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Spatial distribution of legacy pesticides in river sediment from the Republic of Moldova

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ABSTRACT

Historical use of organochlorine pesticides (OCPs) in the Republic of Moldova could pose a potential risk for the aquatic environment due to the persistence, bioaccumulation and toxic properties of these environmental pollutants. However, knowledge on environmental concentrations of legacy OCPs in Moldova is limited. In this study, surface sediment from the two main rivers; Dniester (8 sites, $n = 15$) and Prut (6 sites, $n = 12$), and two tributary rivers; Bîc (11 sites, $n = 11$) and Răut (6 sites, $n = 6$), were collected during 2017–2018 and analyzed for hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethanes (DDTs) and their transformation products (DDDs and DDEs) using gas chromatography coupled to mass spectrometry (GC-MS/MS). Sediment concentrations of Σ_6DDX (1.9–140 ng g^{-1} dry weight (dw)) and Σ_4HCHs (n.d–2.5 ng g^{-1} dw) were found. In the big rivers, the average Σ_6DDX concentration (18 ng g^{-1} dw) were 35 times higher than Σ_4HCHs (0.51 ng g^{-1} dw). Whereas, in the small rivers the average Σ_6DDX concentration (32 ng g^{-1} dw) was approximately 41 times higher than Σ_4HCHs (0.77 ng g^{-1} dw). Compared to previous studies from Eastern Europe, the sediment levels were generally similar as found in Moldova's neighboring countries (Romania and Ukraine). Overall, the contamination profile indicates long-term ageing of OCPs used in the past in the agricultural sector. Less than half of the sites (45%) had levels that pose a potential risk for benthic organisms. Hence, further work is needed to determine the bioaccumulation of OCPs in the aquatic food web in this region and the associated risks to ecosystems and human health.

1. Introduction

Organochlorine pesticides (OCPs), such as dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) were extensively used in the agricultural and forestry sector in the past (Li et al., 2004, 2006). However, these compounds undergo widespread distribution due to their resistance to degradation in the environment and long-range transport in the atmosphere (Wong et al., 2021). Due to their persistency, bioaccumulative and toxic properties, these compounds are classified as persistent organic pollutants (POPs) under the Stockholm Convention, and their use is nowadays banned or restricted (Stockholm Convention, 2001a). OCPs can enter the aquatic environment through many pathways, e.g. runoff from contaminated soils, sewage effluents and atmospheric deposition. In the water, hydrophobic OCPs (such as DDTs and HCHs) tend to absorb to particulate organic matter and deposit in sediments (Karickhoff et al., 1979). Hence, sediment act as a sink where hydrophobic OCPs accumulate, but the sediment can also be a secondary source for dispersal of OCPs through particle resuspension (Roberts, 2012), diffusion from sediment pore water to bottom water (Valsaraj et al., 1996) and bioaccumulation in benthic biota, which often leads to biomagnification in the food web (Nfon et al., 2008). Therefore, assessment of OCPs in sediments provides important information on the contamination profile and associated ecological risks in the aquatic environment in a region.

The use of OCPs was extensive in the former Soviet Union (FSU) from the 1950's to the end of the 1980's (Li et al., 2004). Great efforts have been done to study residue levels of OCPs and other POPs in Central and Eastern European Countries in more recent time (Holoubek et al., 2000; Bojakowska et al., 2014). However, information about environmental concentrations is still scarce from some FSU countries, e.g. the Republic of Moldova. Technical DDT and HCH formulations were the most produced and used pesticides in the FSU during the 1940'-50's. The use was mainly focused to the southern regions of the FSU, where the major agricultural activity occurred, i.e. in Moldova, Ukraine, Volga River

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basin, the North Caucasus region, and the Central Asian region (Li et al., 2004, 2006). The Republic of Moldova is a small country (33,843 km^2, 4 million people) in southeastern Europe. It is characterized by mild climate and fertile soils. These favorable agrarian conditions contributed to an intensive development of the agricultural sector in the 1960's-1980's, and today the agricultural land makes up about 75% of the Moldovan territory (Cumanova et al., 2007). It has been estimated that during 1950's–1990's, a total amount of 560,000 tons of pesticides was used for agricultural purposes in Moldova, including 22,000 tons of OCPs. After the 1990's, the pesticide use decreased dramatically, from 38,000 tons of active ingredients in 1984 to 2800 tons in year 2000 (Cumanova et al., 2007). During the period 1981–1987, the approximate amount of pesticide washout from agricultural fields was estimated to 1.1–2.2 tons of ΣDDTs (DDT, DDD and DDE), 2.6–3.0 tons of α-HCH (dominant isomer in technical HCH) and 1.7 tons of γ-HCH (lindane; the insecticidal isomer in technical HCH and a pesticide of its own) (Sinelnikova and Davidova, 1990). In 2001, the Republic of Moldova signed the Stockholm Convention on persistent organic pollutants (POPs), which includes prohibition and/or elimination of the production, use, and import/export of DDT and HCHs (Stockholm Convention, 2001b). However, after decades of pesticide use, Moldova is still contaminated with high levels of POPs (>50 mg kg^{-1}) at hundreds of terrestrial sites, comprising mainly DDT, HCH, and other OCPs such as chlordane, heptachlor and toxaphene (Duca et al., 2010). Moreover, a recent study found high levels of DDTs (mean: 35 μg g^{-1} dry weight (dw)) and HCHs (mean: 34 μg g^{-1} dw) in urban and rural soils collected in the proximity of former pesticide storage sites in North-Eastern Moldova, and concluded that these contaminated sites act as continuous point sources to the environment (Culighin, 2020). High levels of OCPs in soil has also been reported from Romania (Covaci et al., 2006; Dragan et al., 2006; Ene et al., 2012; Tarcau et al., 2013) and other Eastern European countries e.g. Czech Republic (Holoubek et al., 2009) and Poland (Falandysz et al., 2001; Maliszewska-Kordybach et al., 2014).

Given the historically extensive use of OCPs in Moldova, it is

Table 1
Concentrations of ΣHCHs and ΣDDTs (ng g^{-1} dw) in sediment and soil from Moldova and it's neighboring countries (Romania and Ukraine) and other Eastern European countries (Czech Republic and Poland).

Country/region	Sampling year	Matrix	ΣHCH	ΣDDT	References
Moldova					
Dniester River, Moldova	2017–2018	sediment	0.10–1.2[a]	6.2–36[b]	This study
Prut River, Moldova	2017–2018	sediment	0.093–1.0[a]	2.6–38[b]	This study
Răut River, Moldova	2018	sediment	0.38–1.6[a]	7.4–140[b]	This study
Bîc River, Moldova	2018	sediment	n.d – 2.5[a]	1.9–60[b]	This study
Prut River, Moldova	2014	sediment	n.d. – 0.92[c]	n.d – 9.4[b]	State Hydrometeorological Service (2015)
Bîc River, Moldova	2013	sediment	n.a.	n.d. – 68[b]	Gillefalk and Lindberg (2013)
Dniester and Prut Rivers, Moldova	2003–2005	sediment	n.d. – 0.9[c]	0.4–12[b]	Cumanova et al. (2007)
Dniester River, Moldova	2001	sediment	n.a.	8.2–35[b]	Sapozhnikova et al., 2005a
Soroca district, Northern Moldova	2012	soil	n.d. – 1,100,000[c]	n.d. – 840,000[b]	Culighin (2020)
Romania					
Someşu Mic River, Romania	2017	sediment	0.8–12[d]	1–39[b]	Barhoumi et al. (2019)
Bahlui River, Romania	2006–2007	sediment	0.4–3[e]	0.18–4.0[b]	Neamtu et al. (2009)
Bahlui River, Romania	2002	sediment	0.5–6[c]	16–78[b]	Dragan et al. (2006)
Danube Delta, Romania	2001	sediment	0.9–6.8[f]	0.9–17[g]	Covaci et al. (2006)
Danube Delta, Romania	1993	sediment	2.2–40[c]	0.83–72[h]	Fillmann et al. (2002)
North-Eastern Romania	2005	soil	1.1–9.8[d]	4.4–79[b]	Tarcau et al. (2013)
Eastern Romania	2005	soil	0.7–12[d]	0.9–670[b]	Drăgan et al. (2007)
South-Eastern Romania	2009	soil	n.d. – 6,800[c]	n.d. – 5,800[b]	Ene et al. (2012)
Various sites, Romania	NI	soil	0.7–90[c]	3.5–1,500[b]	Covaci et al. (2001)
Ukraine					
The Dnipro–Bug estuary, the Danube delta, the Balaklava and Sevastopol bays, Ukraine	2006–2009	sediment	0.4–2,200[i]		Milyukin and Goncharuk (2019)
Danube Delta, Ukraine	2006–2008	sediment	n.a.	0.30–210[b]	Burgess et al. (2011)
Dnieper and Boh Estuaries, Ukraine	2006–2008	sediment	n.a.	2.0–340[b]	Burgess et al. (2011)
Danube Delta, Ukraine	1995	sediment	1.3–2.0[c]	9.2–43[b]	Fillmann et al. (2002)
Odessa bay, Ukraine	1995	sediment	1.2–2.2[c]	34–65[b]	Fillmann et al. (2002)
Poland					
Various lakes, Poland	2010–2013	sediment	n.d. – 61[d]	0.7–600[g]	Bojakowska et al. (2014)
Southern Poland	1994	sediment	0.85–4.7[c]	18–120[j]	Falandysz et al. (2001)
Various sites, Poland	2005	soil	0.11–150[c]	0.24–450[g]	Maliszewska-Kordybach et al. (2014)
Southern Poland	1994	soil	0.36–110[c]	4.3–2,400[j]	Falandysz et al. (2001)
Czech Republic					
Various sites, Czech Republic	NI	soil	0.26–4.0[d]	2.0–1,900[g]	Holoubek et al. (2009)

n.a. – not analyzed.
n.d. – not detected.
NI – No Information.
[a] Sum of *α*- and *β*-HCH.
[b] Sum of *o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD and *p,p′*-DDD.
[c] Sum of *α*-, *β*- and *γ*-HCH.
[d] Sum of *α*-, *β*-, *γ*- and *δ*-HCH.
[e] Sum of *β*-HCH and *γ*-HCH.
[f] Sum of *α*- and *γ*-HCH.
[g] Sum of *p,p′*-DDT, *p,p′*-DDD and *p,p′*-DDE.
[h] Sum of *p,p′*-DDT, *o,p′*-DDD, *o,p′*-DDD, *p,p′*-DDD and *p,p′*-DDE.
[i] Sum of α-, β-, γ- and δ-HCH and p,p′-DDT, o,p′-DDD, p,p′-DDD and p,p′-DDE.
[j] Sum of *o,p′*-DDT, *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD.

important to assess also the contamination levels in the aquatic environment in this region today. Studies from Moldova's neighboring countries have reported high levels of DDTs in sediments ranging from 0.3 to 340 ng g^{-1} dw (Ukraine) and 0.18–78 ng g^{-1} dw (Romania) (see references in Table 1), while levels of HCHs were found to be in the range 1.2–2.2 ng g^{-1} dw (Ukraine) and 0.4–40 ng g^{-1} dw (Romania) (see references in Table 1). Furthermore, combined levels of HCHs and DDTs has also been reported in sediment from Ukraine with up to 2200 ng g^{-1} dw (Milyukin and Goncharuk, 2019). However, scientific literature and reports on exposure and levels of OCPs in the aquatic environment in Moldova is very limited. Apart from a report from the State Hydrometeorological Service of Moldova on OCPs in sediments from Moldovan rivers and lakes (State Hydrometeorological Service, 2015), only four other studies are available on OCP contamination of sediment or fish from Moldova (Cumanova et al., 2007; Gillefalk and Lindberg, 2013; Sapozhnikova et al., 2005a,b). In these studies, Σ_6DDT concentrations ranged from not detected to 68 ng g^{-1} dw in sediments, while in fish, levels up to 28 and 34 ng g^{-1} wet weight (ww) were recorded in muscles and gonads, respectively. Lindane (γ-HCH) was also detected in fish gonads, in levels up to 76 ng g^{-1} ww (Sapozhnikova et al., 2005b)

This study is the first one that aims to provide a comprehensive overview of the concentration levels and profiles of legacy OCPs in the aquatic environment in Moldova. Sediment samples from the two main rivers (Dniester and Prut) and two smaller tributary rivers (Bîc and Răut) were collected and analyzed for HCHs, DDTs and their transformation products. The DDT and HCH levels were compared to corresponding levels reported from Moldova and other countries in Eastern Europe and the origin and dominating pathways of the pesticides in Moldova were assessed through contamination profile analysis. Additionally, an assessment of the ecological risk of the OCPs in sediments in Moldova was performed by comparing the detected levels of the targeted pesticides with international sediment quality guidelines.

2. Materials and methods

2.1. Chemicals

The following OCPs were included in the chemical analysis: α-, β-, γ- and δ-HCH, *o,p'*- and *p,p'*-DDT and their transformation products; *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD and *o,p'*-DDD. Details about authentic reference standards, mass-labeled internal standards (ISs) and mass labeled recovery standards (RSs) are given in Tables S1 and S2 in Supporting Information (SI).

2.2. Study area

The Dniester River is shared between Ukraine and Moldova (Fig. 1). It is the main river in Moldova and the 10th longest river in Europe with a total length of 1380 km. It has its spring at Carpathian Mountains in Ukraine, runs through Moldova and finally discharges into the Black Sea. The river basin has a total area of 72,100 km^2 and approximately 7 million people live in this basin with the main cities Mohyliv-Podolskyi in Ukraine, and Soroca, Rybnitsa, Chișinău and Tiraspol in Moldova. Around 27% (19,000 km^2) of the river catchment area belongs to Moldova. More than 14,000 small tributaries are estimated to enter the Dniester River. There are two hydroelectric plants situated along the Dniester River: Dniester Hydroelectric Power Station near Novodnistrovsk (Ukraine, built 1981) and Dubossari Hydroelectric Power Station near Dubossari (Moldova, built 1954) (Gorbatenky and Byzgu, 1990).

The Bîc and Răut rivers are tributaries of Dniester River and flow

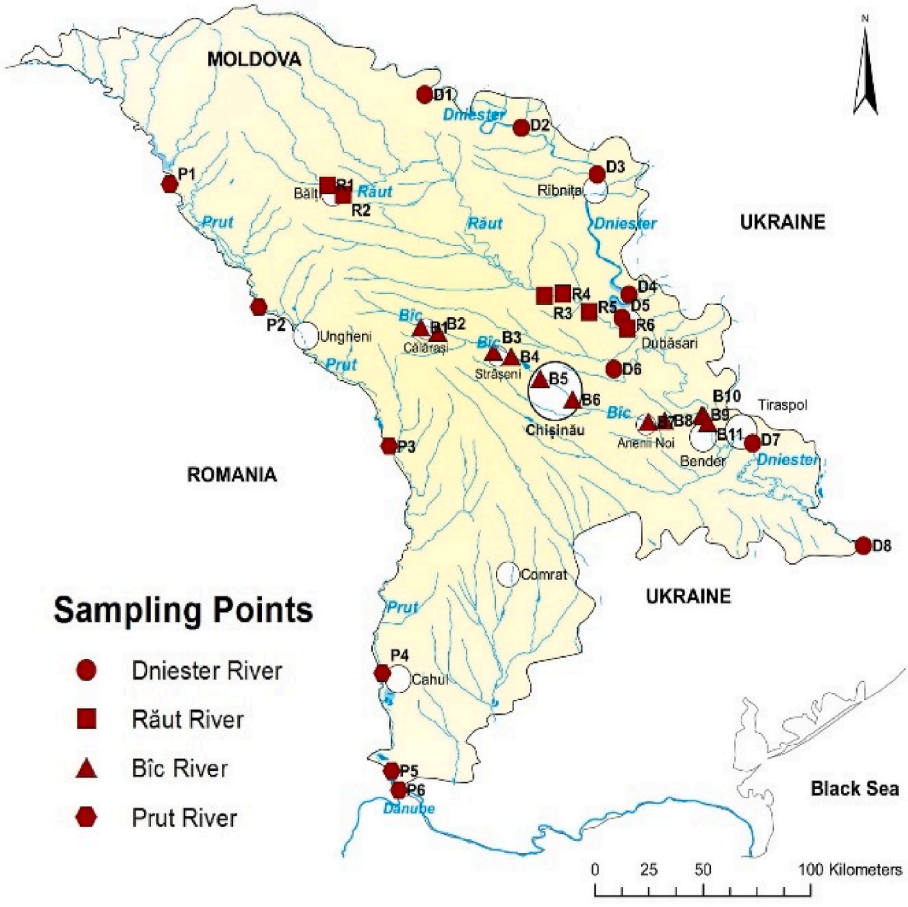

Fig. 1. The sediment sampling sites in four rivers in Moldova.

completely within Moldovan borders. The Răut River, with a length of 286 km, flows through cities such as Florești, Orhei, Bălți with a total population of 150,000 people. Most of the basin area of Răut is covered by agricultural fields (Dobrojan et al., 2014). The Bîc River, with a length of 155 km, flows through several big cities including the capital Chișinău, with a total population around 1.1 million people, and receives discharges from several urban wastewater treatment plants (WWTPs). Sixty percent of the land in the Bîc River basin is being used for agricultural purposes, meaning that arable land without buffer zones is used in close proximity to the river.

The Prut River, the second longest tributary of the Danube River, with a length of 953 km, starts at Carpathian Mountains, and runs southeast through the territory of three states: Ukraine, Moldova and Romania. The total area of the Prut River basin is 27,500 km^2, of which 8240 km^2 belongs to Moldova (Rusu et al., 2012). Over 681 km of the Prut River presents a natural border between Moldova and Romania. Approximately 3 million people live in the river basin area including 0.8 million people in Moldova. Major cities in the region are Chernivtsi (Ukraine), Iasi (Romania), Ungheni, Leova and Cahul in Moldova.

2.3. Sediment sampling

Composite sediment samples were collected from Dniester River ($n = 15$; sites D1-D8) and Prut River ($n = 12$; sites P1–P6) during summer sampling campaigns in year 2017 and 2018. In addition, composite sediment samples were collected from Dniester tributaries; Răut River ($n = 6$; sites R1-R6) and Bîc River ($n = 11$; B1-11) in May and June 2018 (Fig. 1, Table S3 in SI). Sediment was collected using an Ekman dredge at 1–3 m distance from the shore. At each site, top layer (0–5 cm) samples were taken in triplicate and pooled to form a composite sample. In total, 44 composite samples were collected from the 31 sampling sites. Each sample was air-dried at room temperature, sieved (1 mm) and grinded using mortar grinder within 3–4 days from sampling. The samples were sealed in polyethylene bags and stored at −20 °C until chemical analysis.

2.4. Sample extraction and clean-up

Sediment samples (3 g dw) collected in summer 2018 were Soxhlet extracted for 16 h in acetone:*n*-hexane (225 mL, 1:1, v/v) based on a standardized method (method 3540C US EPA, 1996). Samples collected in summer 2017 were extracted by means of automatic Soxhlet (Soxtec® Avanti, 2050) for 2 h in acetone: *n*-hexane (60 mL, 1:1, v/v). Eight samples were Soxhlet extracted and cleaned up in triplicate, whereas the rest of the samples ($n = 36$) were analyzed as single samples. Procedural solvent blanks ($n = 8$) were included for quality assurance/quality control. Before extraction, each sediment sample was spiked with isotope-(^{13}C)-labeled ISs (Table S2 in SI). After extraction, a Biotage TurboVap II® system was used to reduce the extract to ~1 mL under a gentle stream of nitrogen, while keeping a temperature of 40 °C (temperature bath). Subsequently, 3 g of activated granular copper was added to the extract to remove sulfur. The extract was further purified on a multilayer column (glass column; 30 cm × 10 mm i.d.) composed of activated silica gel (3 g), sulfuric acid treated silica gel (40% H_2SO_4: SiO_2, 6 g) and sodium sulfate (Na_2SO_4, 3 g). The analytes were eluted with 60 mL of *n*-hexane:dichloromethane (4:1, v/v). The eluate volume was then reduced to 0.5 mL using the Biotage TurboVap II® system. The solvent was exchanged to isooctane and then transferred into amber GC vials. Isotope-(^{13}C)-labeled RSs were added (Table S2 in SI) and the sample was solvent reduced to 150 μL using an Organomation N-EVAP nitrogen evaporator.

2.5. Instrumental analysis of OCPs

All compounds were analyzed by gas chromatography (GC 7890A, Agilent Technologies) coupled to a triple quadrupole mass spectrometer (7010 GC-MS/MS Triple Quad, Agilent Technologies) equipped with an autosampler (7693, Agilent Technologies). The GC injection system operated in split-less mode and the injection volume was 2 μL. The GC column was a fused silica capillary column DB5 (60 m × 250 μm id x 0.25 μm, Agilent Technologies) and the temperature program was as follows: 190 °C (held for 2 min), 3 °C/min until 250 °C, and 6 °C/min until 310 °C (held for 1 min). Helium was employed as a carrier gas at a flow rate of 2 mL/min. The mass spectrometer was operated in electron ionization (EI) mode at 70 eV. The ion source temperature was held at 300 °C and the transfer line was kept at 310 °C. Nitrogen (N_2) was used as a collision gas, and helium (He) was used as quench gas in the collision cell. The target compounds were monitored in multiple reaction monitoring (MRM) using the same settings as presented elsewhere (Dahlberg et al., 2020). Identification and quantification was performed using authentic reference standards. Agilent MassHunter Quantitative Analysis (for QQQ) software was used for data evaluation.

2.6. Organic carbon analysis

An aliquot of the sediment was used to determine the dry weight of the sediment samples and the total organic carbon (TOC) content, using the Swedish standard procedure SS-ISO 10694. The TOC procedure was performed by dry combustion at 1350 °C and elemental analysis using a TruMac instrument (Leco Corporation, St-Joseph, USA). The dry weight was determined gravimetrically by heating a sample at 105 °C until constant weight.

2.7. Quality assurance and quality control

Quality assurance and quality control were applied to all samples. In order to reduce the risk of any background contamination during sample preparation, all glassware was cleaned and heated at 400 °C prior to use. Prior to each batch of samples being extracted, the Soxhlet equipment including the Soxhlet extractor, the cellulose thimble and the 500 mL round bottom flask, were cleaned by running the Soxhlet overnight with acetone:*n*-hexane (200 mL, 1:1, v/v). For every batch of 8 samples, a blank solvent sample was used to check for background contamination. The blanks generally showed low contamination, but blank correction was applied for batches that contained a few target compounds (i.e. *p,p'*-DDE and *o,p'*-DDE). Samples P1, P6, D1, D8, B1, B11, R1, and R6 were extracted in triplicates and the relative standard deviation (RSD) for these triplicates were on average 8.0 ± 6.1% (α-HCH), 9.3 ± 7.2% (beta-HCH), 9.4 ± 5.9% (*o,p'*-DDD), 8.9 ± 5.2% (*o,p'*-DDE), 11 ± 4.2% (*p,p'*-DDD), 7.3 ± 4.3% (*p,p'*-DDE), 2.7 ± 5.0% (*o,p'*-DDT) 15 ± 12% (*p,p'*-DDT). The method detection limit (LOD) was set to a signal-to-noise ratio of 3 and ranged from 11 to 12 pg g^{-1} dw for HCHs, DDDs, DDTs and from 1.9 to 12 pg g^{-1} dw for DDE. The lowest calibration point that could be quantified reliably by the GC-MS/MS was used as the limit of quantification (LOQ). For all compounds, LOQ was in the range 38–40 pg g^{-1} dw, except for *o,p'*-DDE and *p,p'*-DDE, where LOQ ranged from 6.3 to 40 pg g^{-1} dw. The recoveries for isotopic-labeled compounds used in Soxhlet extraction were on average; 54 ± 35% (α-HCH), 72 ± 35% (γ-HCH), 98 ± 14% (*p,p'*-DDE), and 168 ± 49% (*p,p'*-DDT). The automatic Soxhlet analyzer showed recoveries of 36% ± 37% (α-HCH), 58 ± 35% (γ-HCH), 72 ± 5% (*p,p'*-DDE) and 104 ± 32% (*p,p'*-DDT).

2.8. Statistical analysis

For statistical analysis and calculations of sums and geometric means, values below LOD were assigned a value of half the LOD. To test for significant differences in TOC content between rivers a non-parametric test was used (Kruskal-Wallis test) with Dunn's multiple comparison post-test. Spearman rank test was also used to investigate the correlation between HCH, DDX and TOC levels. Prior to further statistical evaluation of the HCH and DDX concentrations the data was log-transformed to achieve normal distribution. Differences in HCH and

DDX concentrations between groups were then evaluated using parametric tests; un-paired t-tests and one-way ANOVA together with Tukey's multiple comparison post-test.

3. Results and discussion

3.1. TOC in sediments

The average TOC content in sediment from the big rivers (sampled in 2017–2018) ranged from 0.48% to 1.5% for Prut River and 0.67%–3.7% for Dniester River, while corresponding values for the small rivers (sampled in 2018) ranged from 0.80% to 1.9% for Răut River and 0.085%–3.0% for Bîc River (Table S4 in SI). There were no significant differences in the median TOC content between any of the rivers (Kruskal-Wallis test, $p > 0.05$).

3.2. HCHs in sediments

The concentrations of Σ_4HCH (ng g^{-1} dw) in the four rivers are presented in Fig. 2 and Table S4 in SI. In the big rivers (Dniester and Prut), the average concentration of Σ_4HCH ranged from 0.053 to 1.2 ng g^{-1} dw, with the highest average levels found at the sites D5 (1.2 ng g^{-1} dw) and P2 (1.0 ng g^{-1}), respectively. Sediment samples taken along the Dubossari reservoir (D2-D5) showed significantly higher Σ_4HCH concentrations (0.81 ± 0.30 ng g^{-1} dw) than samples taken downstream the dam (D6-D8, 0.19 ± 0.10 ng g^{-1} dw) (un-paired *t*-test, $p < 0.05$). The overall average concentrations for Dniester River were 0.57 ± 0.37 ng g^{-1} dw and 0.42 ± 0.37 ng g^{-1} dw for Prut River.

In the small rivers (Răut and Bîc), the levels of Σ_4HCH ranged from not detected to 2.5 ng g^{-1} dw. The highest concentrations in each river was found at sites R1 (1.6 ng g^{-1}) and B4 (2.5 ng g^{-1} dw). Several sampling sites situated downstream the cities Călărași, Strășeni and Chișinău (B2, B4 and B6) showed significantly higher levels of Σ_4HCHs (average 2.1 ± 0.30 ng g^{-1} dw) compared to sites upstream (B1, B3, B5; 0.70 ± 0.27 ng g^{-1} dw) (un-paired *t*-test, $p < 0.05$). The overall average concentrations for Răut River was 0.76 ± 0.40 ng g^{-1} dw and 0.77 ± 0.90 ng g^{-1} dw for Bîc River. The concentrations of Σ_4HCHs did not differ significantly between the four rivers (one-way ANOVA, $p > 0.05$).

It is known that hydrophobic contaminants, such as DDTs and HCHs, sorb to organic material in sediments (Karickhoff et al., 1979; Lohmann et al., 2007). A strong significant correlation between Σ_4HCH and TOC levels was found for all rivers (Spearman $r = 0.66$, $p < 0.0001$, Figure S1 in SI), suggesting lack of current point sources and that the HCHs have reached equilibrium partitioning between water and sediment TOC. Sediment concentrations of Σ_4HCH found in this study were comparable with those reported previously from Moldova and Ukraine, but lower than levels reported from Romania (see references in Table 1).

The pesticide HCH was commercially available in two formulations: lindane and technical HCH (Breivik et al., 1999). Lindane contained mostly γ-HCH (90%), the isomer with the highest insecticidal activity, while the major constituents in technical HCH were: α-HCH (55–80%), β-HCH (5–14%), γ-HCH (8–15%), δ-HCH (2–16%), and ε-HCH (3–5%). In this study, only α-HCH and β-HCH were detected in the sediment samples, except for one site (P6) that also showed occurrence of γ-HCH. The isomer β-HCH was the predominating isomer comprising, on average, 74 ± 21%, thus significantly higher than in technical HCH (Fig. 3). Among the HCH isomers, α-HCH is more likely to partition to air and being transported over long distances in the atmosphere (Concha-Graña et al., 2006). On the other hand, β-HCH is characterized by having the lowest vapor pressure and water solubility compared to other HCH isomers (Zhang et al., 2003; Willett et al., 1998). β-HCH also has the highest relative resistance to microbial degradation, making it the most persistent HCH isomer in sediment (Ramesh et al., 1991; Willett et al., 1998). The dominance of β-HCH in almost every sample could potentially also be explained by the isomerization of γ-to α- and then α-to the more stable β-HCH (Wu et al., 1997). After long-term occurrence in the environment (ageing), β-HCH therefore often has a high contribution in marine and freshwater sediments (Yang et al., 2005; Lee et al., 2001; Sudaryanto et al., 2011). The predominance of β-HCH in the sediments from Moldova is also in agreement with a previous study from Bahlui River in eastern Romania (Dragan et al., 2006). Overall, elevated levels and isomer composition indicates that the main source of HCH in this region is long-term aged technical HCH emitted in the past and now recirculating in the environment, likely also combined with some inputs of diffuse pollution through long range air transport (LRAT), but with no or minor inputs of fresh technical HCH or lindane from primary sources.

3.3. DDTs in sediments

The concentrations of Σ_6DDTs in the four rivers are shown in Fig. 4 and Table S4 in SI. In the big rivers (Dniester and Prut), the average Σ_6DDX concentrations were ~38 times higher than Σ_4HCHs, with levels ranging between 6.2 and 45 ng g^{-1} dw in Dniester River (highest level at D2, only sampled in 2018) and 2.6 and 38 ng g^{-1} dw in Prut River. Similar to the HCH results, sites D2-D5 situated along the Dubossari reservoir, where most of the suspended solids accumulate (Gorbatenky and Byzgu, 1990), showed significantly higher levels of Σ_6DDTs (average 34 ± 8.6 ng g^{-1} dw) than sites situated downstream the dam (D6-D8, average 7.9 ± 1.5 ng g^{-1} dw) (un-paired *t*-test, $p < 0.05$). A study of soil sampled in the Soroca district, in the north-eastern part of Moldova, in the proximity of the Dniester River (sites D1 and D2), revealed levels of ΣDDTs and ΣHCHs up to 1100 and 640 mg kg^{-1} dw, respectively, which is significantly higher than the national allowed concentration in soil (0.1 mg kg^{-1} dw for ΣDDTs and ΣHCHs,

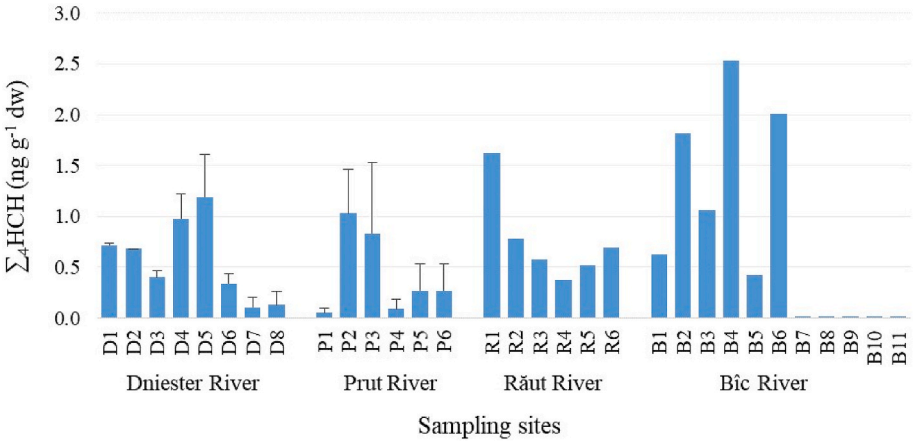

Fig. 2. Concentrations of Σ_4HCH (ng g^{-1} dw) in sediment from the Dniester River (D1-D8), Prut River (P1–P6), Răut River (R1-R6) and Bîc River (B1–B11). The Dniester (0.57 ± 0.37 ng g^{-1} dw) and Prut (0.42 ± 0.37 ng g^{-1} dw) values represent average concentrations from the sampling campaigns in 2017 and 2018 (except D2 that was only sampled in 2018), whereas the Răut (0.76 ± 0.40 ng g^{-1} dw) and Bîc (0.77 ± 0.90 ng g^{-1} dw) were only sampled in 2018. Error bars show the min and max values at each site for the 2017 and 2018 sampling campaigns. HCHs were below limit of detection (LOD) at sites B7–B11.

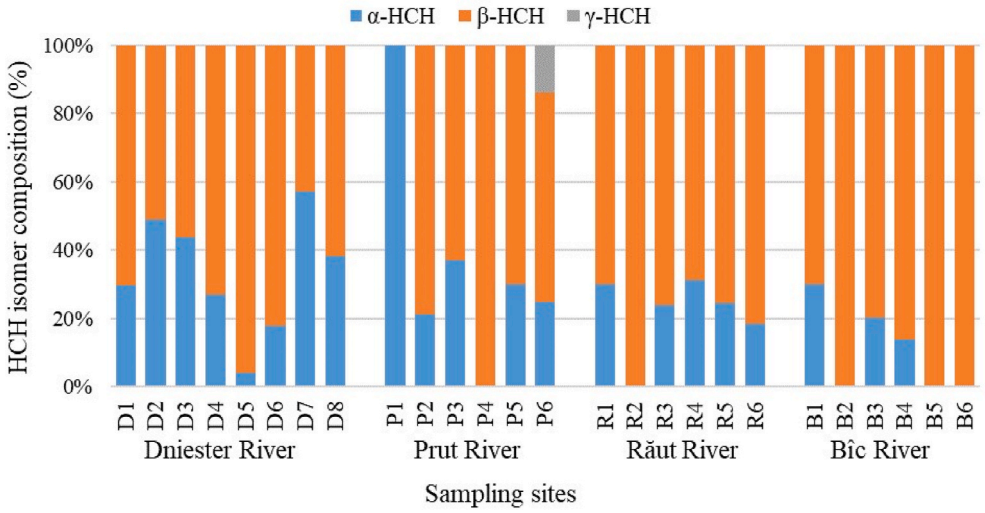

Fig. 3. Composition of HCH isomers in sediment from the Dniester (D1-D8), Prut (P1–P6), Răut (R1-R6), and Bîc (B1–B6) rivers. The composition in Dniester and Prut represent average values from the sampling campaigns in 2017 and 2018, except D2 that was only sampled in 2018, whereas the Răut and Bîc were only sampled in 2018. Sites (B7–B11) are not included since all HCH isomers were below LOD.

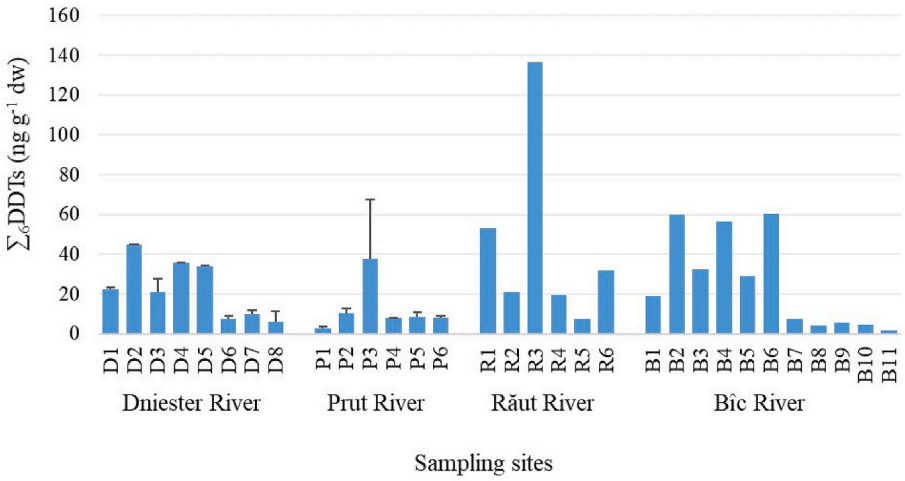

Fig. 4. Concentration of Σ_6DDTs in sediment from the Dniester (D1-D8), Prut (P1–P6), Răut (R1-R6) and Bîc (B1–B11) rivers. The Dniester (23 ± 13 ng g^{-1} dw) and Prut (13 ± 11 ng g^{-1} dw) values represent average concentrations from the 2017 and 2018 sampling campaigns, except D2 which was only sampled in 2018, whereas Răut (45 ± 43 ng g^{-1} dw) and Bîc (25 ± 23 ng g^{-1} dw) were only sampled in 2018. Error bars show the min and max value at each site for the 2017 and 2018 sampling campaigns.

respectively) (Culighin, 2020). It is possible that contaminated soil particles may contribute to OCP accumulation in the Dubossari reservoir through surface run off (Sinelnikova and Davidova, 1990).

The average concentrations of Σ_6DDTs found in sediments from Dniester River (23 ± 13 ng g^{-1} dw) and Prut River (13 ± 11 ng g^{-1} dw) did not differ significantly (un-paired *t*-test; $p>0.05$). In Prut River, the highest value (38 ng g^{-1} dw) was detected at the site P3, which potentially could be explained by discharges from the tributary Jijia. This small river flows in northeastern Romania, crossing areas with both agricultural and industrial activities, with Jassy as the biggest city (791,000 inhabitants) in the region.

The average Σ_6DDT concentrations in the small rivers were in the same range as in the large ones, with, on average, 45 ± 43 ng g^{-1} dw in Răut River and 25 ± 23 ng g^{-1} dw in Bîc River. Although the averages were higher than in the big rivers, there were no statistically significant differences (one-way ANOVA, $p > 0.05$). The concentrations of Σ_6DDT for the Răut River ranged from 7.4 to 140 ng g^{-1} dw, with the highest value at site R3 (Fig. 4). The concentrations in the Bîc River ranged from 1.9 to 60 ng g^{-1} dw with peak concentrations at B2, B4, B6 (Table S4 in SI), i.e. downstream of the cities Călărași, Strășeni and Chișinău. The DDT concentrations at these sites were in the same order of magnitude as previously reported for the Bîc River (Gillefalk and Lindberg, 2013) (Table 1). The 'downstream city' concentrations were significantly higher than the 'upstream city' concentrations (i.e. B2, B4 and B6; average 59 ± 1.6 ng g^{-1} dw *vs.* B1, B3 and B5; average 27 ± 5.7 ng g^{-1} dw; unpaired *t*-test, $p < 0.05$).

As for the HCHs, a strong significant correlation between Σ_6DDT and TOC levels was observed for all rivers (Spearman, $p < 0.0001$, Figure S2 in SI). The sediment concentrations of Σ_6DDT found in this study were also similar with those reported previously from Moldova, Romania and Ukraine (see references in Table 1).

The composition of DDT transformation products in sediment are shown in Fig. 5. In the big rivers (Dniester and Prut), *p,p′*-DDE was the predominant compound comprising on average 45 ± 11% of all analytes, followed by *p,p′*-DDD (28 ± 7%), *o,p′*-DDD (14 ± 12%), *p,p′*-DDT (9 ± 5%), *o,p′*-DDE (3 ± 1%) and *o,p′*-DDT (2 ± 2%). In the small rivers (Răut and Bîc), the pattern was quite similar to the big rivers, i.e. *p,p′*-DDE and *p,p′*-DDD were the predominant compounds. Technical DDT contains high fractions of the parent compounds in relation to the transformation products (parent compounds: 77% *p,p′*-DDT, 15% *o,p′*-DDT and transformation products: 4% *p,p′*-DDE and <5% *p,p′*-DDD (WHO, 1989)). The ratio between the parent compound DDT and its transformation products DDD and DDE can serve as an indicator for the time lapse of DDT usage (Pérez-Maldonado et al., 2010). For example, if

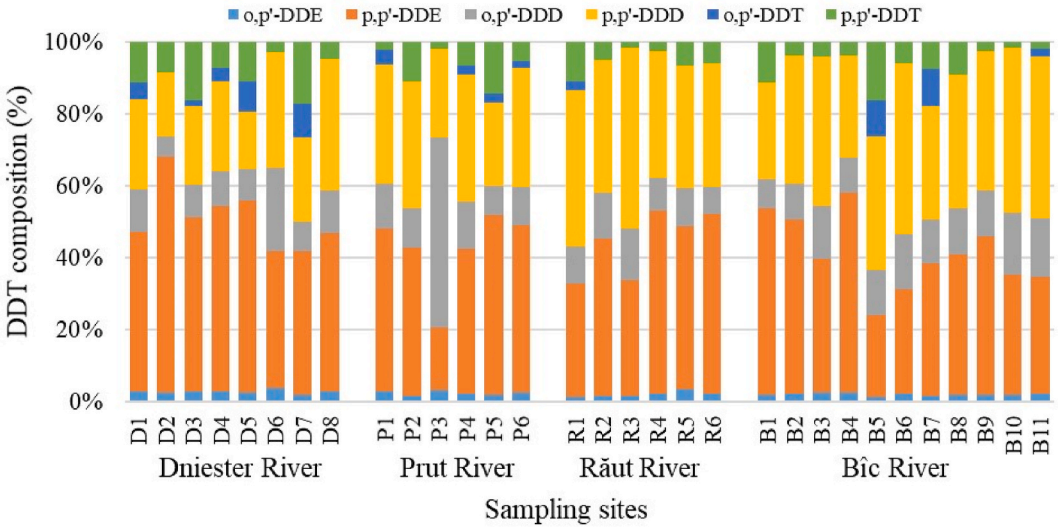

Fig. 5. Composition of DDT-related compounds in sediment from the Dniester (D1-D8), Prut (P1–P6), Răut (R1-R6) and Bîc (B1–B11) rivers. The composition of samples from Dniester and Prut represent average values from the sampling campaigns in 2017 and 2018, except D2 that was only sampled in 2018, whereas Răut and Bîc were only sampled in 2018.

the ratio of (ΣDDE + ΣDDD)/ΣDDTs is greater than 0.5, it suggests that accumulated DDT have undergone long-term degradation; whereas a lower ratio indicates recent DDT input (Sudaryanto et al., 2011). In the present study, the ratio between the transformation products (ΣDDE + ΣDDD) and ΣDDTs ranged from 0.74 to 0.98, indicating that accumulated DDTs have undergone long-term degradation. The degradation of DDT in the environment is influenced by the *in situ* redox state. DDT is transformed to DDE by dehydrochlorination under aerobic conditions and into DDD by reductive dechlorination under anaerobic conditions (Aislabie et al., 1997). A ΣDDD/ΣDDE ratio of >1 indicates anaerobic degradation of DDT, while a ratio of <1 indicates the predominance of aerobic degradation (Hitch and Day, 1992). In this study, half of the sampling sites (51%) showed a ΣDDD/ΣDDE ratio value of >1, and the other half (49%) of the sites showed ratios <1, indicating that the transformation products were formed both under anaerobic and aerobic conditions.

3.4. OCP concentrations in sediments normalized to TOC

Since the TOC content was shown to strongly influence the levels of Σ_4HCH and Σ_6DDT in the sediments, the OCP concentrations were normalized to sediment TOC for comparison (Figures S3 and S4 in SI). This kind of information can be useful as it allows us to distinguish true differences in contamination levels between sites from artifacts caused by differences in sediment characteristics. By normalizing the OCP concentrations to sediment TOC, the concentrations become directly comparable between sites regardless of sediment TOC levels (Dahlberg et al., 2020; Ouyang et al., 2003) and can be used to pinpoint contaminated sites for further investigations in the future. In this study, the TOC normalized contaminant concentrations were found to differ between sites, which suggests that local pollution can play a role in addition to diffuse pollution at some sites. For example, sites D5 and R3 showed high concentrations of Σ_4HCH and Σ_6DDT. The probable reason for the increased concentrations of these substances at site D5 may be the proximity to the Dubossari reservoir dam, where the water flow rate decreases resulting in increased deposition of suspended particles in this area. Most of the Răut River catchment and especially the R2-R3 section are surrounded by agricultural lands, and rain washout increases the risk of soil particles contaminated with pesticides entering the river from the farmland in this area.

3.5. Potential biological effects of OCPs

To assess ecotoxicological risks associated with the OCP contamination in the studied rivers, the sediment levels were compared with international sediment quality guidelines (SQGs). The Republic of Moldova has not established national sediment quality guidelines, and therefore, the Canadian Environmental Quality Guideline for freshwater sediments (Canadian Council of Ministers of the Environment, 1998) and the Norwegian Environmental Quality Standards (EQS) for freshwater sediments (MiljØdirektoratet 2016) were used.

According to the Canadian interim sediment quality guideline (ISQG), 18 sites (58%) exceeded the ISQG value for *p,p'*-DDD (3.5 ng g^{-1} dw), 29 sites (94%) for *p,p'*-DDE (1.4 ng g^{-1} dw) and 16 sites (52%) for *p,p'*-DDT (1.2 ng g^{-1} dw) (Table S5 in SI). The concentrations of *p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT were also higher than the probable effect level (PEL) (8.51, 6.75, 4.77 ng g^{-1} dw, respectively (Canadian Environmental Quality Guidelines, 1998), for 10 (32%), 15 (48%) and 1 (3%) site(s), respectively, indicating possible adverse effects to benthic organisms at those locations (Table S5 in SI). Some sites showed concentration values 2 to 4 times greater than the PEL value for *p,p'*-DDE and *p,p'*-DDD (sites D2, B2, B4 and B6). At site R3, PEL values were exceeded by a factor of 7 and 8 for *p,p'*-DDE and *p,p'*-DDD, respectively.

The Norwegian environmental quality guideline categorizes sediments into 5 classes from background values (Class I) to severe contamination (Class V) (Fig. 6 and Table S6 in SI). The sum of *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT and *o,p'*-DDT and the total HCHs were used to evaluate the possible ecotoxicological risks of OCPs in the study area. About one third of the sites (35%) had Σ_4DDT concentrations in the range of Class III, which may cause chronic effects at long-term exposure. The rest of the sites (65%) were classified as Class II, having no toxic effect. Since only α- and β-HCH were found in the sediment samples in this study, the sum of these 2 isomers was used for the risk assessment. HCH concentrations at 21 sites (68% of all sites) were in the range of Class II (no toxic effects) and 6 sites (19% of all sites) were in the range of Class III (chronic effects of long-term exposure). HCH values at 4 sites (R1, B2, B3, and B6) were in the range of Class IV and may cause acute toxic effects at short-term exposure (13% of all sites). Overall, in total 14 sites (45% of all sites) were found to contain either Σ_4DDT and/or ΣHCH at levels that are considered to cause a risk for benthic organisms. Based on these results, it can be concluded that *p,p'*-DDE, *p,p'*-DDD and HCHs are compounds of ecotoxicological concern in the studied area. Therefore, further studies on possible adverse effects in

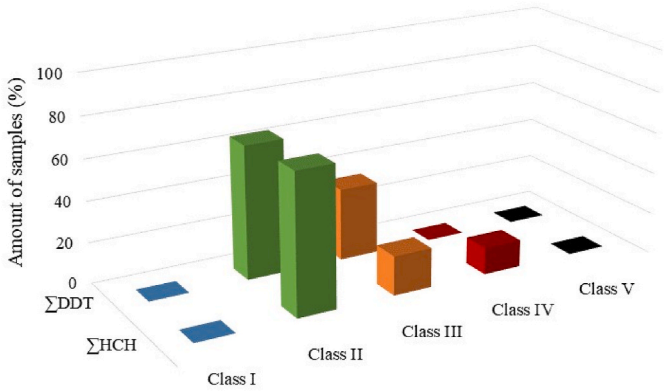

Fig. 6. Distribution of samples (%) in each risk category according to the Norwegian Environmental Quality Guideline for freshwater sediments. The classes correspond to; Class I (background levels), Class II (no toxic effect), Class III (chronic effects at long time exposure), Class IV (acute toxic effects at short time exposure), Class V (severe toxic effects).

benthic fauna caused by the analyzed OCPs are needed.

4. Conclusions

This study provides the first comprehensive overview of some legacy OCPs in sediments from big and small rivers in the Republic of Moldova. Intensive usage of pesticides in agricultural practice in the past is reflected as elevated levels and aged profiles of HCHs and DDT-related compounds in Moldova's river sediments. DDT transformation products (DDD and DDE) were the predominant compounds in all sediment samples, suggesting that this OCP contamination is mainly from previous, weathered agricultural deposition that had undergone degradation under aerobic and anaerobic conditions. The sediment concentrations of Σ_6DDT found in this study were also similar as those reported previously from Moldova, Romania and Ukraine. Similarly, the presence of α-HCH and β-HCH isomers in sediment samples indicates long-term aging of technical HCH used in the past in the agricultural sector and likely combined with input from atmospheric deposition. The levels of Σ_4HCH in this study were comparable with those reported previously from Moldova and Ukraine, but lower than levels reported from Romania. Some locations in the studied rivers are of concern as their sediments contain OCP concentrations that exceeded international sediment quality guidelines, indicating that the level of contamination present a risk for aquatic organisms. Further work is needed to investigate the potential bioaccumulation of the studied OCPs in the aquatic food web in this region and the associated risks to the ecosystems and human health.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.130923.

Author statement

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