ORGANOCHLORINE COMPOUNDS (DDT, HCH) CONCENTRATION IN SEDIMENTS COLLECTED FROM THE LOWER SECTOR OF THE ARGES RIVER, ROMANIA

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Introduction

River ecosystems contamination with persistent organic pollution represents an issue that has been reported all over the world, not few cases mentioning serious damages of the ecosystems functionality or even generating important risks to the human communities located in their watersheds. This situation appears mainly in the regions in which agricultural activities are intense and using important amounts of chemical compounds as fertilizers or for pest control[1, 2, 3, 4]. Romania makes no exception, a study on the pesticides occurrence in the water of Danube River and its tributaries emphasising concentrations 1 or 2 order of magnitude higher than in the other countries from the river basin[5].

Although it is the fifth river in Romania in terms of watershed surface, due to the complex usage of the water (water supply for domestic, industrial or agricultural use, fishing, energy producing, leisure) the Arges River holds a watershed with one of the highest anthropogenic influence. The most important tributary is the Dambovita River, which collects all the non-treated wastewaters from the Bucharest and surrounding areas. Arges River is one of the two tributaries of Danube for which gamma-HCH has been reported in water[6].

Although the use of organochlorine pesticides has been banned in most of the European countries and North America since the late '70s or the beginning of the '80s, high amounts are still quantified in samples all over the world, on one hand due to the illegal possession and use in private households and their continuous use in the developing countries[7].

Materials and methods

Samples collection. The sediment samples were collected in March 2006 from four sampling points along the lower part of the Arges River (Hotarele, Gostinari, Radovanu, Clatesti) and two from the main tributaries from the region (Sabar River and Budesti – Dambovita River – See Fig. 1). The sampling points were chosen in order to consider different flowing regimes of the river (in the late '80s, Arges River was planned to become available for navigation, in order to have Bucharest as a harbour in communication with the Danube River – dredging works were performed in the Gostinari sector, bank consolidation etc.), to emphasise the contribution of the main tributaries in terms of pollutants transport and possible pollution sources on the considered sector.

The samples were collected from the upper layer of the sediments bed and were frozen as soon as possible after sampling, prior of being analysed.

Samples processing. Soil samples processing has been performed as it follows: 30 g of wet soil and 30 g of anhydrous Na_2SO_4 were homogenised in a closed vial. After drying, it was well grinded in a pestle and then stirred for 30 minutes in a shaker. 50 mL of hexane has been added and stirred for 30 minutes. The sample was filtered on a 0,45 μ paper and collected in a 500 ml separation funnel containing 250 mL of distilled water. The funnel was stirred for 5 minutes, the aqueous layer was eliminated and the organic extract was again washed with 250 mL of distilled water. The organic extract was finally passed over anhydrous Na_2SO_4.

The filtrate volume was measured and then was chromatographied on fluorisyl column (80-100 mesh), for purification, as it follows: the column was washed with 50 mL hexane (4 mL/min), then the sample was passed through the column with a rate flow of 3 mL/min. The column was eluted with 50 mL hexane and the first fraction was collected (non-polar compounds). Then, another 75 mL hexane containing 5% ethylic ether were passed, and the second fraction was collected (organochlorine pesticides).

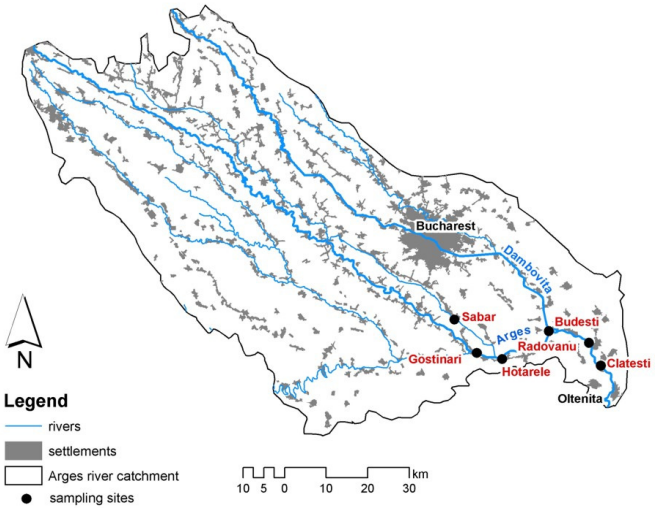

Fig. 1. Location of the samples collection sites.

The column was finally washed with another 75 mL hexane with 50% ethylic ether content, in order to remove any remained polar compound. The eluted fractions were evaporated and then dissolved in 1 mL petroleum ether and hexane and a volume of 5 – 10 µL was injected to the chromatographic column. A pesticide standard was also injected into the column.

Method of analysis. The organochlorine pesticides that were extracted from the samples were determined by electron capture detector gas chromatography (GC - ECD). The following analytes were determined: hexachlorocyclohexane – HCH (4 isomers – alpha, beta, gamma, delta), Aldrin, Endrin, Endrin Aldehyde, 4, 4' – dichlordiphenyltrichlorethane (4, 4' – DDT), 4,4' – dichlordiphenyltrichlorethylene (4, 4' – DDE), 4, 4' – dichlorodiphenyldichloroethane (4, 4' – DDD).

A CARLO ERBA gas-chromatograph was used, equipped with a packed column, splitless injector and Electron Capture Detector. The mobile phase was N_2. The operational parameters are shown in Table 1. The detection limit was of 1 ng/g.

Table 1. Operational parameters of the instruments

Pressure:	**Temperature:**	**Column**
Column: 0,8 kPa	**Column:** 215 ^{0}C (Starting temperature 30 ^{0}C, temperature gradient – 9,5 ^{0}C/min, 5 minutes stationary temperature)	Glass (L = 1,85 D. I. 3 mm), package 1,5% OV17; 1,95%% QF-1, bonded on Chromosorb PAW-DMCS 0,125 - 0,150 mm.
Detector: 1,5 kPa	**Detector:** 275 ^{0}C	
	Injector: 225 ^{0}C	

Results and discussions

The concentrations of the considered analytes in the sediments of the Arges River are presented in the Table 2. The comparison for the DDT group and gamma-HCH has been made with the threshold effect level (TEL) and probable effect level (PEL) (as defined by Smith et al., 1996[8]) from MacDonald et al. (2000)[9]. For Endrin, the Canadian references were used[10].

Table 2. Organochlorine pesticides concentration in the sediments samples (ng/g dryweight)

	Sabar	Gostinari	Hotarele	Radovanu	Dambovita	Clatesti	TEL	PEL
Alpha-HCH	1,047	1,299	2,060	2,397	1,297	4,009	–	–
Beta-HCH	3,658	2,435	1,929	10,873	2,086	11,462	–	–
Gamma-HCH	3,310	1,639	2,588	11,686	3,133	7,242	0.94	1.38
Delta-HCH	3,133	2,971	3,913	18,943	5,316	7,995	–	–

∑HCH	11,148	8,344	10,49	43,899	11,832	30,708	–	–
Aldrin	1,092	1,157	2,301	6,388	3,036	8,256	–	–
Endrin	38,817	102,87	2,673	1,146	44,151	8,443	2.64	62.4
Endrin Aldehyde	4,452	6,268	5,074	2,187	2,082	3,635	–	–
4, 4' – DDE	11,966	8,951	13,117	31,197	16,584	39,741	1.42	6.75
4, 4' – DDD	9,725	2,838	4,242	34,559	18,825	20,320	3.54	8.51
4, 4' – DDT	46,757	33,555	44,395	115,724	64,100	130,302	NG*	NG*
∑DDT	68,448	45,344	61,754	181,48	99,509	190,363	7	4450
DDT/DDE	3,9075	3,749	3,38454	3,709	3,865	3,279	–	–
DDT/DDD	4,8079	11,823	10,46558	3,3486	3,4050	6,4125	–	–

* NG – No Guideline; "–" not available

The data has been statistically tested for normality, distribution with Skewness test and the results are shown in Table 3.

Table 3. Statistical analysis of the results.

	Mean	Confidence limit		Range	Variance	Standard deviation	Standard error	Skewness test
		–95%	**+95%**					
Alpha-HCH	2.01817	0.860	3.176	2.9620	1.218	1.10355	0.45052	1.402292
Beta-HCH	5.40717	0.677	10.137	9.5330	20.311	4.50683	1.83990	0.901084
Gamma-HCH	4.93300	0.919	8.947	10.0470	14.632	3.82513	1.56160	1.401826
Delta-HCH	7.04517	0.624	13.466	15.9720	37.433	6.11825	2.49777	1.993274
Aldrin	3.70500	0.604	6.806	7.1640	8.730	2.95462	1.20622	0.885369
DDE	20.25933	7.318	33.200	30.7900	152.069	12.33164	5.03437	1.003376
Endrin	33.01683	-7.837	73.871	101.7250	1515.518	38.92965	15.8930	1.359108
DDD	15.08483	2.519	27.651	31.7210	143.384	11.97430	4.88849	0.754084
DDT	72.47217	29.846	115.09	96.7470	1649.849	40.61834	16.5824	0.786302
Endrin Aldehyde	3.94967	2.220	5.679	4.1860	2.717	1.64835	0.67294	0.133019

The set of data are quite heterogeneous, especially for the DDT and Endrin Aldehyde, but it is necessary to mention that the sampling was influenced by the flooding that affected the river regime during the sampling period – which might induce changes in the oxygenation rate and dislodging of the sediments from the river bed.

Depending on the oxygen conditions, DDT can be metabolised to DDD (reducing environment) or DDE (aerobic conditions), the resulting degradation product being a clue in what regards one of the two metabolism paths [11, 12].

Very interesting is the fact that even if there are big differences between the concentration of DDT, DDE, DDD and ∑DDT in each sample (Table 3), the DDT/DDE report variation is rather reduced, which might suggest that the percentage of each compound is similar in all the samples and their concentration is influenced by factors like river regime, concentration of dissolved oxygen and dissolved organic matter[13] or the organic matter content of the sediments bed[14] rather than the different metabolic activity of the microorganisms in sediments.

The reports DDT/DDD and DDT/DDE can provide sometimes information of the relative degree of degradation and subsequently of the period of time the DDT residues are present in the analysed sample(s) [15, 16]. For the samples collected from the Arges River lower sector, the values of the two reports vary between 3.279 and 3.9075 (DDT/DDE) and 3.3486 and 11,823 (DDT/DDD). These data may lead to the conclusion that the DDT introduction in the environment has been performed more recent than the period when it was officially banned in Romania[17] (for a half-life time of DDT of approximated to a period of 20 years under moderate climatic conditions[18]). In Dambovita River, the important content or dissolved organic matter provided by the untreated wastewater input that generated local anoxic conditions determined a predominance of the anaerpbic transformation of DDT.

Of a great concern are the important amounts of alpha and beta HCH, reported to be toxic for mammals and fish species[19]. The presence of both DDT and HCH in the samples is not surprising, as the literature mentions that the use of lindane (gamma isomer of HCH) was performed in Romania as mixtures with other pesticides, DDT being one of them[20].

The comparison with the standard values (where available) are emphasising that threat posed by the sediments to the aquatic ecosystem. Thus, the DDE and lindane (gamma-HCH) concentration exceeded the probable effect level in all the analysed samples, while just 4 of the 6 samples exceeded the PEL for DDD. Just one of the samples for Endrin exceeded the probable effect level for the freshwater sediments.

Conclusions

The pesticides analyses performed on sediments samples collected from the Arges River ecosystem emphasised a significant contamination of this component of the aquatic environment which might pose o great risk on the aquatic biota. Despite the big differences between analytes concentrations in different samples, the DDT/DDE report seems to be quite constant across the analysed sector. An influence of the flooding that affected the river, which induced changes in the oxygenation rate and dislodgement of the sediments from the riverbed, was also stressed out by the results. Nonetheless, the Dambovita River water significantly influences the environmental fate of the organochlorine pesticides from the riverbed sediments.

The DDT/DDE and DDT/DD reports were higher than unit, which might support the presumption that although they have been officially banned, the organochlorine pesticides, mainly DDT and gamma-HCH are still illegally used in private households.

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References

1. Brown, LR, *Arch. Environ. Contam. Toxicol.* 1997, 33: 357–368
2. Gil, O and Vale, C, *Aquatic Ecology* 1999, 33**:** 263–269
3. Hyland, JL, Balthis, WL, Hackney, CT and Posey, M, *Journal of Aquatic Ecosystem Stress and Recovery* 2000, 8**:** 107–124
4. Anh, MT, Hong, LCD, Nguyen, NV, Thi, CLT, Minh, TL, Becker-Van Slooten, K and Tarradellas, J, *Chimia*, 2003, 57: 537–541
5. Holoubek, I , Kočan, A, Holoubková, I, Hilscherová, K, Kohoutek, J, Falandysz, J, Roots, O, *Persistent, Bioaccumulative and Toxic Chemicals in Central and Eastern European Countries - State-of-the-art Report,* 2000, Brno, Czech Republic
6. Bujis, L, Uzunov, Y, Tčankov, K, *Water quality profile of the Danube river along the Bulgarian-Rumanian stretch,* 1992, ICWS Report, Amsterdam, The Netherlands
7. Forget, G, J. *Toxicol. Environ. Health*, 1991, 32: 11–31
8. Smith, SL, MacDonald, DD, Keenleyside, KA, Ingersoll, CG, Field, J, *J. Great Lakes Res*., 1996, 22: 624–638
9. MacDonald, DD, Ingersoll, CG, Berger, TA, *Arch. Environ. Contam. Toxicol.*, 2000, 39: 20–31
10. Canadian Council of Ministers of the Environment, Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, 2002, www.ccme.ca/assets/pdf/e1_06.pdf
11. Garrison, AW, Nzengung, VA, Avants, JK, Ellington, JJ, Jones, WJ, Rennels, D and Wolfe, NL, *Environ. Sci. Technol.* 2000, 34: 1663 – 1670
12. Meikle, RW, 1972, *Decomposition: Qualitative Relationships in Organic Chemicals in the Soil Environment*, Vol. 1, Goring, C. A. I. and Hamaker, J. W. (eds.) Marcel Dekker, New York
13. Van den Hoop, MAGT, Kreule, P and Loch, JPG, *Water, Air, and Soil Pollution*, 1999, 110**:** 57–66
14. Karickhoff, SW, Brown, DS and Scott, TA, *Water Res*, 1979, 13: 241–248
15. Vashchenko, MA, Syasina, IG and Zhadan, PM, *Russian Journal of Ecology*, 2005, 36 (1): 57–61
16. Tavares, TM, Beretta, M and Costa, MC, *Chemosphere*, 1999, 38: 1445–1452
17. Comanita, E, Soldea, C, Dumitrescu, E, *Chimia si tehnologia pesticidelor*, Ed. Tehnica, Bucuresti, 1986, Cap. 3
18. Martijn, A. Bakker, H. and Schreuder, R. H.: 1993, *Bull. Environ. Contam. Toxicol.* 51, 178
19. Willett KL, Ulrich EM and Hites, RA, *Environ. Sci. Technol.* 1998, 32: 2197–220
20. Baicu, T, Alexandri, AV, *Îndrumar pentru folosirea pesticidelor*, Ed. Ceres, Bucureşti, 1973, 20