J. Int. Environmental Application & Science, Vol. 3 (2): 66-73 (2008)

The level concentration of lead, cadmium, copper, zinc and phenols in the water river of Sitnica

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Received January 29, 2008; Accepted February 27, 2008

Abstract: The Sitnica River is surrounded by agricultural land and settlements with unresolved wastewater discharge positioned downstream from the significant industrial plants. The purpose of this work was to determine the amount of lead, cadmium, copper, zinc and phenols in the water of River Sitnica and to identify potential pollutants in the flow of this River. For this reason four sample places were chosen: Fushë Kosova (A_1), Obiliq (A_2), Vragolia (A_3) and Mitrovica (A_4). Managing and water protection from pollution have a strategic importance for our country. Experimental results show that quality of this water is endangered from heavy metals (Pb, Cd, Cu, Zn) and phenols. The concentration level of phenols in A_2 and A_3 ample places and heavy metal concentration in all sample places exceeded allowed values of the fourth category of the quality of surfaced waters. Supporting these values we can conclude that water of this river is polluted in such level so that it can't be used for supply, irrigation, recreation, etc. To this condition contributed considerably industrial water from Kosovo power plants in Obiliq and urban central water which with no pretreatment flow into the river Sitnica. To prevent the pollution and to begin the revitalization of the bed of this river it is the last moment for the adequate measures to be undertaken.

Keywords: *The Sitnica River, Heavy metals, Phenols, Water quality.*

Introduction

The river Sitnica flows up in the village Sazli of Ferizaj and is characterized with a low hydrological regimen, with an average flow of 0.8 m^3/sec (Anonim., 2003**)**. Since historically this river is surrounded by a lot of dwellings, river Sitnica is an important factor for their development. Until lately, the water of this river was an important flow for them and was used for different destinations like, water supply, irrigation, fishing and recreation. The last period of time the river Sitnica is converted into a natural recipient of waste waters like the ones coming from Kosovo power plants in Obiliq, waters from bigger and smaller central urban canalization systems, through which river flows down, and which have unresolved problems of treatment and purification of discharged waters. To the flow of the river Sitnica subjoined small rivers like Graçanka, Drenica, Llapi and Prishtevka, which are also recipients of the waste waters of different urban and industrial centres (Korça, *et. al*., 2002; Anonim., 1989).

Parallel with this in the river Sitnica and other small rivers that flow down, it comes a considerable amount of raw waters from the agricultural wrought surfaces. In the middle part of its flow, river Sitnica percolates the city of Obiliq where objects of Kosovo power plants and their activity are dislocated, starting from the exploitation of the natural resources (lignite) until the production, carriage and distribution of electrical energy which considerably indicates in the environment, and in the condition of the river Sitnica as well. Natural waters, in different concentrations, practically contain all chemical elements. Usually ecotoxicological metals in natural waters are in small amounts. In the last decades different methods are used for determination of the concentration of solved metals and ionic types of their traces in water. Contemporary development of the electrochemical analysis enables analysis with high sensitivity; specified analysis and reproducibility for a number of water samples with a minimal

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displacement of chemical equilibrium of the sample even in the levels lower than 10^{-9}M. The concentration of mobile forms of the solvable metals can be obtained directly from the samples of raw natural water, while their total concentrations can be obtained by measuring total metal concentrations in raw acidified samples, (Branica, 1989)

Moreover, today electrochemical instrumentation has been computerized and the analytical procedure is completed automatically. Despite all these analytical and technical capabilities, most of the developments reported until now deal with on-line automatic voltametric analyzers for laboratory and/or field measurements. Development of the experimental procedure for natural waters is still a professional and scientific challenge.

Some metals in aquatic environment react in a specific way which is to be followed with a wide spread of their endurance solvable in water. Their interactions are mainly connected with dominant physical-chemical mechanism. Trace metals in aquatic environment are spread out through abiotic and biotic accretion. Their relative amount in each surface depends from its physical chemical reactivity, respectively from the scale of achieved balance (dynamic equilibrium) (Branica, 1990).

Trace metals species in waters are spread between different physicochemical forms (i.e. simple inorganic species, organic, labile and inert complexes and metal ions adsorbed onto a variety of solid and colloidal particles). Variation in the chemical speciation of an element will affect its bioavailability. Thus, not only total concentration, but also metal speciation measurements are required to understand and predict the role and fate of ecotoxic trace metals in aquatic systems (Branica *et.al*., 1995).

Study Field and Methodology

The purpose of this study was determination of the quantity of lead, cadmium, copper, zinc and phenols (as total phenols) in the water of the Sitnica River as well as identification of the potential pollutants of this water. For this reason in the period of 2005-2007 samples of water in four sample places along the downstream of this river are taken. Along the flow in the bed of the river Sitnica considerable amounts of urban and industrial waters discharge straight from dwellings and different industries.

According to this, sample places are chosen to notice the indication of potential pollutants and its self- purification capability. Samples were taken in four following points: Fushë Kosovë (A1), after the discharge of urban waters in Prishtina and the suburb; Obiliq (A2), after the discharge of the waters of Kosovo's power plants "A" and "B"; Vragoli (A3) before the reunion of the water of the rivers Drenica with Sitnica and Mitrovica (A4), closeness to the city of Mitrovica, before the reunion of river Sitnica with river Ibër (Figure 1).

Samples of the water for analyses are taken and prepared according to the standards methods (Anonim., 1992; Dalmacija, 2000). Heavy metals are determined from the acidic aquatic solutions with voltametric method with anodic stripping voltametry (Branica *et. al.* 1998).

Phenols are determined with spectrophotometer, measuring colour intensity of condense products of phenols compounds from chloroform extract with 4-aminoantipyrin in 460 nm. With this method all o-phenols and m-phenols can be detected, while p- phenols substituting. The sensitiveness of the method depends on the nature of substituting. Preliminarily phenols must be separated with distillation, from various organic and inorganic substances. Only volatile phenols were included in determination. Taking into consideration that water samples contain different phenol compounds, obtained results were expressed as a phenol equivalent. The applied methodology is a standard method and it is acceptable in many world laboratories (Balvay**,** 1991; Lee & Jones-Lee, 1999; Jusufi *et. al*. 2004).

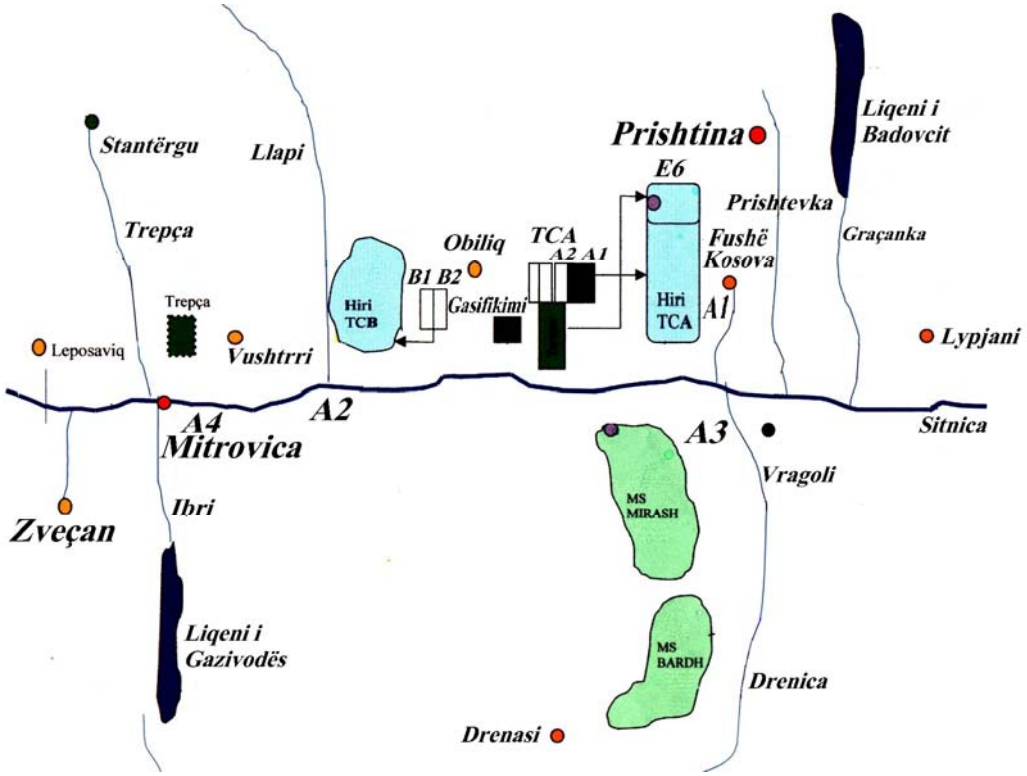

Figure 1. *Schematic sample places in water flow the river of Sitnica*

Results and Discussion

Natural water contains low concentrations of eco-toxic metals and any contaminations may present a severe hazard to the normal functioning of the aquatic ecosystem. Something like that is happening with the water of river Sitnica. Trace metals are not biodegradable and are involved in biogeochemical cycles by which they are concentrated in sediment and biota, by very high distribution coefficients. Different anthropogenic and biogeochemical sources indicate in the content of trace metals in different aquatic surfaces and that: (i) by, direct input of the pollutants that contain metals, or by inputting other reactive reagents (ii) which have an indication in spreading trace metals within chemical types and their surfaces in the aquatic system. (Organic ligands, active superficial material, redox reagents) and indirect, like thermal pollution (iii). When it comes to the point of river Sitnica, it is evident that in this river all used waters from Kosovo power plants (Kosova "A" and "B") are discharged there, and exude waters of all ash disposals and two surface open mine (Mirash and Bardh) of these two power plants also.

Direct input of different pollutants in aquatic system indicates in the content of the general amount of metals within the entire system, while two others (ii) and (iii) show how evidently can be indicated in the amount and spreading of ionic types in different surfaces of the aquatic system.

Repeated mobilization of previous deposed metals in the lower levels of the aquatic system causes increase of risky indication in human nutrition especially with its concentration in the edible chain.

Obtained experimental results in this research improve data from literature (Rugova *et.al.* 1989; Rugova *et.al.*, 2003; Jusufi *et. al.*, 2004; Arbneshi, *et al.*, 2004) according to which concentration of heavy metals and phenols in the river Sitnica is disquietude.

Analysis of the content of the amount of Lead, Cadmium, Copper and Zinc in water of river Sitnica show that the highest concentrations for lead, zinc and cadmium are registries in the sample place A4 (Mitrovicë) during all year (Figures 2, 3 and 4).

This condition can be explained with the fact that this sample place presents reunion point of both rivers Sitnica with Ibër in which waters of the combine Trepça are discharged. Although most of the producible capacities of this combine are not in function, pollution with heavy metals is evident.

Heavy metals (Pb, Zn and Cd) come from the existing disposals of the combine objects especially after the rainfalls.

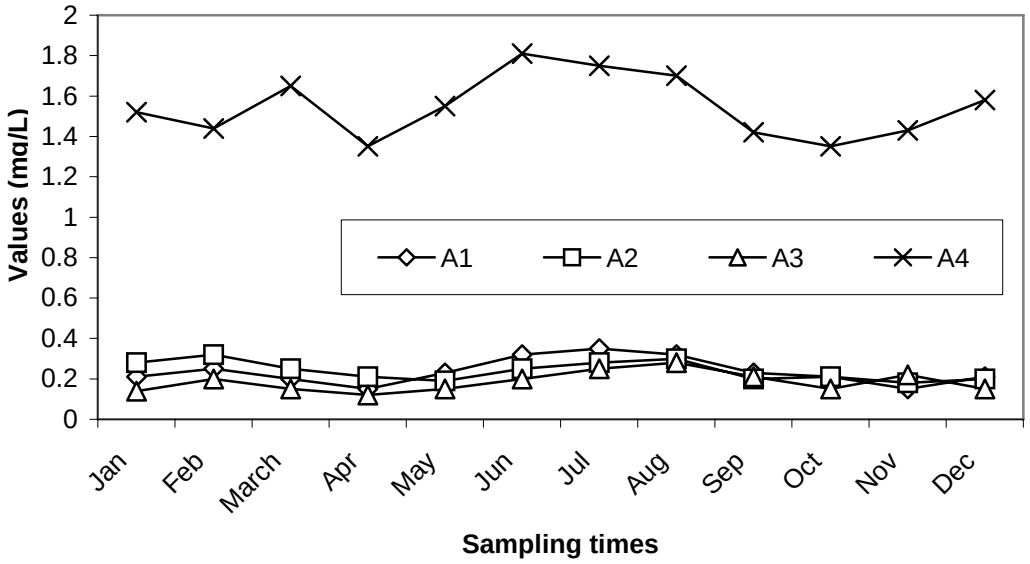

Figure 2. The level concentration of lead in the water river of Sitnica.

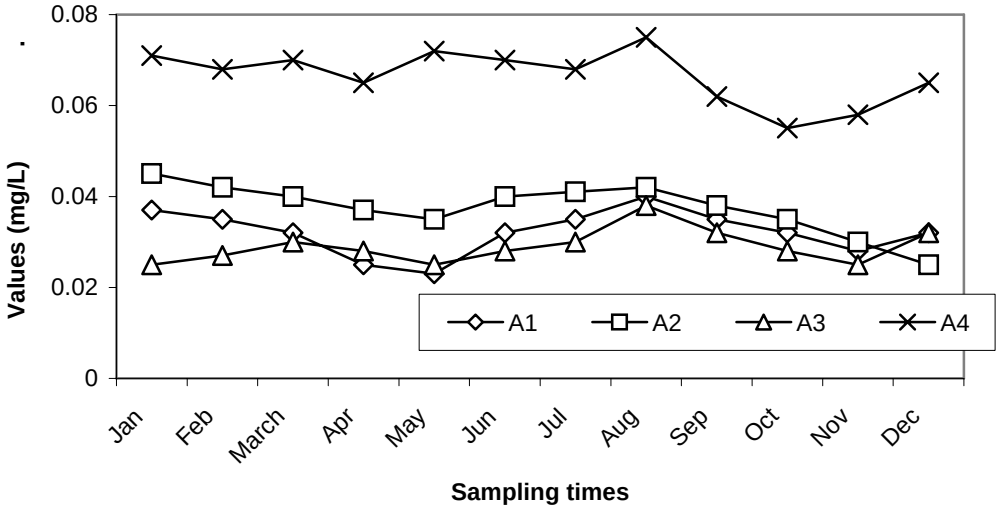

Figure 3. The level concentration of cadmium in the water river of Sitnica

In three other sample places (A1, A2 and A3) which are near Kosovo power plants, the amount of lead and zinc has a relatively small variability (fig 2 and 4), while cadmiums and Coppers shows an emphatic variability (Figures 3 and 5), especially the coppers one Figure 5.

The presence of heavy metals in the river Sitnica in these three sample places is in fact as a result of the producible activity of Kosovo power plants which use lignite as a combustible material and which after combustion releases a considerable amount of ash. Created disposals from residues after the combustion of lignite are near river Sitnica and in the permanent way indicate in the quality of its water.

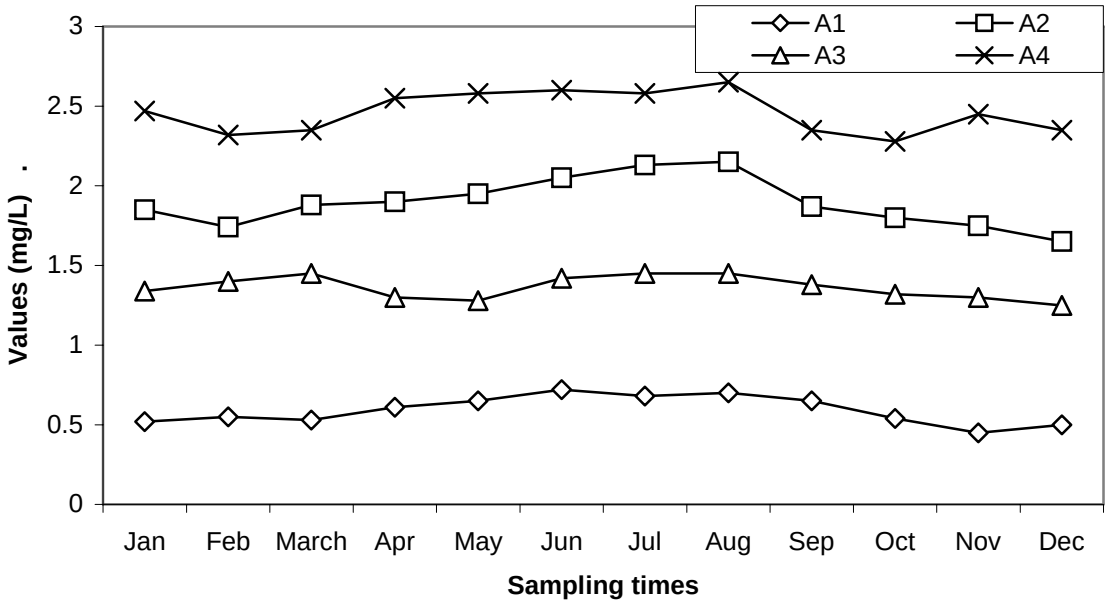

Figure 4. The level concentration of zinc in the water river of Sitnica

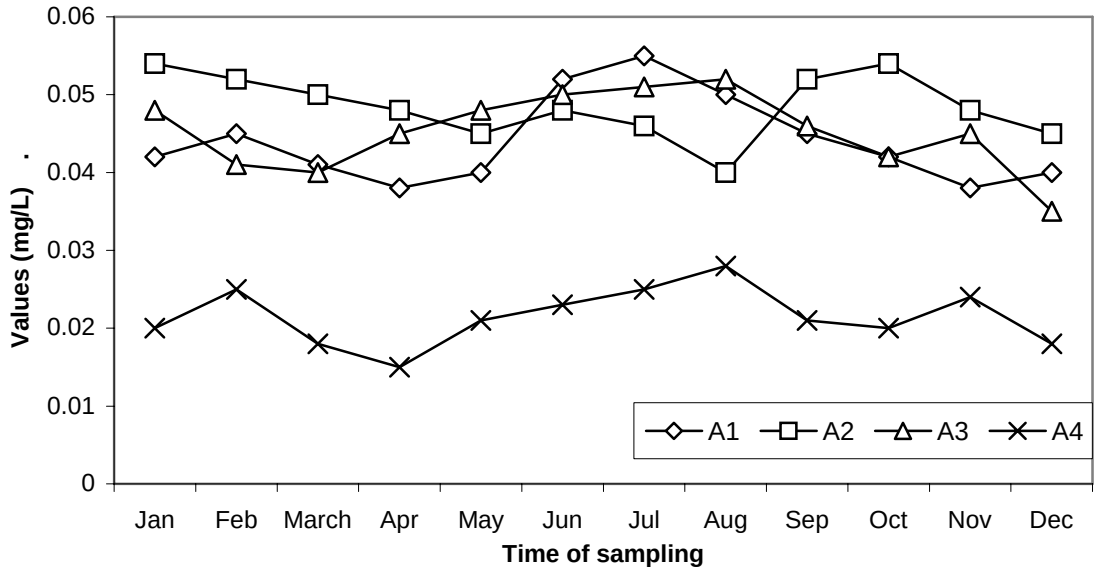

Figure 5. The level concentration of copper in the water river of Sitnica

High quantity of copper in these sample places can be described as a variety of agricultural activities in this region. Farmers, with their activity in agro production, use different

chemical preparations, which contain copper, and which together with raw waters from agricultural surfaces, arrive till the river Sitnica.

In the case of Kosovo Electrical Company (KEC) large quantities of phenols are present in waters, coming from Thermal Power Plant, production and process of lignite, and ash disposal site. Cooling manner, type of secondary fuel (diesel oil or petroleum), transportation technology, ash disposal and water chemical preparation, are factors that determine type and waste waters. In water preparation facilities in all Thermal Power Plants wastewaters are obtained, and after being neutralized are used for hydraulic transportation or flow into natural recipients.

Besides lignite, Thermal Power Plants use naphtha or diesel oil as a secondary fuel; therefore a considerable amount of polluted water with phenols is obtained. All Thermal Power Plants using lignite, for the ash transportation carry out hydraulic technology, which is unacceptable from aspect of water pollution. In facilities for coal production in Kosova`s mine basins a waste waters are obtained which require multiple purification.

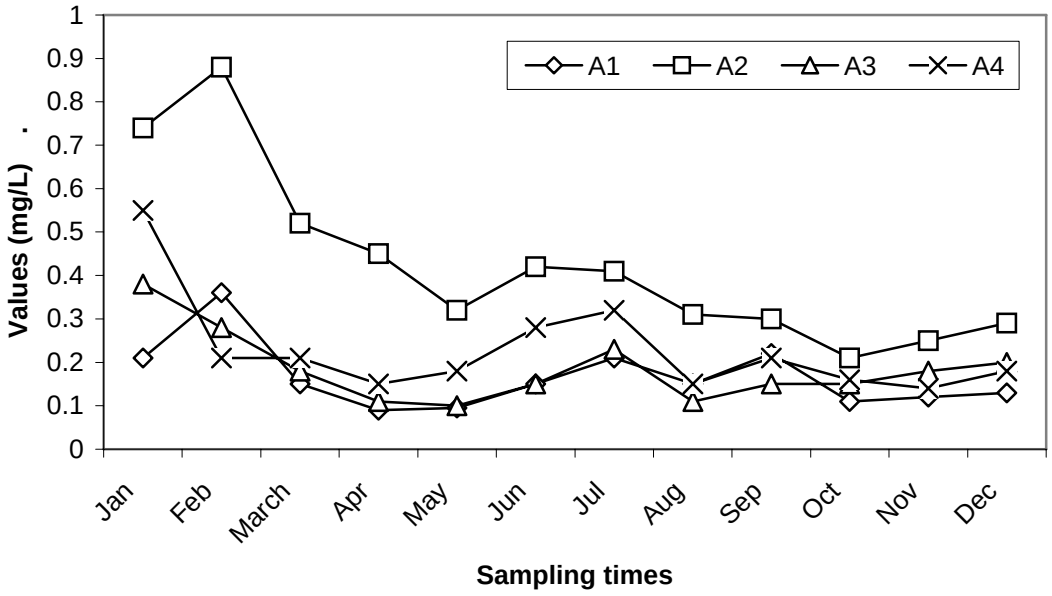

Figure 6. The level concentration of phenols in the water river of Sitnica

Obtained results are shown graphically in Figures 6. Phenols concentration was carried out for a long period of time in four taken samples. In this work only phenols concentration during the rainfall will be discussed. This has resulted in increasing of phenols concentration in all locations from where samples were taken. Water alongside the river has been over concentrated with phenols, which often exceeded maximal allowed concentration.

Thus, in the end of January 2005 and beginning of February 2005 is noticed slightly increase of phenols concentration in sample taking A1 in the entrance of Sitnica River, after outfall of the sewage coming from Prishtina town (0.12-0.21 mg/L). In sample taking A2 when Sitnica River enters KEC area, a great increase is noticed which is observed till the last point in Mitrovica. These concentrations are 0.20-0.74 mg/L in sample taking A2; 0.12-0.88 mg/L in sample taking A3; 0.13-0.69 mg/L and 0.12-0.55 in sample taking A6 (figure 6). After the rainfall break the situation becomes stabilized, which is noticed with decreasing of phenol concentration in all taken samples.

Conclusions

In this research an effort has been made only to improve the differences between concentration of heavy metals and phenols in different sample places along the river Sitnica. From the obtained data we can see that concentrations of heavy metals are higher in the sample place A4 (Figures 2, 3 and 4) except the copper, which has higher concentration in the A3 sample place (Figure 5).

The highest level of phenol concentration is a registry in the sample place A2 (fig. 6) in the period January-march 2003, period followed with a lot of rainfalls.

According to this we can conclude that the quantity of phenols grew as a result of water level, which infiltrated till the disposal of phenol waters in Obiliq by taking with a considerable amount of phenols. A great contribution to this condition has the rinse of ash and coal disposals that are near river Sitnica.

In reference to comparative analyses of the content of metals and phenols in different sample places from the period January- December 2005 we can conclude that obtained results can serve as indicators of water pollution of river Sitnica with micro pollutants as a result of a direct anthropogenic indication.

Even though a lot of damage has been done, in aspect of letting water of river Sitnica be polluted with heavy metals and phenols, there is still time for changes. In fact it is the last time for the adequate measures to be undertaken.

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