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Organic pollution in sediment-water systems on the Ratno Ostrvo location in Novi Sad, Serbia and Montenegro

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ABSTRACT: Two-year (2001-2002) monitoring was conducted to determine residues of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in sediment-water systems of three types of watercourses on the location of Ratno Ostrvo in Novi Sad (Serbia and Montenegro). Types of watercourses were established on the basis of the flow regime: drainage ditches with 1-2 m^3/s (four sampling points), the DTD Canal with up to 10 m^3/s (three sampling points) and the Danube River with 1500-3000 m^3/s (five sampling points). Water quality was compared with the requirements given by the national and Dutch regulations, and the quality of sediment with the Dutch and Canadian quality guidelines, due to the lack of national legislaton. Based on the concentrations of organic pollutants in the samples of sediments and water from selected sampling points, average annual values were computed for the three types of watercourses. Great differences regarding the level of pollution between two years of monitoring were in smaller watercourses – drainage ditches and the DTD Canal, which might be a consequence of water flow, increased anthropogenic activity, decrease of self-purification potential. Concentrations of both PAHs and pesticides were below national maximum permissible levels in water and below Dutch intervention levels in sediment. Standard deviations of average annual concentrations were very high (up to 30-300%), probably because of the increased anthropogenic effect.

KEYWORDS: monitoring, polycyclic aromatic hydrocarbons, pesticides, water, sediment

Introduction

The location of “Ratno Ostrvo” is of the paramount importance for the City of Novi Sad, because here, on the Danube alluvion, are located the wells of the water supply for preparation of drinking water for the city population. However, it is situated in a very risky surroundings endangering the water source quality, which at the present has no alternative water source. The water catchment “Ratno Ostrvo” stretches along the left bank of the Danube River, from the confluence of the Danube-Tisza-Danube (DTD) canal further downstream in a total lenght of about 400 m. The whole area of Ratno Ostrvo lies on a generally flat land consisting of sedimentary plain of the Danube (Holocene). The alluvial deposits (Danube terraces) consist of sand and silty clay more or less interbedded. The major bed of the Danube consists of mixed mud and sand. A large old meander of the Danube is visible on the north-east of the City, surrounding a big plain where the Oil Refinery and the water catchment “Ratno Ostrvo” are located. Besides large meander some other old sedimentary structures, somewhat smaller, are possibly existing and may cause bypass of high permeability in a relatively more impervious matrix. In terms of hydrogeology, the area consists mostly of an alluvial plain of gravely sandy-silt deposits, which are more or less permeable. The impervious basal layer consists of clays. The groundwater aquifer, spread in whole area of “Ratno Ostrvo” has a very high permeability (around 10 E-3 m/sec) and a high vulnerability to superficial pollution. At the west border of the water supply source there is Oil Refinery “Novi Sad”, which was bombed several times during the NATO campaign in the period March-June 1999. In the vicinity there are heating plant, residential area Šangaj, discharge points of the municipal sewer system and the inflow of the DTD canal (with several industrial discharges of treated water) into the Danube further upstream (south border of the “Ratno Ostrvo”). Parallel to the series of wells, wastewater collector for carrying storm and oiled treated water from the Oil Refinery has been constructed [1]. This wastewater collector discharges into the Danube. At the Ratno Ostrvo area there are numerous drainage ditches.

Within the policy of water protection the European Union replaced the “user” approach by “ecosystem” approach in 1992 [2]. The EU Framework Directive (2000) [3] acquires “combined” approach within integrated water management of river basins. For the first time it emphasises the importance of the sediment quality for the entire aquatic system, but for the time being the EU does not regulate the quality criteria [4]. The Netherlands and Canada have long legislative tradition in this area. They have developed criteria and regulations on sediment quality [5-11]. In Serbia and Montenegro there is no continual monitoring of the sediment quality, and neither there are regulations concerning the quality standards. Harmonization of the legislation in the filed of environmental protection with EU requirements will increase the significance of the monitoring activities regarding this issue. The monitoring is equally important in various stages of environmental quality improvement during integrated water management and, if necessary, in all stages of restoration (planning, during and after the restoration) [12]. Water Framework Directive deals with three types of monitoring activities: surveillance, operational and investigative monitoring. Lot of data for European rivers have been gained regarding nutrients and organic loads (in terms of BOD) [13] and monitoring is broadened to micropollutants as well [14, 15]. Beside industrial acitivities lot of problems still origins from illegal dumps, runnoffs, railroads, insufficient treatment of the sewage, usage of the septic systems, diffuse pollution due to the use of pesticides and fertilizers in farming activities.

The aim of this work was to collect the data on specific organic pollution in surface waters (PAHs and organochlorine pesticides) at the sensitive area of Ratno ostrvo in Novi Sad (at the banks of the Danube River) through two-year surveillance monitoring. These data should serve as the basis for decision making on futher improvement of the environment quality.

Materials and methods

Two-year (2001-2002) monitoring was conducted to determine PAHs and organochlorine pesticides in sediment-water systems of three types of watercourses on the location of Ratno Ostrvo in Novi Sad (Serbia and Montenegro). Types of watercourses were established on the basis of the flow regime: drainage ditches with 1-2 m^3/s, the DTD Canal with up to 10 m^3/s and the Danube River with 1500-3000 m^3/s. Water and sediment quality was compared with the requirements given by the national, Dutch and Canadian regulations [5, 6, 11, 16]. Monitoring network consisted of four sampling sites at drainage ditches, five locations at the river Danube (at the river kilometers: 1270, 1257, 1255, 1250 and 1240) and three locations at the DTD Canal (0+550, 0+650 and 0+800).

Measurements were carried out two times in a quarter: I (March – April), II (May – June), III (August – September) IV (November – December). Water sampling was performed according to the standard procedure [17]. Sediment samples were taken with the aid of the Eckman sediment sampler. PAHs and pesticides in water were measured after the solid phase exctraction [18], by GC/MS analysis according to modified method 6410 B [19]. Details of the method can be found elsewhere [20]. After completing the procedure of sediment sample preparation (extracting, adding copper, fractionation and concentration) extracts were analysed by HP 5890GC SERIES II with 5971 MSD pursuant to splitless procedure. Results were calculated on dry weight of sediment.

Results and discussion

Based on the concentrations of organic pollutants in samples of sediment and water from selected sampling points, average annual values were computed for the three types of watercourses. The results are given in Tables 1, 2 and 3.

Water from the drainage ditches in year 2002 was mostly polluted with PAHs (average annual concentration was 570 ng/l) and pesticides (average annual concentrations: aldrin-20 ng/l, dieldrin-17 ng/l and delta HCH-120 ng/l). National standard for six cancerogenic PAHs is 200 μg/l in water. Concentrations of the most abundant PAHs for the year 2002 (fluorene, phenanthrene, anthracene) are not regulated by the national low [16]. According to the national legislative the quality of water is satisfactory. Contents of anthracene, phenanthrene and benz(a)anthracene exceeded the Dutch values for maximum permissible level (MPL) [4]. Significant difference between two years for the drainage ditches might be a consequence of anthropogenic influence.

Regarding sediment quality (Tables 2 and 3) significant differences were observed between two years for all types of watercourses.

The highest difference was observed for the watercourses with smaller waterflow. For the year 2001 average annual concentration of PAHs was the highest in the Danube sediment (440 ⎕g/kg). In the second year of this study, the concentration of PAHs in both draining ditches and Canal DTD showed an increase (measured concentrations were 2100 and 1800 μg/kg, respectively). High concentrations in drainage ditches were in accordance with higher concentrations observed in water, while for the DTD Canal only sediment was more polluted. Sediment from the Danube had lower concentration in year 2002 (120 μg/kg) compared to the year 2001. Some PAHs (phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene) were detected most frequently with average annual concentration from 4.2 to 450 mg/kg. Dutch intervention value is 40 mg/kg for ten selected PAHs [5]. This intervention value is defined for standard sediment (10% organic matter and 25% clay). Comparing measured values to Canadian sediment quality guidelines [6] it can be concluded that PAH concentration theoretically can have possible effect (it is above interim sediment quality guideline-ISQGs). Some locations within the same watercourse type had significant differencies. So, high concentration of PAHs was found in Koviljski rit (average annual concentration-840 mg/kg), most probably due to slow water flow of the Danube. Also high concentrations of PAHs were found at the pump station “Kalište” (average annual concentration-6700 mg/kg), due to acumulations formed at all drainage ditches at the end of the drainage system before its discharge into the Danube.

Table 1. Average annual values for PAHs and pesticides concentrations in water (ng/l) with standard deviations (±sd) and number of measurements (n).

Parameter	Units	Drainage ditches		Danube		Canal DTD	
		2001	2002	2001	2002	2001	2002
		$\bar{x}$ ± sd, (n)					
Naphtalene	ng/l	8.2±28 (12)	5.7±19 (15)	<2.2 (20)	<2.2 (8)	<2.2 (4)	<2.2 (9)
Acenaphthylene		<2.7 (12)	11±28 (15)	<2.7 (20)	<2.7 (8)	<2.7 (4)	<2.7 (9)
Acenaphthene		<1.3 (12)	26±73 (15)	<1.3 (20)	<1.3 (8)	<1.3 (4)	<1.3 (9)
Fluorene		<4.0 (12)	180±480 (15)	<4.0 (20)	<4.0 (8)	<4.0 (4)	<4.0 (9)
Phenanthrene		<1.5 (12)	220±820 (15)	<1.5 (20)	<1.5 (8)	<1.5 (4)	3.9±8.1 (9)
Anthracene		<1.7 (12)	110±420 (15)	<1.7 (20)	<1.7 (8)	<1.7 (4)	<1.7 (9)
Fluoranthene		<3.4 (12)	<3.4 (15)	<3.4 (20)	<3.4 (8)	<3.4 (4)	<3.4 (9)
Pyrene		<3.4 (12)	13±30 (15)	<3.4 (20)	<3.4 (8)	<3.4 (4)	<3.4 (9)
Benz[a]anthracene		<2.5 (12)	13±29 (15)	<2.5 (20)	<2.5 (8)	<2.5 (4)	<2.5 (9)
Chrysene		<1.9 (12)	3.7±12 (15)	<1.9 (20)	<1.9 (8)	<1.9 (4)	<1.9 (9)
Benzo[b]fluoranthene		<4.5 (12)	<4.5 (15)	<4.5 (20)	<4.5 (8)	<4.5 (4)	<4.5 (9)
Benzo[k]fluoranthene		<4.5 (12)	<4.5 (15)	<4.5 (20)	<4.5 (8)	<4.5 (4)	<4.5 (9)
Benzo[a]pyrene		<4.1 (12)	<4.1 (15)	<4.1 (20)	<4.5 (8)	<4.5 (4)	<4.5 (9)
ΣPAHs		10±14 (12)	570±910 (15)	3.9±6.3 (20)	0.2±0.3 (8)	1.2±1.0 (4)	6.2±8.1 (9)
Aldrin		<5.0 (12)	20±15 (15)	<5.0 (20)	<5.0 (8)	<5.0 (4)	<5.0 (9)
Dieldrin		<5.0 (12)	17±64 (15)	<5.0 (20)	<5.0 (8)	<5.0 (4)	<5.0 (9)
4,4'-DDT		<5.0 (12)	<5.0 (15)	<5.0 (20)	<5.0 (8)	<5.0 (4)	<5.0 (9)
delta-BHC		<5.0 (12)	120±390 (15)	<5.0 (20)	<5.0 (8)	<5.0 (4)	<5.0 (9)
Endrinaldehyde		<5.0 (12)	<5.0 (15)	<5.0 (20)	<5.0 (8)	<5.0 (4)	<5.0 (9)

Table 2. Average annual values of PAHs concentration in sediment of water courses (mg/kg) standard deviations (±sd) and number of measurements (n).

Parameter	Canadian theoret. possible effect level (ISQSs)		Drainage ditches 2001	Drainage ditches 2002	Danube 2001	Danube 2002	Canal DTD 2001	Canal DTD 2002
			$\bar{x}$ ± sd, (n)					
Acenaphthylene	5.87	Units µg/kg	<3.0 (9)	31±66 (12)	<3.0 (19)	<3.0 (6)	<3.0 (12)	<3.0 (8)
Acenaphthene	6.71		<2.0 (12)	3.2±8.8 (12)	<2.0 (19)	<2.0 (6)	<2.0 (12)	<2.0 (8)
Fluorene	21.2		<4.4 (9)	15±33 (12)	<4.4 (19)	<4.4 (6)	<4.4 (12)	5.1±12 (8)
Phenanthrene	41.9		<2.0 (9)	340±490 (15)	16±33 (19)	12±13 (6)	<2.0 (12)	120±180 (8)
Anthracene	46.9		<2.0 (9)	8.9±17 (12)	2.6±4.1 (19)	10±14 (6)	<2.0 (12)	9.0±13 (8)
Fluoranthene	111		7.1±14 (9)	200±590 (12)	61±110 (19)	23±16 (6)	4.2±12 (12)	250±400 (8)
Pyrene	53.0		3.9±7.9 (9)	450±860 (12)	170±330 (19)	20±17 (6)	31±61 (12)	240±380 (8)
Benz[a]anthracene	31.7		4.4±8.8 (9)	300±710 (12)	37±56 (19)	6.7±5.2 (8)	<2.1 (12)	36±72 (8)
Crysene	57.1		4.2±8.5 (9)	110±240 (12)	69±120 (19)	6.8±8.9 (6)	11±25 (12)	150±260 (8)
Benzo[b]fluoranthene	-		<5.0 (9)	100±250 (12)	39±63 (19)	12±11 (6)	<5.0 (12)	290±570 (8)
Benzo[k]fluoranthene	-		<5.0 (9)	150±290 (12)	<5.0 (19)	8.2±10 (6)	<5.0 (12)	420±780 (8)
Benzo[a]pyrene	31.9		<5.0 (9)	150±250 (12)	27±40 (19)	6.0±5.8 (6)	<5.0 (12)	91±240 (8)
Dibenzo[a,h]anthracene	6.22		<5.0 (9)	45±91 (12)	19±29 (19)	6.5±5.1 (6)	<5.0 (12)	74±130 (8)
Benzo[g,h,i]perylene	-		<5.0 (9)	<5.0 (12)	<5.0 (19)	<5.0 (6)	<5.0 (12)	<5.0 (8)
Indeno[1,2,3-cd]pyrene	-		<5.0 (9)	100±250 (12)	<5.0 (19)	7.0±6.4 (6)	ND (12)	110±190 (12)
ΣPAH	-		35±71 (9)	2100±3100 (12)	440±380 (19)	120±91 (8)	46±120 (12)	1800±3000 (9)

Regarding pesticides the DDTs (DDD, DDE, DDT), endosulphane, endrinaldehyde, lindane, aldrin and dieldrin were detected in most sediment samples and always below Dutch intervention values. Sediment pesticide content in 2001 was highest in the Danube River. This was a consequence of the elevated concentration of lindane (110-150 mg/kg) at two sampling points. In the next year of monitoring, content of pesticides was highest in the DTD Canal because of the elevated content of dieldrin at one sampling point (150 mg/kg).The average annual concentrations of lindane in the Danube sediment (16 μg/kg) and of dieldrin in the DTD Canal sediment (15 μg/kg) were above Canadian probable effect levels. Dutch intervention values are: for DDT 4 mg/kg, for drins (aldrin, dieldrin and eldrin) 4 mg/kg, for total HCH 2 mg/kg, for alpha endosulphane 4 mg/kg.

Table 3. Average annual values for pesticide concentrations in sediment (mg/kg) with stand ard deviations (±sd) and number of measurements (n).

Parameter	Canadian theoretical possible effect level (ISQSs)		Drainage ditches		Danube		Canal DTD	
			2001	2002	2001	2002	2001	2002
			$\bar{x}$ ± sd, (n)					
Lindane	0.94	Units μg/kg	<0.5 (11)	<0.5 (12)	16±42 (19)	<0.5 (7)	1.1±3.7 (12)	0.6±1.9 (10)
Endosulphane1(alfa)	-		<0.5 (11)	<0.5 (12)	3.8±9.6 (19)	<0.5 (7)	<0.5 (12)	<0.5 (10)
Endosulphane2(beta)	-		<0.5 (11)	<0.5 (12)	3.9±9.8 (19)	<0.5 (7)	<0.5 (12)	<0.5 (10)
Aldrin	-		<0.5 (11)	<0.5 (12)	0.1±0.3 (19)	<0.5 (7)	<0.5 (12)	7.6±24 (10)
Dieldrin	2.85		<0.5 (11)	<0.5 (12)	<0.5 (19)	<0.5 (7)	<0.5 (12)	15±47 (10)
4,4'-DDD	3.54		<0.5 (11)	0.8±3.1 (12)	4.0±3.5 (19)	<0.5 (7)	<0.5 (12)	<0.5 (10)
4,4'-DDE	1.42		<0.5 (11)	2.6±9.4 (12)	3.8±3.5 (19)	<0.5 (7)	<0.5 (12)	<0.5 (10)
4,4'-DDT	1.19		<0.5 (11)	0.6±2.2 (12)	2.9±2.4 (19)	<0.5 (7)	0.5±0.9 (12)	<0.5 (10)
Endrinaldehyde	-		0.8±2.7 (11)	<0.5 (12)	1.2±1.9 (19)	<0.5 (7)	0.6±1.6 (12)	<0.5 (10)

It is probable that the results were influenced by water flow, increased anthropogenic activity, decrease of self-purification potential, etc. Average annual concentrations are not characterized by a satisfactory accuracy (standard deviation up to 30-300%), both for low and high concentrations. Possible explanation might be anthropogenic influence on the area. Such a result pointed out to the problem of defining the monitoring network and frequency on particular locations that may appear in the future application of WFD. According to the Directive the monitoring network shall be designed so as to provide a coherent and comprehensive overview of quality within each watercourse and to detect the presence of long-term anthropogenically induced upward trend in pollutants. Variations of organic parameters suggest that some difficulties can be expected in the determination of background values. It is necessary to design very carefully the monitoring network and sampling frequency with the aim to obtain reliable results.

Conclusion

Water quality of the surface waters on the area of "Ratno Ostrvo" is satisfactory according to the national law. PAHs and pesticides concentrations found in sediment are below Dutch intervention values, although sometimes above Canadian probable effect levels. The samples of the slower watercourses (drainage ditches and Canal DTD) have higher differences for average concentrations between years 2001 and 2002, probably due to anthoropogenic influence. Sediment quality have got worsened during the second year of monitoring for those watercourses. This contamination does not demand remediation actions but it is urgent to stop further degradation of the aquatic environment due to anthropogenic activities, and to organize better system of environmental protection of the location with the top priority of groundwater supply source protection. The basis for the efficient management should be the legislation harmonized with EU requirements.

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