Organochlorine pesticides in Baikal bivalve mollusc Colletopterum ponderosum sedakovi

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Abstract. For the first time, the bivalve mollusc Colletopterum ponderosum sedakovi (Siemaschko, 1848) was used as a universal bioindicator of pollution of Lake Baikal ecosystem with organochlorine pesticides (OCPs). OCPs were identified and quantified in soft tissue samples, collected from Lake Baikal. Dichlorodiphenyltrichloromethylmethane (DDT) and its metabolites, isomers of hexachlorocyclohexane (HCH) and hexachlorobenzene (HCB) were identified using modern gas-chromatography-mass spectrometry. The obtained data on OCPs levels have been compared with those reported earlier for molluscs from other world regions. Levels, sources and trends of OCPs contamination of Lake Baikal ecosystem and its basin were established. The recommendations on using Colletopterum ponderosum sedakovi as a bioindicator of OCPs in aquatic ecosystems in further research have been proposed.

1. Introduction
Organochlorine pesticides (OCPs) are highly hazardous ecotoxicants, which have a pronounced mutagenic and carcinogenic activity, a high bioaccumulation degree and environmental stability. OCPs were recognized by the world community as especially dangerous ecotoxictants and were defined as persistent organic pollutants (POPs) by the Stockholm Convention on Persistent Organic Pollutants in 2001 [1].

Shellfish are widely used as bioindicators of organochlorine contamination of marine and freshwater ecosystems [2,3]. It is known that molluscs are one of the most convenient test organisms, which are widely used in modern world practice as bioindicators of a large number of pollutants due to, the ability to accumulate them to high concentrations during filtration of water. In the present work, a bivalve mollusc Colletopterum ponderosum sedakovi, is first used as a universal bioindicator of pollution of Lake Baikal ecosystem by OCPs [4,5]. This species is widespread in Baikal region; it inhabits mainly the silty sand at a depth of 0–3 m [6].

2. Materials and methods
Bivalve samples (45 specimens) were collected in Cherkalov Sor Bay and Chivyrkuisky Bay of Lake Baikal during summer season in 2008-2010 (Figure 1). All animals were wrapped separately in aluminium foil, put in zip-lock bags and frozen until analyses.
The mollusc population in Chivyrkuy Bay is characterized by low density and inhabits the silty soils with thickets of aquatic vegetation. The population was represented mainly by 7-year-old individuals with an average linear size of 63.9 ± 5.5 mm (lim 18.8–85.3 mm) and a mass of 24.6 ± 4.3 g (lim 0.3–45.1 g) (n = 12).

In Cherkalov Bay, molluscs inhabit all area, but the largest accumulations were noted on silty sands at depths of 1.5–2 m. The Baikal bivalve molluscs population was predominantly represented by 6–7-year-old individuals with an average linear size of 72.6 ± 2.2 mm (lim 49.1–100.6 mm) and a mass of 29.7 ± 2.6 g (lim 9.5–77.3) (n = 33).

The tissue samples were analyzed after extraction for OCPs by gas-chromatography-mass spectrometry (Agilent 6890N gas chromatograph with mass-selective detector AT 5975N and autosampler AT 7683B). Dichlorodiphenyltrichloroethane (DDT) and its metabolites (p, p'-DDE, p, p'-DDD), hexachlorocyclohexane (HCH) and its isomers (α-HCH, β-HCH, γ-HCH), hexachlorobenzene (HCB) were identified. Quantitative determination of OCPs in extracts was carried out to establish the nature of their intake, distribution, and accumulation.

Tissue samples were integrated by habitat. OCPs were extracted twice from homogenized soft tissues (10 g) with a mixture of acetone and hexane (5:2) using an ultrasound disperser (model UZDN-A, Russia) with a frequency of 22 kHz for 20 min. The extracted OCPs were redistributed into hexane by washing the combined extract with distilled water. The obtained hexane extract was purified with concentrated sulfuric acid (washing the extract with 5 mL acid portions until the acid layer became decolored) and dried with anhydrous sodium sulfate. Afterwards, the extract was fractionated by passing through a column with activated alumina a mixture of dichloromethane and hexane (1:1) at a liquid rate of 5 mL/min. The obtained fraction was subjected to concentration and GC-MS analysis to determine OCPs.

3. Results and discussion
The total concentration of ΣHCH and ΣDDT in soft tissues of Baikal mollusc varied from 0.4 to 0.9 ng/g wet weight (average concentration 0.7 ng/g) and from 0.4 to 6.1 ng/g wet weight (average
concentration 2.5 ng/g), respectively. The HCB varied from 0.2 to 0.3 ng/g. The average concentration of HCB was 0.2 ng/g wet weight.

The percentage of OCPs in mollusc tissues was found to be as follows: ΣHCH (20.3%), ΣDDT (73.4%), HCB (6.3%). The pesticides β-HCH, δ-HCH, aldrin, dieldrin and endrin were not identified. The ratio of DDT/DDE was 0.3-4.4.

A comparative analysis of the obtained results and literature data on the OCPs levels in molluscs from various marine ecosystems showed that the pollution level of *Colletopterum ponderosum sedakovi* is relatively low, and significantly lower than that observed for molluscs from Southeast Asia [7-12].

**HCB.** Hexachlorobenzene levels in mollusc tissues (0.2-0.3 ng/g wet weight) were comparable with those found for molluscs from other world regions [2,3,12-15]. The found levels were lower than the highest concentrations, reported for *Mytilus edulis* (edible mussel) collected from coastal waters of South Korea (up to 50 ng/g) [16,17]. The average values and relatively uniform distribution of HCB concentrations in tissues of Baikal molluscs suggest that the presence of HCB is due to global atmospheric transport, and there were no local sources of HCB in Baikal region. We suppose that these levels are background levels. HCB has a relatively high vapor pressure of about 10^{-3} Pa, which contributes to its redistribution in the northern hemisphere as a result of air transport.

**Aldrin, dieldrin and endrin.** These pesticides were not found in mollusc tissues. Aldrin and dieldrin were used in Russia in small quantities (in 1966-1967 years of high usage) and have never been used in Baikal region.

**DDT.** The total concentration of DDT group compounds (ΣDDT) in mollusc tissues ranged from 0.4 and 6.1 ng/g wet weight. These values were relatively low and comparable with those of total DDT levels in *Mytilus galloprovincialis* (Black Sea mussel) (1.6–6.6 ng/g) collected from natural waters of Balear Isles [14] and in *Mytilus galloprovincialis* (0.2-1.7 ng/g) from Spain [18]. But were significantly lower than the highest levels found for species collected from seas, washing China, Korea, Thailand [3,7,8,19,20] and Adriatic Sea [21]. Notably, the total DDT levels in *Mytilus edulis* from coastal waters of Korea reached 2680 ng/g [16]. Such enormous concentrations of DDT can be attributed to the fact that DDT is currently used in China and India against the malaria mosquito. Taking into account the long life-time of DDT in the environment, its concentrations were apparently due to the intensive use of DDT in agriculture in the past.

Another possible source of DDT in Lake Baikal basin ecosystem is an atmospheric transport from countries that produce and use DDT today. Although most countries (more than 80 countries) signed a convention on the prohibition of DDT production and use in 1970, the pesticide is still used for sanitary purposes and in agriculture by some developing countries (to control disease insects). DDT is capable at entering the atmosphere in the form of vapors or aerosol associates from the surface of water bodies or soil and can be transported over considerable distances from the places of initial release into the environment, being involved in repeated evaporation-condensation cycles.

The detection of DDT and other persistent organochlorine compounds in environmental objects in Arctic and Antarctic indicates a global redistribution of OCPs [22-24]. In Russia DDT was prohibited for application in 1969-1970 years; therefore, the most probable source of DDT input in Lake Baikal basin is a transboundary air transfer from India and China, where DDT are being used and produced. Note that geographically these countries are located near Lake Baikal basin, which in Mongolia extends into the state border with China.

**HCH.** This pesticide was identified in mollusc tissues at concentrations of 0.4–0.9 ng/g wet weight, which were comparable with those found in molluscs collected from various parts of World Ocean [16]. These levels were lower than the highest concentrations found in *Mytilus edulis* from coastal waters of Korea (up to 38 ng/g) [16], *Brachiodontes sp.* from Egypt (up to 115.4 ng/g) [25]. A similar variation in the concentration of HCH indicates a local intake of HCH. This pesticide was widely used in agriculture in Lake Baikal basin against the meadow moth, as well as to destroy the unpaired silkworms.
Therefore, this pesticide is washed out and inflow into the ecosystem of Lake Baikal. The sufficiently high concentrations of HCH in bivalves indicate the primary contribution of local sources of its input in lake ecosystem.

The sources of OCPs in the Lake Baikal basin can be ranged as follows:

- global air transport (HCB);
- transboundary air transfer from neighboring countries (DDT);
- local transport (HCH).

4. Conclusions

1. The levels of OCPs in *Colletopterum ponderosum sedakovi* were relatively low, and Baikal region can be attributed to the low-polluted area.

2. A comparison of HCB levels in mollusc tissues with the corresponding data for molluscs from various world regions showed, that its levels in Lake Baikal ecosystem can be considered as a background, and its intake is due to global air transport.

3. Total DDT levels in mollusc tissues were due to the long life-time of previously introduced DDT and transboundary (regional) air transport from countries, where DDT are being used and produced.

4. The presence of HCH is the result of local sources.

We presume that the use of *Colletopterum sedakovi* as universal bioindicator of pollution of aquatic ecosystems by persistent organic pollutants is an informative and promising approach for further research and environmental protection practice. Firstly, the bivalve mollusc is a quite common in aquatic ecosystems. Secondly, the large linear dimensions and small depth of habitat makes them easy to collect. Thirdly, a high degree of OCPs accumulation allows one to reliably establish the degree of ecosystem pollution by these ecotoxins.

The POPs data in environment objects and biota may be used for regional ecological-geochemical and ecological-hygienic assessments of the environmental state, effective identification of sources and areas of anthropogenic environmental impact strengthening and weakening, design of bioaccumulative POPs models for aquatic ecosystems and environmental risk assessment [5].

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