INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES
(p-ISSN: 2348-5213: e-ISSN: 2348-5221)
www.ijcrcps.com
Coden: IJCROO(USA) Volume 3, Issue 4 - 2016

Research Article

SOI: http://s-o-i.org/1.15/ijcrcps-2016-3-4-10

The distribution of metals in sediments in the Likova, Kumanova and Pçinja rivers

Nazmi Ejupi[1], Bardha Korça[2],*Bujar H. Durmishi[1], Zehra Hajrullai - Musliu[3], Murtezan Ismaili[1], Ahmed Jashari[1], Agim Shabani[1]

[1]State University of Tetova, Faculty of Mathematics and Natural Sciences, R. of Macedonia
[2]University of Prishtina, Faculty of Mathematics and Natural Sciences, Republic of Kosova
[3]University Kiril and Metodij, Faculty of Veterinary, Republic of Macedonia

*Corresponding Author: bujar.durmishi@unite.edu.mk

Abstract

Rivers are one of the most important components of the environment and play a crucial role in the development of the respective regions. They are getting more and more polluted because of the rapid urbanization, industrialization and other developmental activities. The pollution of rivers is a very serious issue because the usage of polluted water has direct and long-lasting effects on people's health and the existence of other animals and creatures. The sediment is characterized with its own capacity to concentrate the trace metal levels and represents a very suitable indicator for the monitoring and detection of pollution sources in river waters. The aim of this paper was to examine the contents of some metals in the sediments of rivers Likova, Kumanova and Pçinja, in order to assess the suitability of their water for general usage purposes. The water and sediment samples were gathered in February 2014 from six sampling stations. Initially, some physical-chemical parameters of the water from these rivers were obtained, such as their color, turbidity, pH, electrolytic conductivity, chemical oxygen demand, ammonia, nitrites, nitrates, and chlorides. Based on the physical-chemical quality assessment of the water from these rivers, we conclude that it belongs to the first/second category as determined by the state regulations, and in general it resulted in being very little polluted. The sediment samples were characterized with the composition of twenty two metals in river sediments and international guidelines were implemented in order to assess the pollution level. According to them, the sediments were most polluted by Al, Fe, Ca, Na, Mg and Mn. The content of metals in river sediments in the examined area pursued the following order: Al > Fe > Ca > Na > K > Mg > Mn > Ba > Zn > Sr > V > Cr > Ni > Pb > Cu > Li. Metals that surpassed the Dutch standard on sediments were the following: Ba, Ni, and Cu. Pollutants from the industry, agriculture, and households were deposited in rivers and this contributed to the increase of pollution levels in these rivers. Based on the study results, we came to conclude that this mild pollution of the rivers was caused by urban actions, agricultural works and some industrial discharge.

Keywords: Metals, Pollution, Physical-Chemical Parameters, Sediment, River Water.

Introduction

The pollution of rivers and the sediments in them occurs everywhere in the world because of the rapid increase of the population, urbanization, industry and intensive agricultural practices. This has therefore alarmed the scientists and other experts dealing the issue of water pollution in rivers. Surface waters are crucial for the existence of people, animals, the flora and fauna in waters, the industry, agriculture, sailing and other outdoor activities.

Nowadays, the quality of water in rivers is becoming worse and worse, and in developing countries the pollution of rivers represents a serious threat. In this context, a key challenge of water resources management is the identification of the main anthropogenic pollution sources and the assessment of their downstream ecological and socio-economic impacts [1], since rivers and lakes are very important par t of our natural heritage [2]. Industrial growth has led

© 2016, IJCRCPS. All Rights Reserved

to increase in quantity of chemical materials used in industry, as well as in industrial facilities which use the chemicals as raw materials [3]. As a result, an increased emission of heavy metals in waters and sediments of the rivers can be noticed. Industrial wastes have a negative influence in water habitats and pollution is caused by their direct and/or indirect toxic activity, thus changing the quality of the water.

The pollution of rivers is a matter of concern in Macedonia too. The studies of heavy metals and other pollutants in river water and sediments have multiplied in recent years, especially for large rivers [4, 5, 6]. In many papers it is reported that dumping at trace levels by inorganic and organic pollutants have constantly polluted the water in rivers and the sediments in them; therefore, one of the important results of stability is metal expansion in food chain [7, 8].

Seen from the perspective of the persistence and potential for the bio-accumulation of many micro-pollutants, sediments are considered an important source of danger against water ecosystems. Unlike organic pollutants, heavy metals do not undergo the process of natural decomposition and as such they entering natural waters become part of the water sediment system and their distribution processes are controlled by a dynamic set of physical and chemical interactions and equilibria [9]. In this way, the pollution of rivers with heavy metals deteriorates the delicate equilibrium of water systems. Unlike organic pollutants, heavy metals are also known for their long half-life and as such their negative effects on water organisms last quite a long time. Heavy metals are important polluters of environment and determination of the concentration of heavy metals in different environments shows the pollution grade of those environments [10].

Heavy metals, including essential and non-essential elements play an important role in ecotoxicology, because they are toxic to living organisms. The bioaccumulation and biomagnification of these metals in fishes and other creatures at toxic levels is possible even when their exposure is low. Recently, anthropogenic activities have caused an increase in the amount of heavy metals in water ecosystems and the pollution of heavy metals in aquatic system is growing at an alarming rate and has become an important worldwide problem [11]; on the other hand, trace elements have expanded effect on environment because of their uses in Human's life [12].

Heavy metals in aquatic ecosystem and sediments have natural and anthropogenic origin; distribution and accumulation of metals are influenced by sediment texture, mineralogical composition, oxidation-reduction state, adsorption - desorption processes and physical transport [13]. As a consequence of anthropogenic pollution, the biochemical cycle and equilibrium of heavy metals in rivers has changed drastically. Anthropogenic sources of pollution mainly come from various different industrial branches and intensive agricultural practices, without leaving behind urban pollution too. That is why the pollution of the environment with metals is considered a huge concern – the toxicity of heavy metals in different habitats has been reported by many authors [14, 15, 16]. In recent years, there have been extraordinary attempts to characterize the fate, weight and distribution of heavy metals in sediments [5]. The pollution of sediments with heavy metals in many European rivers has been a study focus of many researchers and scientists; many such studies have focused on the industrialized parts of Europe [17]. Some studies have shown that water sediments have been polluted with heavy metals in these industrialized areas. Therefore, the assessment of the distribution of metals in sediments is useful to understand the pollution level in water systems[18], specifically in the above-mentioned areas. Similarly, research carried out by [19, 20], has widely confirmed the pollution of river sediments with heavy metals. Another factor that makes the whole situation even worse is the discharge of wastewaters in rivers, without their prior adequate treatment. In this context, the weak water quality does not influence only the water fauna, but it also considerably increases the cleaning costs of the water used for various different purposes [21].

The research on the concentration of heavy metals in river sediments in Macedonia has not been that frequent and in most of the rivers is still unknown. The aim of this paper was to study the distribution of some metals in the sediments of rivers Likova, Kumanova and Pçinja, in order to assess the suitability of their water for general usage purposes. Metals, as pollutants, have been purposefully selected, because their concentrations can cause serious toxic effects in the surrounding industrialized and urbanized environment.

Materials and Methods

The study area

The Likova, Kumanova, and Pcinja rivers all in the region of the city of Kumanovo, Republic of Macedonia, were chosen for purposes of this study because there have been some indications lately that they have been affected by the urban, agricultural and industrial pollution (Figure 1). The Likova River is in the northwestern part of Macedonia and is a tributary of the Kumanova River. This river is created in the village of Goshince with the conjunction of the Goshince river and Breshtani river, whereas the Slupcane river serves as its left tributary. In the upper flow, it has a mountainous character whereas in the lower flow up to the spill, it has a field character. This river is 17.5 km long, whereas its basin covers an area of 300 km^2. Two artificial lakes have been created in this basin – the artificial lake of Likova and Glazhnja. The average flow of this river is 1.42 m^3/s.

© 2016, IJCRCPS. All Rights Reserved

The Kumanova River is situated in the northeastern part of Macedonia and flows out east to the Skopska Crna Gora. It flows through the city of Kumanova and ends as a right tributary of Pçinja River. It is 44 km long with an overall fall of 1060 m. Its basin covers an area of 460 km^2. The Likova River is its most important tributary. The basin of this river is bare and therefore its bed is porous, causing frequent floods. The Pçinja River is the left tributary of the Vardar River. This river belongs to the Aegean basin and it covers an area of 3140 km^2 (1247 km^2 in Serbia and 1893 km^2 in Macedonia). Other left tributaries include the Bistrica, Petroshnica and Kriva Reka rivers, whereas the Kumanova River is its right tributary.

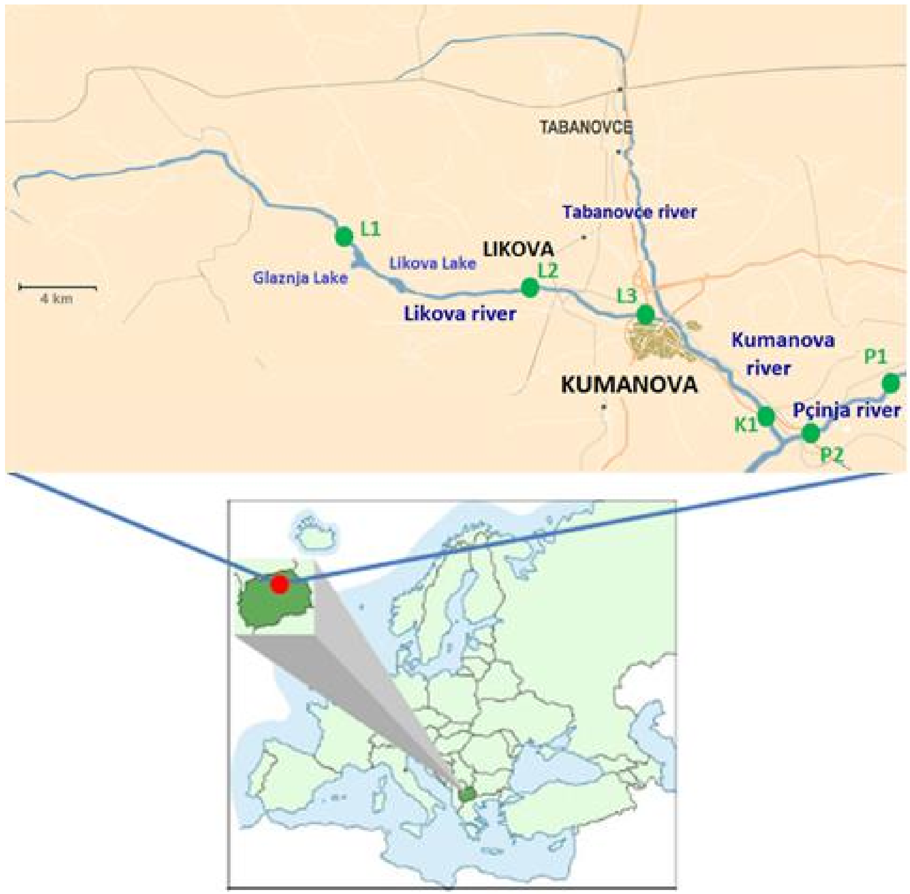

Figure 1. Map of monitoring stations.

Acquisition of samples and their preparation

In order to achieve the research objectives, samples for the physical-chemical analysis of the water and sediments were obtained on 20.02.2014 from six sampling stations: L1, L2, L3, K1, P1 and P2. Three of these stations are situated along the flow of the Likova River (L1, L2, and L3), one is situated along the flow of the Kumanova River (K1) and two along the flow of the Pçinja River (P1 and P2) (Figure 1). The L1 station was before the Glazhnja accumulation, the L2 station was after the Likova accumulation, the L3 station was at the exit of the village of Likova before getting to the city of Kumanova; the K1 station was outside the city of Kumanova and the plant for urban wastewater treatment ahead of the debouchments in the Pçinja River. The P1 and P2 stations are situated before the conjunction of rivers Kumanova and Pçinja. The selection of stations was based on the probable pollution indicators.

Water samples were taken using clean and sterilized polyethylene bottles of 1L. All of these bottles had spent the night in 10% nitric acid and then were rinsed out several times with ultrapure water before sampling took place. Before being filled, bottles were washed with the river water three times and then were filled with flowing river water along the river flow. Sample bottles were labeled with the name of the respective station as well as the filling time and date. Sediment samples from the river beds were taken in accordance with the methods used for shallow rivers [22]. These methods include the usage of respective sampling equipment under water at a depth of 10 cm to 20 cm. Two sub-samples were taken at every station, which were then joined into one single sample, and then it was placed in the polyethylene bottles.

© 2016, IJCRCPS. All Rights Reserved

Treatment and analysis of waters

Physical-chemical parameters of the water in the mentioned rivers were analyzed at the Public Healthcare Center in Kumanova. Each water sample was analyzed on nine parameters: color, turbidity, pH, electrolytic conductivity (EC), chemical oxygen demand (COD), ammonia, nitrites, nitrates, and chlorides. After getting into the laboratory, water samples were filtered through the Whatman membrane filter, with 0.45 μm pore diameter. The above-mentioned parameters were determined by referring to standardized methods as cited in the literature review [23]. The color was determined colorimetrically using a comparator; the pH value was measured using a pH-meter; EC was measured using conductometer; COD was measured using the H_2SO_4 and $H_2C_2O_4$ method; ammonia, nitrites, and nitrates were measured with a UV-Vis spectrophotometer and chlorides were measured with a silvermetric titration.

Treatment and analysis of sediments

Metals in sediments were analyzed at the Chemistry Institute laboratories in the city of Skopje. Sediment samples were characterized by the composition of the following metals: Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, Tl, V and Zn. The analyses were carried out by using standard analytical methods. The samples were initially taken to laboratories where they were dried in fully aired rooms for 8 to 10 days. Afterwards they underwent a sieving process. 0.2528 g sieved sediment was measured from every sediment and 5 mL of HNO_3 65 % solution was added to it. This composition was heated until only 1mL of the sample solution remained. This was then cooled for 5 to 10 minutes; 5 mL of HF 40 % solution and 1.5 mL of $HClO_4$ 60 % solution were added to the newly formed solution and it was again heated until another 1mL of the sample solution remained. Next, 2 mL of HCl 37 % and 5 mL distilled water were added to the latter and it was cooled for 1 to 2 minutes; then it was filtered using a plastic funnel. The obtained filtrate was put in a normal plastic flask with 5 mL volume. This is how the sample was prepared for a spectrometric measurement.

Instrumentation

Twenty two metals in the sediments from the selected rivers were examined. Metals such as Ca, Fe, K, Mg, and Na were analyzed with the atomic emission spectrometer Varian ICP-AES 715S, in a process known as inductively coupled plasma atomic emission spectrometry, whereas other remaining metals were analyzed with inductively coupled plasma mass spectrometry (ICP-MS).

Quality control

The quality control of the applied techniques was performed by standard addition method, and it was obtained that the recovery for the analysed elements ranges for ICP-AES between 98.0% and 101.5%. The same method was applied for the determination of some trace elements in the reference standard materials JSAC 0401 (soil) and SARM 3 (rock), yielding values very close to those certified.

Results and Discussion

The results of physical-chemical analyses of the water from the Likova, Kumanova and Pçinja rivers are shown in Table 1, whereas the results of the analyses of metals in sediments in Table 2 and Figures 2 – 4.

Table 1. Results of physical-chemical analyses of the water from the Likova, Kumanova and Pçinja rivers.

Phisico-chemical parameters	Unit	L1	L2	L3	K1	P1	P2	Maximal values
Color	º Pt-Co	nd*	nd	nd	nd	nd	nd	**20**
Turbidity	NTU	0.310	0.436	1.18	1.300	0.663	0.378	**4**
pH	/	7.55	7.44	7.75	7.85	7.83	7.66	**6.8 - 8.5**
EC	μS/cm	330	465	282	290	250	241	**1000**
COD	mg/L	0.82	0.82	1.61	1.22	1.77	1.73	**5**
Ammonia	mg/L	nd	nd	nd	nd	nd	nd	**0.50**
Nitrites	mg/L	0.01398	nd	nd	nd	nd	0,01064	**0.10**
Nitrates	mg/L	1.627	2.908	0.559	0.558	0.341	0.483	**50**
Chlorides	mg/L	3.54	12.4	5.31	6.73	2.48	2.48	**250**

*nd - not detected

© 2016, IJCRCPS. All Rights Reserved

Table 2. Concentration of metals in sediments from the Likova, Kumanova and Pçinja rivers (mg/kg) and descriptive statistics

Stations	Ag	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K
L1	< 1	34315	<5	195,8	7575	<1	<1	204,2	40,4	29407	14588
L2	< 1	32921	<5	64,7	14501	<1	<1	44,9	64,8	33458	2978
L3	< 1	38758	17,3	138,5	34453	<1	<1	95	25,1	26291	6913
K1	< 1	44555	<5	214	49070	<1	<1	111,1	43,6	27649	7299
P1	< 1	26459	<5	270	13132	<1	<1	38,5	21,4	23460	12114
P2	< 1	33103	<5	344,3	17181	<1	<1	45,8	24,6	25455	13478
Minimum	/	26459	/	64,7	7575	/	/	38,5	21,4	23460	2978
Maximum	/	44555	/	344,3	49070	/	/	204,2	64,8	33458	14588
Median	/	33709	/	204,9	15841	/	/	70,4	32,8	26970	9706,5
Average	/	**35018,5**	**/**	**204,6**	**22652**	**/**	**/**	**89,9**	**36,7**	**27620**	**9561,7**
Stand. Dev.	/	**6111,6**	**/**	**97,9**	**15820,8**	**/**	**/**	**63,5**	**16,5**	**3493,9**	**4529,8**

Table 2. Concentration of metals in sediments from the Likova, Kumanova and Pçinja rivers (mg/kg) and descriptive statistics (continued)

Stations	Mg	Mn	Mo	Na	Ni	Pb	Sr	Tl	V	Zn	Li
L1	11338	515	<1	5854	126,6	10.0	49,1	<1	106,2	95,9	28,8
L2	6862	601	<1	14452	24,1	18,5	43,5	<1	206,5	129,8	7
L3	8320	640	<1	8907	44,7	9,4	83,7	<1	87,6	102,3	8,3
K1	11319	571	<1	7733	60	29,5	146,5	<1	71,8	219,8	9,5
P1	6891	411	<1	12447	16,9	75,2	154	<1	74,7	100,9	11
P2	6962	516	<1	11770	24,3	83,1	173	<1	88,6	135,1	11,6
Minimum	6862	411	/	5854	16,9	9,4	43,5	/	71,8	95,9	7
Maximum	11338	640	/	14452	126,6	83,1	173	/	206,5	219,8	28,8
Median	7641	543,5	/	10338,5	34,5	24	115,1	/	87,6	116,1	10,3
Average	**8615,3**	**542,3**	**/**	**10193,8**	**49,4**	**37,6**	**108,3**	**/**	**105,9**	**130,6**	**12,7**
Stand. Dev.	**2172,1**	**80,6**	**/**	**3232,3**	**41**	**33,1**	**56,6**	**/**	**50,8**	**46,6**	**8,1**

© 2016, IJCRCPS. All Rights Reserved

Physical – chemical parameters of the water in rivers

The color of the water is an organoleptic parameter of the water, which provides a preliminary assessment of pollution. The notion of "the color of the water" refers to its nuance that is produced by the presence of metal ions, humus compositions and particles suspended from pollutants. The results from the analysis of this parameter show that the water in the selected rivers was of relatively high quality because the color of the water could not be detected in any of the sampling stations (Table 1).

pH is classified as secondary tap water pollutant, whose impact is considered as aesthetic [24]. The high or a low pH value shows the alkaline or acidic conditions of the water, respectively. The pH value is affected by the geology and types of soil, by natural organic acids present in water, as well as by the acidic rain, which usually has a pH value between 3.5 and 5.5. pH values of the water from the selected rivers varied between 7.44 and 7.85, which is within the normal range and do represent pollution (Table 1). The lowest value of 7.44 was measured at the L2 station and this slight deviation of the pH from the increasing trend between L1 and K1 was, in our opinion, because of the accidental penetration of acidic substances in the water in the Likova River. The highest value of 7.85 was measured at the K1 station, which can be attributed to the pollution caused by urban waste waters from the city of Kumanova. There was an increasing trend of the pH values from L1 (except L2) to K1, and then a slight decrease from P1 to P2 could be noticed.

Electrolytic conductivity (EC) is the measure of a material's ability to accommodate the transport of an electric current and it largely depends on the amount of salts dissolved in water. EC is an important measure of the water quality, because it gives very concrete information about the amount of dissolved materials in the water. EC can also help to find potential pollution sources, because polluted water usually has higher values compared to clean water. EC values quite often show pollution from road salts, septic systems, waste water management plants, or urban/agricultural drainages. High EC values show pollution of the water in rivers. These values, in our concrete case, ranged between 241.00 – 465.00 μS/cm, which were within the range of recommended values, pointing at very low pollution levels. The highest value was measured at the L2 station and the lowest at the P2 station.

Turbidity is a measure of the amount of material suspended in water. It is the cloudiness or haziness of a fluid caused by large numbers of individual particles that are generally invisible to the naked eye, similar to smoke in air. The measurement of turbidity is a key test of water quality. This material, comprising of particles from clay, mud, algae, floating sediments and rotten plant substances, cause distribution and absorption of light, increase water temperature and decrease dissolved oxygen concentration. High turbidity can also lower the amount of light that can penetrate in the water, which in turn reduces the process of photosynthesis and the production of dissolved oxygen. Clean waters have low turbidity in general. Rainfalls increase turbidity in surface waters by washing the sediments, organic matters and other substances away. Human activity such as destruction of vegetation and soil can lead to dramatic increase of turbidity levels. In our concrete case, the measured level of turbidity was lower than 1.5 nephelometric turbidity units (NTU). Results have been shown in Table 1 and they are all within the limits of the recommended values, ranging from 0.310 to 1.300 NTUs. The highest results were recorded at L3 (1.180 NTU) and K1 (1.300 NTU).

Chemical Oxygen Demand (COD) is a measurement of the oxygen required to oxidize soluble and particulate organic matter in water. COD is used to determine the amount of organic pollutants in surface waters and wastewaters, making it a useful measurement tool for the quality of the water. COD is the amount of oxygen that is needed to oxidize the organic pollution by using strong oxidizing agents. The examined water samples contained COD values ranging from 0.82 – 1.77 mg/L (Table 1). The lowest value was measured at L1 and L2 stations, whereas the highest value was measured at the P1 station. Results show that the water in the selected rivers is not polluted with organic substances.

Ammonia, nitrites and nitrates – the presence of substances that are created from the decomposition of wastes of animal origin is of crucial importance in terms of the assessment of the quality of surface waters. Waters containing products from this decomposition are usually microbiologically polluted. In polluted waters, different products can be created, such as compositions of C and S, as well as those of N, which are of particular importance. Nitrogen in these products appears in the form of ammonia, nitrites, and nitrates, coming from outflowing waters from industries and households. These parameters are the most usual indicators for the assessment of the quality of water in rivers. The concentration levels of nitrites and nitrates and the ammonia, expressed in mg/L have been given in Table 1.

The presence of ammonia in water is a very dangerous occurrence. The allowed amount of ammonia in surface waters, according to the regulations in Macedonia, cannot exceed 0.5 mg/L. Fortunately, we could not detect the presence of this substance in any of the examined stations. Nitrites are also toxic and their amount in water is maximally

© 2016, IJCRCPS. All Rights Reserved

limited to 0.1 mg/L. They are created in water from the dissolution of biological and industrial pollutants. The composition of nitrites in stations ranged from 0.01064-0.01398 mg/L. The lowest value was measured at P2 and the highest at L1. Nitrites could not be detected at L2, L3, K1 and P1. Nitrates represent a higher degree of oxidation in the circulation of nitrogen in nature. High levels of nitrates are not desirable, because they can be reduced to nitrites under the influence of the red flora, and nitrites are toxic, as mentioned earlier. Nitrates represent the final product of the biological oxidation of organic pollutants. This shows that the water had been polluted earlier. The range of values of nitrates at stations was 0.341-2.908 mg/L, which means within the allowed limits. The lowest value was measured at P1 and the highest at L2. Low values of nitrates show that water in rivers is not anthropogenically polluted. Results show that the presence of ammonia, nitrites, and nitrates was within the recommended and the allowed levels for water in rivers of the first/second category. This is due to the low urban pollution and the reduction of the production of industrial items.

Chlorides are less dangerous pollutants in river waters. According to the recommended standards, their presence in river waters is quite high and may reach up to 250 mg/L. The concentration of chlorides in river waters in our case ranged from 2.48 - 12.4 mg/L. The lowest vale was measured at P1 and P2 and the highest at L2. The composition of chlorides in river waters was low and this indicates a minimal anthropogenic pollution.

Metals in sediments

Metals in general and heavy metals in particular play a crucial role in the pollution of rivers; however, the concentration of some of those metals are beneficial whereas of some others harmful and toxic. The toxicity of heavy metals depends on the type of the metal and the compound, on the amount of metal that reaches the organism and the length of its activity. This group of metals consists of Hg, Pb, Cd, Cr, Cu, Ni, As, Zn. The process of absorption is responsible for the elimination of metal traces from water in rivers and sediments.

The descriptive statistics of results obtained from the analysis of the sediments in respective rivers has been presented in Table 2, whereas the distribution of metals in sediments from the sampling stations has been presented in Figures 2 – 4. Since the legislation in Macedonia does not cover the issue of metals in sediments, our results were compared to the Dutch standards [25] as well as global average values of sediments in rivers [26]. Based on the analyses, it was found that Al was the most represented, followed by Fe, Ca, Na, K, Mg. The presence of other metals such as Mn, Ba, Zn, Sr, V, Cr, Ni, Pb, Cu, and Li ranged from 12.7 – 542.3 mg/kg, whereas the presence of Ag, As, Cd, Co, Mo and Tl was less than 1 mg/kg, meaning that the pollution with these metals was very low. Metals that surpassed the Dutch standard were Ba, Ni, and Cu. The sustainability of metals in river sediments in the examined area pursued the following order: Al > Fe > Ca > Na > K > Mg > Mn > Ba > Zn > Sr > V > Cr > Ni > Pb > Cu > Li.

The concentration of Al was higher and it varied between 26459 and 44555 mg/kg, whereas the average value with standard deviation was 35018.5±6111.6 mg/kg. The lowest level was measured at P1 and the highest at K1 (Figure 2). The distribution of Al in stations of concern had an increasing trend from L1 to K1, and lower values at P1 and P2. The content of Al is not included in the Dutch standards or in the global averages of sediments in rivers.

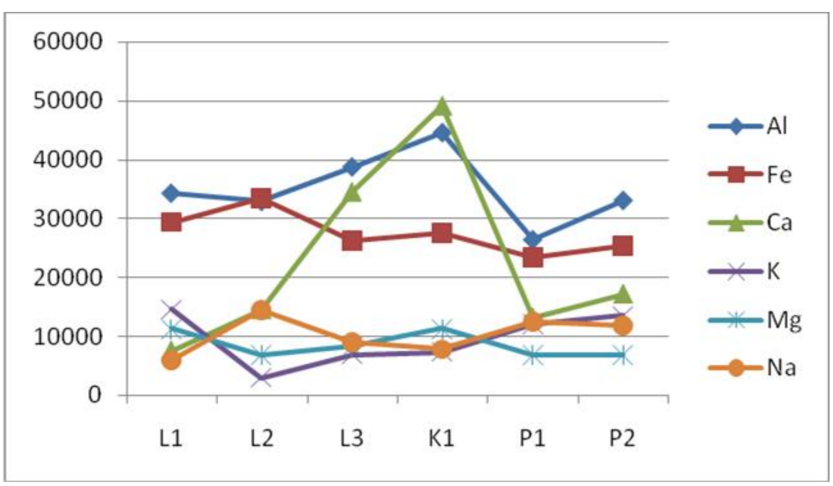

Figure 2. Spatial distribution of Al, Fe, Ca, K, Mg and Na in sediments (mg/kg)

© 2016, IJCRCPS. All Rights Reserved

The concentration of Fe was high and it varied between 23460 and 33458 mg/kg, whereas the average value with standard deviation was 27620±3494 mg/kg. The lowest level was measured at P1 and the highest at L2 (Figure 2). The distribution of Fe content in stations of concern had a slightly decreasing trend from L1 to P2. The content of Fe is not included in the Dutch standards whereas it was below the global averages of sediments in rivers (57405.9 mg/kg).

The concentration of Ca varied between 7575 and 49070 mg/kg, whereas the average value with standard deviation was 22652±15821 mg/kg. The lowest level was measured at L1 and the highest at K1 (Figure 2). The distribution of Ca in stations of concern had an obvious increasing trend from L1 to K1, and lower values with a slight decreasing trend at P1 and P2. The content of Ca is not included in the Dutch standards or in the global averages of sediments in rivers.

The concentration of Na varied between 5854 and 14452mg/kg, whereas the average value with standard deviation was 10193.8±3232.3 mg/kg. The lowest level was measured at L1 and the highest at L2 (Figure 2). The distribution of Na in stations of concern had an almost constant trend. The content of Al is not included in the Dutch standards or in the global averages of sediments in rivers.

The concentration of K was relatively high and varied between 2978 and 14588mg/kg, whereas the average value with standard deviation was 9562±4530 mg/kg. The lowest level was measured at P1 and the highest at L2 (Figure 2). The distribution of K in stations of concern had a sensitive decreasing trend from L1 to L2 and then an increasing trend from L3 to P2. The content of Al is not included in the Dutch standards or in the global averages of sediments in rivers.

The concentration of Mg was moderately high and varied between 6862 and 11338mg/kg, whereas the average value with standard deviation was 8615±2172 mg/kg. The lowest level was measured at L2 and the highest at L1 (Figure 2). The distribution of Mg in stations of concern had a decreasing trend from L1 to P2, except for the value at K1 where a considerable jump was noticed. The content of Mg is not included in the Dutch standards or in the global averages of sediments in rivers.

The concentration of Mn was moderately high and varied between 411 and 640 mg/kg, whereas the average value with standard deviation was 542.3±80.6 mg/kg. The lowest level was measured at P1 and the highest at L3 (Figure 3). The distribution of Mn in stations of concern had a progressive trend, then decreasing and increasing again from P1 to P2. The content of Mn is not included in the Dutch standards whereas it was below the global averages of sediments in rivers (975.3 mg/kg).

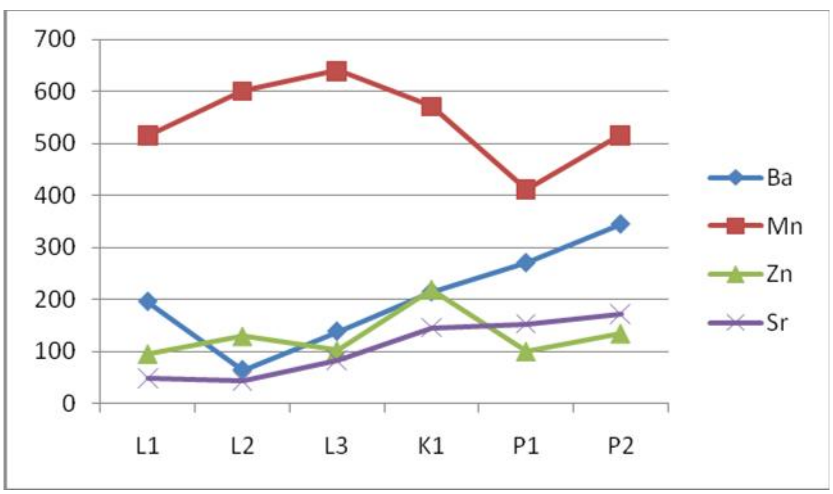

Figure 3. Spatial distribution of Ba, Mn, Zn and Sr in sediments (mg/kg)

The concentration of Ba was moderate and varied between 64.7 and 344.3 mg/kg, whereas the average value with standard deviation was 204.6±97.9 mg/kg. The lowest level was measured at L2 and the highest at P2 (Figure 3). The distribution of Ba in stations of concern had an increasing trend from L2 to P2, with an exception of the value of 195.8 mg/kg at L1. This shows that the concentration of Ba in sediments has increased gradually along the downstream basin of the rivers. The concentration of Ba was above the recommended Dutch standards (200 mg/kg), but it is not included in the global averages of sediments in rivers.

The concentration of Zn was moderate and varied between 95.9 and 219.8 mg/kg, whereas the average value with standard deviation was 130.6±46.6 mg/kg. The lowest level was measured at L1 and the highest at K1 (Figure 3).

© 2016, IJCRCPS. All Rights Reserved

The distribution of Zn in stations of concern had an increasing trend, with an exception of the higher value at K1. The concentration of Zn in sediments was below the recommended Dutch standards (140 mg/kg), and below the global averages of sediments in rivers (303 mg/kg).

The concentration of Sr was moderate and varied between 43.5 and 173 mg/kg, whereas the average value with standard deviation was 108.3±53.6 mg/kg. The lowest level was measured at L2 and the highest at P2 (Figure 3). The distribution of Sr in stations of concern had an increasing trend from L1 to P2. The content of Sr is not included in the Dutch standards or in the global averages of sediments in rivers.

The concentration of V was moderate and varied between 71.8 and 206.5 mg/kg, whereas the average value with standard deviation was 105.9±50.8 mg/kg. The lowest level was measured at K1 and the highest at L2 (Figure 4). The distribution of V in stations of concern had a decreasing trend, except from the higher value at L2. The content of V is not included in the Dutch standards or in the global averages of sediments in rivers.

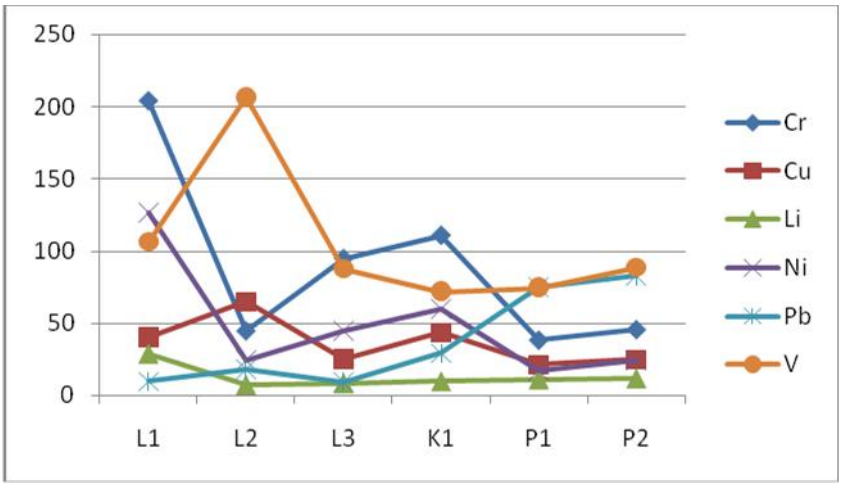

Figure 4. Spatial distribution Cr, Cu, Li, Ni, Pb and V in sediments (mg/kg)

The concentration of Cr was moderate and varied between 38.5 and 204.2 mg/kg, whereas the average value with standard deviation was 89.9±63.5 mg/kg. The lowest level was measured at P1 and the highest at L1 (Figure 4). The distribution of Cr in stations of concern had a decreasing trend from L1 to P2. The concentration of Cr in sediments was below the recommended Dutch standards (100 mg/kg), and below the global averages of sediments in rivers (126 mg/kg).

The concentration of Ni was moderate and varied between 16.9 and 126.6 mg/kg, whereas the average value with standard deviation was 49.4±41 mg/kg. The lowest level was measured at P1 and the highest at L1 (Figure 4). The distribution of Ni in stations of concern had a drastically decreasing trend from L1 to L2 and then an increasing trend from L2 to K1 and again a decreasing trend from K1 to P2. The concentration of Ni in sediments was allowed the recommended Dutch standards (35 mg/kg), and below the global averages of sediments in rivers (102.3 mg/kg).

The concentration of Pb was low and varied between 9.4 and 83.1 mg/kg, whereas the average value with standard deviation was 37.6±33.1 mg/kg. The lowest level was measured at L3 and the highest at P2 (Figure 4). The distribution of Pb in stations of concern initially had a constant trend from L1 to L2 and then an highlighted increasing trend from L3 to P2. The concentration of Pb in sediments was below the recommended Dutch standards (85 mg/kg), and below the global averages of sediments in rivers (230.75 mg/kg).

The concentration of Cu was moderately low and varied between 21.4 and 64.8 mg/kg, whereas the average value with standard deviation was 36.7±16.5 mg/kg. The lowest level was measured at P1 and the highest at L2 (Figure 4). The distribution of Cu in stations of concern had a generally decreasing trend from L1 to P2. The concentration of Cu in sediments was above the recommended Dutch standards (36 mg/kg), and below the global averages of sediments in rivers (122.9 mg/kg).

The concentration of Li was low and varied between 7 and 28.8 mg/kg, whereas the average value with standard deviation was 12.7±8.1 mg/kg. The lowest level was measured at L2 and the highest at L1 (Figure 4). The distribution of Li in stations of concern had a drastically decreasing trend at the beginning from L1 to L2, and then a mild increasing trend from L2 to P2. The content of Li is not included in the Dutch standards or in the global averages of sediments in rivers.

© 2016, IJCRCPS. All Rights Reserved

The Likova River, Kumanova River and Pçinja River are the most important rivers in the region of Kumanova. They have mainly carbonate basins, which give bicarbonate characteristics to their water. A very few studies have been carried out about the waters and sediments in these rivers [27]. Just outside the city of Kumanova, the urban wastewater treatment plant is situated, which cleans the water from the pollutants thus contributing to the preservation of the water in the rivers of Kumanova and Pçinja. Based on the physical-chemical parameters, it resulted in low levels of pollution of these waters, meaning that they belong to the first/second class.

In general, the pollution of rivers with metals has varied at different monitoring stations; the content of some metals was higher at the upper flows whereas of the others at lower flows of the rivers in question. The pollution in river basins is caused by the rinsing of soil from the water in rivers, by the regional erosion from rainfalls, by black waters flowing from residential areas that accumulate more at river basins, by out flowing waters from the few factories in the city (even though they operate at reduced capacity) as well as by the general pollution of the environment in the region of the municipality of Kumanova. Industrial, agricultural and household pollutants are deposited in rivers, which has caused some pollution to occur. Based on the obtained results, we concluded that this mild pollution in rivers was caused by urban, agricultural and industrial activities.

Conclusion

In order to explore the pollution level of sediments with metals, twenty two metals were analyzed in sediment samples taken from six sampling stations in the rivers of Likova, Kumanova and Pçinja. The sustainability of metals in river sediments in the examined area pursued the following order: Al > Fe > Ca > Na > K > Mg > Mn > Ba > Zn > Sr > V > Cr > Ni > Pb > Cu > Li. International sediment quality assurance guidelines were used in assessing the pollution levels. According to them, sediments were mostly polluted by Al, Fe, Ca, Na, Mg and Mn. Average presence was detected for Ba, Zn, Sr, V, Cr, Ni, Pb, Cu and Li, whereas the presence of Ag, Cd, Co, Mo, Tl and As was very low (< 1 mg/kg). Metals that surpassed the Dutch standard on sediments were the following: Ba, Ni, and Cu. The distribution of metals in sediments showed very low presence of anthropogenic elements (Cu, Cr, Mn, Ni, Pb, V and Zn) poured off in river sediments by the industry, agricultural activities and households. Based on the physical-chemical quality assessment of the water from these rivers, we conclude that it belongs to the first/second category as determined by the state regulations, and in general it resulted in being very little polluted.

References

1. Jürgen Hofmann, Michael Rode & Philipp Theuring (**2013**). Recent developments in river water quality in a typical Mongolian river basin, the Kharaa case study. *Proceedings of H04, IAHS-IAPSO-IASPEI Assembly, Gothenburg, Sweden, July 2013 (IAHS Publ. 361, 2013)* (pp. 123-131). Gothenburg: IAHS-IAPSO-IASPEI Assembly.
2. Muniyan G. A. and Ambedkar M. (**2012**). Analysis of heavy metals in water, sediments and selected freshwater fish collected from Gadilam river, Tamilnadu, India. *International Journal of Toxicology and Applied Pharmacology*, 2 (2): 25-30.
3. Shanur Jahedul Hasan, Mohosena Begum Tanu, Md. Istiaque Haidar, Tayfa Ahmed and AKM Shafiqul Alam Rubel (**2015**). Physico-chemical characteristics and accumulation of heavy metals in water and sediments of the river Dakatia, Bangladesh. *International Journal of Fisheries and Aquatic Studies*, 300-304.
4. Woitke P., J. Wellmitz, D. Helm, M. Kube, P. Lepom, P. Litheraty (**2003**). Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. *Chemosphere 51(8)*, 633-642.
5. Camusso M., Galassi S., Vignati D. (**2002**). Assessment of river Po sediment quality by micropollutant analysis. *Water Research, 36*, 2491.
6. Sakan S. M., D. S. Đorđević, D. D. Manojlović, P. S. Polić (**2009**). Assessment of heavy metal pollutants accumulation in the Tisza river sediments. *Journal of Environmental Management 90 (11)*, 3382-3390.
7. Seyed Mohammad Derakhshesh and Ebrahim Rahimi (**2012**). Determination of Lead Residue in Raw Cow Milk from Different Regions of Iran by Flameless Atomic Absorption Spectrometry. *American-Eurasian Journal of Toxicological Sciences, 4(1)*, 16-19.
8. Mehdi Hosseini, Afshin Abdi Bastami, Javad Kazemzadeh Khoei, Maryam Esmailian, Elmira Janmohammadi Songhori and Mina Najafzadeh (**2012**). Concentrations of Heavy Metals in Selected Tissues of Blue Swimming Crab, Portunus pelagicus (Linnaeus, 1758) and Sediments from Persian Gulf. *World Applied Sciences Journal, 19(10)*, 1398-1405.
9. Jain C. K. (**2004**). Metal fractionation study on bed sediments of River Yamuna, India,*Water Research,* Vol. 38, Issue 3, 569–578.
10. Bekteshi A., E. Myrtaj (**2014**). Heavy metals in the Shkodra lake ecosystem. *Journal of Environmental Protection and Ecology 15, No 3*, 834–841.
11. Malik N, Biswas AK, Qureshi TA, Borana K, Virha R (**2010**). Bioaccumulation of heavy metals in fish tissues of a freshwater lake of Bhopal. *Environ. Monit. Assess. 160*, 267-267.

© 2016, IJCRCPS. All Rights Reserved

12. Mandalia, Chintan Pathak and Hiren C. (**2011**). Impact of Environmental Pollution on Human Future. *World Journal of Environmental Pollution, 1(2)*, 08-10.
13. Mollazadeh N., F. Moattar, A.R. Karbassi and N. Khorasani (**2013**). Distribution of Metals, Chemical Partitioning, Pollution and Origins in Riverbed Sediment. *World Applied Sciences Journal*, 21 (5): 674-680.
14. Mason R. P. (**2013**). *Trace Metals in Aquatic Systems.* John Wiley & Sons, Ltd.
15. Albulescu M., H. Popovici, L. Turuga, S. Masu, A. Chiriac (**2012**). Analysis of Heavy Metals Content of Soil and Vitis Vinifera in Two Vineyard Areas of the Caras-Severin County, Romania. *J Environ Prot Ecol, 13 (1)*, 48 .
16. Neziri A., W. Gössler (**2008**). Determination of heavy metals in water and sediments of Drini river, Buna river and lake Shkodra. *Balwois.* Ohrid.
17. Oetken Matthias, Burkhard Stachel, Markus Pfenninger, Jörg Oehlmann (**2005**). Impact of flood disaster on sediment toxicity in a major river system – the Elbe flood 2002 as a case study. *Environmental Pollution, 134*, 87-95.
18. Gehan, M. el Zokm, Soaad el-Gohary and D.E. Abd-el-Khalek (**2012**). Studies of some heavy metals in water and sediment in el-max fish farm, Egypt. *World Applied Sciences Journal,18(2)*, 171-180.
19. Karbassi A.R., S.M. Monavari, Gh.R. Nabi Bidhendi, J. Nouri and K. Nematpour (**2008**). Metal pollution assessment of sediment and water in the Shur River. *Journal of Environ. Monit. Assess., 147*, 107-116.
20. Alireza Safahieh, Hossein Zolgharnein, Mahmood Hashemi Tabar, Bita Archangi and Sima Sarmadyan (**2012**). The levels of essential (Cu) and nonessential (Cd) heavy metals in crassostrea gigas, sediment and water. *American-Eurasian Journal of Toxicological Ssciences, 4(3)*, 143-146.
21. Nyamangara J., C. Bangira, T. Taruvinga, C. Masona, A. Nyemba, D. Ndlovu (**2008**). Effects of sewage and industrial effluent on the concentration of Zn, Cu, Pb and Cd in water and sediments along waterfalls stream and lower Mukuvisi river in Harare, Zimbabwe. *Physics and Chemistry of the Earth, 33*, 708–713.
22. Lewis D.W. and D.M. McConchie (**1994**). *Analytical Sedimentology.* New York, USA, Chapman and Hall.
23. APHA, AWWA, WEF (**1995**). *Standard methods for the examination of water and wastewater, 19th ed.* Washington, DC: American Public Health Association/America Water Works Association/Water environment federation.
24. Bujar H. Durmishi (**2013**). The study of the trihalomethanes (THMs) content variation with advanced analytical methods in the drinking water in the city of Tetova. *Disertation.* University of Tirana, Faculty of Natural Sciences, Chemeistry Department, Tirana, Albania.
25. Dutch Ministry of Housing, Spatial Planning and Environment. Available at http://www.contaminatedland.co.uk/std-guid/dutch-l. htm (Accessed sep **2015**)
26. Emad A. Mohammad Salah, Tahseen A. Zaidan, Ahmed S. Al-Rawi (**2012**). Assessment of heavy metals pollution in the sediments of Euphrates river, Iraq. *Journal of Water Resource and Protection, Vol. 4*, 1009-1023.
27. Stanko Ilić Popova, Trajče Stafilov, Robert Šajnc and Claudiu Tanaselia (**2015**). Distribution of trace elements in sediment and soil from river Vardar basin, Macedonia/Greece. *Journal of Environmental Science and Health, Part A*, 1-14.

Access this Article in Online	
	Website: **www.icrcps.com**
	Subject: **Water Pollution**
Quick Response Code	

How to cite this article:

Nazmi Ejupi, Bardha Korça,Bujar H. Durmishi, Zehra Hajrullai - Musli, Murtezan Ismaili, Ahmed Jashari, Agim Shabani. (2016). The distribution of metals in sediments in the Likova, Kumanova and Pçinja rivers. Int. J. Curr. Res. Chem. Pharm. Sci. 3(4): 99-109.

© 2016, IJCRCPS. All Rights Reserved