Specific organic pollutants in Serbian rivers-current state and the actions required

Ivana Ivančev-Tumbas[1], Emira Maljević[2], Jelena Tričković[1], Aleksandra Tubić[1], Jelena Molnar[1], Branislav Gavrić[2], Zoran Stojanović[2]

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1 Introduction

In accordance with the Water Framework Directive (WFD, 2000/60/EC) specific pollutants are all priority substances and other substances identified as being discharged in significant quantities into water bodies. The list has to be identified during development of the River Basin Management Plan. Both priority pollutants and specific organic pollutants are just a part of the puzzle called "organic micropollutants in water". Those chemicals are released into the aquatic environment by various routes (e.g. inadequate or insufficient waste and wastewater treatment, agriculture). According to the literature (Schwarzenbach et al., 2006: Loos et al., 2009) there are more than 100,000 registered chemicals in the EU, of which 30,000-70,000 are in daily use. Emerging compounds that enter the environment in various ways differ in biodegradability, emission loads and the effects they can cause to aquatic eco-systems and humans. They might be polar or non polar in their nature. In both groups one can find persistent compounds. If they are not persistent their continuous emission or transformation products might pose a problem. Their presence in water in small concentrations and in various mixtures is a great challenge for research related to both their effects in eco-systems and implementation of appropriate water treatment technologies (Schwarzenbach et al., 2006). Traditionally persistent organic pollutants (POPs) are hydrophobic molecules that tend to accumulate in sediments and enter food chains with a tendency to accumulate in organisms. Recently the significance of polar compounds has also been shown: polar herbicides, pharmaceuticals, complexing agents, surfactant metabolites etc. (Reemtsma & Jekel, 2006; Loos et al., 2010), which endanger water quality and might have a negative impact on water supply sources. Although the WFD is not yet implemented in Serbia, a certain amount of data referring to some organic pollutants has been obtained by official monitoring programmes of the Republic Hydrometeorological Service of Serbia (RHMS). This paper presents an overview relating to the presence of specific organic pollutants in Serbian watercourses obtained by the RHMS in 2004-2008 and the results of several GC/MS screening surveys performed by the Faculty of Sciences, Novi Sad.

2 Official monitoring performed by the Republic Hydrometeorological Service of Serbia

The hydrographic network of the Republic of Serbia is part of the Danube River Basin; it can be further divided into several sub-basins: the basins of the River Tisa, the River Sava, the Hydrosystem Danube-Tisa-Danube, the River Drina, the River Velika Morava, the River Zapadna Morava and the River Južna Morava. Between 2004-2008, RHMS monitored in total 17 pesticides and PAHs (fluoranthene,

1 Department for Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg D. Obradovica 3, 21000 Novi Sad, Republic of Serbia, e-mail: ivana.ivancev-tumbas@dh.uns.ac.rs
2 Republic Hydrometerological Service of Serbia, Kneza Višeslava 66, 11000 Belgrade, Republic of Serbia, e-mail: emira.maljevic@hidmet.gov.rs

benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)-perylene, indeno (1,2,3-c,d)-pyrene). Since 2005, PCBs were also included in the programme (PCB 28, 52, 101, 138, 153, 180 and 194). Among those compounds, 9 pesticides, 6 PAHs and fenanthrene are listed in Annex I of Directive 2008/105/EC. Additional data was collected regarding heptachlor, heptachlor epoxide, DDE, p,p'DDD, o,p'-DDT and methoxychlor. During 2009, the official monitoring programme was changed adding 20 new parameters: pentachlorophenol, octylphenol, nonylphenol, hexachlorobutadiene, pentachlorobenzene, terbutryne, prometryne, desethylatrazine, desisopropylatrazine, chlorphenvinphos, chlorpyriphos, alachlor, diuron, linuron, monuron, isoproturon, α-endosulphane, β-endosulphane, isodrin, trifluralin. Among those compounds, 14 are from the list of priority substances and 6 are additional. However, another 14 organic pollutants from the list of priority substances, including certain other pollutants, are still not included in the monitoring programme: anthracene, benzene, brominated diphenylether, carbon-tetrachloride, chloroalkanes, 1,2-dichlorethane, dichlormethane, di(2-ethylhexyl)-phtalate, naphthalene, tetrachloro-ethylene, trichloro-ethylene, trichloro-benzenes, tributyltin compounds and trichloro-methane.

The results analyzed below originate from the official monitoring and represent a synthesis of 139 sampling sites, located on 66 rivers. The monitoring was performed with a sampling frequency of 0-12 samples per year per location; the list of analytical methods is presented in Table 1.

Table 1. *Analyzed organic pollutants and their corresponding methods of analysis*

Parameter	**Analytical Method**	**Limit of detection**
Pesticides		μg/l
αHCH, βHCH, Lindane, Hexachlorbenzene, Heptachlor, Heptachlorepoxide, Aldrin, Endrine, Dieldrine, DDE, p,p'-DDD, p,p'-DDT, o,p'-DDT, Metoxychlor	1. EPA Method 8081A (GC-ECD), 2. EPA Methods: 8270 and 3510 (GC-MS, liquid-liquid extraction)	0.001, 0.001, 0.002, 0.001, 0.001, 0.001, 0.001, 0.002, 0.002, 0.002, 0.002, 0.002, 0.002, 0.003
Atrazine, Simazine, Propazine	1. EPA Method 507, Determination of Nitrogen- and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector 2. EPA Methods: 8270 and 3510 (GC-MS, liquid-liquid extraction)	0.009 0.0020, 0.0030, 0.0015
PCB		
PCB 28, 52, 101, 138, 153, 180, 194	1. EPA Method 8082A (GC-ECD), 2. EPA Methods: 8270 and 3510 (GC-MS, liquid-liquid extraction)	0.001 0.0002-, 0.0002, 0.0003, 0.0002, 0.0002, 0.0002, 0.0003
PAH		
Fluroanthene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Benzo (g,h,i) perylene, Indeno (1,2,3-c,d)pyrene	1. EPA Method 8100, Summary: Polynuclear Aromatic Hydrocarbons (GC-FID) 2. EPA Methods: 8270 and 3510 (GC-MS, liquid-liquid extraction)	0.1 0.0001-0.0002

The total number of samples analyzed between 2004-2008 increased (Fig.1), and an increasing trend was recorded for the number of locations with at least one positive finding (Table 2). The term "positive finding" is used for samples where at least one compound was detected above the limit of detection of the method used. The list of pesticides detected between 2004-2008 is presented in Table 3. The most frequently detected pesticides in 2006 were hexachlorobenzene with a positive finding in 47 samples (15% of the analysed samples), followed by DDE in 34 samples (11% of total number of samples) and heptachlor in 20 samples (6% of total number of samples). In 2007, the highest frequency was recorded for triazine herbicides and β-HCH (40% of positive samples for atrazine, 12% propazine, 8% simazine, 6% β-HCH), while in 2008, the most abundant were triazine herbicides (49% of samples was positive for atrazine and 3% for simazine and propazine). In general, only a small number of samples exceeded the annual average environmental quality standards (EQS) for inland surface waters (2008/105/EC). The comparison was made based on each sample concentration and not on the annual averages.

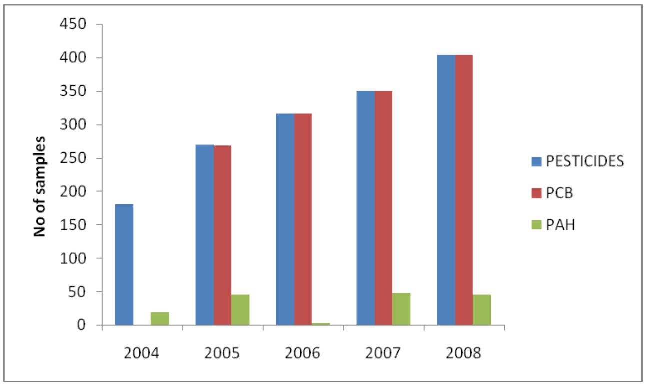

Figure 1. *Total number of annual analyses*

Table 2. *Number of locations with positive pesticide findings*

Year	Investigated locations	Positive locations	Ratio of positive locations (%)
2004	94	4	4.3
2005	100	12	12
2006	111	65	58.6
2007	114	81	71.1
2008	101	79	78.2

Table 3. *Number of positive samples*

	2004	2005	2006	2007	2008
Total number of samples	181	269	316	350	404
α-HCH	0	0	1	3	2
β-HCH	0	0	4	20	8
Lindan	2	3	11	8	0
Hexachlorbenzene	0	1	47	9	0
Heptachlor	0	5	20	15	0
Heptachlorepoxide	0	0	18	17	0
Aldrin	0	4	13	4	0
Endrin	0	0	12	5	1
DDE	1	0	34	6	4

Dieldrin	0	0	9	10	1
p,p'-DDD	0	0	6	11	1
p,p'-DDT	0	0	8	4	3
o,p-DDT	0	0	3	0	0
Metoxychlor	0	0	14	11	8
Atrazine	0	0	4	141	197
Simazine	0	0	0	27	14
Propazine	0	0	1	42	14

In total, there were 11 samples above EQS in 2006, 15 samples in 2007 and 3 samples in 2008; the values are listed in Table 4. For all other samples, positive findings values were below EQS. The concentrations of compounds which are not regulated by Directive 2008/105/EC were below 0.1 µg/l which is the maximum allowed concentration for drinking water. Regarding positive findings for PAHs and PCBs, there was 1 positive sample for PAHs in 2007 and 11 positive samples in 2008. There were 4 positive samples for PCBs in 2006, 4 in 2007 and 1 in 2008.

Table 4. *Pesticides concentrations above AA-EQS (Directive 2008/105/EC)*

Year	Results	AA-EQS [µg/l]
2006	**Hexachlorbenzene**: 3 samples with 0.011µg/l **Aldrin**: 1 sample with concentration 0.27 µg/l and 1 sample with 0.018 µg/l **DDT**: 1 sample 0.04 µg/l, 1 sample 0.053 µg/l **Atrazine**: 1 sample 0.889 µg/l and 1 sample 0.612 µg/l ***Pesticides not included in Dir. 2008/105/EC, above 0.1 µg/l*** **DDE**: 1 sample with concentration of 0.146 µg/l **Propazine**: 1 sample with value 0.1 µg/l	0.01 0.01 sum for cyclodiene pesticides 0.025 (total) 0.6
2007	**Dieldrin**: 5 samples (0.025-0.195 µg/l) **Endrin**: 2 samples (0.01 and 0.023 µg/l) **DDT**: 1 sample 0.087 µg/l **Atrazine:** 3 samples (0.6-2.4 µg/l) ***Pesticides not included in Dir. 2008/105/EC, above 0.1 µg/l*** **Methoxychlor:** 1 sample 0.931 µg/l and 1 sample 1.1 µg/l **Heptachlor:** 1 sample 0.24 µg/l **Propazine:** 1 sample 0.11 µg/l	0.01 sum for cyclodiene pesticides 0.025 (total) 0.6
2008	**Atrazine**: 1 sample 0.805 µg/l and 1 sample 0.788 µg/l ***Pesticides not included in Dir. 2008/105/EC, above 0.1 µg/l*** **Methoxychlor:** 1 sample 0.122 µg/l	0.6

3 Results of GC/MS screening surveys performed by the University of Novi Sad Faculty of Sciences

GC/MS screening surveys are a useful tool for tentative identification of a great variety of organic xenobiotics. The University of Novi Sad, Faculty of Sciences has performed several such surveys in the territory of the Autonomous Province of Vojvodina since 2004. A hydrographic characteristic of this region is its dense network of canals within the DTD Hydrosystem (a total length of 20,000 km). Non-purified or insufficiently purified wastewaters are discharged to the watercourses. They originate from about 500 point sources and agriculture as an important diffuse source of pollution. One of the earliest surveys was the investigation of organic xenobiotics in the Vrbas region which represents a “hot spot” with respect to contamination of the canals of the DTD Hydrosystem by industrial wastewaters (Ivančev-Tumbas, 2004). Various compounds were identified: phthalates, phenols (also including nonyl phenol), hydrocarbons, benzene derivates, methyl esters of fatty acids, PAHs and caffeine. Tentative identification was made after liquid-liquid extraction by HP5890 GC series II with 5971 MSD. Recently, screening of the Krivaja River (109 km) and the Tisa River was performed. Details on methodology and results are given in Agbaba et al., 2008, Ivančev et al., 2008. An Agilent Technologies 7890 A GC system with a 5975C Mass Selective Detector was used for screening. Results evaluation was made by Deconvolution Reporting Software (DRS) which combines the results from the Agilent GC/MS Chemstation with the NIST Mass Spectral Library and Automated Mass Spectral Deconvolution and Identification System (AMDIS). Search matches for all identified compounds were higher than 70%. The main classes of organic chemical compounds tentatively identified in the Krivaja River were hydrocarbons, phthalates, aldehydes, alcohols and their derivates, organic acids and esters, PAHs, substituted PAHs and phenols. Some of the identified compounds are priority pollutants: anthracene, atrazine, benzene, di-(ethylhexyl)-phthalate (DEHP), fluoranthene and naphthalene. Additionally, several emerging contaminants were tentatively identified as being present: organophosphate flame retardants (tributyl phosphate), personal care products (benzophenone), pesticides (carbofurane and atrazine), fragrances (vanillin), antioxidative agents (p-tert-butyl phenol) and caffeine, the detailed results being presented in Agbaba et al., 2008. In the Tisa samples, tentatively identified compounds were aromatic and aliphatic hydrocarbons, toluene, styrene, acetamide, indene, acetophenone, 1,4-dichlorbenzene, phenol and its derivates, vanillin, various phthalates, DEHP, fluorene, organic alcohols and organic acids, benzothiazole, tributyl phosphate, diphenylamine, benzophenone, anthracene, caffeine, pyrene, cholesterol, squalene, etc. In total, 81 compounds were identified, the results being presented in Ivančev-Tumbas et al. (2009).

4 Conclusions

The data presented in this paper shows that there is a certain number of positive pesticide findings in Serbian watercourses, as well as the presence of some other priority and emerging pollutants. The content of pesticides in rivers exceeded the annual average values defined by Directive 2008/105/EC in a very small number of samples (3.5% in 2006, 4.3% in 2007 and 0.7% in 2008). However, further revision of the Serbian list as well as the frequency and objectives of the official monitoring programme is required in accordance with EU lists and EU water policy. The presence of the tentatively identified compounds has yet to be confirmed and further investigation on the presence and relevance of organic micropollutants must be undertaken.

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