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ORGANOCHLORINE PESTICIDES IN FISH OF THE KILIYA DELTA OF THE DANUBE (2003–2005)

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Purpose. Identification and analysis of the content of organochlorine pesticides (OCP) in organs and tissues of benthivorous and predatory fish species of the Kiliya delta of the Danube (Eastern mouth) and their comparison with previous years.

Methodology. The analysis of the samples of aquatic organisms for the content of residual organochlorine pesticides was carried out by gas-liquid chromatography (GLH) based on a unified methodology. The chromatographic analysis was carried out on the gas chromatograph "Color 5" with electron capture detector at the Institute of Hydrobiology of the National Academy of Sciences of Ukraine.

Findings. The effect of stable organochlorine pesticides on aquatic organisms is characterized by marked persistence in the environment and by high ability for migration and accumulation on different levels of food chains in aquatic ecosystems.

The continuous presence of OCP in all investigated organs and tissues of selected species with the presence of a certain amount of fat and consequently, the fixation of residual organochlorine pesticides. Among benthivorous fishes, the content of OCP in organs and tissues (total) is as follows: vimba → roach → wild carp → bream → gibel carp. Among the predators: asp → perch → European catfish → pikeperch.

Originality. Recently, a significant number of scientists all around the world returns to the problem of the accumulation and distribution (redistribution) of OCP in the components of aquatic ecosystems. This is associated with certain threats to the environment and human health, that could lead to negative consequences as a result of the consumption of fish as the highest trophic level in fresh waters of Ukraine.

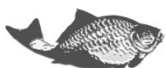
Practical value. The obtained data indicate that the major commercial fish species of the Kiliya delta of the Danube river contains residual quantities of pesticides. This indicates to the need for continuous hygienic and toxicological monitoring of fish caught and sold. There is a tendency that smaller amounts of OCP are accumulated in less active species benthivorous (bream, gibel carp) compared to active ones (vimba, roach, wild carp), and these patterns are confirmed to the current study.

Keywords: pollution, organochlorine pesticides (OCP), DDT and its metabolites, α - and γ -isomers of HCH.

PROBLEM STATEMENT AND ANALYSIS OF LAST ACHIEVEMENTS AND PUBLICATIONS

The Danube is the largest river in the Central and South-Eastern Europe, which belongs to the Black Sea basin. By its length and catchment area, the Danube is the second river in Europe after the Volga. Only small part of the Danube River (169 km) goes across the territory of Ukraine — from Reni to its mouth. Approaching the Black Sea, the river, upstream Romanian city Tulcha, is divided into three branches:

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Kiliyskyi, Sulynkyi, and Georgiivskyi. Water volume in the Danube delta is divided as follows: Kiliyskyi branch — 58%, Sulynskyi branch — 19%, Georgiivskyi branch — 23%. The most high water of them, Kiliyskyi branch (129 km³/year), goes along the border territory of Romania and Ukraine [1].

Lately, high number of scientists all over the world turns again to the studies the problem of organochlorine pesticide (OCP) accumulation and distribution (redistribution) in the components of aquatic ecosystems [6–8].

HIGHLIGHT OF THE EARLIER UNRESOLVED PARTS OF THE GENERAL PROBLEM. AIM OF THE STUDY

For a long enough period of time, especially in 1980–1990-ies, scientific circles and general public of Ukraine artificially supported the idea that the problems of organochlorine pollutants for the environment does not exist anymore and applied pesticides disintegrated virtually completely. First studies of the content of DDT and its metabolites in the mouth part of the Danube were carried out in May 1972 by scientists of the Department of Radiation and Chemical Biology of the Institute of the Biology of South Seas of the National Academy of Sciences of Ukraine [9]. In 1970–80-ies, DDT was the main pollutant of the Danube, while its quantity significantly decreased in 1990-ies. At the same time, there was an increase in HCH concentrations [2, 5].

The results of studies carried out at the of XX and beginning of XXI centuries showed that the part of water samples in the Danube contained the residues of organochlorine pesticide or the products of their decomposition — metabolites, at quantities significantly lower than the maximum allowable concentrations, but virtually all the time. E.g., the concentration of α -HCH in the Danube water varied from 0 to 0.000141 mg/dm³, γ -HCH — from 0 to 0.000117 mg/dm³, DDT — from 0 to 0.000672 mg/dm³, DDE – from 0 to 0.00008 mg/dm³. At the same time, no pesticide content was detected in 62-69.4% of samples [3].

OCP is a problem of the pollution of virtually all rivers both small and large. Last studies carried out in the Dnieper River basin found stable organochlorine pesticides and their metabolites in all examined samples of organs and tissues of aquatic invertebrates and fish [4].

The levels of OCP accumulation are different for different aquatic species and different types of hydroecosystems, however, they are recorded everywhere and did not disintegrated or degraded at all and are continuously redistributed along hydroecosystem components by accumulating in fish as the highest trophic component in freshwaters of Ukraine [10].

It is known [5] that the residues of pesticides in aquatic organisms can act both directly and cause remote toxic consequences (genetic, teratogenic, etc.). If threshold concentrations of pesticides are present in fish, their cumulative actions with heavy metals, other toxic and radioactive substances can have severe effects. During spawning period, as a result of the mobilization of fat depots, earlier accumulated OCPs will pass to blood that will lead to the intoxication of fish and their offspring. The presence of pesticides in fish as food products of humans can result in negative effects on health.



SanPiN 42-123-4540-87 currently acting on the territory of Ukraine regulates the sanitary norms of pesticide content in food products. According to them, the total content of hexachlorocyclohexane isomers should not exceed 0.03 mg/kg for freshwater fish, while for DDT and its metabolites — 0.3 mg/kg.

MATERIALS AND METHODS

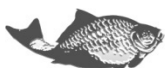
The work is based on the results of field studies, which were carried out by the Institute of Hydrobiology of Ukraine of the National Academy of Sciences and Institute of Fisheries of the National Academy of Agrarian Sciences in the Kiliya delta of the Danube. Samples were taken in summer period of 2003 and 2005, in particular in the Eastern mouth. In total, 205 samples of fish organs and tissues were taken. The analysis of fish samples for the content of residual OCPs was carried out using gas-liquid chromatography (GLC) according the unified technique. GLC is based on the recovery of OCPs from biological samples by the extraction with organic solvents and following refining of the obtained extracts depending on the content of extracting substances. In the case of the high content of the latters, refining was carried out using sulfuric acid saturated with anhydrous sodium sulfate. We used the chromatography with aluminum oxide or ACK silica gel columns, the chromatographic analysis was carried on gas chromatograph “Color-5” with electrone capture detector at the Institute of Hydrobiology. Detection sensitivity for the biosubstrate was 1×10^{-3} mg/kg of wet weight.

STUDY RESULTS AND THEIR DISCUSSION

Stable organochlorine pesticides (OCP), which pass to water bodies, ultimately accumulate in different components of aquatic ecosystems but mainly concentrate in hydrobionts, especially in fish. They become the carriers of stable toxicants and at the same time the biomonitors of the state of the water body. For assessing the ecological-toxicological situation, determining the content of stables pesticides, which migrate in aquatic environment, the degree of their effects on aquatic organisms, it is important to know the levels of their accumulation in different components of aquatic ecosystem, their distribution in the tissues and organs hydrobiont and especially fish. The accumulation of stable pesticides in the organs and tissues of hydrobionts and the tendency of their transfer across throphic chains is an additional factor, which increases the ecological risk of water pollution.

Stable pesticides were found in all samples of different fish species and other hydrobionts. Stable organochlorine pesticides in the examined samples were represented by DDT and its metabolites *o.n.1* – DDE and *n.n.1* – DDE; *o.n.1* – DDE and *n.n.1* – DDD; *o.n.1* – DDT and *n.n.1* – DDT; (α - and γ -isomers of hexachlorocyclohexane (HCH), the contents of which are represented as a total amount. The prevalence of metabolites indicates on the fact that there is a DDT degradation process, while the presence of HCH is related to the continued use of it in agriculture of some countries of the Danube basin [6, 7].

Figures 1–8 show the results of the studies carried out on the Eastern mouth of the Kiliya delta of the Danube river (one of the Starostambul mouth located east to the Black Sea) in August 2003 [6, 7].



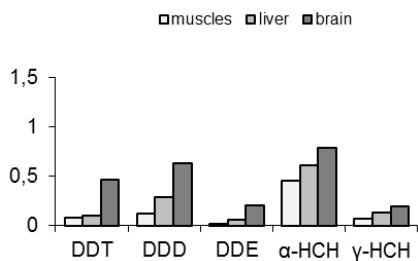


Fig. 1. OCP content in the organs and tissues of gibel carp

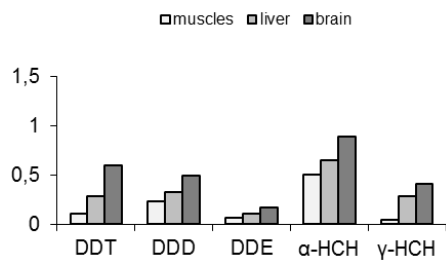


Fig. 2. OCP content in the organs and tissues of bream

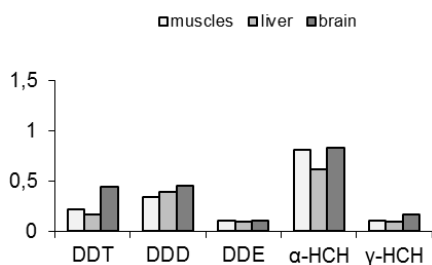


Fig. 3. OCP content in the organs and tissues of wild carp

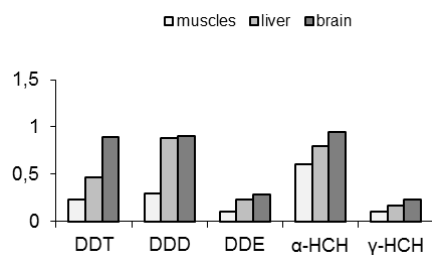


Fig. 4. OCP content in the organs and tissues of roach

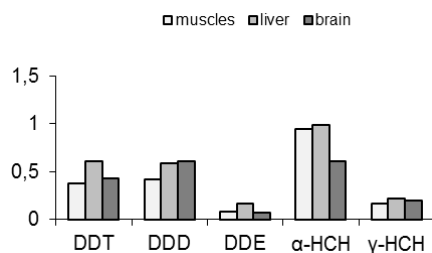


Fig. 5. OCP content in the organs and tissues of vimba

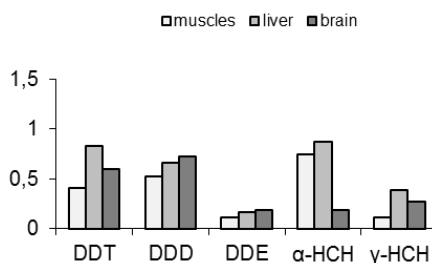


Fig. 6. OCP content in the organs and tissues of European catfish

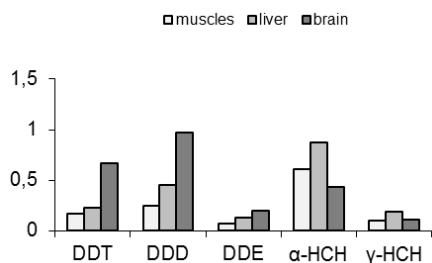


Fig. 7. OCP content in the organs and tissues of pikeperch

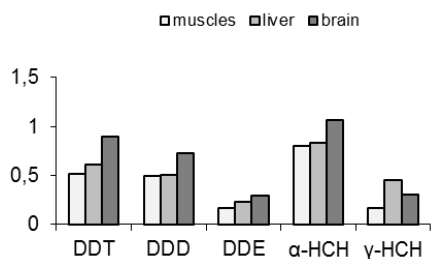


Fig. 8. OCP content in the organs and tissues of asp



By the level of accumulation of stable toxicants, the first top position is occupied by predators — pikeperch, pike, perch, asp. There is no legalized normative values of OCP content in fish from the point of view of their biological hazard for fish. Experimental works and observations during mass kill of fish in the Dnieper reservoirs [5] show that such accumulation in stress situations (e.g., in temperature extremes, spawning, etc.) can result in fish intoxication and kill, while chronic contamination — in gradual reduction in the level of metabolic processes, increases in parasite infestations and infectious diseases.

The provided data show that the main commercial fish species of the Kiliya delta of the Danube contain high enough residual quantities of organochlorine pesticides. It indicates on the necessity for continued hygienic and toxicological monitoring of fish caught and sold. The carried out studies allow providing insight into current ecological-toxicological situation of the Kiliya delta of the Danube. Currently, there is a clear picture of the pollution of the studied aquatic ecosystems with stable pesticides (OCP) resulting in the accumulation of toxicants in aquatic biota, especially in spring–summer period.

The materials of the study allow attesting continuous presence of OCP in all examined fish tissues. The typical sign of the examined tissues is the presence of certain amount of fat (muscles, liver). Vimba has especially high fat content in all tissues and as a result we observed the highest quantities of OCP in this species. As a whole, there is tendency of OCP content for all studied species: muscles > liver > brain > internal fat (with some exceptions). The same tendencies were described earlier by some authors [2, 5, 10].

Among benthivorous fish (Fig. 1–5), the following tendency for OCP content in fish tissues and organs is observed (pooled values): vimba → roach → wild carp → bream → gibel carp. Among predators (Fig. 6–8): asp → perch → European catfish → pikeperch. Perch were the youngest and smallest fish examined. Earlier [2], a tendency was observed that lower OCP levels accumulate in less active benthivorous fish (bream, gibel carp) compared to more active ones (vimba, roach, wild carp). The results of our studies of 2005 (Table 1) confirms these tendencies.

In 2005, the studies were continued. Tables 1 and 2 show the results of the studies carried out in the Eastern mouth of the Kiliya delta of the Danube in August 2005.

Table 1. OCP content in organs and tissues of benthivorous fish of the Kiliya delta of the Danube river (Eastern mouth), 20.08–25.08.2005, M, n = 4, mg/kg of wet weight

Species	Organs or tissues	DDT	DDD	DDE	α-HCH	γ-HCH
Gibel carp	Muscles	0.07	0.10	0.03	0.45	0.08
	Liver	0.12	0.25	0.07	0.60	0.10
	Brain	0.40	0.60	0.25	0.75	0.25
Bream	Muscles	0.12	0.25	0.08	0.52	0.07
	Liver	0.32	0.30	0.15	0.61	0.24
	Brain	0.53	0.55	0.21	0.80	0.42
Wild carp	Muscles	0.20	0.36	0.14	0.74	0.15
	Liver	0.19	0.43	0.25	0.52	0.12
	Brain	0.46	0.49	0.17	0.75	0.14



Species	Organs or tissues	DDT	DDD	DDE	α -HCH	γ -HCH
Roach	Muscles	0.20	0.32	0.15	0.54	0.40
	Liver	0.34	0.89	0.28	0.68	0.16
	Brain	0.80	0.79	0.32	0.91	0.20

Table 2. OCP content in organs and tissues of predatory fish of the Kiliya delta of the Danube river (Eastern mouth), 20.08–25.08.2005, M , $n = 4$, mg/kg of wet weigh

Species	Organs or tissues	DDT	DDD	DDE	α -HCH	γ -HCH
Perch	Muscles	0.40	0.65	0.32	1.16	0.20
Pikeperch	Muscles	0.35	0.45	0.13	0.83	0.14
	Liver	0.56	0.63	0.21	0.87	0.18
	Brain	0.45	0.72	0.12	0.57	0.16
European catfish	Muscles	0.45	0.59	0.13	0.70	0.15
	Liver	0.82	0.69	0.19	0.85	0.36
	Brain	0.64	0.79	0.21	0.25	0.16

Comparing the obtained results with the previous ones (Fig. 1–8) [6, 7], we can say that that the OCP contents did not change significantly for such a short period of time.

CONCLUSION AND PERSPECTIVES OF FURTHER DEVELOPMENT

The results of the performed studies indicate on the continuous presence and circulation of OCPs in the components of the hydroecosystem of the Ukrainian part of the Danube river, including Kiliya delta. The organs and tissues of all examined fish contained OCPs. The same as in previous years, the highest OCP content was observed in fat-containing organs and tissues. The tendency of their distribution in fish did not change.

The analysis of scientific literature and materials of own investigations allows drawing a conclusion that the most toxic stable organochlorine pesticides for hydrobionts are those, which are characterized by the highest persistence in the environment and high ability to migrate and accumulate in the different links of the food web of aquatic ecosystems.

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ХЛОРООРГАНІЧНІ ПЕСТИЦИДИ У РИБАХ КІЛІЙСЬКОЇ ДЕЛЬТИ ДУНАЮ (2003–2005 РР.)

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Мета. Визначення та аналіз вмісту хлорорганічних пестицидів (ХОП) у органах та тканинах бентофагів та хижих видів риб Кілійської дельти Дунаю (гирло Восточне) та порівняння їх з результатами попередніх років.

Методика. Проведення аналізів проб гідробіонтів на вміст залишкових хлорорганічних пестицидів проводили за допомогою газорідної хроматографії (ГРХ) за єдиною методикою. Хроматографічний аналіз проводився на газовому хроматографі «Цвет-5» з електронно-захоплювальним детектором в Інституті гідробіології Національної академії наук України.

Результати. Стійкі хлорорганічні пестициди, вирізняються вираженою персистенцією у навколишньому середовищі і характеризуються високою здатністю до міграції та накопичення у різних ланках трофічних ланцюгів водних екосистем.

У досліджуваних органах і тканинах відібраних видів риб, за наявності певної кількості жиру — фіксація залишкової кількості хлорорганічних пестицидів. Серед бентофагів за вмістом ХОП в органах і тканинах (сумарно) ряд виглядає наступним чином (у порядку зростання): рибець → тарань → сазан → ляц → карась сріблястий. Серед хижаків: білізна (жерех) → окунь → сом → судак.

Наукова новизна. В останні роки багато вчених у всьому світі знову повертається до вивчення проблеми накопичення та розподілу (перерозподілу) ХОП у компонентах водних екосистем. Це пов'язано з наявністю певних загроз для довкілля та здоров'я людини, що може призвести до негативних наслідків у результаті споживання риби як вищої трофічної ланки прісноводних екосистем України.

Практична значимість. Отримані дані свідчать про те, що основні промислові види риб Кілійської дельти Дунаю містять залишкову кількість пестицидів. Це вказує на необхідність проведення постійного гігієнічного та токсикологічного контролю риби, що вилловлюється та реалізується. Відмічена закономірність нижчого рівня накопичення ХОП у менш рухливих видів бентофагів (ляц, карась сріблястий) порівняно із активнішими (рибець, тарань, сазан), підтверджується даними цього дослідження.

Ключові слова: забруднення, хлорорганічні пестициди (ХОП), ДДТ та його метаболіти, α - і γ -ізомери ГХЦГ.

ХЛОРООРГАНИЧЕСКИЕ ПЕСТИЦИДЫ В РЫБАХ КИЛИЙСКОЙ ДЕЛЬТЫ ДУНАЯ (2003–2005 ГГ.)

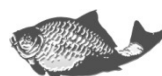
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Цель. Определение и анализ содержания хлорорганических пестицидов (ХОП) в органах и тканях бентофагов и хищных видов рыб Килийской дельты Дуная (устье Восточное) и сравнение их с результатами предыдущих лет.

Методика. Проведение анализов проб гидробионтов на содержание остаточных хлорорганических пестицидов проводили с помощью газожидкостной хроматографии (ГЖХ) по единой методике. Хроматографический анализ проводился на газовом хроматографе



«Цвет-5» с электронно-захватывающим детектором в Институте гидробиологии Национальной академии наук Украины.

Результаты. Стойкие хлорорганические пестициды, отличающиеся выраженной персистентностью в окружающей среде, характеризуются высокой способностью к миграции и накоплению в разных звеньях трофических цепей водных экосистем.

В исследуемых органах и тканях отобранных видов рыб, при наличии определенного количества жира — фиксация остаточного количества хлорорганических пестицидов. Среди бентофагов по содержанию ХОП в органах и тканях (суммарно) ряд выглядит следующим образом (в порядке возрастания): рыбец → тарань → сазан → лещ → серебряный карась. Среди хищников: белизна (жерех) → окунь → сом → судак.

Научная новизна. В последние годы множество ученых во всем мире снова возвращаются к изучению проблемы накопления и распределения (перераспределения) ХОП в компонентах водных экосистем. Это связано с наличием определенных угроз для окружающей среды и здоровья человека, что может привести к негативным последствиям, в результате потребления рыбы как высшего трофического звена пресноводных экосистем Украины.

Практическая значимость. Полученные данные свидетельствуют о том, что основные промысловые виды рыб Килийской дельты Дуная содержат остаточное количество пестицидов. Это указывает на необходимость проведения постоянного гигиенического и токсикологического контроля вылавливаемой и реализуемой рыбы. Отмеченная закономерность — меньшие количества ХОП накапливаются у менее подвижных видов бентофагов (лещ, карась серебрястый) по сравнению с активными (рыбец, тарань, сазан) — подтверждается данными настоящего исследования.

Ключевые слова: загрязнение, хлорорганические пестициды (ХОП), ДДТ и его метаболиты, α - и γ -изомеры ГХЦГ.

