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ORGANIC POLLUTANTS IN STREAM SEDIMENTS OF KUPA RIVER DRAINAGE BASIN

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SUMMARY

This paper presents the first results of distribution of organic pollutants in 44 sediment samples (fraction <63 µm) of Kupa River drainage basin, which is a significant water resource for Croatia, Slovenia and BiH (Bosnia and Herzegovina). The investigated region aimed to be used as a model for future studies, necessary to meet Decision No. 2455/2001/EC. Some parts of the drainage basin are national parks (Risnjak and Plitvice Lakes). Also, a great part was affected by war 1991-1995 and is still under mines, what makes it difficult to sample.

Sediments have shown a good record of pollution. Concentrations of total polychlorinated biphenyls (PCBs) were found above toxic levels (>0.02 ppm) for 7 sediment samples. Total phenols were determined above 0.65 ppm for 23 sediment samples, which was characterized as heavily polluted sites. Mineral oils above 100 ppm were found in 13 sediment samples, which are, therefore, moderately polluted. Total lindane isomers in all sediments were below the detection limit of 0.0004 ppm, and, therefore, far below the toxic level of 0.0009 ppm.

Results have shown unexpectedly that the western part of Kupa River drainage basin, with karst aquifers of high risk located in the boarder area of Croatia and Slovenia, has sediments, which were more polluted with organic contaminants from those affected by the war in the middle and eastern part of the basin. Further studies of sediments and protection of karst aquifers in this region is suggested.

KEYWORDS: PCBs, phenols, total oils, mineral oils, lindane, stream sediments, Kupa River drainage basin, Croatia, Slovenia, Bosnia and Herzegovina.

INTRODUCTION

Kupa River drainage basin is a very poorly investigated area in terms of geochemistry and organic pollution. As Kupa River is rich in water resources significant for both Croatia and Slovenia, it is very important to investigate its state of pollution. Also, some parts of drainage basin are National Parks, so that it is very important to investigate the quality of water and sediments.

In this work, 5 organic pollutants (PCBs, lindane isomers, phenolic index, total oils and mineral oils) were studied in Kupa River drainage basin. PCBs (polychlorinated biphenyls) are the most harmful of all of them [1]. They have the general chemical formula $C_{12}H_{10-n}Cl_n$, in which n = 1-10. There are 209 congeners of PCBs (chemicals with the same basic structure), where biphenyl structure has atoms of chlorine changed with atoms of hydrogen in various degrees. From them, about 100 congeners are present in different technical mixtures of PCBs, which were commercially produced in big amounts until the end of the 1970-decade [2]. PCBs were mostly used in electric equipments, as transformers and capacitors, in hydraulic fluids, etc [2]. It is one of the most toxic organic pollutants, due to their low degradation rate. PCBs stay in environment and animals, and bioaccumulate in food chain and present a risk for human health and environment [3]. PCBs, but also other organic pollutants, are being transported by streams and rivers over big distances and are often precipitated in areas, where they have never been produced [4].

The state of organic contamination of the Kupa River ecosystem is not known yet. Generally, a limited number of studies concerning organic contamination has been performed. Picer and Holoubek [5] and Picer et al. [6] have investigated PCBs in karstic environment of Slovenia and Croatia. In the last 20 years in Slovenia and Croatia were two serious incidents, in which significant amounts of PCB were introduced into the bioecological cycle of karstic environment.

The first incident was at the beginning of the 1970-ties, because of inadequate PCB disposal from the capacitor factory "Iskra" in Semič, Bela Krajina, Slovenia. This pollution was discovered in 1983, during research of water samples of the small Krupa River, as potential drinking water source for Bela Krajina region in Slovenia. The pollution spread to Lahinja River and then to Kupa River and continued about 200 km downstream. It is estimated that 1962-1985 about 3-6 t of PCBs were emitted into the atmosphere, and a similar amount was lost during different technological processes. Also, 65-75 t were inadequately disposed, mostly into karstic holes in the vicinity of the factory. In 1986 was a big remediation of the area, and 30-50 t of PCB waste were collected. In the same time, it was assumed that 30-40 t of PCB waste still exist in the karstic area of Bela Krajina, Slovenia [5]. For comparison, in the whole UK environment their amount was estimated to be 400 t [7].

The second incident occurred during the war in Croatia (1991-1995), when unknown amounts of PCBs were released into the environment by destruction of many transformer stations, and from explosives and their side products. By non-controlled burning of PCB and other organohalogens, polyhalogenated dibenzofurans and dibezodioxins are formed, which makes the area of war activities even more dangerous. In Croatia there are several locations, at which is suspected on pollution as result of war activities. One of them is located in Kupa River drainage basin, because in Delnice a 5/10 kV transformer station was bombed. However, the soil samples have not shown significant pollution. There could be also many more sites in war-affected areas, where minor pollution could be present, as described in a recent study "Inventory of polychlorinated biphenyls (PCBs) in the Republic of Croatia, Summary" [8].

Besides PCBs, phenols are one of the main organic pollutants in sediments. According to Omuro Lupetti et al. [9], the presence of phenols in aquatic environment indicates anthropogenic pollution, whose main sources are colors, petroleum, cellulose, paper industry, pesticides` production and their use. Phenols are very toxic for humans, and they damage blood, liver and kidneys [10]. As several different phenols can be present in aquatic environments, their monitoring can be performed by total phenols` determination.

The aim of the present work

The aim of the work was to present a model pollution study of the chosen Kupa River drainage basin, and to determine the concentrations of organic pollutants in stream sediments. The preliminary results can give a clear picture about the current state of the water resources of interest for Croatia, Slovenia and Bosnia and Herzegovina. The growing importance of this research is to prove the quality of water, because according to Biondić et al. [11] karst aquifers of the western part of Kupa River drainage basin are of high risk. There are zones of major traffic corridors, oil pipelines, railways, wood industry, saw and flower mills. Middle and eastern parts of the basin were affected by the war activities 1991-1995, what is assumed to contribute to pollution.

We aim to define the regions of further necessary research and protection.

MATERIALS AND METHODS

The study area of the Kupa River drainage basin, together with a location map for Slovenia, Croatia and Bosnia and Herzegovina is presented in Figure 1. Kupa River itself is 296 km long, from its source under Risnjak Mountain in Gorski Kotar to its inflow to Sava River in Sisak. The drainage basin covers 10.052 km^2. Most of its part is situated in Croatia, and minor parts are in Slovenia and in Bosnia and Herzegovina. It is very asymmetric: north from Kupa it is narrow (approximate width is < 20 km), while southwards it stretches up to 80 km from Kupa River flow. The main tributaries flowing from south are Kupica, Dobra, Mrežnica, Korana, Glina and Petrinjčica, whereas those flowing from north are Čabranka, Lahinja and Kupčina rivers.

The hydrogeological characteristics of Kupa River drainage basin are as follows: From Slovenia to Bosnia there is a 120 km long series of anticline structures with Jurassic dolomites in the core, which represent the total barrier and force the groundwaters to flow northward and spring from the series of 12 permanent springs with minimal flows of 0.1-1.0 m^3/s. Those springs form the streams Ogulinska Dobra, Zagorska Mrežnica, Dretulja, Lička Jasenica and, occasionally, Lake Begovac. These springs sink when they pass dolomite bedrock, and groundwater again springs at new lower series of 12 strong permanent sources, which form permanent rivers: Kupa, Čabranka, Dobra, Mrežnica, Korana, their tributaries, and Plitvice Lakes National Park. In such a way there are formed two large karstic hydrogeological "stairs". The line of lower springs represents also the boarder between high-karstic and fluvio-karstic sub-regions and it extends far away in the drainage basin of Krka River in Slovenia.

Sampling in Kupa River drainage basin was performed during three summer months of 2003, between 4th June and 29th August. In Figure 1 the sketch-map of the investigated area is presented, with the numbers of 44 sampling stations, in which organic pollutants have been analyzed.

The summer of 2003 was extremely dry and warm, so water levels of most streams and rivers were low, which was a very suitable time for sampling. Sampling was complicated by the fact that a big part of Kupa River drainage basin was affected by war, and also mined. Therefore, the Croatian center for de-mining in Sisak was consulted before all field trips, and planned locations of some samples were modified, according to the mine situation in the field. Surface sediments in contact with running water were collected manually, using an acrylic glass tube, 20 cm long and of 6 cm diameter. It was looked out that the sampling locations were representative, to exclude contamination of sediment by sliding down of the material from the riverbanks. At each sampling site 3-5 kg of sediment was collected, so that it would be possible to obtain enough fractions < 63 μm, on which all analyses were performed. Samples were dried in open air, in the shadow, at the air-temperature of about 30-35 ºC, and then dry-sieved using three standard sieves of diameter 63, 500 and 2000 µm (Fritsch, Germany). The 500 and 2000 µm mesh sieves were used to eliminate coarse grains, and that with 63 µm was used for obtaining the fraction f < 63 µm (silt + clay), on which all analyses were performed.

To obtain the mineralogical composition of sediments, semi-quantitative mineralogical analysis was performed, as described by Boldrin et al. [12]. A diffract meter Philips 3040/60, X-pert MPD was used, with the following conditions: Start position: 2θ 4.01; End position: 2θ 62.99; Generator settings: 40 kV, 40 mA. The mineral phases were identified using the program X-pert.

Analysis of total PCBs and lindane was performed in an authorized institution, according to German standard method DIN 38 414-20, based on extraction and gas chromatography. The detection limit was 0.005 ppm (mg/kg of dry weight) for PCBs and 0.0004 ppm (mg/kg of dry weight for lindane, as described by Šmit et al. [13].

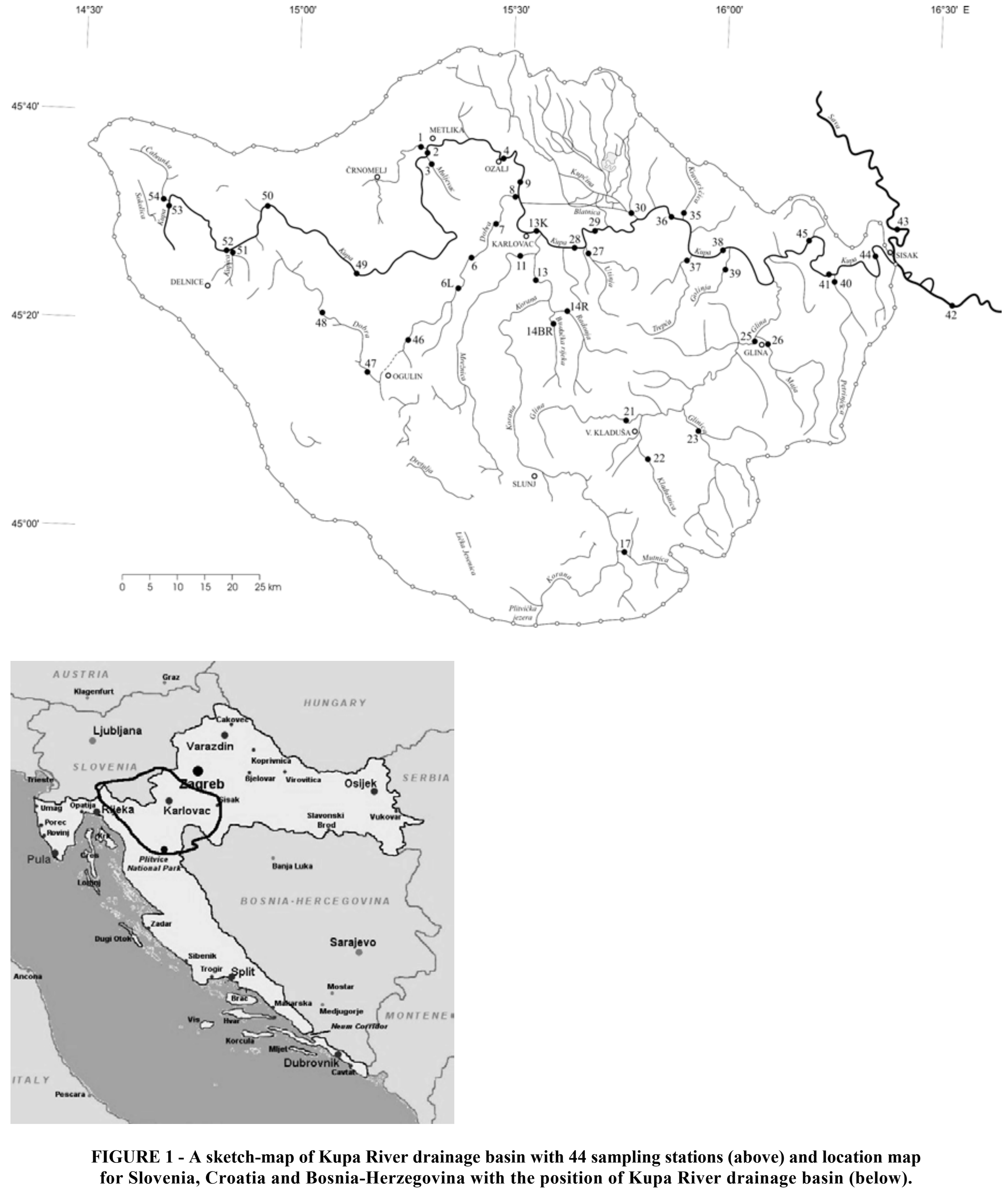

FIGURE 1 - A sketch-map of Kupa River drainage basin with 44 sampling stations (above) and location map for Slovenia, Croatia and Bosnia-Herzegovina with the position of Kupa River drainage basin (below).

Analysis of total and mineral oils was performed in an authorized institution, according to German standard method DIN 38 409-18. As medium for extraction of oils, 1,1,2–trichlorotrifluorethane (freone-113) was used. For quantitative determination with infrared spectroscopy, the characteristic adsorption of CH_3-group (υ=2968 cm^{-1}), CH_2-group (υ=2924 cm^{-1}) and CH-aromate group (υ= 3030 cm^{-1}) was used. This extraction mean does not cause disturbances during determination of the oils.

Analysis of total phenols was carried out in an authorized institution, according to the German standard method DIN 38409-16. Phenol index (in µg/L) is determined spectrophotometrically at 510 nm, after distillation and with adding the reagent 4-AAP (4-aminoantipirine) in alkaline solution. Phenol detection limit in sediment was 0.1 ppm (mg/kg of dry weight).

RESULTS

Determination of organic pollutants

Table 1 is presenting sample numbers and description of sampling locations, together with the concentrations of organic pollutants determined. Each group of organic pollutants is described separately.

From the distribution of total PCBs in sediments it is obvious that, in the middle and most of the eastern part of Kupa River drainage basin, PCBs have concentration levels below the detection limit. Low concentrations (0.005-0.010 ppm) are present in sediments of Čabranka at Osilnica (Slovenia), Kupa at Severin, Ozalj, Levkušje-Zorkovac and at Lijevo Sredičko. Concentrations of 0.010-0.020 ppm were determined in Kupa at Žaga and at Letovanić. Concentrations of 0.020-0.025 ppm were measured in Trepča River at Trepča, and 0.025-0.030 ppm were obtained in Dobra at Trošmarija and Petrinjčica at Petrinja. High concentrations of 0.055-0.065 ppm were found in Lahinja at Primostek (Slovenia), while the highest concentrations in the whole Kupa River drainage basin were measured in Kupa at Hrvatsko in National Park Risnjak, upstream from Čabranka River inflow (0.066 ppm), and in Kupa at Brod na Kupi (0.072 ppm), at the boarder of Croatia and Slovenia.

Total lindane isomers were not detected in any of the 44 sediments, namely, they were below the detection limit.

Concentrations of total phenols are the lowest in the eastern part of Kupa River drainage basin, where amounts of <0.3 ppm prevail. Concentrations of 0.3-0.7 ppm were found in Kupa River at Žaga and in Dobra before its inflow in Kupa. Concentrations of 0.7-1 ppm were determined in Budačka Rijeka at Donji Budački and Mutnica at Pjanići (Bosnia and Herzegovina). Increased levels of total phenols (1-2 ppm) were obtained in Kupica at Brod na Kupi, Čabranka at Osilnica (Slovenia), Kupa at Brod na Kupi and at Čabranka inflow, Kupa at Jurovo, Ozalj, Karlovac, Letovanić and Petrinja, Dobra at Jarče Polje, and in Korana at Belajske Poljice. Concentrations of 2-3 ppm were determined in Dobra at Vrbovsko. Higher concentrations of phenols were measured in Kupa at Severin na Kupi and in Lahinja at Primostek, Slovenia (3-4.5 ppm), and 4.5-5 ppm are found in Dobra river at Ogulin and Donje Stative. The highest concentration of total phenols (9.7 ppm) was measured in Dobra at Trošmarija.

In the eastern part of Kupa River drainage basin, the concentrations of total oils are <200 ppm. In this part are only two localities (Kupa at Lijevo Sredičko and Glina at Glina), where the concentrations were <100 ppm. Concentrations of 200-250 ppm were determined in Kupa at Severin, Muljevac at Brihovo and Mrežnica at Mala Švarča. Concentrations of 250-300 ppm were observed in Kupa at Žaga, Dobra at Trošmarija and Donje Stative, Kupa at Levkušje-Zorkovac, Kupčina at Donja Kupčina and Kladušnica at Barake-Velika Kladuša (Bosnia and Herzegovina). Concentrations of 300-350 ppm were in Kupa at Hrvatsko, Dobra at Lipa and at Jarče Polje, and high concentrations (350-400 ppm) of total oils were measured in Kupa at Brod na Kupi and Karlovac, in Kupica at Brod na Kupi, Lahinja at Primostek (Slovenia) and in Dobra at Ogulin. The highest concentrations of total oils in the whole Kupa River drainage basin were found in Čabranka (432.0 ppm) at Osilnica, Slovenia and in Dobra River (504.4 ppm) at Vrbovsko.

The lowest concentrations of mineral oils (<80 ppm) were found in the eastern part of Kupa River drainage basin, where only at two localities (Glina at Glina and Glinica at Glinica, Bosnia and Herzegovina) concentrations of <50 ppm were measured. 80-100 ppm were determined in Kupa at Žaga and Severin na Kupi, in Muljevac at Brihovo, Dobra at Donje Stative and in Glina at Gejkovac, whereas 100-120 ppm of mineral oils were obtained in Kupa at Hrvatsko, in Lahinja at Primostek (Slovenia), Kupa at Levkušje-Zorkovac, Dobra at Jarče Polje and Mrežnica at Mala Švarča. Rather high concentrations of 120-140 ppm were measured in Kupa at Brod na Kupi and in Kladušnica at Barake-Velika Kladuša (Bosnia and Herzegovina), and 140-160 ppm in Kupica at Brod na Kupi. High concentrations of mineral oils (160-180 ppm) were determined in Čabranka at Osilnica (Slovenia), Dobra at Vrbovsko, and in Kupa at Karlovac. The highest concentration of mineral oils in the whole Kupa River drainage basin was measured in Dobra at Ogulin (185.9 ppm), before the sinking hole.

Mineralogical composition

Mineralogical composition was determined in each sediment sample semi-quantitatively, and the details will be presented elsewhere. The results in this work are presented only for samples with the highest concentrations of pollutants.

In sample 52, which has the highest content of PCBs, silica (33-1161) was found as predominant mineral, >30%; and calcite (05-0586), dolomite (11-0078) and muscovite (07-0032) were less abundant, 10-30%; and clinochlore ferroan (07-0076) and albite (09-0466) were trace minerals.

TABLE 1 - Sampling locations and results of analysis of organic pollutants in sediments (f<63 µm) from Kupa drainage basin.

Smpl. No.	Sampling site	River	flows into	Geographic coordinates	height (m)	Total PCBs (ppm)	Total phenols (ppm)	Total oils (ppm)	Mineral oils (ppm)	Lindane (ppm)
1	Primostek (SLO)	Lahinja	Kupa	45º38'51" N 15º17'57" E	136	0.059	3.250	363.2	118.3	<DL
2	Jurovo (bathing site)	Kupa	Sava	45º36'38" N 15º18'40" E	135	<DL*	1.856	143.6	67.0	<DL
3	Brihovo	Muljevac	Kupa	45º35'41" N 15º19'48" E	138	<DL	1.111	224.1	93.6	<DL
4	Ozalj (downsteram hydr. power pl.)	Kupa	Sava	45º36'57" N 15º29'09" E	122	0.005	1.869	132.6	62.4	<DL
6	Jarče Polje	Dobra	Kupa	45º28'35" N 15º26'23" E	148	<DL	1.769	306.2	119.5	<DL
6L	Lipa	Dobra	Kupa	45º24'29" N 15º23'34" E	187	<DL	<DL	304.6	61.3	<DL
7	Donje Stative	Dobra	Kupa	45º30'01" N 15º27'18" E	121	<DL	4.516	272.4	96.1	<DL
8	Donje Pokupje – Priselci	Dobra	Kupa	45º32'15" N 15º30'50" E	114	<DL	0.481	124.2	58.8	<DL
9	Levkušje – Zorkovac	Kupa	Sava	45º35'54" N 15º31'40" E	116	0.008	<DL	254.5	100.6	<DL
11	Mala Švarča	Mrežnica	Korana	45º28'16" N 15º31'40" E	116	<DL	0.163	221.5	109.3	<DL
13	Belajske Poljice	Korana	Kupa	45º24'47" N 15º32'11" E	142	<DL	1.341	139.6	72.4	<DL
13K	Karlovac – Vodostaj	Kupa	Sava	45º31'28" N 15º33'57" E	111	<DL	1.596	362.8	175.4	<DL
14R	Zimić – Okić	Radonja	Korana	45º22'35" N 15º38'52" E	137	<DL	<DL	147.2	68.1	<DL
14BR	Donji Budački	Budačka Rijeka	Radonja	45º22'21" N 15º36'40"E	113	<DL	0.990	125.1	70.3	<DL
17	Pjanići (BiH)	Mutnica	Korana	44º58'39" N 15º49'04" E	275	<DL	0.766	141.4	78.8	<DL
21	Maljevac – Gejkovac	Glina	Kupa	45º12'10" N 15º47'39" E	151	<DL	<DL	191.9	94.1	<DL
22	Barake – Velika Kladuša (BiH)	Kladušnica	Glina	45º08'46" N 15º50'26" E	135	<DL	0.210	276.1	135.4	<DL
23	Glinica (BiH)	Glinica	Glina	45º11'52" N 15º56'47" E	143	<DL	<DL	100.6	47.0	<DL
25	Glina	Glina	Kupa	45º20'30" N 16º05'03" E	121	<DL	<DL	69.7	33.2	<DL
26	Glina – Majske Poljane	Maja	Glina	45º19'44" N 16º06'28" E	122	<DL	<DL	113.2	60.8	<DL
27	Brežani	Utinja	Kupa	45º28'30" N 15º41'33" E	110	<DL	<DL	119.0	54.4	<DL
28	Donja Rečica	Kupa	Sava	45º28'51" N 15º39'60" E	122	<DL	<DL	163.8	79.7	<DL
29	Zamršlje – Gorenjski Kraj	Kupa	Sava	45º30'24" N 15º41'42" E	121	<DL	<DL	137.7	78.4	<DL
30	Gornje Selo (Donja Kupčina)	Kupčina	Kupa	45º32'01" N 15º47'24" E	117	<DL	1.272	292.8	79.2	<DL
35	Lijevo Sredičko	Kravaršćica	Kupa	45º32'20" N 15º54'26" E	102	<DL	<DL	119.5	61.8	<DL
36	Lijevo Sredičko	Kupa	Sava	45º31'49" N 15º53'04" E	100	0.008	<DL	161.4	69.4	<DL
37	Trepča	Trepča	Kupa	45º27'39" N 15º54'53" E	104	0.021	<DL	127.2	60.5	<DL
38	Pokupsko (Sunčani Brijeg)	Kupa	Sava	45º29'16" N 16º00'35" E	90	<DL	<DL	97.4	54.6	<DL
39	Donje Taborište	Golinja	Kupa	45º27'08" N 16º00'13" E	98	<DL	<DL	196.0	63.0	<DL
40	Petrinja	Petrinjčica	Kupa	45º26'05" N 16º16'22" E	101	0.025	<DL	136.3	64.4	<DL
41	Petrinja (bathing site)	Kupa	Sava	45º26'41" N 16º16'10" E	91	<DL	1.388	109.3	62.8	<DL
42	Lukavec Posavski	Sava	Danube	45º24'04" N 16º32'24" E	90	0.043	1.717	171.4	98.9	<DL
43	Strelečko	Sava	Danube	45º31'02" N 16º23'60" E	92	<DL	0.920	450.5	241.8	<DL
44	Sisak (Zibel bathing site)	Kupa	Sava	45º28'33" N 16º21'35" E	108	<DL	0.273	116.0	68.4	<DL
45	Letovanić	Kupa	Sava	45º30'15" N 16º12'03" E	108	0.013	1.911	133.3	59.6	<DL
46	Trošmarija	Dobra	Kupa	45º19'26" N 15º16'38" E	180	0.027	9.700	271.6	79.7	<DL
47	Ogulin (Puškarić Selo)	Dobra	Kupa	45º16'07" N 15º11'55" E	325	0.009	4.935	352.1	185.9	<DL
48	Vrbovsko (Kamačnik)	Dobra	Kupa	45º22'03" N 15º04'21" E	368	0.008	2.073	504.4	177.2	<DL
49	Severin na Kupi	Kupa	Sava	45º25'30" N 15º09'27" E	158	0.006	3.073	223.7	90.5	<DL
50	Žaga (SLO)	Kupa	Sava	45º31'41" N 14º55'24" E	223	0.016	0.625	250.0	85.2	<DL
51	Brod na Kupi	Kupica	Kupa	45º27'49" N 14º51'22" E	249	<DL	1.183	364.8	150.4	<DL
52	Brod na Kupi	Kupa	Sava	45º27'53" N 14º51'22" E	246	0.072	1.840	370.2	120.4	<DL
53	Hrvatsko	Kupa	Sava	45º31'26" N 14º42'02" E	262	0.066	1.624	356.1	103.1	<DL
54	Osilnica – Sela (SLO)	Čabranka	Kupa	45º31'32" N 14º41'31" E	276	0.007	1.489	432.0	160.8	<DL

*<DL: below detection limit

In sample 46, which has the highest amount of phenols, the predominant minerals (>30%) were quartz (46-1045), calcite (24-0027) and dolomite ferroan (34-0517). Less abundant (10-30%) was albite (41-1480), and phlogopite (16-0344) was only trace mineral.

In sample 48, which has the biggest amount of total oils and also a very high one for mineral oils, the predominant minerals (>30%) were silica (33-1161) and dolomite ferroan (34-0517). Numbers in parenthesis are of JCPDF (Powder Diffraction File) cards.

These minerals alone, with hydrophilic surfaces do not seem to be good adsorbents for the studied organic pollutants. The adsorption mechanism is complex, particularly for hydrophobic substances, and needs further research.

DISCUSSION

To illustrate distribution of organic pollutants in the two most-polluted rivers, Kupa and Dobra, concentrations are presented as histograms along the flow direction (km) in Figure 2. Sediment quality will be discussed in view of the available sediment quality criteria and guidelines for the protection of aquatic life, issued by the University of Waterloo, Canada [14].

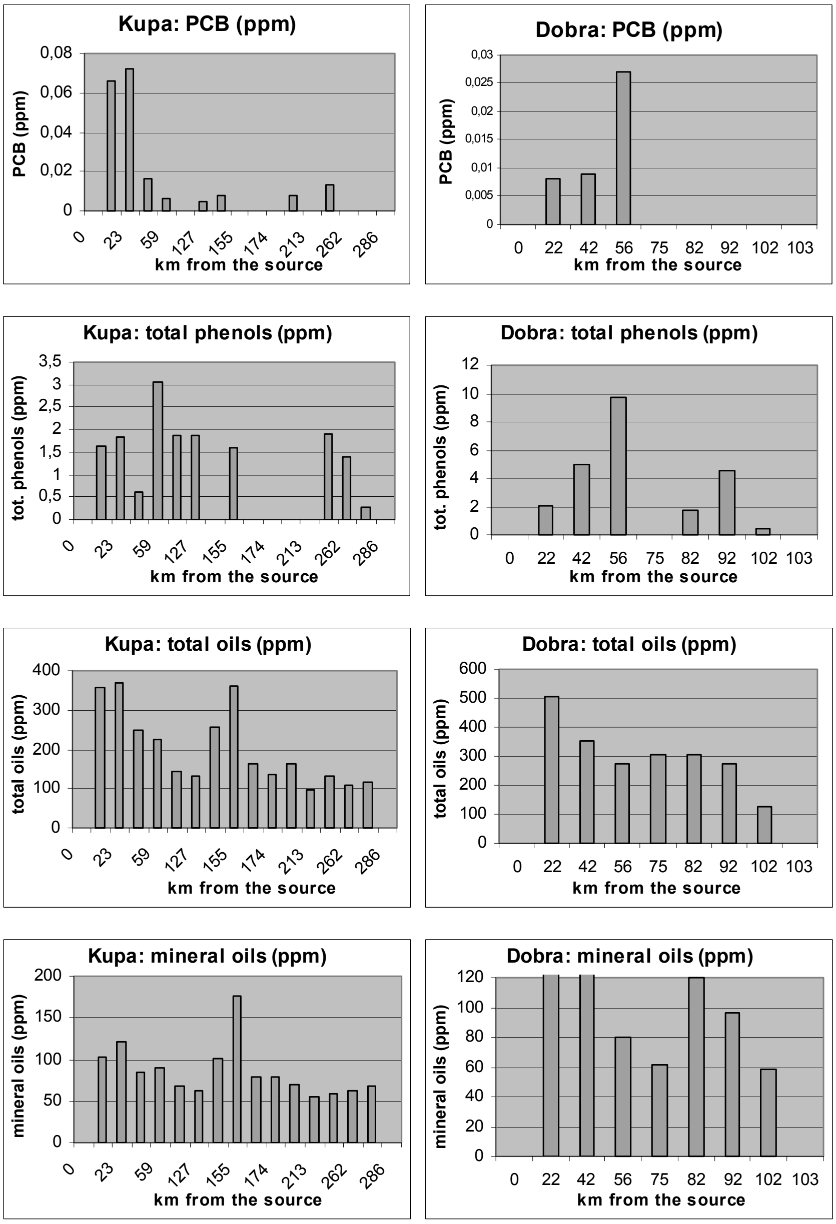

FIGURE 2 - Histograms showing downstream distribution of organic pollutants in Kupa River (left) and in Dobra River (right).

State and origin of PCBs

PCBs are the most harmful of all organic pollutants, which were determined in this work. Their concentrations were measured above detection limit of 0.005 ppm in 36% of the analyzed samples. According to American standards, toxic level threshold for PCBs in sediments is 0.02 ppm [14]. Concentrations above this level were measured in 16% of the samples. Increased levels of PCBs in Lahinja River (Slovenia) are resulting from wastes of Iskra capacitors factory in Semič, Bela Krajina (Slovenia), which have polluted Krupa, Lahinja and Kupa rivers before 1985, when the factory was closed [5]. PCBs, found in levels below toxic threshold at Ozalj and Levkušje-Zorkovac, further downstream Kupa River after inflow of Lahinja, also originated from Iskra factory in Semič, and partly from hydro-power plant in Ozalj. Rather high concentrations of PCBs in sediments from Trepča at Trepča, Petrinjčica at Petrinja, and Sava at Lukavec Posavski are results of war activities in this region, from destroyed transformer stations or oils from numerous destroyed tanks. PCBs in samples of sediment from Dobra River at Trošmarija have their origin from the nearby hydro-power plant Gojak, located upstream. Surprisingly, the two highest concentrations of PCBs in the whole Kupa River drainage basin were found in samples from the upper most part of Kupa River, one of them located in Risnjak National Park. In this area, upstream from Hrvatsko to Kupa source, there were no settlements, roads, nor industry. Also, there were no direct war activities. So, the only explanation is that the pollution has come to Kupa River by groundwaters from the broader area, as it is a typically karstic area, and ground-waters are flowing fast from rather big distances. Looking for possible pollution sources, the sinking river Velika Voda at the outskirt of National Park Risnjak was observed. According to Biondić et al. [11], karst aquifers are of high risk and should be protected.

Pollution with PCBs should not be ignored, because it was present above the toxic levels in the region used for tourism, sport and fishing, at the Croatian-Slovenian border. According to findings of Gevao et al. [15] the sediment-water flux is upward for PCBs, indicating that the sediments may be acting as a secondary source for PCBs. Also, Wolska et al. [4] reported that transport of PCBs in the river takes place both with the aqueous phase and the suspended matter.

State and origin of total phenols

Concentrations of total phenols were found above detection limit (0.1 ppm) in 64% of analyzed samples. According to American standards [14] as unpolluted are considered sediments with <0.42 ppm, as moderately polluted those with 0.42-0.65 ppm, and heavily polluted that with >0.65 ppm of total phenols. Only three samples in the whole Kupa River drainage basin were found to be unpolluted, while all the other samples were moderately to heavily polluted. The most-polluted sediment sample with phenols in the whole Kupa River drainage basin was from Dobra River at Trošmarija (9.7 ppm). The high phenol concentration at this site resulted from Gojak hydro-power plant. The next two most-polluted samples were measured also in Dobra River: one at Ogulin (4.9 ppm) and at Donje Stative (4.5 ppm). Furthermore, a high concentration of phenols was determined in Dobra at Vrbovsko (2.1 ppm). From this can be concluded that Dobra is the most-polluted river with phenols in the whole Kupa River drainage basin. In the upper part of its course, the pollution originated from the industry in Vrbovsko, and especially from wagon wash of the Croatian Railways located in Moravice, upstream from Vrbovsko, where washed tank wagons are used for the transport of chemicals. Wastewaters, originating from these sites, are discharged directly into Dobra River without any treatment. Increased concentrations of phenols in the upper course of Kupa River, the same as PCBs, came there from underground flows of settlements in Gorski Kotar. The high concentration of phenols in Lahinja River, Slovenia (3.1 ppm) was caused by the pollution from the capacitors factory Iskra in Semič.

The highest peak of total phenols in Dobra coincided with the highest peak of PCBs.

State and origin of mineral oils

No quality criteria for mineral oils in sediments and soils are available. Aesthetic or phytotoxicity considerations were typically the basis for the development of standards, while little or no consideration was given to the human health risks associated with the contaminant levels. Numerical criteria for maximum concentrations range from 1,000 to 20,000 ppm for oil and grease [16]. For mineral oils used criteria [17] are the following: unpolluted sediments contain <100 ppm of mineral oils, moderately polluted contain 100-1000 ppm, while heavily polluted sediments contain >1000 ppm of mineral oils. When in sediments concentration of mineral oils exceed 5000 ppm, a recovery of the area is necessary. In Kupa River drainage basin there were no heavily polluted sediments. Mineral oils, determined in concentrations > 100 ppm, which correspond to moderately polluted sediments, were found in 30% of the samples analyzed. The highest concentration of mineral oils was in Sava at Strelečko (242 ppm), due to upstream pollution from Zagreb industry. In Kupa River drainage basin, the highest concentration of mineral oils was found in the upper coarse of Dobra River: at Ogulin (186 ppm) and at Vrbovsko (177 ppm). Mineral oil pollution in Vrbovsko is due to upstream wagon wash of the Croatian Railways in Moravice. In Ogulin, in addition to this pollution source, mineral oils come partly from the water mill in Puškarić Selo, below which was sampled. In this mill the owners used waste mineral oils for lubricating the mill wheel, and entering into water and sediment. In Kupa River near its source (National Park Risnjak), mineral oils came via an underground way from a sinking tributary, Velika Voda, along which numerous mills are situated. The high mineral oil levels in Kupica River originate from tributary Delnički Potok, bringing wastewaters from Delnice. Pollution in Dobra River at Jarče

Polje could come either from the nearby road and its upstream bridge, or from the mill near the sampling point.

CONCLUSIONS

The following conclusions could be drawn:

- Stream sediments showed stable records of occasional and special pollution and are suggested to be used in future monitoring of water quality;
- Analysis of organic pollutants in sediments has clearly shown that the western part of Kupa River drainage basin is more affected than its war-exposed middle and eastern parts;
- At several locations, particularly in the upper flow of Kupa (at Croatian-Slovenian border) and Dobra, concentrations of PCBs, total phenols and mineral oils were above the toxic levels;
- The karst aquifers of high risk, described by Biondić et al. [11], seem to be partly polluted. They should be further studied including stream sediments, and possibly protected by joint efforts of Croatia and Slovenia.
- Results are aimed to be a small contribution from South Europe to the recent global contamination study of Breivik et al. [18].

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