOUAND, G. 2017. The environmental issues of DDT pollution and bioremediation: a multidisciplinary review. In: *Applied biochemistry and biotechnology*, vol. 181, nr. 1, pp. 309-339. ISNN 2732289.
18. NEAMTU, M., CIUMASU, I. M., COSTICA, N., COSTICA, M., BOBU, M., NICOARA, M. N., CATRINESCU, C., VAN SLOOTEN, K. B., DE ALENCASTRO, L. F. 2009. Chemical, biological, and ecotoxicological assessment of pesticides and persistent organic pollutants in the Bahlui River, Romania. In: *Environmental Science and Pollution Research International,* vol. 16, nr. 1, ISNN 16147499.
19. NOLLET, L., RATHORE, H. S. 2019. Pesticides Evaluation of Environmental Pollution. Copyright Year 2012, Published December 10, 2019 by CRC Press 659 p. ISBN 9780367865191.
20. POZO, K., URRUTIA, R., MARIOTTINI, M., RUDOLPH, A., BANGUERA, J., POZO, K., PARRA, O., FOCARDI, S. 2014. Levels of Persistent Organic Pollutants (POPs) in sediments from Lenga estuary, central Chile. In: *Marine Pollution Bulletin*, vol. 79, nr. 1–2, pp. 338–341. ISNN 0025326X.
21. *Priority Pollutant List.* 2014. United States Environmental Protection Agency. [citat: martie 2019]. Disponibil: https://www.epa.gov/sites/default/files/2015-09/documents/priority-pollutant-list-epa.pdf
22. SAPOZHNIKOVA, Y., ZUBCOV, N., HUNGERFORD, S., ROY, L. A., BOICENCO, N., ZUBCOV, E., SCHLENK, D. 2005b. Evaluation of pesticides and metals in fish of the Dniester River, Moldova. In: *Chemosphere*, vol. 60, nr. 2, pp. 196–205. ISNN 00456535.
23. SAZAKLI, E., SIAVALAS, G., FIDAKI, A., CHRISTANIS, K., KARAPANAGIOTI, H. K., LEOTSINIDIS, M. 2016. Concentrations of persistent organic pollutants and organic matter characteristics as river sediment quality indices. In: *Toxicological and Environmental Chemistry*, vol. 98, nr. 7, pp. 787–799. ISNN 10290486.
24. SOLIMAN, Y. S., ALANSARI, E. M. A., SERICANO, J. L., WADE, T. L. 2019. Spatio-temporal distribution and sources identifications of polycyclic aromatic hydrocarbons and their alkyl homolog in surface sediments in the central Arabian Gulf. In: *Science of the Total Environment*, vol. 658, pp. 787–797. ISNN 18791026.
25. STANCHEVA, M., GEORGIEVA, S., MAKEDONSKI, L. 2013. Persistent organic pollutants - PCBs and DDTs in fish from Danube River and from Black Sea, Bulgaria. In: *CBU International Conference Proceedings*, vol. 1, pp. 354–361. ISNN 1805-997X.
26. TCACIUC, A. P., BORRELLI, R., ZANINETTA, L. M., GSCHWEND, P. M. 2018. Passive sampling of DDT, DDE and DDD in sediments: accounting for degradation processes with reaction–diffusion modeling. In: *Environmental Science: Processes & Impacts*, vol. 20, nr. 1, pp. 220-231. eISNN 2050-7895.
27. Tehnici analitice de înaltă performanță pentru monitorizarea substanțelor toxice din mediu. Ghid metodologic = High-performance analytical techniques for the monitoring of toxicants in environment.

Methodological guide. 2021. Ed. Ene Antoaneta. Casa Cărții de Știință, Cluj-Napoca, 178 p., CIORNEA, V., **IVANOVA, A.,** ZUBCOV, E., ENE, A. 2021. Cromatografia gazoasă cu detector de masă (GC-MS) pentru analize de mediu. pp. 142-155. ISBN 978-606-17-1848-1.
28. VAN AEL, E., COVACI, A., BLUST, R., BERVOETS, L. 2012. Persistent organic pollutants in the Scheldt estuary: Environmental distribution and bioaccumulation. In: Environment International, vol. 48, pp. 17–27. ISNN 18736750.
29. VOSNIAKOS, F., PASCU, L. F., PETRE, J., CRUCERU, L., VASILE, G., IANCU, V., DINU, C. 2012. The temporal and spatial monitoring of water and sediment physical-chemical quality from Saint George Branch in the period February 2009-February 2011. In: *Fresenius Environmental Bulletin*, vol. 21, nr. 2, pp. 233-245. ISSN: 10184619.
30. YUNKER, M. B., MACDONALD, R. W., VINGARZAN, R., MITCHELL, R. H., GOYETTE, D., SYLVESTRE, S. 2002. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. In: *Organic Geochemistry*, vol. 33, nr. 4, pp. 489–515. ISNN 01466380.
31. Региональный норматив. Нормы и критерии оценки загрязненности в водных объектах Санкт-Петербурга, 1996. 19 с.
32. СЫТНИК, Ю. М., КОЛЕСНИК, Н. Л., БЕРСАН, Т. А. 2012. Хлорорганические пестициды в органах и тканях рыб устьевого участка Днестра и Днестровского Лимана (обзор). В: *Рибогосподарська наука України*, №. 3, с. 8–13. ISSN 2312-9581.

LIST OF PUBLICATIONS ON THE THESIS TOPIC

1. Articles in scientific journals:

1.2 in journals from databases accepted by ANACEC (with indication of the database):

1. **IVANOVA, A.,** WIBERG, K., AHRENS, L., ZUBCOV, E., DAHLBERG, A-K. Spatial distribution of legacy pesticides in river sediment from the Republic of Moldova. In: *Chemosphere*, 279 (2021) 130923. ISSN: 0045-6535. SCIENCE DIRECT

2. **IVANOVA, A**. Organochlorinated compounds in the Prut river sediments. In: *Analele Universității ”Dunărea de Jos” din Galați. Fascicula II, Matematică, fizică, mecanică teoretică / Annals of the ”Dunarea de Jos” University of Galati. Fascicle II, Mathematics, Physics, Theoretical Mechanics,* 41(1), 2018, pp. 40-47. ISSN: 2067-2071. doi: https://doi.org/10.35219/ann-ugal-math-phys-mec.2018.1.06. EBSCO

3. CIORNEA, V., **IVANOVA, A.,** ZUBCOV, E. AND ENE, A. Determination of some organochlorine pesticides in the waters of the Prut River. In: *Annals of the University Dunarea de Jos of Galati: Fascicle II, Mathematics, Physics, Theoretical Mechanics, 39(1),* 2016, pp.81-85. ISSN: 2067-2071.EBSCO

1.3 in journals from the National Register of specialized journals:

1. **IVANOVA, A**. Conținutul unor pesticide organoclorurate în *Abramis brama* L. (Cyprinidae) din fluviul Nistru. În: *Buletinul AŞM. Ştiinţele vieţii*. Nr. 3(342), 2020, pp. 136-142. ISSN 1857-064X

2. Articles in the proceedings of conferences and other scientific events:

2.1 in the papers of scientific events included in the Register of materials published on the basis of organized scientific events in the Republic of Moldova:

1. **IVANOVA, A**. Long-term residue of DDT compounds in surface sediments from the Dniester River. In: *Tendințe contemporane ale dezvoltării științei: viziuni ale tinerilor cercetători*. Ediția 7, Vol.1, 15 iunie 2018, Chișinău. Chișinău, Republica Moldova: Tipogr. „Biotehdesign”, 2018, pp. 154-159. ISBN 978-9975-108-45-4.

2. JURMINSCAIA, O., ZUBCOV, E., ANDREEV, N., **IVANOVA, A**. Evaluarea stării ecologice a fluviului Nistru conform unor parametri fizico-chimici. In*: Functional Ecology of Animals70th anniversary from the birth of academician I.Toderas.* 21 septembrie 2018, Chișinău. Chișinău, Republica Moldova: Institutul de Zoologie, pp. 433-443. ISBN 978-9975-3159-7-5.

3. UKRAINSKIY, V., KOVALYSHYNA, S., DENGA, Y., **IVANOVA, A.,** ANDREEV, N., ZUBCOV, E., ENE, A. Concentration of organochlorine pesticides in water and bottom sediments of the Dniester River

ecosystem. In: *Sustainable use and protection of animal world in the context of climate change dedicated to the 75th anniversary from the creation of the first research subdivisions and 60th from the foundation of the Institute of Zoology*. Ediția 10, 16-17 septembrie 2021, Chișinău, 2021, pp. 109-112. ISBN 978-9975-157-82-7.

3. Other works and achievements specific to different scientific fields:

3.1 conference abstracts:

1. UKRAINSKIY, V., DENGA, Y., KOVALYSHYNA, S., **IVANOVA, A**., ZUBCOV, E., ENE, A. Organochlorine pesticides in water and bottom sediments of the Dniester River ecosystem. In: *Environmental Toxicants in Freshwater and Marine Ecosystems in the Black Sea Basin BSB27-MONITOX*. 8-11 septembrie 2020, Kavala, Greece: International Hellenic University, 2020, pp. 26-28.
2. **IVANOVA, A**. HCH and DDT residues in sediments from rivers in Moldova, *Abstract Book, International Conference "Environmental Toxicants in Freshwater and Marine Ecosystems in the Black Sea Basin BSB27-MONITOX "*, September 8-11, 2020, Kavala, Greece, Organotiki OE, p.38, ISBN 978-618-85036-0-1.
3. **IVANOVA, A.,** AHRENS, L., WIBERG, K., DAHLBERG, A-K. Persistent Organic Pollutants in sediments from rivers in Moldova. In: *SETAC Europe 29th Annual Meeting. Abstract Book*, 26-30 May 2019, Helsinki, Finland, pp.341-342. e-ISNN 2310-3043
4. **IVANOVA, A.,** CIORNEA V., ZUBCOV, E. Organochlorinated Compounds in the Prut River Sediments. In: *Book of abstracts. Scientific Conference of Doctoral Schools*. SCDS-UDJG. The Sixth Edition, Galaţi, 7th-8th of June 2018, p.164.
5. CIORNEA, V., **IVANOVA,** A., ZUBCOV, E. AND ENE, A. Determination of some organochlorine pesticides in the waters of the Prut River. In: *Book of abstracts. Scientific conference of doctoral schools from UDJ GALAȚI. CSSD-UDJG 2016, Fourth Edition*. Romania, Galați, 2nd-3th of June 2016, pp.106-107
6. **IVANOVA, A**. POPs and their migration into the environment. In: *Life sciences in the dialogue of generations: "Connections between universities, academia and business community". The International Conference dedicated to the 70th anniversary of foundation of first research institutes of the ASM and the 55th anniversary of the inauguration of the Academy of Sciences of Moldova*, Chisinau, March 25, 2016, p. 172. ISBN 978-9975-933-78-0.

3.2 methodological guidelines:

1. CIORNEA, V., **IVANOVA, A**., ZUBCOV, E., ENE, A. Cromatografia gazoasă cu detector de masă (GC-MS) pentru analize de mediu. În: *Tehnici analitice de înaltă performanță pentru monitorizarea substanțelor toxice din mediu. Ghid metodologic*. Ed. Ene A. Casa Cărții de Știință, Cluj-Napoca, 2021, pp. 142-155. ISBN 978-606-17-1848-1.
2. ZUBCOV, E., BAGRIN, N., ZUBCOV, N., BORODIN, N., CIORNEA, V., JURMINSKAIA, O., **IVANOV, A.** Componenţa chimică a apelor naturale. În: *Monitoringul calităţii apei şi evaluarea stării ecologice a ecosistemelor acvatice*. Chişinău: Elan-Poligraf., 2015, pp. 16-34. ISBN 978-9975-66-503-2.
3. JURMINSKAIA, O., BAGRIN, N., ZUBCOV, N., BORODIN, N., **IVANOV, A**. Sampling of suspensions and sediments. In: *Hydrochemical and hydrobiological sampling guidance. // Prelevarea suspensiilor şi sedimentelor*. În: *Ghid de prelevare a probelor hidrochimice şi hidrobiologice.* Chişinău: Elan-Poligraf., 2015, pp. 40-42. ISBN 978-9975-66-480-6

ADNOTARE

Ivanova Anastasia „Poluanții organici persistenți în ecosistemele acvatice ale Republicii Moldova". Teză de doctor în științe biologie, Chișinău, 2022.

Structura tezei. Teza include adnotare, introducere, patru capitole, concluzii generale și recomandări, referințe bibliografice care includ 290 surse. Materialul ilustrativ cuprinde 59 figuri, 10 tabele și 8 anexe, volumul total al lucrării constituie 148 pagini. Rezultatele obținute sunt publicate în 13 lucrări științifice.

Cuvinte-cheie: poluanți organici persistenți, ecosistem acvatic, Nistru, Prut

Domeniu de studiu: 166.01. Ecologie

Scopul tezei constă în investigarea poluanților organici persistenți și proceselor de acumulare a lor în unele componente ale ecosistemelor acvatice ale fluviului Nistru și râului Prut prin implementarea metodelor, tehnicilor moderne de laborator și echipamentului analitic performant.

Obiectivele de cercetare: Studiul, testarea și implementarea metodelor analitice moderne pentru determinarea poluanților organici persistenți în componentele ecosistemelor acvatice, conform standardelor și metodelor internaționale; determinarea dinamicii conținutului pesticidelor organoclorurate și altor POP în apele ecosistemelor acvatice transfrontaliere în limitele Republicii Moldova; stabilirea nivelului de acumulare în depunerile subacvatice a reziduurilor de pesticide organoclorurate, bifenili policlorurați și difenileteri polibromurați, estimarea calității ecologice a depunerilor acvatice după conținutul POP; precizarea aspectelor metodologice privind determinarea pesticidelor în țesuturile de pești și analiza lor în mușchii corpului, ficat și gonade la 2 specii cu diferit tip de nutriție (bentofagi și răpitori).

Noutatea și originalitatea științifică constă în stabilirea dinamicii conținutului reziduurilor de $\sum_4$HCH, $\sum_6$DDT, $\sum$HAP în apele, depunerile subacvatice și țesuturile de pești din ecosistemele acvatice transfrontaliere, descifrarea migrației acestor substanțe în timp și spațiu fiind temeiul pentru dezvoltarea teoriei funcționării ecosistemelor acvatice. În premieră, au fost stabilite unele legități de acumulare a $\sum_{20}$BPC și $\sum_{34}$DEPB în depunerile subacvatice și evaluată starea ecologică a acestora după conținutul POP. Prin ajustarea, implementarea tehnicilor și instrumentului analitic performant a fost determinat nivelul POP în țesuturile a 2 specii de pești.

Problema științifică soluționată constă în fundamentarea științifică a monitoringului complex al migrației POP în ecosistemele acvatice transfrontaliere ale Republicii Moldova, prin implementarea tehnicilor și echipamentului analitic de performanță care permit evidențierea reziduurilor acestor poluanți în mediul acvatic, ceea ce va contribui la dezvoltarea aspectelor teoretice ale funcționării ecosistemelor acvatice.

Semnificația teoretică. Metodele testate, tehnicile analitice performante implementat în cercetare, aprobate în Republica Moldova și Suedia, au permis obținerea rezultatelor veridice și stabilirea unor legități privind acumularea și migrația POP, a reziduurilor formate în procesul transformării acestora în depunerile subacvatice și materialul biologic.

Valoarea aplicativă. Rezultatele testării tehnicilor de analiză a POP în componentele ecosistemelor acvatice contribuie la dezvoltarea bazei metodologice a studiilor ecotoxicologice. Rezultatele privind conținutul POP sunt valoroase pentru estimarea calității apelor de suprafață și a stării ecologice a depunerilor subacvatice.

Implementarea rezultatelor științifice. Rezultatele cercetărilor privind starea ecosistemelor acvatice prezintă interes pentru Ministerul Mediului și agențiile subordonate. Ele sunt implementate la Universitatea "Dunărea de Jos" din Galați. Rezultatele au devenit parte componentă a 2 proiecte internaționale (BSB27 MONITOX, BSB165 HydroEcoNex) și a 1 proiect național în cadrul Programului de Stat 2020-2023 (20.80009.7007.06 AQUABIO).

АННОТАЦИЯ

Иванова Анастасия „Стойкие органические загрязнители в водных экосистемах Республики Молдова”. Диссертация на соискание ученой степени доктора биологических наук, Кишинэу, 2022

Структура работы: введение, 4 главы, общие выводы и рекомендации, библиографию, включающую 290 источников, 59 рисунков, 10 таблиц, 8 приложений, 148 страниц. Результаты исследований опубликованы в 13 научных работах.

Ключевые слова: стойкие органические загрязнители, экосистема, Днестр, Прут.

Область исследования: 166.01. Экология

Цель работы: состоит в исследовании стойких органических загрязнителей (СОЗ) и процессов их накопления в отдельных компонентах водных экосистем рек Днестр и Прут с применением современных методов, и современного аналитического оборудования.

Задачи: тестирование и внедрение современных аналитических методов определения СОЗ в водных экосистемах соответствие с международными стандартами и методиками; определение динамики содержания хлорорганических пестицидов и других СОЗ в трансграничных водных экосистемах Молдовы; исследование накопления СОЗ в донных отложениях и экологическая оценка их состояния по содержанию СОЗ; уточнение методических аспектов и определение пестицидов в тканях рыб.

Научная новизна и оригинальность работы заключается определении динамики концентрации $\sum_4$ГХЦГ, $\sum_6$ДДТ, ПАУ в воде, донных отложениях и тканях рыб Днестра, его притоков Реут и Бык, реки, Прута. Оценка миграции СОЗ во времени и пространстве является важным звеном развития теории функционирования водных экосистем в современных условиях. Впервые определены и установлены отдельные закономерности накопления в донных отложениях $\sum_{20}$ПХБ и $\sum_{34}$ПБДЭ и дана их экологическая оценка по содержанию СОЗ. Путем тестирования, уточнения и внедрения современных методик и оборудования получены материалы о динамике содержания, миграции и накоплении стойких хлорорганических пестицидов в мышцах тела, печени и гонадах 2-х видов рыб. Полученные результаты имеют теоретическое значение для проведения комплексного мониторинга и расширения знаний функционирования водных экосистем.

Научное направление, которому служат результаты диссертации, состоит в научном обосновании проведения комплексного мониторинга миграции СОЗ путем внедрения современных методов и оборудования, дающие новые знания о состоянии экосистем, необходимых для развития теории водных экосистем и снижения риска воздействия СОЗ.

Теоретическая значимость диссертации состоит в получении новых знаний по исследованию СОЗ в компонентах водных экосистем путем внедрения современных методов (методики и оборудование, тестированные в Швеции и Молдове), установленных закономерностях накопления и миграции СОЗ.

Прикладная ценность работы. Результаты тестирования и апробации методик анализа СОЗ в компонентах водных экосистем способствуют развитию методологической базы экотоксикологических исследований. Результаты исследований содержания СОЗ важны при оценке качества поверхностных вод и экологического состояния донных отложений.

Внедрение научных достижений. Результаты исследований состояния водных экосистем представляют интерес для Министерства Окружающей Среды и подведомственных ведомств. Они внедрены в учебный процесс в университете «Dunărea de Jos» в Галац. Результаты являются частью 2 международных проекта (BSB27 MONITOX, BSB165 HydroEcoNex) и 1 национального проекта в рамках Государственной программы 2020-2023 (20.80009.7007.06 AQUABIO).

ANNOTATION

Ivanova Anastasia „Persistent organic pollutants in the aquatic ecosystems of the Republic of Moldova", PhD thesis in biological sciences, Chisinau, 2022

Structure of the thesis. The thesis consists of introduction, four chapters, conclusions and recommendations, bibliography (290 titles), 59 Figures, 10 tables, 8 annexes, 148 pages. The obtained results were published in 13 scientific papers.

Keywords: persistent organic pollutants, aquatic ecosystem, Dniester River, Prut River.

Field of investigation: 166.01. Ecology.

The purpose of the research consists in investigation of persistent organic pollutants and their accumulation processes in some components of the aquatic ecosystems of the Dniester River and the Prut River by implementing modern methods, laboratory techniques and high-performance analytical equipment.

Objectives of the thesis: study, testing and implementation of modern analytical methods for the POP determination in the components of aquatic ecosystems according to international standards and methods; determining the dynamics of the content of organochlorine pesticides and other POPs in the waters of transboundary aquatic ecosystems within the limits of the Republic of Moldova; establishing the level of POPs accumulation in the sediments and estimating the ecological quality of the sediments according to the POP content; specifying the methodological aspects regarding the determination of pesticides in fish tissues.

Scientific novelty and originality consists of establishing the dynamics of the residue content of $\sum_4$HCH, $\sum_6$DDT, $\sum$HAP in water, sediments and fish tissues in transboundary aquatic ecosystems; determination of the migration of these substances in time and space being the basis for the development of the theory of the functioning of aquatic ecosystems in the current conditions. For the first time, some legitimacies of accumulation in the sediments of the industrial compounds $\sum_{20}$BPC and $\sum_{34}$PBDEs were determined and established; the ecological status of the sediments was evaluated according to several ecological guidelines on POPs content. By adjustment, specifying and implementing high-performance techniques and equipment, results were obtained on the level of accumulation of persistent organochlorine pesticides in the muscles of the body, liver and gonads in 2 species of fish. The investigations and the results obtained expand the knowledge regarding the complex monitoring of the functioning of the aquatic ecosystems.

The solved scientific problem consists of the scientific argumentation of the migration of POPs in the aquatic ecosystems of the Republic of Moldova, which led to highlighting of the importance of POPs investigations on the pollution of aquatic components.

The theoretical significance. The tested methods, and high-performance equipment implemented in research, approved in Sweden and Moldova allowed to obtain results on accumulation and migration of POPs, including forms of transformation, are theoretical points in the development of ecological science of the functioning of aquatic ecosystems and their complex monitoring.

The applicative value of the work. The results of testing POP analysis techniques in the components of aquatic ecosystems contribute to the development of the methodological basis of ecotoxicological studies. The results on the POP content are valuable for estimating surface water quality and the ecological status of sediments.

Implementation of scientific results. The results of research on the state of aquatic ecosystems are of interest to the Ministry of Environment and subordinate agencies. They are implemented at the "Dunărea de Jos" University of Galați. The results became part of 2 international projects (BSB27 MONITOX, BSB165 HydroEcoNex) and 1 national project on the State Program 2020-2023 (20.80009.7007.06 AQUABIO).

IVANOVA ANASTASIA

PERSISTENT ORGANIC POLLUTANTS IN AQUATIC ECOSYSTEMS OF THE REPUBLIC OF MOLDOVA

166.01. Ecology

Summary of the doctoral thesis in biological sciences

Approved for printing: 4.03.2022	Paper size: 60×84 1/16
Offset paper. Digital printing.	Copies ex. 25
Printing sheets: 1.0	Order no.

Typography "REAL PRINT" SRL

29/2 Nicolae Dimo str., Chișinău, MD-2004, Republic of Moldova