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ORIGINAL PAPER

Metal concentration and particle size distribution of stream and river water polluted from copper rolling mill industry

M. Vučnić Vasić · J. Kiurski · S. Aksentijević · U. Kozmidis-Luburić

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Abstract Concentrations of heavy metals, pH, and particle size distribution parameters were measured in Dragica stream and Djetinja River water receiving wastewaters from copper rolling mill industry, Sevojno. The concentrations of copper, zinc, lead, and mercury were determined for water samples collected in summer 2009. It was found that Copper Rolling Mill Sevojno was the significant source of water pollution with copper and zinc. Considering that copper rolling mill industry, one of the larger emitters of sulfur dioxide, pollutes the area, the water pH was surprisingly alkaline. The particle size analysis results showed that particles from oil-in-water emulsion evidently got into stream water in spite of the purification devices used. In order to assess the possible relations between the measured parameters, a correlation analysis was performed. The correlation analysis showed a significant positive correlation between the total metal concentrations of copper and zinc, as well as between particle size distribution parameters and the concentration of lead and copper.

Keywords Correlation · Fine particles · Heavy metal · Water pollution

M. Vučnić Vasić (✉) · J. Kiurski · U. Kozmidis-Luburić
Faculty of Technical Sciences, University of Novi Sad,
Trg D. Obradovica 6, 21000 Novi Sad, Serbia
e-mail: milicavv@uns.ac.rs

S. Aksentijević
Business Technical College, Trg Svetog Save 34,
31000 Uzice, Serbia

Introduction

Industrialization and urbanization, which are becoming more and more intensive, represent one of the greatest factors endangering the environment. Heavy metals, once introduced into the environment, can spread to different components of the environment which is caused by the nature of the interactions going on in natural systems. Because of the effects that their toxicity might have on the living world and because of their persistence in the environment due to the impossibility of their biological decomposition, the detection of heavy metals in waters and sediment is extremely important. Water and sediment pollution is a problem present all over the world, especially in the industrial regions.

Metal concentration in river water is mainly affected by the geology of the area, bedrock compositional, and anthropogenic factors. Anthropogenic heavy metal pollution of surface waters results from various sources, mostly from industrial wastewaters, mining and smelter wastes, urban run-off, agricultural run-off (where copper is still used as a pesticide), atmospheric deposition, and leaching from solid waste dumps (Berner and Berner 1996; Fernandez-Calvino et al. 2008). In surface waters, at normal pH and redox conditions, most of the trace elements are readily adsorbed onto the particulate matter (Meybeck et al. 1992). Consequently, the actual dissolved elements concentrations are very low. Valuable information for the estimation of the pollution status of the river water is the total (dissolved + particulate bound) metal concentration (Alonso et al. 2004; Moore and Ramamoorthy 1984). It is also well-known that metal concentration in river water drastically depends on dilution effect due to the variation in water level and discharge (Philips and Rainbow 1993).

In general, heavy metals from metallurgical industry plants pollute the surrounding soil, surface/groundwater, and atmosphere in spite of the purification devices used. Soil investigation near the ore mining, roasting, and processing plants established an extreme enrichment with metals in the upper soil layer (humus) (Reimann et al. 1998). Aquatic plants in surface water polluted by copper mining and metallurgical industries showed serious level of heavy metal concentration (Samecka-Cymerman and Kempers 2004). The mining industry as well as Cu and Ni smelter industry in the Kola Peninsula district increased the risk of the Kola River metal pollution, the reported results indicated relatively low contamination except in headwaters close to the mining areas where the highest concentration of metals were detected (Pekka et al. 2008). Also, the chemical composition of groundwater near nickel–copper smelting industry shows the signs of incipient contamination from surface waters with heavy metals (Caritat et al. 1998).

Industrial wastewaters, in contrast to communal, contain the wider spectra of pollutants, with both seasonal and daily variations. In the copper industry, water is mainly used for cleaning and cooling, as well as for oil-in-water emulsion. All these different tasks produce wastewaters. The object of investigation was groundwater directly polluted by the wastewater from the copper rolling mill. First sampling campaign was done during the spring of 2009. This determined the concentration of Al, Fe, Cu, Cr, Ni, and Zn in the water and sediment.

The results from this campaign (Kiurski et al. 2010) showed high concentrations of Cu and Zn in both water and sediment which required further monitoring. The results from the second sampling campaign carried out during the summer of 2009 are reported in this paper.

The aims of this research were to assess pollution status regarding Hg and Pb determined for the first time, to ascertain the difference in copper and zinc concentration in water samples collected during different seasons, and to distinguish which of the investigated metals is preferably bound to fine particles. Lead and mercury were introduced within the investigation due to the facts that Copper Rolling Mill Sevojno produces and processes, among other, leaded brass and that mercury nitrate is used for brass waste treatment. In order to access the investigation aims, metals concentration, pH, and particle size distribution parameters were measured, and the evaluation of theirs correlation is done. The research was carried out during July of 2009 in the western part of Serbia at sites in the Djetinja River and in the Dragica spring.

Materials and methods

The sampling object was the Djetinja River basin. Its source is on the eastern and south-eastern slopes of Tara Mountain. The Djetinja River together with the Golijska Moravica River forms the Zapadna Morava, one of the most significant water basin in Serbia. The samples were taken at the Dragica stream and along the Djetinja River, as it is shown in Fig. 1 (sampling sites are denoted by S1–S8). Samples S1–S4 were taken at the Dragica stream, starting from the place where the wastewaters from the industrial plant are discharged into it (site S1 on Fig. 1) at 50 m

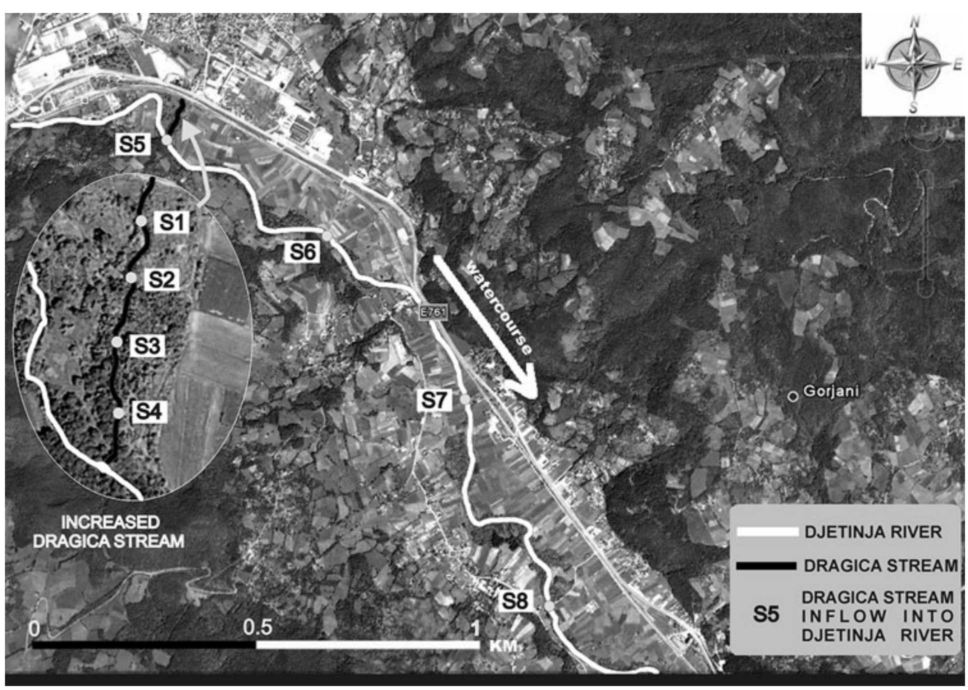

Fig. 1 Sampling sites in the Dragica spring and the Djetinja River

intervals; sample S5 was taken at the place where the Dragica stream flows into the Djetinja River; while samples S6–S8 were taken along the Djetinja River, at 500 m intervals. It was noticed that the water was grey, oily, and with unpleasant odor. On the banks, as well as in the water itself, there was a lot of waste (plastic bags, metal and textile items, rotten agricultural products). All this waste was carefully avoided during sampling. The handling, storage, and preparation of the samples were done in compliance with the standard EPA method 200.7, in plastic bottles of 1 L cleaned with the 10 % solution of nitric acid before usage. All plastic bottles were factory new. The bottles were filled with water by holding them several centimetres under the water surface. Before sampling, each bottle was thoroughly rinsed several times with river water. The water samples were not filtered, only sieve was used to remove coarse impurities. After sampling, pH value was determined by a pH-meter.

Prior to chemical analysis, the particle size distribution (PSD) analysis of the water samples was performed using a Malvern Mastersizer 2000 Particle Size Analyzer capable of analyzing particles between 0.02 and 2,000 μm. The result from the analysis is the relative distribution of volume (number) of particles in the range of size classes. The measurement parameters were pump speed = 2500 rpm; ultrasonic = off. For this measurement, the water samples required 100-fold preconcentration by evaporation before the analysis.

The total amount of metal concentration in water samples was determined with the instrument ICAP 6500 Duo ICP after their laboratory acidification with nitric acid. The following heavy metal concentrations were measured (detection limits are indicated in brackets): Cu (0.49 μg/L), Zn (0.19 μg/L), Pb (1.39 μg/L), and Hg (0.09 μg/L).

Non-parametric correlation analysis was performed due to the non-normal distribution of some parameters and because it is less sensitive to outliers. Spearman rank correlation coefficients between analyzed variables were calculated by the software package Statistica 10. Only correlation coefficients significant at the 0.05 level are discussed within the paper.

Results and discussion

The previous results of biological and chemical analysis indicated that the degradation of the Djetinja River ecosystems occurred in the following fashion: upstream from the town of Uzice, the quality of water was mildly degraded; while downstream from Uzice to Pozega, the quality of water was very heavily polluted (Milijasevic and Jojic Glavonjic 2009). The quality of water had been defined by 12 parameters: dissolved oxygen, percentage of saturation by oxygen, biochemical oxygen demand, chemical oxygen demand, saprobic degree, the most probable number of coli-germs, suspended substances, dissolved substances, pH, visible waste substances, and colour and smell (Milijasevic and Jojic Glavonjic 2009).

The polluters of the Djetinja River are the plants from the Krcagovo and Sevojno industrial zones as well as the settlements (especially Uzice and Pozega), farms, agriculture, etc. The plants from the Krcagovo industrial zone are: "Metaloprerada"—the production of coolers, heat exchanger sand lamp holders; "Namenska proizvodnja"—the production of military, sports and hunting ammunition, and medical equipment; "ABC proizvod"—the production of boilers and heaters; "WOKSAL"—the production of heavy metals, high-voltage contacts, and fishing material. The Sevojno industrial zone includes giants such as Aluminium Mill and Copper Rolling Mill, where sheet metal, strips, boards, plates, coils, wires, and other various profiles made of aluminium, copper, and copper alloys are produced. Wastewater from the Copper Rolling Mill Sevojno was directly discharged into the Dragica stream that inflows into the Djetinja River. The average quantity of wastewater from the Copper Rolling Mill Sevojno is around 100 m^3/h (Milijasevic and Jojic Glavonjic 2009).

The results of heavy metal concentrations are given in Table 1 and Fig. 2. Maximum allowable heavy metal concentrations were established by the Regulation on Dangerous Substances in Water (Official Gazette RS 1982). The results of the present study showed that the concentrations of copper determined in the water samples

Table 1 Metal contents, pH and particle size distribution parameters in surface water from the Dragica spring and the Djetinja River

	Cu (mg/L)	Zn (mg/L)	Pb (mg/L)	Hg (mg/L)	pH	$d(0.1)_{v.b.}$ (μm)	$d(0.5)_{v.b.}$ (μm)	$d(0.9)_{v.b.}$ (μm)	D[4.3] (μm)	$d(0.1)_{n.b}$ (μm)	$d(0.5)_{n.b}$ (μm)	$d(0.9)_{n.b}$ (μm)	D[1.0] (μm)
S1	0.663 (4)	0.540 (4)	0.008 (2)	0.0001 (1)	7.4	20 (1)	76 (2)	191 (6)	99 (3)	0.45 (2)	0.54 (1)	0.84 (3)	0.65 (2)
S2	0.660 (4)	0.190 (2)	0.007 (2)	0.0002 (1)	7.4	8 (1)	50 (2)	149 (5)	76 (3)	0.40 (2)	0.53 (1)	0.92 (3)	0.65 (2)
S3	0.556 (4)	0.760 (5)	0.006 (1)	0.0001 (1)	7.4	21 (1)	88 (2)	204 (6)	120 (3)	1.78 (2)	2.45 (1)	6.46 (4)	3.75 (7)
S4	0.150 (3)	0.110 (3)	0.005 (1)	0.0001 (1)	7.4	38 (1)	132 (2)	343 (7)	168 (4)	2.78 (2)	3.72 (1)	10.44 (5)	5.86 (9)
S5	0.059 (2)	0.006 (1)	0.006 (1)	0.0004 (1)	8	31 (1)	95 (2)	248 (7)	124 (3)	2.39 (2)	3.20 (1)	8.59 (4)	5.14 (9)
S6	0.188 (3)	0.160 (3)	0.005 (1)	0.0006 (1)	8.2	26 (1)	89 (2)	223 (6)	114 (3)	2.07 (2)	2.83 (1)	7.33 (4)	4.34 (9)
S7	0.328 (3)	0.148 (3)	0.005 (1)	0.0002 (1)	8.2	33 (1)	89 (2)	202 (6)	106 (3)	2.13 (2)	2.88 (1)	7.16 (4)	4.60 (9)
S8	0.092 (3)	0.038 (2)	0.006 (1)	0.0001 (1)	8.2	19 (1)	67 (2)	210 (6)	97 (3)	0.45 (2)	0.56 (4)	0.90 (3)	0.69 (2)

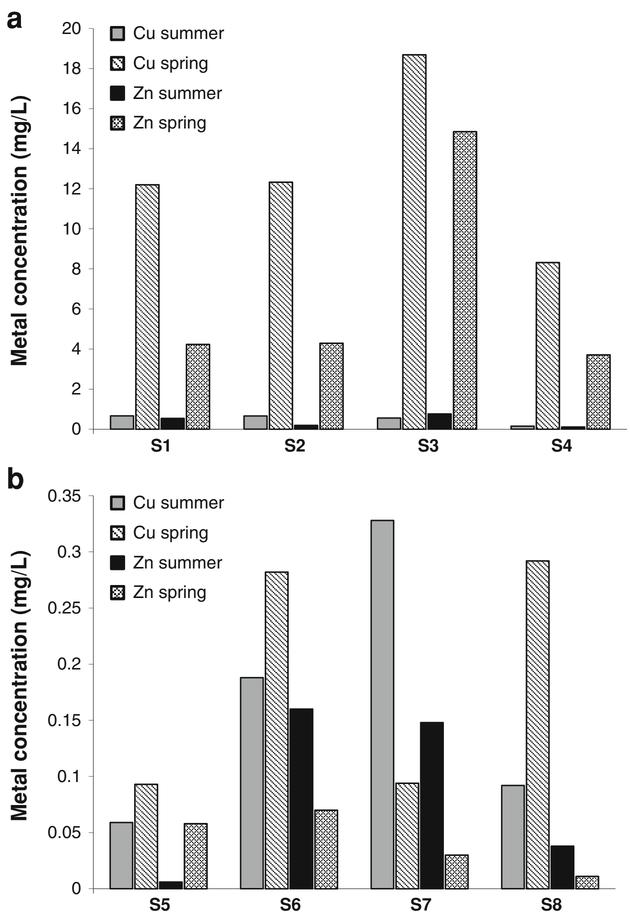

Fig. 2 Summer and spring (Kiurski et al. 2010) concentrations of Cu and Zn: **a** sites S1–S4, **b** sites S5–S8

exceeded the maximum allowed values of 0.1 mg/L, except on sites S5 and S8. The concentrations of other metals did not exceed the allowed limits. The total concentrations of Cu and Zn at sites near to the direct inflow of wastewater into the Dragica stream (sites S1–S3) were two to four times higher compared with sites S6–S8 in the Djetinja River. On the other hand, Pb and Hg did not show significant differences in concentration regarding the distance from the wastewater inflow. Obviously, wastewater from the Copper Rolling Mill Sevojno was not the significant source of pollution with Pb and Hg. The total Cu and Zn concentrations showed an almost continuous decrease with the increase in the distance from the wastewater inflow up to the sampling site S5, where the Dragica stream flows into the Djetinja River. This is the consequence of a continuous dilution and the fact that particulate Cu and Zn settle down downstream the Dragica stream (particle size distributions will be discussed below). The concentrations of these two metals at the sampling sites in the Djetinja River (sites S6–S8) exceeded the concentrations at the sampling site S5. The metal concentrations at sampling sites in the Djetinja River (S6–S8) were the result of the accumulation of metals from the Dragica spring and the Djetinja River upstream from the sampling site S5. Total metal concentration for Zn, Pb, and Hg, at all sites, did not exceed the maximum allowable concentrations of heavy metal concentrations according to the European Standards for Fisheries and Aquatic Life (Chapman and Kimstach 1992). Copper concentration at all sites, except at the sampling site S8, was higher than the mentioned standard.

The seasonal variations of the chemical composition of surface water are generally influenced by water level (i.e., dilution), as well as by anthropogenic factors: mining, industrial, urban, and agricultural activities (Reza and Singh 2010; Zare Garizi et al. 2011). Heavy metal concentrations for samples collected in summer 2009 were compared with the results collected during the spring season 2009, at the same sites, reported in (Kiurski et al. 2010). It was observed that at sites S1–S4, Cu and Zn concentrations were approximately 10 to 50 times lower during the summer, while at sites S5–S8, the summer and spring values were on the same order of magnitude, as could be seen in Fig. 2. It is known that metal content in surface water reaches their maximum during springtime snow melting (Caritat et al. 1998), and it is also known that the amount of heavy metals is higher in the spring rains than in the summer ones (Changling et al. 2005; Sermin Örnektekin and Cakmakli 2003). If the above mentioned had an influence on metals concentrations, this would be detected at all sampling sites in the same way. However, half of the sites within the area of investigation showed significant seasonal variations, while other half did not. The sites which showed significant seasonal difference in metal concentrations were at the Dragica stream. The possible reasons for such results could primarily be attributed to the fluctuations in wastewater inflow from the copper rolling mill as well as to the local anthropogenic emission sources from the surrounding agricultural land (the use of pesticides, fertilizers, etc.).

The results of the present study were also compared with the results pertaining to the metal pollution in the Kola River in the north western Russia (Pekka et al. 2008). The total concentrations of Cu and Zn in the Dragica stream and in the Djetinja River exceeded for two orders of magnitude the maximum values reported for the Kola River (2.84 µg/L for Cu and 1.82 µg/L for Zn) except on sites S5 and S8. The total concentrations of Pb, at all sites (S1–S8), were the order of magnitude higher than the maximum reported value for the Kola River (0.14 µg/L). Hg was not observed by Pekka et al. (2008) in the Kola River. The observed pollution with heavy metals was also compared with metal concentrations in unpolluted reference rivers. Unfortunately, any reports indicating the values for an unpolluted river in the geographical vicinity of the Uzice district could not been found. For that reason, the results that were reported by Meybeck et al. (1992) were used as a reference for average unpolluted river water. This comparison showed that the total concentrations of Cu, Zn, and Pb were two to three times orders of magnitude higher, if compared with the dissolved metal concentration values for average unpolluted river water. Although geology, climate, and vegetation are important factors determining river water chemistry, the comparison of the results reported here with the reference for average unpolluted river water showed that Cu and Zn concentrations were governed by the high input from the pollution sources at the copper rolling mill.

The alkaline pH of river water (from 7.4 up to 8.2) was observed within the area of investigation. Considering pH value, there were two groups with the identical value within group. One group (pH = 7.4) consisted of the Dragica spring sites (S1–S4). The second one, pH = 8.2 included the Djetinja River sites S6–S8. For the site S5, pH value was 8. The Krcagovo industry zone is located upstream from the site S5 where the Dragica stream inflows into the Djetinja River. Wastewaters from industry plants in Krcagovo are also discharged into the Djetinja River and highly affect the pH value of water. Sites S6–S8 were under the influence of wastewaters from both the Krcagovo industry zone and the copper rolling mill as well, while sites S1–S4 were highly affected by the copper rolling mill only. This is considered to be the most possible reason for less alkaline pH value at the Dragica spring sites.

The acidification of surface waters is often ascribed to the phenomenon of "acid rain", usually attributed to anthropogenic emissions of sulfur and nitrogen gaseous oxides, such as that from the Copper Rolling Mill Sevojno. However, it is most likely that the river water in the immediate vicinity of the copper rolling mill might be influenced by the fallout of ash or other alkaline particulates. While gaseous emissions from mineral processing works tend to be enriched in volatile gaseous phases which release acid on hydrolysis (e.g., SO_2, CO_2), fly ash phases are enriched in semi-volatiles and alkaline oxides, yielding a high pH on hydrolysis. According to the available data pertaining to 2009, the average annual concentration of SO_2 in air measured in Uzice was 11 μg/m^3, which does not exceed the permissible limit of 50 μg/m^3 (the maximum daily concentration in Uzice in 2009 was 189 μg/m^3) (Report 2010). The results that were reported by Trumbulovic-Bujic and Acimovic-Pavlovic (2008) showed that the concentration of SO_2 in flue gases emitted from the Copper Rolling Mill Sevojno were below the regulative boundary levels of emission (Official Gazette RS 30/97 and 35/97 1997).

According to the 2009 official investigation of the Agency of Environmental Protection of Serbia, the highest ash concentration, among all control points in Serbia, was measured in Uzice, with the highest ash daily concentration being 409 μg/m^3 (Report 2010). The annual average value of ash exceeded the permissible limit of 50 μg/m^3 only in Uzice (77 μg/m^3) (Report 2010). During 2009, there were 193 days with ash concentration above the maximum allowed value (Report 2010). If released, potentially basic ash phases would be likely to fall nearer the plant than the potentially acidic gaseous phases and might result in the rise of pH in the river water. The pH values of river water are also a consequence of alkaline pH values (9–9.5 (Fernandez et al. 2005)) of oil-in-water emulsions. Oil-in-water emulsions (smoothing emulsion and finishing emulsion) are used as lubricants and coolants in the industrial copper rolling process, to reduce friction between the metal pieces and mechanical equipment and to avoid corrosion (Springborn and Silliman 1992). The results of the research on wastewaters of the Copper Rolling Mill Sevojno, after the treatment on purification devices, also indicated the alkaline character of wastewaters (Milijasevic and Jojic Glavonjic 2009).

Laser diffraction is one of the most widely used methods of particle size analysis for wastewater (Houghton and Stephenson 2002; Kim and Lee 2003; Weidong et al. 2009). The results of PSD analysis are given in Table 1 and in Fig. 3. Each sample was analyzed in three replicates, average PSD parameter values are given in Table 1. The results were recorded as the particle volume percent in 100 discrete size ranges between 0.02 and 2000 μm. After measurement, the results were recalculated as the particle number percent. The d(0.1), d(0.5) and d(0.9) values indicate that 10, 50, and 90 % of the particles measured were smaller than or equal to the size stated. D[4,3] and D[1,0] are the volume-weighted and number-weighed means calculated from the volume-based (v.b.) and number-based (n.b.) results, respectively. The number-based PSD (averaged results) of the analyzed samples are illustrated in Fig. 3a, while Fig. 3b shows the percentage of particles by volume.

The number-based PSD showed that the fraction of particles >50 μm was negligible for all samples. The most common values of the frequency distribution curve (mode) for water samples S3–S7 were in the size range of 2–3 μm, while for samples S1, S2 and S8 mode values were approximately one order of magnitude lower (400–600 nm). Mode value shift toward smallest values, for samples S1 and S2, was less obvious but also present for volume-based results. The volume-based PSD showed that the fraction of particles smaller than 2 μm was negligible for samples S3–S7. For samples collected at sites S1 and S2 (two sites closest to the wastewater inflow), the fraction of particles smaller than 2 μm was small but not negligible as could be seen in Fig. 3b. The literature

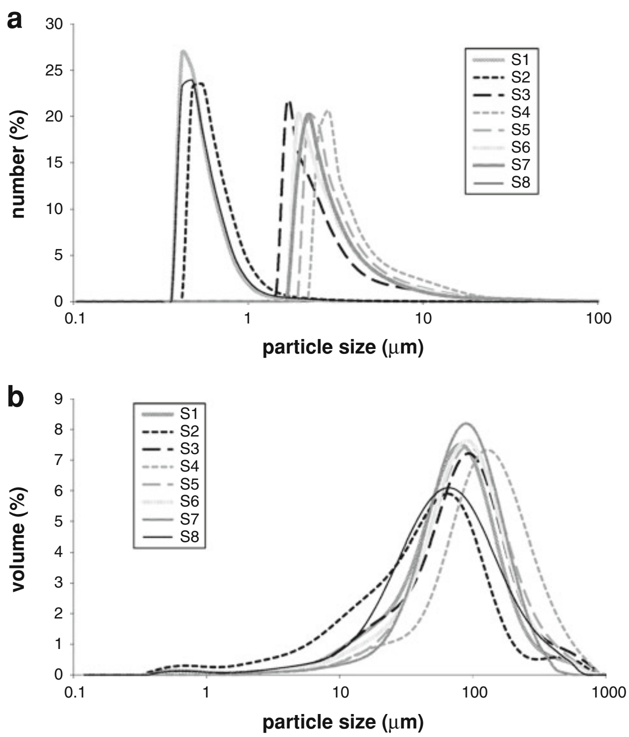

Fig. 3 Number-based (**a**) and volume-based (**b**) particle size distribution

reported mode value for volume-based particle size distribution curves for oil-in-water emulsions used in the copper rolling process were in the range 0.7–2.5 μm (Fernandez et al. 2005), depending on the emulsion ageing. It is known that after usage, oil-in-water emulsion becomes less effective because of thermal and mechanical degradation and contamination by components in suspension (Bataller et al. 2004). Considering previously mentioned, it was concluded that particles from oil-in-water emulsion evidently get into the wastewater and the Dragica stream. The shift of the mode of the number- and volume- based PSD curves toward smaller particles, for samples S1 and S2, could be explained in terms of particles from oil-in-water emulsion. The fractions of these "small" particles were visible only near wastewater inflow at distances smaller than 100 m. The volume-based results indicate where most of the mass of suspended material is located in terms of particle size. As seen from Fig. 3b, most of the mass were located in the broad interval from 10 to 1000 μm. As it was indicated earlier, the samples were not filtered but only a sieve was used. The particles with the size larger than 5 μm, so called biological particles, were assigned to natural sources. Biological particles can be produced by various mechanisms such as pollen, spores, bacteria, algae, parotozoa, fungi, fragments of leaves, etc. (Görner et al. 2006).

Correlation analysis is often used in detecting relationships between metals and suspended particulate matter (Okafor and Opuene 2006; Reimann et al. 1998). To investigate how metals (Cu, Zn, Pb and Hg) were associated, a non-parametric correlation analysis was done for the concentrations of metals themselves and against the particle size distribution parameters. The values of the obtained Spearman correlation coefficients are given in Table 2. As expected, Cu and Zn very strongly correlated to each other indicating that these elements originated from the same sources.

The specific surface area is a key particle property which controls the adsorption capacity. It is inversely proportional to particle size and decreases over three orders of magnitude from clay-sized particles to sand grains (Thomas and Meybeck 1992). Therefore, the finest particles are generally the richest in trace elements. This effect is particularly evident when separate chemical analyses are made on different size fractions (Herngren et al. 2006; Thomas and Meybeck 1992). In many studies, it was also found that the correlations between suspended solids and chemical element content decreased as the particle size increased (German and Svensson 2002; Westerlund and Viklander 2006). One of the aims of the present research was to investigate the correlation between metal concentration and PSD parameters. Both number- and volume-based PSD parameters were considered. When total particulate matter is considered, the trace element content is usually directly proportional to the amount of the finest fraction (Fernandez-Espinosa and Ternero-Rodrıguez 2004; Madrid et al. 2008). In our case, larger amount of the fine particle fraction would result in particle size distribution parameters shifting toward smaller values. This means that the increase in the amount of fine particle fraction would be followed with the decrease of particle size

Table 2 Spearman correlation coefficient for parameters measured

	Zn	Pb	Hg	$d(0.1)_{v.b.}$	$d(0.5)_{v.b.}$	$d(0.9)_{v.b.}$	D[4.3]	$d(0.1)_{n.b.}$	$d(0.5)_{n.b.}$	$d(0.9)_{n.b.}$	D[1.0]
Cu	**0.9048**	0.4910	–0.2426	–0.4286	–0.5238	**–0.8333**	–0.4762	–0.6667	–0.6667	–0.5952	–0.6826
Zn		0.4051	–0.2554	–0.3809	–0.4524	–0.6428	–0.2619	–0.5714	–0.5714	–0.4762	–0.5868
Pb			–0.1975	**–0.8224**	**–0.7365**	–0.6015	–0.5647	**–0.8102**	**–0.8102**	**–0.7488**	**–0.8274**
Hg				0.1660	0.2043	0.1149	0.0511	0.2043	0.2043	0.4214	0.2441

Bold values are statistically significant at 0.05 level distribution parameters. In other words, negative correlation between concentration and PSD parameters is expected for metals preferentially bound to the fine particle fraction. Negative correlation coefficient values were found between Cu, Zn, and Pb concentrations and all PSD parameters, while positive values were found between Hg and all PSD parameters. Statistically significant correlation was ascertained between both types of PSD parameters and the concentration of Pb, as well as between Cu concentration and $d(0.9)_{v.b.}$ only. This indicated that lead and copper concentrations were preferentially bound to the fine particle fraction.

Conclusion

Water composition in the study area can be viewed as a consequence of pollution; a strong influence of anthropogenic sources is visible for Cu and Zn. The Cu and Zn concentrations very strongly correlated to each other (at the 0.05 level of significance), indicating that these elements originated from the same source. The concentrations of copper in the water exceeded the maximum allowed values of 0.1 mg/L, except on sites S5 and S8. The level of water pollution with Zn, Pb, and Hg was lower, but very close to maximum allowed values, especially for Zn.

Particle size analysis results showed that particles from oil-in-water emulsion evidently got into wastewater and consequently, into the Dragica stream in spite of the purification devices used for the purification and filtration of wastewaters emitted from the Copper Rolling Mill Sevojno. Statistically significant correlation ascertained between the PSD parameters, and the concentrations of Pb and Cu indicated that lead and copper concentration were preferentially bound to the fine particle fraction.

Although the area strongly affected by the industry wastewaters appears rather small, especially considering that the Copper Rolling Mill Sevojno is one of the largest plants for copper rolling process on the Balkan peninsula, the hardly tolerable metal contamination in the Dragica stream and the Djetinja River require further constant analyses of the water with sampling carried out at regular intervals over a longer time period.

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References

Alonso E, Santos A, Callejón M, Jiménez JC (2004) Speciation as a screening tool for the determination of heavy metal surface water pollution in the Guadiamar river basin. Chemosphere 56(6): 561–570

Bataller H, Lamaallam S, Lachaise J, Graciaa A, Dicharry C (2004) Cutting fluid emulsions produced by dilution of a cutting fluid concentrate containing a cationic/nonionic surfactant mixture. J Mater Process Technol 152(2):215–220

Berner EK, Berner RA (1996) Global environment: water, air and geochemical cycles. Prentice-Hall, New Jersey, pp 1–376

Changling L, Guosen Z, Hongbo R, Jing Z (2005) Distribution of heavy metals and nutrients in rainwater in coastal regions between the southern Yellow Sea and East China Sea. Chin J Ocean Limnol 23(2):230–237

Chapman D, Kimstach V (1992) Selection of water quality variables. In: Chapman D (ed) Water Quality Assessments—a guide to use of biota, sediments and water in environmental monitoring. Chapman and Hall, London, pp 74–133

de Caritat P, Danilova S, Jaeger Ø, Reimann C, Storr¢ G (1998) Groundwater composition near the nickel–copper smelting industry on the Kola Peninsula, central Barents Region (NW Russia and NE Norway). J Hydrol 208(1–2):92–107

Fernandez E, Benito JM, Pazos C, Coca J, Ruiz I, Rıos G (2005) Regeneration of an oil-in-water emulsion after use in an industrial copper rolling process. Colloids Sur A 263(1–3): 363–369

Fernandez-Calvino D, Rodriguez-Suarez JA, Lopez-Periago E, Arias-Estevez M, Simal-Gandara J (2008) Copper content of soils and river sediments in a winegrowing area and its distribution among soil or sediment components. Geoderma 145:91–97

Fernandez-Espinosa AJ, Ternero-Rodrıguez M (2004) Study of traffic pollution by metals in Seville (Spain) by physical and chemical speciation methods. Anal Bioanal Chem 379(4):684–699

German J, Svensson G (2002) Metal content and particle size distribution of street sediments and street sweeping waste. Water Sci Technol 46(6–7):191–198

Görner P, Fabris JF, Duquenne P, Witschger O, Wrobel R (2006) Bioaerosol sampling by a personal rotating cup sampler CIP 10-M. J Environ Monit 8(1):43–48

Herngren L, Goonetilleke A, Ayoko GA (2006) Analysis of heavy metals in road-deposited sediments. Anal Chim Acta 571(2): 270–278

Houghton JI, Stephenson T (2002) Particle size analysis of digested sludge. Water Res 36(18):4643–4647

Kim JS, Lee CH (2003) Effect of powdered activated carbon on the performance of an aerobic membrane bioreactor: comparison between cross-flow and submerged membrane systems. Water Environ Res 75(4):300–307

Kiurski J, Vučinić-Vasić M, Aksentijević S, Kozmidis-Luburić U, Vojinović-Miloradov M (2010) Metals distribution and particle size analysis in water and sediment of the Djetinja River and Dragica spring (Serbia). Chem Ind Chem Eng Q 16(4):363–372

Madrid F, Biasioli M, Ajmone-Marsan F (2008) Availability and bioaccessibility of metals in fine particles of some urban soils. Arch Environ Contam Toxicol 55(1):21–32

Meybeck M, Friedrich G, Thomas R, Chapman D (1992) Rivers. In: Chapman D (ed) Water quality assessments—a guide to use of biota, sediments and water in environmental monitoring. Chapman and Hall, London, pp 246–324

Milijasevic D, Jojic Glavonjic T (2009) Water quality of the Djetinja River. J Geog Inst Cvijić 1(59):63–74

Moore JW, Ramamoorthy S (1984) Heavy metals in natural waters. Springer, Berlin

Official Gazette RS 31/82 (1982) Regulation on dangerous substances in water. Ministry of Environment and Spatial Planning

Official Gazette RS 30/97 and 35/97 (1997) Regulations on emission limit values, methods and time frame for measuring and recording. Ministry of Environment and Spatial Planning

Okafor ECh, Opuene K (2006) Correlations, partitioning and bioaccumulation of trace metals between different segments of Taylor Creek, southern Nigeria. Int J Environ Sci Tech 3(4):381–389

Pekka L, Halmeenpää H, Ecke F, Vuori KM, Mokrotovarova O, Öhlander B, Ingri J (2008) Assessing pollution in the Kola River, northwestern Russia, using metal concentrations in water and bryophytes. Boreal Env Res 13(1):15–30

Philips D, Rainbow P (1993) Biomonitoring of trace aquatic contaminants. Chapman and Hall, London

Reimann C, de Caritat P, Niskavaara H, Finne TE, Kashulina G, Pavlov VA (1998) Comparison of elemental contents in O- and C-horizon soils from the surroundings of Nikel, Kola Peninsula, using different grain size fractions and extractions. Geoderma 84:65–87

Report on the State of the Environment in Republic of Serbia for 2009 (2010) Agency for environmental protection—Ministry of Environment and Spatial Planning

Reza R, Singh G (2010) Assessment of heavy metal contamination and its indexing approach for river water. Int J Environ Sci Tech 7(4):785–792

Samecka-Cymerman A, Kempers AJ (2004) Toxic metals in aquatic plants surviving in surface water polluted by copper mining industry. Ecotoxicol Environ Saf 59:64–69

Sermin Örnektekin S, Cakmakli S (2003) Chemical composition and acidity of rain at the Gulf of Iskenderun, North-East Mediterranean. Water Air Soil Pollut 3(5–6):157–172

Springborn RK, Silliman JK (1992) Cutting and grinding fluids: selection and application. American society of tool and manufacturing engineers, Dearborn

Thomas R, Meybeck M (1992) The use of particulate material. In: Chapman D (ed) Water Quality Assessments—a guide to use of biota, sediments and water in environmental monitoring. Chapman and Hall, London, pp 134–181

Trumbulovic-Bujic Lj, Acimovic-Pavlovic Z (2008) Influence of air pollutants on air quality in industrial environment. Metalurgija-J Metall 14(3):229–240

Weidong L, Weifeng L, Haifeng L, Zunhong Y (2009) Influence of sewage sludge on the slurryability of coal–water slurry. Fuel 88(11):2241–2246

Westerlund C, Viklander M (2006) Particles and associated metals in road runoff during snowmelt and rainfall. Sci Total Environ 362(1–3):143–156

Zare Garizi A, Sheikh V, Sadoddin A (2011) Assessment of seasonal variations of chemical characteristics in surface water using multivariate statistical methods. Int J Environ Sci Tech 8(3): 581–592