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POLLUTION INDICES FOR ASSESSMENT OF ORGANOCHLORINE PESTICIDES CONTAMINATION IN DANUBE WATER AND SEDIMENTS, CALAFAT-TURNU MAGURELE SECTOR, ROMANIA

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ABSTRACT. The distribution of 18 organochlorine pesticides (OCPs) in the aquatic ecosystem from Danube River (Calafat - Turnu Măgurele sector), Romania was investigated. A total of 16 samples, comprising of 6 surface water and 10 sediment samples, was collected in October 2012 to evaluate the residue of OCPs in Danube River and its two tributaries (Jiu and Olt) using solvent extraction followed by capillary gas chromatography with electron capture detector. The pollution indices were calculated to evaluate OCP's pollution potential, as follows: concentration factor and degree of contamination for sediments, and also contamination factor and contamination index for surface water. The obtained concentrations were below their corresponding threshold values set in Romanian legislation, indicating that harmful effects are unlikely to occur. The calculated values for pollution indices suggested no potential environmental risk.

Key words: *organochlorine pesticides, contamination indexes, Danube River, water, sediment*

INTRODUCTION

The application of an organochlorine pesticide (OCPs) on land enters the aquatic environment by runoff or atmospheric deposition. Due to their hydrophobic characteristics, these pesticides are removed from the surface of the water column and settle at the bottom sediment. Sediment thus serves as a primary repository for majority of applied pesticides (Kuranchie-Mensah et al., 2012). Organochlorine pesticides contamination in aquatic environment is of great concern, due to their persistence, bioaccumulation and toxicity, being able to produce adverse effects in extremely low doses (Tajkarimi et al., 2008). Due to their persistence and widespread use, these pollutants are ubiquitous, low levels being detected in the entire ecosystem. Some OCPs can be involved in human reproductive toxicity, cancer development, neurodevelopment and intellectual dysfunction in infants (Wang et al., 2009).

The Danube, the second longest European river, after the Volga, originates in Germany and then flows southeast for 2,872 km, passing through four Central European capitals before emptying into the Black Sea via the Danube Delta in Romania and Ukraine.

This study reports the values of pollution indices calculated to reveal the OCPs pollution potential in the aquatic environment, in the studied area, based on the concentrations of 18 OCPs (α-, β-, γ-, δ-, ε-isomers of hexachlorocyclohexane - expressed as HCHs, dichloro-diphenyltrichloro-ethane and its metabolites - expressed as DDTs, aldrin, dieldrin, heptachlorepoxide (isomers A and B), α-endosulfan, β-endosulfan, hexachlorobenzene - HCB) in surface water and sediments along the Danube River and in two tributaries, namely Jiu and Olt Rivers, between Calafat and Turnu Magurele towns, situated on the Romanian side of the Danube. In order to assess the contamination degree of the water environment in the studied area, the following pollution indices were calculated: concentration factor (CF) and degree of contamination for sediments, and also contamination factor and contamination index (C_d) for surface water.

MATERIALS AND METHODS

Study area and sample collection

The sampling stations along Danube River and its two tributaries (Jiu and Olt) are illustrated in figure 1. A total of 16 samples, comprising of 6 surface water and 10 sediment samples, was collected in October 2012. Among the 6 surface waters, 4 were collected along the mainstream of the Danube (W1-W4) and 2 from the tributaries Jiu (W5) and Olt (W6) Rivers, from near surface (0-20 cm depth). A number of 7 sediments (S1-S7) were collected from the Danube, 2 from Jiu River (S8-S9) and 1 from Olt River (S10) from the surface (0-20 cm). Throughout sampling a global positioning system (GPS) was used to locate the sampling positions. The water samples were directly collected from the rivers using pre-cleaned glass bottles and the sediments, using a grab sampler. The samples collected at each station were placed on ice after sampling. All the samples were transferred directly to the laboratory.

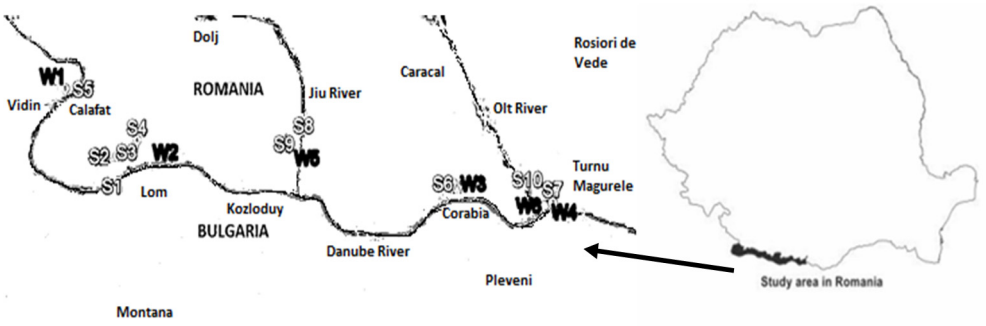

Fig. 1. *Location of sampling points*

Sample preparation and instrumentation

For OCPs determination, water samples were liquid-liquid extracted with hexane, according to the method SR EN ISO 6468:2000 and the sediments were ultrasonic extracted according to EPA method 3550 with acetone: hexane (1:1 vol/vol) in an ultrasonic bath (Bandelin, Sonorex, Germany). The extracts were dried on anhydrous sodium sulphate (Merck, Darmstadt, Germany), cleaned-up with Florisil (Merck, Darmstadt, Germany), then evaporated on a rotary evaporator (Laborota 4010, Heidolph, Germany) near dryness and the residues were re-dissolved in 1 ml of hexane. The solvents were gas chromatography grade of quality (LGC Standards, Germany). The amount of extracted OCPs was determined by gas chromatographic system with an electron capture detector (GC-μECD), Agilent Technologies 6890N equipped with a capillary column DB1 (Agilent J&W), 30 m L×0.32 mm ID×0.50 μm. High purity Helium at a flow rate of 1 mL/min was used as carrier gas. The oven temperature program consists of 4 stages: from 80°C to 196°C (rate 4°C/min, 2 min), from 196°C to 224°C (rate 4°C/min, 2 min), from 224°C to 240°C (rate 4°C/min, 2 min) and from 240°C to 275°C (rate 4°C/min, 2 min). The injector and the detector were 280 and 300°C, respectively.

RESULTS AND DISCUSSION

OCPs concentrations in water samples

The range of concentrations of the investigated OCPs in surface water samples were shown in Table 1.

Table 1. *The range of OCPs concentrations (μg/l) in surface water of the Danube, Jiu and Olt Rivers*

Compound	Range	MAC*
α-HCH	<0.001 – 0.005	-
β-HCH	<0.001 – 0.006	-
γ-HCH	<0.001 - 0.001	0.02
δ-HCH	all <0.001	-
ε-HCH	all <0.001	-
Σ(α-, β-, γ-, δ-HCH)	0.001 – 0.009	0.042
HCB	all <0.002	0.05**
2,4'-DDT	all <0.009	-
4,4'-DDT	all <0.002	0.01
2,4'-DDE	<0.001 - 0.004	-
4,4'-DDE	all <0.001	-
2,4'-DDD	all <0.001	-
4,4'-DDD	all <0.001	-
Σ DDTs***	<0.001 - 0.004	0.025
Aldrin	<0.002 – 0.002	0.01
Dieldrin	all <0.001	0.01

Compound	Range	MAC*
Heptachlor epoxide A	<0.001 – 0.004	-
Heptachlor epoxide B	all <0.001	-
Endosulfan α	all <0.001	-
Endosulfan β	all <0.001	-
Endosulfan Σ(α, β)	<0.001 - 0.001	0.004

**maximum admitted concentration (MAC) for the hazardous substances and priority hazardous substances in surface waters, according to the Romanian legislation (Ministerial Order 161/2006), for the quality class I (Order 161/2006)*
***environmental quality standard (EQS) for priority substances and certain other pollutants, according to the Water Framework Directive 2000/60/EC (WFD 60/2000)*
**** ΣDDTs= Σ(2,4'-DDT, 4,4'-DDT, 2,4'-DDE, 4,4'-DDE, 2,4'-DDD, 4,4'-DDD)*

The maximum admitted concentrations for OCPs, regarded as threshold value or quality standard are stipulated in the Romanian legislation (Order 161/2006), comprising the list of relevant hazardous substances and priority hazardous. Related to these values, the all obtained concentrations of 4,4'-DDT, ΣDDT regarded as Σ(2,4'-DDT+4,4'-DDT+2,4'-DDE+4,4'-DDE+2,4'-DDD+4,4'-DDD), aldrin, dieldrin, γ-HCH (lindane), Σendosulfan [Σ(endosulfan-α + endosulfan-β)], ΣHCH [Σ(α-HCH+β-HCH+γ-HCH+δ-HCH)] were below their corresponding threshold values.

The concentrations of heptachlor epoxides A and B are not stipulated in the Ministerial Order 161/2006. All the concentrations of hexachlorobenzene (HCB) were below the threshold value set by WFD 60/2000.

OCPs concentrations in sediment samples

Basic statistic for the obtained concentrations of OCPs in surface sediment samples were shown in Table 2. For the calculation of mean and stdev. values, the concentrations below quantification limit were considered as ½ from quantification limit.

Table 2. *Basic statistic for OCPs concentrations in sediment samples (μg/kg dw) in Danube, Jiu and Olt Rivers*

Compound	Min	Max	Mean	Standard Deviation (stdev)
α-HCH	1.00	13.3	5.37	4.81
β-HCH	0.13	0.64	0.24	0.17
γ-HCH	0.33	1.14	0.72	0.28
δ-HCH	0.34	0.61	0.44	0.10
ε-HCH	<0.05	0.32	0.20	0.08
2,4'-DDT	<0.05	0.15	0.04	0.04
4,4'-DDT	<0.05	0.57	0.19	0.23
2,4'-DDE	<0.05	0.23	0.16	0.06
4,4'-DDE	0.16	0.74	0.31	0.20
2,4'-DDD	<0.05	0.93	0.16	0.28

Compound	Min	Max	Mean	Standard Deviation (stdev)
4,4'-DDD	<0.05	0.99	0.36	0.32
Aldrin	<0.05	0.22	0.14	0.07
Dieldrin	<0.05	0.33	0.09	0.11
Heptachlor epoxide A	0.10	0.43	0.23	0.10
Heptachlor epoxide B	<0.05	0.13	0.05	0.04
Endosulfan α	<0.05	<0.05	0.02	0.01
Endosulfan β	<0.05	0.39	0.06	0.12

The concentration of α-, β-, γ-, δ-HCH, 2,4'-DDE, 4,4'-DDE and heptachlor epoxide B were detected in all samples. Also, ΣHCH regarded as [Σ(α-+β-+γ-+δ-+ε-HCH)] ranged between 1.88 (in Jiu River) and 14.81 ng/g dw (in Danube River), with an average of 6.97 ng/g dw and ΣDDT expressed as Σ(2,4'-DDT+4,4'-DDT+2,4'-DDE+4,4'-DDE+2,4'-DDD+4,4'-DDD) ranged between 0.28 (in Danube River) and 3.19 ng/g dw (in Jiu River) with an average value of 1.15 ng/g dw. The total concentration of OCPs in the investigated samples ranged from 2.99 and 16.78 ng/g dw.

Pollution indices

Pollution index represents a powerful tool for ecological assessment. The commonly used pollution indices were classified as: single index and integrated index, in an algorithm point of view (Gong et al., 2008).

For the assessment of the contamination extent in the catchment, several indices were calculated for the OCPs: concentration factor (CF) and degree of contamination for sediments, and also contamination factor and contamination index (C_d) for surface water.

The *concentration factor* (*CF_i*) is defined as (Cabrera et al., 1999, Liu et al., 2005):

$$CF_i = \frac{C_i}{C_{ri}} \quad (1)$$

where:

C_i = the content of the contaminant *i*

C_{ri} = the reference value, baseline or national criteria of contaminant *i.*

For the present work as *C_{ri}* is taken the national criteria of contaminant *i* (the Romanian Normal Value).

The *degree of contamination* (*C_d*) was originally defined as the sum of all concentration factors (Pekey et al., 2004):

$$C_d = \sum_{i=1}^{m} CF_m^i \quad (2)$$

where:

CF^i_{fm} = the single index of concentration factor,

m = the count of the contaminants species.

For the description of contamination degree, the following terminologies have been used:

$C_d < m$	low degree of contamination
$m \leq C_d < 2m$	moderate degree of contamination
$2m \leq C_d < 4m$	considerable degree of contamination
$C_d > 4m$	very high degree of contamination

For surface water quality assessment, the method evaluated in this study is represented by calculation of the Contamination index (Cd) developed by Backman et al. (1998). The C_d is computed separately for each sample of water analyzed, as a sum of the contamination factors of individual components exceeding the upper permissible value. Hence, the C_d summarizes the combined effects of several quality parameters considered harmful to household water. The contamination index is calculated from equation 3:

$$C_d = \sum_{i=1}^{n} C_{fi} \tag{3}$$

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$$

where:

C_{fi} = contamination factor for the i-th component

C_{Ai} = analytical value for the i-th component

C_{Ni} = upper permissible concentration of the *i*-th component (N denotes the 'normative value').

The upper permissible concentration value (C_{Ni}) was taken as the Romanian maximum admissible concentration (MAC).

The organic species with analytical values below the upper permissible concentration value are not considered, since their concentration of heavy metals below this limit does not pose any hazardous problem to the quality of groundwater. The resultant C_d value identifies areas of varying contamination levels which are grouped into three categories as follows:

$C_d < 1$	low
$C_d = 1–3$	medium
$C_d > 3$	high

Pollution indices for sediments

Concentration factor (CF) – total OCPs

The results obtained for the concentration factor of the total OCPs in sediments are presented in the figure 2 and table 3.

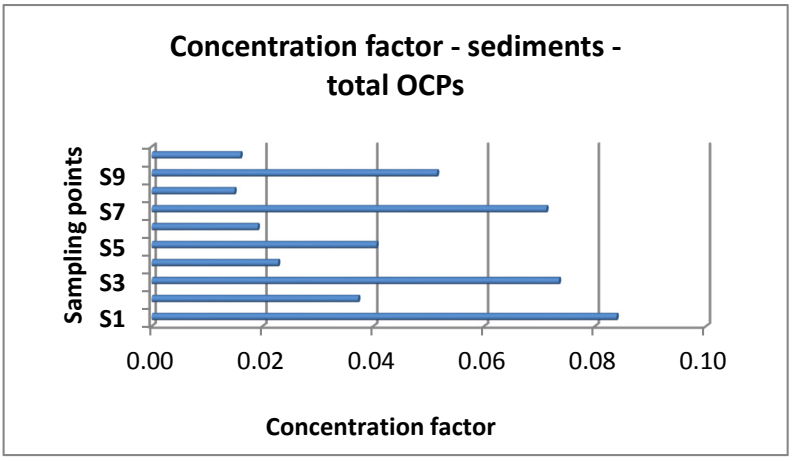

Fig. 2. *The concentration factor – total OCPs – sediments*

Table 3. *The concentration factor of the total OCPs of sediments, in the studied area*

Sampling point	CF Total OCPs
S1	0.08
S2	0.04
S3	0.07
S4	0.02
S5	0.04
S6	0.02
S7	0.07
S8	0.01
S9	0.05
S10	0.02

Pollution indices for water

The results obtained regarding the contamination index of the surface waters concerning the pollution with total OCPs are presented in the Fig. 3 and Table 4.

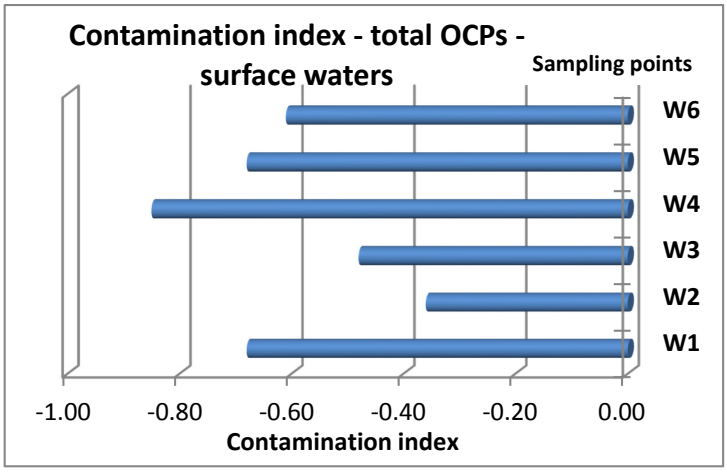

Fig. 3. *The contamination index of the surface water in the studied area – Total OCPs*

Table 4. *The contamination index of the surface water – total OCPs*

Sampling points	W1	W2	W3	W4	W5	W6
Contamination index	-0.68	-0.36	-0.48	-0.85	-0.68	-0.61

The obtained values of pollution indices indicated that Danube, Jiu and Olt Rivers are low contaminated with organochlorine pesticides and they pose no potential risk to the environment, therefore harmful effects are unlikely to occur.

CONCLUSIONS

In this study, the level of contamination with OCPs in surface water and sediment from Danube River (Calafat-Turnu Magurele sector), Romania was studied. The concentrations were below their corresponding threshold values set in Romanian legislation, indicating that harmful effects are unlikely to occur and the calculated pollution indices indicated a low contamination with OCPs of the aquatic environment in the studied area.

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