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ORGANOCHLORINE PESTICIDES IN THE TISZA RIVER (SERBIA): DISTRIBUTION AND RISK ASSESSMENT

ABSTRACT: Paper provided the systematic data on the distribution and risk assessment status of organochlorine pesticides (OCPs) in sediment of the Tisza River (Serbia). The α-HCH, endrin ketone and methoxychlor are the most commonly found OCPs compounds. According to Serbian regulation concentrations of dieldrin, α-HCH, β-HCH and heptachlor were below limit values. In the Tisza River, sediment samples concentrations of aldrin, endrin, γ-HCH, endosulfans, heptachlor epoxide, p,p'-DDD, p,p'-DDE, p,p'-DDT were above limit values but below maximum concentration. Adverse effects are expected occasionally and slight potential health risks may exist to organisms based on the sediment quality guidelines. Upon exposure to organochlorine pesticides through non-dietary routes, results reported no potential cancer risk. The highest risk of cancer was through ingestion of contaminated sediments and minimal through inhalation routes.

KEYWORDS: chronic daily intake assessment model, distribution, incremental life time cancer risk, organochlorine pesticides, sediment

INTRODUCTION

Organochlorine pesticides (OCPs) are a large group of structurally different compounds. There is still an indication of excessive use of pesticides, regardless of the worldwide attempts to exclude or decrease releases of the pesticides (Kuranchie-Mensah et al., 2012).

The Tisza River (longest tributary of the Danube River) is facing a serious increase in the concentration of pesticides due to agricultural activities. The

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countries in the Tisza Basin (Ukraine, Romania, Slovakia, Hungary and Serbia) have taken great efforts to adopt, adjust and implement the EU Directives in support of implementing of measures to reduce the pressures from agricultural activities on water resources (ICPDR, 2007). The main initiatives are grouped around the Directive 2009/128/EC to establishing a framework for Community action to achieve the sustainable use of pesticides – by reducing the risks and impacts of pesticide on human health and the environment.

Valuing human health risk that may arise from exposure to pesticides is imperious. Some studies include estimates of the potential risk to human health from the consumption of pesticide contaminated food (dietary intake) (Jiang et al., 2005; Ezemonye et al., 2015). However, there is the need to estimate the risk to human health through non dietary exposures. These risks are predicted by chronic daily intake assessment model (CDI) (Huang et al., 2014; Ogbeide et al., 2016) and the incremental life time cancer risk (ILCR) (Qu et al., 2015; Ogbeide et al., 2016).

In this study, 20 compounds were analyzed in sediment samples collected from Serbian part of the Tisza River: α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, α-chlordane, γ-chlordane, endosulfan I, endosulfan II, endosulfan sulphate, DDT, DDD, DDE and methoxychlor.

The main objective of this study is to analyze distribution of the OCPs in sediments of the Tisza River, and to evaluate the risk assessment of OCPs in study area which has not been done so far.

MATERIALS AND METHODS

Study area

This study was carried out in the Tisza River (Serbia). The current investigations include four sediment profiles T, B, S and M. The sampling sites are presented in Figure 1.

Sediment samples were collected by Eijkelkamp core sampler from each sample point, according to standard method ISO 5667-12:1995. Core sediment samples, 80 cm long, were sectioned at 20 cm intervals (T1, B1, S1, M1 = 0–20 cm; T2, B2, S2, M2 = 20–40 cm; T3, B3, S3, M3 = 40–60 cm; T4, B4, S4, M4 = 60–80 cm). The standard USEPA Soxhlet extraction method (3540S) was used for OCP extraction from sediments. Analysis of sediment extracts was done with gas chromatography with electron capture detector (Agilent 7890B) equipped with capillary column HP-5 (Agilent J&W GC Columns, 30 m x 0.30 mm x 0.25 μm).

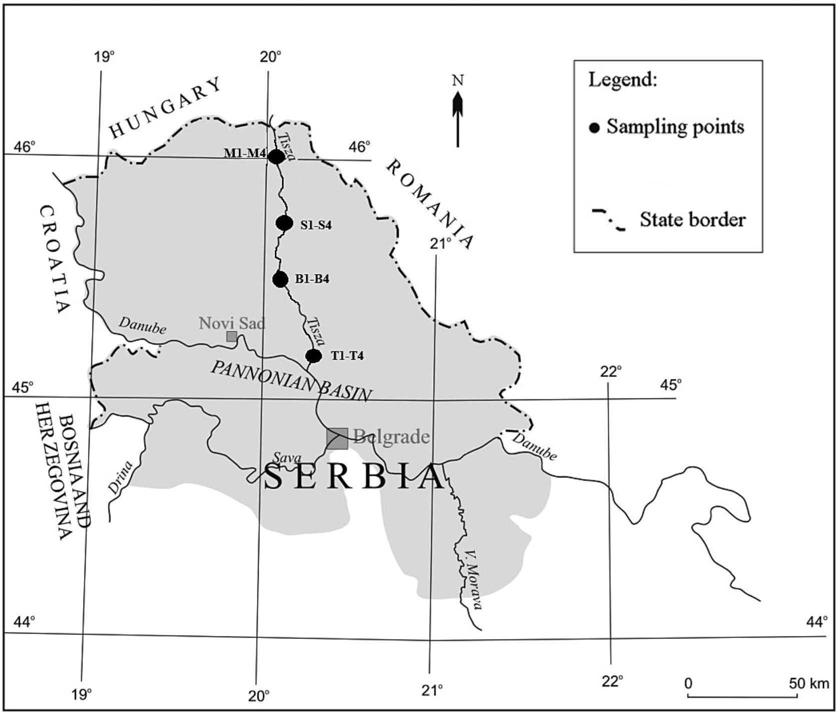

Figure 1. Study area

Risk assessment models

To determine whether the OCPs concentrations in the sediment samples from the Tisza River exceed the permitted values, the concentrations of OCPs were compared to Serbian regulation (*Off. Gazette of RS*, No. 50/12).

Sediment quality guidelines (Long and MacDonald 1998) were established to evaluate the ecotoxicology aspect of sediment contamination. Threshold effects level (TEL) and probable effects level (PEL) have been used to predict biological effects for sediments. Apart from that, effects range-low (ERL) and effects range-median (ERM) values have been used to predict potential impacts of contaminants in sediments (Yang et al., 2010). The non-carcinogenic and carcinogenic risk of detected pesticides to adults and children were calculated using a chronic daily intake (CDI) and the incremental life time cancer risk (ILCR) model. CDI are assessed for ingestion, inhalation and dermal contact (Ogbeide et al., 2016). The CDI was assessed using the following formulae (Ogbeide et al., 2016) (Equations 1–3).

$$CDI_{ingestion}=C_{(sediment)}\times IR_{(sediment)}\times CF\times EF\times ED/BW\times AT \quad (1)$$

$$CDI_{inhalation}=C_{(sediment)}\times (1/PEF)\times IAR\times EF\times ED/BW\times AT \quad (2)$$

$$CDI_{dermal}=C_{(sediment)}\times SA\times CF\times EF\times ED\times ABS\times AF/BW\times AT \quad (3)$$

ILCR for dermal, inhalation and ingestion pathways was calculated using the following equations (Ogbeide et al., 2016) (Equations 4–6).

$$ILCRs_{ingestion}=CS\times(CSF_{ingestion}\times\sqrt[3]{(BW/70)})\times IR_{sed}\times ED\times EF/BW\times AT\times CF \quad (4)$$

$$ILCRs_{dermal}=CS\times(CSF_{dermal}\times\sqrt[3]{(BW/70)})\times SA\times FE\times ABS\times AF\times EF\times ED/BW\times AT\times CF \quad (5)$$

$$ILCRs_{inhalation}=CS\times CSF_{inhalation}\times\sqrt[3]{(BW/70))}\times IRair\times ED\times EF/BW\times AT\times CF \quad (6)$$

The non-cancer and cancer risk was estimated for two age groups: childhood (0–10 y) and adulthood (19–70 y), since several exposure parameters, such as body weight, ingestion rate and inhalation rate, changed with age growth. The values used to derive a CDI and the ILCR and details of exposure parameters are presented in Table 1.

Table 1. Values of the parameters for the estimation of a chronic daily intake (CDI) and the incremental life time cancer risk (ILCR)

Exposure parameters	Unit	Childhood	Adulthood
Body weight (BW)	kg	13.95	58.75
Ingestion rate (IRsoil)	mg d^{-1}	200	100
Exposure frequency (EF)	d yr^{-1}	350	350
Exposure duration (ED)	yr	6	30
Average life span (AT)	d	LT × 365	LT × 365
Lifetime (LT)	yr	72	72
Surface area (SA)	cm^2 d^{-1}	2800	5700
Dermal exposure ratio (FE)	Unitless	0.61	0.61
Dermal surface factor (AF)	mg cm^{-1}	0.2	0.07
Dermal absorption factor (ABS)	Unitless	0.13	0.13
Inhalation rate (IRair)	m^3 d^{-1}	10.9	17.5
Particle emission factor (PET)	m^3 kg^{-1}	1.36 × 109	1.36 × 109

The carcinogenic slope factor of OCPs through ingestion, dermal contact and inhalation are listed in Table 2 (Qu et al., 2015).

Table 2. The carcinogenic slope factor (1/(mg/kg/d)) of OCPs through ingestion, dermal contact and inhalation

Compound	CSFingestion	CSFdermal	CSFinhalation
α-HCH	6.30E+00	4.49E+00	6.30E+00
β-HCH	1.80E+00	1.98E+00	1.86E+00
γ-HCH	1.30E+00	1.34E+00	1.80E+00
p,p′-DDE	3.40E–01	4.86E–01	NA*
p,p′-DDD	2.40E–01	3.43E–01	NA*
p,p′-DDT	3.40E–01	4.86E–01	3.40E–01

*NA indicated that a value was not available

The total risks were assessed as the totality of individual risk for the three exposure pathways in different age groups.

The contaminant level would exert an adverse human health effect or carcinogenic effect when CDI for a contaminant is more than the reference dose (RfD) (Huang et al., 2014; Ogbeide et al., 2016). The ILCR between 10^{-6} and 10^{-4} represents potential risk, while an ILCR larger than 10^{-4} indicates potentially high health risk (Chen and Liao, 2006; Ogbeide et al., 2016). An ILCR of 10^{-6} or less represents virtual safety (Chen and Liao, 2006; Huang et al., 2014; Ogbeide et al., 2016).

Statistical analysis

Principal component analysis (PCA) uses a correlation matrix to define a smaller set of computed values that reflect underlying shared variance in variables present in the original dataset (Wu et al., 2013). For PCA analysis Minitab 12 statistical software was performed.

RESULTS AND DISCUSSION

The α-HCH, endrin ketone and methoxychlor are the most commonly found OCPs compounds (maximal values contributed with 60%). Gamma-chlordane, DDT, and endrin aldehid contributed with 29 %. Concentrations of other OCPs such as β-HCH, γ-HCH, δ-HCH, DDD, DDE, heptachlor, drin, α-chlordane, and endosulfan contributed with 11 %, respectively. The highest level of ΣOCPs was found at site Martonoš (M1-4), while the lowest concentrations were found at site Senta (S1-4). The highest mean value of ΣOCPs concentrations was determined at a depth of 20–40 cm.

The ΣOCPs concentrations in the Tisza River sediments (11.6–21.34 μg kg^{-1}) were lower to those detected in Daya Bay, China (16.66–44.04 μg kg^{-1} Wang et al., 2008), similar to those detected in Honghu lake, China (17.88 μg kg^{-1} Yuan et al., 2013). Higher than those detected in Ariake bay, Japan (4.1 μg kg^{-1} Kim et al., 2007), Minjiang River Estuary, China (1.57–13.06 μg kg^{-1} Zhang et al., 2009), Da-han and Erh-jen River (0.57–14.1 μg kg^{-1} Doong et al., 2002).

Ration of α/γ HCH ranged from 1.50 to 5.49, indicating input of technical HCHs (Zhang et al., 2009; Yuan et al., 2013). HCH residues were resulting mainly from the historical inputs of technical HCHs (the ration of β-HCH/ΣHCHs ranged from 0.06 to 0.31 which was below 0.50) (Wu et al., 2013). Low levels of dieldrin show slow rate of aldrin degradation. Decrease levels of endrin in relation to its degradation products provide indication of the historical input of the OCPs (Kuranchie-Mensah et al., 2012). Average γ/α-chlordane was 5.15, indicating recent input of technical chlordane in the Tisza River sediment (Zhang et al., 2009; Yuan et al., 2013). Rations DDD/DDE was in the range 0.56–2.17, with 69% of the values greater than 1, indicating anaerobic biodegraded condition (Wu et al., 2013). Sediment contamination by DDTs in the

Tisza River came from the historical and recent input of DDT (rations (DDD+DDE)/DDTs in 50 % of samples were greater than 0.5 and 50% of samples were smaller than 0.5). Ratio p,p'-DDT/p,p'-DDE was 0.17–28.14, respectively, also indicating fresh and old input of p,p'-DDT (Wu et al., 2013). Anaerobic biodegraded condition contributes to slower degradation of the parent compound. For this reason, the results indicate recent input of technical chlordane and fresh input of p,p'-DDT.

According to Serbian regulation concentrations of dieldrin, α-HCH, β-HCH and heptachlor in the Tisza River sediment samples were below limit values. On the other hand, concentrations of aldrin, endrin, γ-HCH, endosulfans, heptachlor epoxide, p,p'-DDD, p,p'-DDE and p,p'-DDT in the Tisza River sediment samples were above limit values but below maximum concentration. Therefore, the OCPs levels were categorized as moderate contaminations.

After performing PCA on the datasets, two principal components presented in Figure 2 account for 53.1% of the total variance.

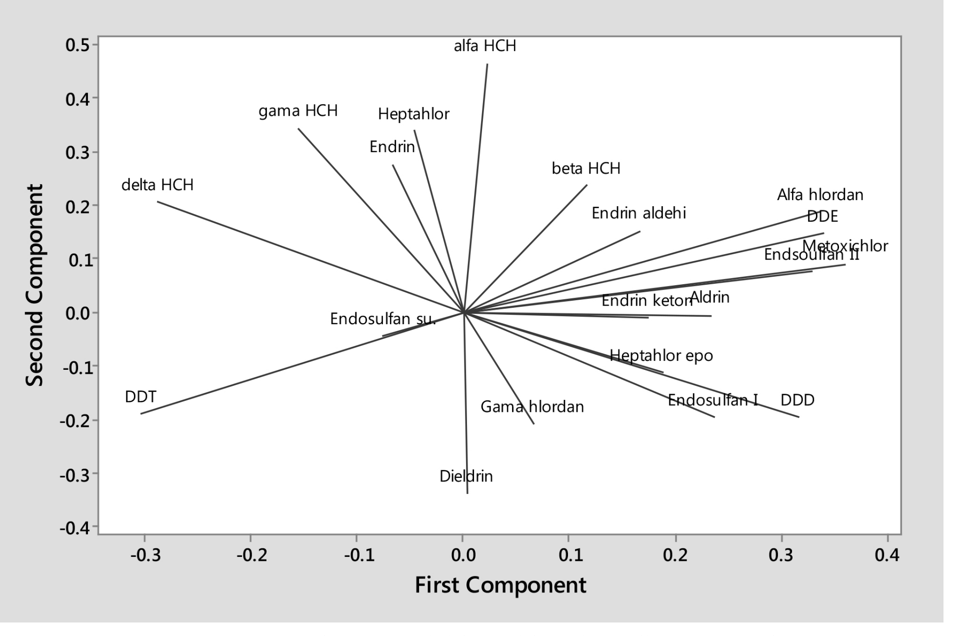

Figure 2. PCA plot of pesticide residues in sediment samples

Positive loadings of pesticides residues such as α-HCH, β-HCH, endrine aldehid, α-chlordane, endosulfan I, endosulfan II, aldrin, endrin ketone and γ-chlordane p,p'-DDD, p,p'-DDE, metoxichlor (Figure 2) imply that those pesticides undergo similar degradation and distribution patterns in sediment samples from the upper and lower reaches of the Tisza River.

Pesticides used many years ago such as DDT and γ-HCH are present in the sediment of the middle course of the river. The obtained results are expected considering that agriculture in this region has been present for at least hundred years. Analyzing the results of PCA there can be determined the impact of agriculture on the presence of pesticides in the Tisza River sediments.

Adverse effects are expected occasionally and slight potential health risks may exist to organisms. Only concentrations of all HCH isomers were higher than PEL values (Table 3).

Table 3. Evaluations of potential ecotoxicological risks of selected OCPs in surface sediments

	Range	ERL	ERM	%< ERL	%ERL-ERM	%> ERM	TEL	PEL	%<TEL	%TEL-PEL	%>PEL
a-HCH	1.38–3.76	N.A.	N.A	–	–	–	0.94	1.38	–	–	100
β-HCH	0.26–1.51	N.A.	N.A	–	–	–	0.94	1.38	68.75	18.75	12.5
γ-HCH	0.34–2.22	N.A.	N.A	–	–	–	0.94	1.38	62.5	18.75	18.75
p,p’ – DDT	0.17–1.99	1	7	50	50	–	1.19	4.77	50	50	–
p,p’ – DDD	0.15–1.62	2	20	100	–	–	1.22	7.81	81.25	18.75	
p,p’ – DDE	0.07–1.11	2.2	27	100	–	–	2.07	374.17	100	–	–
ΣDDTs	1.38–3.55	1.58	46.1	6.25	93.75	–	3.87	51.7	100	–	–
Aldrin	0.10–0.96	N.A	N.A	–	–	–	2	N.A.	100	–	–
Heptachlor	0.08–0.96	0.50	6	62.5	37.5	–	2.26	4.79	100	–	–
Heptachlor epoxide	0.04–0.99	N.A.	N.A.	–	–	–	0.6	2.74	93.75	6.25	–
Endrin	0.03–0.28	0.02	45	–	100	–	2.67	62.4	100	–	–

Results obtained from this study reported no potential cancer risk to humans upon exposure to organochlorine pesticides through non-dietary routes (Table 4).

Table 4. Estimated chronic daily intake (CDI) compared with reference dose for OCPs

	Ingestion		Dermal		Inhalation		Reference dose
	Children	Adults	Children	Adults	Children	Adults	
α-HCH	3.53E-05	5.24E-06	6.44E-06	3.14E-06	6.79E-09	5.18E-08	8.00E-03
β-HCH	1.13E-05	1.67E-06	2.06E-06	1.00E-06	2.17E-09	1.65E-08	8.00E-03
γ -HCH	1.23E-05	1.83E-06	2.25E-06	1.10E-06	2.37E-09	1.81E-08	3.00E-04
ΣDDT	3.25E-05	4.82E-06	5.93E-06	2.89E-06	6.24E-09	4.76E-08	5.00E-04

ILCRs estimates for α-HCH, γ-HCH, β-HCH DDE, DDD and DDT, where higher in children compared to adults when exposed via ingestion, dermally and through inhalation. Cancer risk was highest through ingestion of contaminated sediments and minimal when exposure routes were through inhalation (Table 5).

Table 5. Estimated incremental lifetime cancer risk (ILCRs) for OCPs

	Ingestion		Dermal		Inhalation	
	Children	Adults	Children	Adults	Children	Adults
α-HCH	1.32E-05	4.77E-06	2.04E-05	7.00E-06	5.17E-09	3.99E-09
β-HCH	1.20E-06	4.35E-07	2.88E-06	9.86E-07	4.88E-10	3.77E-10
γ -HCH	9.51E-07	3.44E-07	2.13E-06	7.30E-07	5.16E-10	3.99E-10
DDE	1.71E-07	6.19E-08	5.32E-07	1.82E-07	1.24E-09	9.61E-10
DDD	1.38E-07	5.01E-08	4.30E-07	1.47E-07	1.43E-09	1.10E-09
DDT	2.65E-06	9.60E-07	7.51E-06	2.83E-07	1.04E-10	8.04E-11

CONCLUSIONS

The α-HCH, endrin ketone and methoxychlor are the most commonly found OCPs compounds in the Tisza River sediments, Serbia. Ration of α/γ HCH indicates input of technical HCHs. The ration of β-HCH/ΣHCHs suggests that the HCHs were resulting mainly from the historical inputs of technical HCHs. Also, decrease levels of endrin indicate the historical input of the OCPs. Ration of γ/α-chlordane indicates recent input of technical chlordane in the Tisza River sediments. Sediments contamination by DDTs in the Tisza River came from historical and recent DDT input. Concentrations of dieldrin, α-HCH, β-HCH and heptachlor were below limit values. On the other hand, concentrations of aldrin, endrin, γ-HCH, endosulfans, heptachlor epoxide, p,p'-DDD, p,p'-DDE, p,p'-DDT in Tisza River sediment samples were above limit values but below maximum concentration. The OCPs levels are categorized as moderate contaminations. Adverse effects are expected occasionally and slight potential health risks may exist to organisms. Results obtained from this study reported no potential cancer risk to humans upon exposure to organochlorine pesticides through non-dietary routes. Cancer risk was highest through ingestion of contaminated sediments and minimal when exposure routes were through inhalation.

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ПЕСТИЦИДИ У РЕЦИ ТИСИ (СРБИЈА): ДИСТРИБУЦИЈА И ПРОЦЕНА РИЗИКА

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РЕЗИМЕ: У раду су дати системски подаци о статусу расподеле и процени ризика органохлорних пестицида у седименту реке Тисе (Србија). Најзаступљенији органохлорни пестициди у седименту су α-HCH, ендрин кетон и метоксихлор. Према националној регулативи концентрације диелдрина, α-HCH, β-HCH и хептахлора биле су испод граничних вредности. У узорцима седимента реке Тисе концентрације алдрина, ендрина, γ-HCH, ендосулфана, хептахлор епоксида, p'-DDD, p, p'-DDE, p, p'-DDT биле су изнад граничних вредности, али испод максимално дозвољених концентрација. Нежељени ефекти на организме очекују се повремено. Након излагања органохлорним пестицидима путем недијеталних путева потенцијални ризик од рака се не очекује. Највећи ризик од рака очекује се при гастроинтестиналном уносу седимената и минимално путем инхалације.

КЉУЧНЕ РЕЧИ: дистрибуција, модел процене хроничног дневног уноса, органохлорни пестициди, ризик од рака, седимент