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HEAVY AND TOXIC METALS IN WATER AND SEDIMENTS OF THE VARDAR RIVER IN SKOPJE

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A b s t r a c t: Ninety composite samples (45 samples of surface water and 45 samples of river sediments) were collected from course of the Vardar river, in the urban part of the Skopje valley – City, in the period from 8. 3. 2013 to 17. 5. 2013. Heavy metals concentrations (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, Ti, Zn), some non-metals (B, P), anions and more physico-chemical parameters of water and sediments in the Vardar river, during its course through the urban area, were studied in order to assess and discuss its pollution in Skopje and the origin of this pollution. Besides water, river sediments, as reservoirs of most pollutants, were analyzed, using methods of Geoaccumulation index (I_{geo}) and Enrichment factor (EF).

Key words: heavy metals; Vardar river; pollution; water; sediments

INTRODUCTION

In the course of the Vardar river is situated major urban settlement Skopje, where live about 500,000 people. Increasing urbanization and industrialization results in polluting the river, since the river is preferred waste disposal site for domestic, agricultural and industrial effluents, (Boev and Lepitkova, 2002), sometimes in their unprocessed state, because some industries do not make pretreatment of waste water or sewage, which they discharged to river, so effluents go, directly or indirectly, to river waters, by surface run off or drainage. They are all potential sources of contaminants in the Vardar river. Various substances, organic or inorganic, that can contaminate the river, come to Vardar (many of them come from anthropogenic sources, they are results of various human activities) (Boev and Lipitkova, 2002), but the most common and most dangerous are metals, primarily because they have significant toxicological impact and are particularly resistant to degradation and removal. Heavy metals, derived from natural (geochemical) or anthropological sources, when they come in contact with water systems, are distributed among the various parts of these systems, water, sediments and biological communities in the sediments, their distribution depends of the mineralogical and chemical composition of various substances present, of anthropological influences and processes. Suspended particles in water flows collect contaminants due to their nature of sorption, for example heavy and toxic metals (which are considered the least soluble), coming up to environment from anthropogenic sources in the form of inorganic complexes or hydrated ions, floating in waters or accumulate in sediments of aquatic ecosystems, where they bind to sediment matrices, with weak physical and chemical bonds and sediment at bottom of rivers. Sediments are known as major removers of metals in aquatic environments, but they are also important reservoirs of such substances, from where they are desorbed and transformed to different bioavailable and toxic forms (Imran & Aboul-Enein, 2006). with exposure to various chemical environments. Sorbed on sediments, in aquatic ecosystems, such as the Vardar river, contaminants are transported by river in suspension or like drag sediment and through solubility, they become sources of water pollution with heavy metals. The more heavy metals dissolve and pass easier in the aqueous phase, the more they have greater toxicological significance and bioavailability. Surface sediments provide a good representation and analysis of the current state of anthropogenic input of metals into rivers.

THE STUDY AREA

The study area is located on the northern part of the Republic of Macedonia, in the Skopje valley, its urban part – Skopje City, on about 41˚59' latitude, 21˚25' longitude. Starts from the west entrance of the Vardar river in Skopje, near the settlement of Kondovo, before the bridge on the ring road around Skopje and ends at the southeast of Skopje, near Dolno Lisiče, just before the bridge over the Vardar, on the road that connects Dolno Lisiče with Jurumleri.

Measurement locations were chosen because of the proximity of potential contaminants and availability of measuring points (Table 1 and Figure 1). They are:

1) v. Kondovo – reference point, the first measurement location, comparing the input into Vardar, in terms of what is input and characteristics of the river before entering the city – M1;

2) St. Lazar – located in Đorče Petrov, just before the tributary Treska – M2;

3) Hrom – in the settlement of Hrom, where on the left riverbank, near the river are situated more former, large industrial facilities – M3;

4) Zlokućani – before the tributary Lepenec, in urban neighborhoods Vlae and Karpoš 4, near the great industrial zone – Lepenec – M4;

5) Momin Potok – after the triburaty Serava, near the industrial zone, with more old and currents plants and warehouses – M5

6) Železnička stanica – in the very urban core of the city, with more current and former sources of pollutants. Just before the measurement point is Transport center (railway station) and railway bridge – M6;

7) Novo Lisiče – urban part of the city, on the right bank of the river is a urban settlement and more sites and the left bank of the river has more former, large industrial facilities, some of which are still active – M7;

8) Gorno Lisiče – near one side has a landfill and industrial zone, and on the other side is settlement of Gorno Lisiče and agricultural areas – M8;

9) Dolno Lisiče – near wild dump, on the road connecting settlements Dolno Lisiče and Jurumleri, before the bridge on Vardar, near cultivated, agricultural areas – M9;

The measurement locations are located at the following coordinates, assessed with the GPS.

Table 1

Coordinates of measurement locations

T.	Masurement location	Latitude	Longitude
M1	v. Kondovo	42.00661N	21.31379E
M2	St. Lazar – GP	42.00294N	21.34574E
M3	Hrom	41.99906N	21.37503E
M4	Zlokućani	42.01160N	21.38202E
M5	Momin Potok	42.01397N	21.41670E
M6	Železnička st.	41.99270N	21.45135E
M7	Novo Lisiče	41.99057N	21.47608E
M8	Gorno Lisiče	41.98093N	21.49924E
M9	Dolno Lisiče	41.96273N	21.54423E

Fig. 1. The area of research, with the locations from which samples were taken

MATERIALS AND METHODS

Sampling and preparation

From each one measurement location on the Vardar river, were sampled simultaneously, composite water and composite sediment samples (for composite samples – Mitra, Somenath, 2003; Harvey, 2006). Water and fresh retained sediments (that are sediments before a short time frame and retained and separated by river currents and sediments that the river carries), were taken from shallow, coastal waters of the river, near the right and left banks of the river, at a distance from the coast 1–1.5 m. The waters were collected at a depth of 10–15 cm from the surface of the water and sediments at a depth of 0–10 cm from the bottom of the river, on the same measurement locations. Samples were collected during the period 8. 3. 2013 to 17. 5. 2013 in 5 occasions, with frequency of measurement 18–19 days. Water samples were collected in bottles of inert plastic (polyethylene), with immersion on the specified depth and sediment samples were taken with grab and placed in polyethylene bags, then they were transported under standard conditions to the laboratory. Temperatures of the water and sediments are determined in the field, while the other parameters (pH, turbidity, organic matter, alkalinity, COD, anions, cations) are determined before or after certain preparations were made on them in the laboratory.

Analysis of samples

Concentrations of heavy metals were determined by Liberty – Varian ICP – AES spectrometer, after being extracted from the samples, by the digestion with acids, anions were determined with the spectrophotometer and for the determination of other parameters were used valid, standard analytical methods and equipment (Ahuja & Jespersen, 2006; Van de Wiel, 2003; Boss & Fredeen, 1997).

RESULTS AND DISCUSSION

The purpose of this study is to assess the level of contamination, toxic heavy metals and quality of water and sediments in surface parts of the Vardar river, horizontal distribution of these contaminants and to evaluate the status of pollution around the downstream of Vardar in its urban part – Skopje City, because contamination is most easily accomplished by human activity, so the river water and especially river sediments near urban areas usually contain high levels of contaminants, which is a serious environmental problem.

River water

The measured values for heavy metals in the river water are given in Table 2 and they are compared with the maximum allowable concern of metals under *Uredba za klasifikacija na vodite* – Sl. vesnik br.18/99 (Decree on Water Classification – Gazette No. 18/99), with Dutch (target values – TG and intervention – IntV values, *The New Dutchlist*) and Australian standards for metals in freshwater (ANZECC/ARMCANZ-2000).

The obtained results of surface water in Vardar distribution is shown in Figure 2) compared with Macedonian MAC regulation (*Uredba za clasifikacija na vodite,* Sl. vesnik RM br.18/99 – Decree on Water Classification – Gazette RM No. 18/99), indicate that the waters of the river meet the quality criteria of class I, in terms of Al, Ba, Co, Cr, Fe, Ti, Zn and B, there are no contaminations with these metals. Compared with average measured values of Al, Cr, in 2007 in the Vardar river there is a decrease in the concentration of these metals. There is a slight increase in concentration of Fe and Zn, that measured values show compared to 2007 (*Study on waste water management 2007* – LEAP 2 Skopje City – 2011). However, incurred increased concentrations of Cr, two times in M1 (v. Kondovo) are larger than TG – values from the Dutch list of standards for ground water, but far from IntV–value (intervention), which are requiring action to prevent further pollution. In terms of Mg, Ca, K and Na, results were monitored by MAC for drinking water in emergencies and there is no evidence of contamination (*Pravilnik za bezbednost na vodata*, Sl. vesnik 46/08 – Rules of water safety). It is notable pollution with Pb, especially 29. 4. 2013 at two measuring locations, M1 and M3, with values corresponding to the V class of water, and in M5, on the 17. 5. 2013. The measurement locations M3 and M6 consistently elevated value of Pb, suggesting the existence of a source of ongoing contamination with Pb in these locations. Regarding the previously mentioned Study from 2007, there is some increase of Pb concentration, from then (LEAP 2, 2011). All measured values are smaller than Dutch IntV-value for Pb. Accidental pollution of the Vardar river happens with Mn (M5), As (M2) and Cd (M9), and there is little pollution in M5 with Cu.

Cu pollution is larger to some measurement locations in relation to 2007, according to the Study from 2007. The content of As is in satisfactory limits, except 12. 4. 2013 in M2, but at this point the measured value is less than the Dutch IntV-value, too. The content of Sr is evaluated according to some studies in the United States, after which the values of Sr under 0.5 mg/l for rivers are low values for ambient water (Skougstadt & Horr, 1960; Alfredo, 2014) and from this aspect the measured Sr contents in Vardar are below these values. Pollution of surface waters of Vardar is greater from aspect of P ratio eutrophication, at all measurement locations, especially in M5 (Momin Potok) and M9 (Dolno Lisiče), except for M3 (Hrom), where is close to the value for I and II-class of waters.

T a b l e 2

Concentrations of metals and some non-metals in water of the Vardar

Water (mg/l)	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sr	Ti	Zn
8. 03. 2013															
M1	<0.005	0.019	0.034	<0.005	<0.005	0.008	<0.005	0.069	4.91	0.008	0.028	<0,01	0.104	<0.005	0.020
M2	0.008	<0.005	0.014	<0.005	<0.005	<0.005	<0.005	0.069	5.40	0.005	0.039	<0,01	0.095	<0.005	<0.005
M3	0.010	0.022	0.018	<0.005	<0.005	<0.005	<0.005	0.071	12.00	0.003	0.044	<0,01	0.122	<0.005	<0.005
M4	0.011	0.009	0.015	<0.005	<0.005	<0.005	<0.005	0.051	11.90	0.004	0.016	0.015	0.114	<0.005	<0.005
M5	0.011	0.007	0.024	<0.005	<0.005	<0.005	<0.005	0.049	23.43	0.078	0.028	<0,01	0.226	<0.005	<0.005
M6	0.011	0.013	0.016	<0.005	<0.005	<0.005	<0.005	0.051	12.30	0.008	0.021	0.024	0.120	<0.005	<0.005
M7	0.011	0.027	0.019	<0.005	<0.005	<0.005	<0.005	0.060	14.80	0.007	0.105	<0,01	0.142	<0.005	0.005
M8	0.012	0.030	0.019	<0.005	<0.005	<0.005	<0.005	0.049	14.30	0.009	0.027	<0,01	0.138	<0.005	0.006
M9	0.012	0.020	0.017	<0.005	<0.005	<0.005	<0.005	0.040	13.40	0.008	0.043	<0,01	0.127	<0.005	0.010
Mean	0.011	0.017	0.020	0.005	0.005	0.006	0.005	0.057	12.49	0.015	0.039	0.013	0.132	0.005	0.008
Med	0.011	0.019	0.018	0.005	0.005	0.005	0.005	0.051	12.30	0.008	0.028	0.010	0.122	0.005	0.005
Min	0.005	0.005	0.015	0.005	0.005	0.005	0.005	0.040	4.91	0.004	0.016	0.010	0.095	0.005	0.005
Max	0.012	0.030	0.034	0.005	0.005	0.008	0.005	0.071	23.43	0.078	0.105	0.024	0.226	0.005	0.020
SD	0.003	0.009	0.006	0.000	0.000	0.001	0.000	0.011	5.46	0.024	0.027	0.005	0.039	0.000	0.005
26. 3. 2013															
M1	0.011	0.027	0.021	<0.005	<0.005	<0.005	<0.005	0.039	4.90	0.008	0.017	<0,01	0.132	<0.005	<0.005
M2	0.012	0.007	0.023	<0.005	<0.005	<0.005	<0.005	0.037	5.00	0.006	0.025	<0,01	0.135	<0.005	<0.005
M3	0.010	0.014	0.016	<0.005	<0.005	<0.005	<0.005	0.157	5.30	0.003	0.018	0.011	0.115	<0.005	<0.005
M4	0.011	0.014	0.019	<0.005	<0.005	<0.005	<0.005	0.096	5.40	0.003	0.035	0.010	0.119	<0.005	<0.005
M5	0.011	0.009	0.018	<0.005	<0.005	<0.005	0.011	0.096	7.10	0.056	<0,005	<0,01	0.140	<0.005	<0.005
M6	0.009	0.016	0.018	<0.005	<0.005	<0.005	<0.005	0.104	5.30	0.006	0.039	0.012	0.125	<0.005	<0.005
M7	0.007	<0,005	0.011	<0.005	<0.005	<0.005	<0.005	0.138	4.10	0.001	0.004	<0,01	0.087	<0.005	<0.005
M8	0.008	<0,005	0.012	<0.005	<0.005	<0.005	<0.005	0.018	4.40	0.005	0.039	<0,01	0.089	<0.005	<0.005
M9	0.007	0.021	0.012	0.025	<0.005	<0.005	<0.005	0.047	7.52	0.002	<0,005	0.030	0.093	<0.005	<0.005
Mean	0.010	0.013	0.017	0.008	0.005	0.005	0.006	0.082	5.45	0.010	0.021	0.013	0.115	0.005	0.006
Med	0.010	0.014	0.018	0.005	0.005	0.005	0.005	0.096	5.30	0.005	0.018	0.010	0.119	0.005	0.005
Min	0.008	0.005	0.011	0.005	0.005	0.005	0.005	0.018	4.10	0.001	0.004	0.010	0.087	0.005	0.005
Max	0.012	0.027	0.023	0.025	0.005	0.005	0.011	0.157	7.52	0.056	0.039	0.030	0.140	0.005	0.007
SD	0.002	0.008	0.005	0.007	0.000	0.000	0.002	0.049	1.15	0.018	0.015	0.007	0.021	0.000	0.001

Water (mg/l)	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sr	Ti	Zn
12. 4. 2013															
M1	0.011	0.008	0.023	<0.005	<0.005	0.008	<0.005	0.015	4.2	<0.005	0.002	0.018	0.143	<0.005	<0.005
M2	0.011	0.040	0.029	<0.005	<0.005	<0.005	<0.005	0.009	4.3	<0.005	0.038	<0,01	0.159	<0.005	<0.005
M3	0.010	0.011	0.022	<0.005	<0.005	<0.005	<0.005	0.004	5.3	<0.005	0.009	0.011	0.151	<0.005	<0.005
M4	0.010	0.023	0.020	<0.005	<0.005	<0.005	<0.005	0.005	4.8	<0.005	0.036	<0,01	0.147	<0.005	<0.005
M5	0.010	<0.005	0.021	<0.005	<0.005	<0.005	<0.005	0.019	5.0	<0.005	0.007	0.011	0.162	<0.005	<0.005
M6	0.010	0.017	0.021	<0.005	<0.005	<0.005	<0.005	0.006	4.7	<0.005	0.009	<0,01	0.144	<0.005	<0.005
M7	0.009	<0.005	0.020	<0.005	<0.005	<0.005	<0.005	0.006	4.2	<0.005	0.005	<0,01	0.138	<0.005	<0.005
M8	0.009	0.008	0.017	<0.005	<0.005	<0.005	<0.005	0.001	3.5	<0.005	<0,005	0.020	0.130	<0.005	<0.005
M9	0.009	0.020	0.016	<0.005	<0.005	<0.005	<0.005	0.005	3.7	<0.005	0.007	0.022	0.113	<0.005	<0.005
Mean	0.010	0.016	0.021	0.005	0.005	0.006	0.005	0.008	4.41	0.005	0.014	0.014	0.144	0.005	0.005
Med	0.010	0.012	0.021	0.005	0.005	0.005	0.005	0.006	4.30	0.005	0.007	0.011	0.144	0.005	0.005
Min	0.009	0.005	0.016	0.005	0.005	0.005	0.005	0.001	3.53	0.005	0.002	0.010	0.114	0.005	0.005
Max	0.012	0.040	0.029	0,005	0,005	0.008	0.005	0.019	5.27	0.005	0.038	0.023	0.163	0.005	0.005
SD	0.001	0.012	0.004	0.000	0.000	0.001	0.000	0.006	0.59	0.000	0.014	0.006	0.015	0.000	0.000
29. 4. 2013															
M1	0.007	0.028	0.029	<0.005	<0.005	<0.005	<0.005	0.004	3.1	0.015	0.014	0.034	0.128	<0.005	<0.005
M2	0.008	0.021	0.035	<0.005	<0.005	<0.005	<0.005	0.228	3.8	0.022	0.103	0.010	0.133	<0.005	<0.005
M3	0.008	0.022	0.038	<0.005	<0.005	<0.005	<0.005	0.060	3.7	0.003	<0,005	0.041	0.137	<0.005	<0.005
M4	0.010	0.021	0.021	<0.005	<0.005	<0.005	<0.005	0.033	5.1	0.001	0.034	<0,01	0.132	<0.005	<0.005
M5	0.015	0.011	0.043	<0.005	<0.005	<0.005	<0.005	0.051	12.6	0.133	0.039	0.023	0.349	<0.005	<0.005
M6	0.009	0.011	0.100	<0.005	<0.005	<0.005	<0.005	0.075	4.1	0.005	0.019	0.021	0.125	<0.005	<0.005
M7	0.009	0.006	0.023	<0.005	<0.005	<0.005	<0.005	0.051	4.3	0.003	0.007	0.011	0.125	<0.005	<0.005
M8	0.009	<0.005	0.022	<0.005	<0.005	<0.005	<0.005	0.049	4.1	0.008	0.013	<0,01	0.113	<0.005	<0.005
M9	0.009	0.014	0.029	<0.005	<0.005	<0.005	<0.005	0.066	4.4	0.021	0.011	<0,01	0.127	<0.005	<0.005
Mean	0.010	0.016	0.038	0.005	0.005	0.005	0.005	0.069	5.02	0.024	0.028	0.019	0.153	0.005	0.006
Med	0.009	0.014	0.029	0.005	0.005	0.005	0.005	0.051	4.10	0.008	0.014	0.011	0.128	0.005	0.005
Min	0.008	0.005	0.022	0.005	0.005	0.005	0.005	0.004	3.08	0.002	0.005	0.010	0.113	0.005	0.005
Max	0.015	0.028	0.100	0.005	0.005	0.005	0.005	0.228	12.62	0.133	0.103	0.042	0.349	0.005	0.009
SD	0.003	0.008	0.025	0.000	0.000	0.000	0.000	0.063	2.91	0.042	0.031	0.012	0.075	0.000	0.002
17. 5. 2013															
M1	0.007	0.014	0.021	<0.005	<0.005	<0.005	<0.005	0.052	2.4	0.018	0.050	<0,01	0.102	<0.005	<0.005
M2	0.007	0.004	0.021	<0.005	<0.005	<0.005	<0.005	0.091	2.4	0.015	0.016	0.010	0.111	<0.005	<0.005
M3	0.009	0.001	0.020	<0.005	<0.005	<0.005	<0.005	0.019	3.9	0.008	0.058	<0,01	0.136	<0.005	<0.005
M4	0.009	0.016	0.020	<0.005	<0.005	<0.005	<0.005	0.057	3.5	0.007	0.016	<0,01	0.131	<0.005	<0.005
M5	0.014	0.012	0.037	<0.005	<0.005	<0.005	<0.005	0.092	10.9	0.122	0.014	0.043	0.313	<0.005	<0.005
M6	0.008	0.013	0.021	<0.005	<0.005	<0.005	<0.005	0.066	3.6	0.013	0.045	0.014	0.145	<0.005	<0.005
M7	0.007	<0.005	0.020	<0.005	<0.005	<0.005	<0.005	0.065	3.2	0.013	0.039	<0,01	0.130	<0.005	<0.005
M8	0.009	0.021	0.008	<0.005	<0.005	<0.005	0.006	0.069	3.7	0.016	0.019	<0,01	0.130	<0.005	<0.005
M9	0.008	0.012	0.022	<0.005	<0.005	<0.005	<0.005	0.098	3.2	0.099	0.034	<0,01	0.139	<0.005	<0.005

Water (mg/l)	**Al**	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**Pb**	**Sr**	**Ti**	**Zn**
Mean	0.009	0.011	0.022	0.005	0.005	0.005	0.006	0.068	4.08	0.035	0.033	0.015	0.149	0.005	0.005
Med	0.009	0.013	0.021	0.000	0.005	0.005	0.005	0.066	3.50	0.015	0.034	0.010	0.131	0.005	0.005
Min	0.007	0.001	0.009	0.005	0.005	0.005	0.005	0.020	2.36	0.008	0.015	0.010	0.103	0.005	0.005
Max	0.014	0.021	0.038	0.005	0.005	0.005	0.006	0.099	10.93	0.122	0.059	0.044	0.313	0.005	0.005
SD	0.002	0.007	0.008	0.000	0.000	0.000	0.001	0.025	2.61	0.044	0.017	0.012	0.063	0.000	0.000
MAC Mak I–V class	1.5	0.03–0.05	1–4	0.0001–0.01	0.1–2	0.05–0.1	0.01–0.05	0.3–1	50▲	0.05–1	0.05–0.1	0.01–0.03	–	0.1	0.1–0.2
Dutch (TG–MAC)	–	0.01–0.06	0.05–0.625	0.0004–0.006	0.02–0.1	0.001–0.03	0.015–0.075	–	–	–	0.015–0.075	0.0150–.075	–	–	0.065–0.8
ANZECC	0.2	0.01	2	0.002	–	0.05 Cr(VI)	2	0.3	15	0.5	0.02	0.01	–	–	3
Average values for harmful and hazardous substances in the Vardar river and its tributaries on the territory of the city – river Treska and river of Lepenec [Source: Study on waste water management 2007 – LEAP 2 Skopje City – 2011]															
Saraj	0.0622	–	–	0.00002	–	0.0064	0.0014	0.042	–	–	–	0.003	–	–	0.0069
Vlae	0.0434	–	–	0.00001	–	0.0057	0.0015	0.034	–	–	–	0.004	–	–	0.0059
Kamen	0.0624	–	–	0.00001	–	0.0052	0.0013	0.061	–	–	–	0.003	–	–	0.0102
Saem	0.0503	–	–	0.00002	–	0.0053	0.0019	0.068	–	–	–	0.003	–	–	0.0083
Ohis	0.0392	–	–	0.00001	–	0.0036	0.0021	0.100	–	–	–	0.003	–	–	0.0098
Trubarevo.	0.0412	–	–	0.00002	–	0.0039	0.0021	0.089	–	–	–	0.003	–	–	0.0084
Treska river	0.0299	–	–	0.00003	–	0.0038	0.0013	0.036	–	–	–	0.003	–	–	0.0058
Lepenec	0.1256	–	–	0.00002	–	0.0037	0.0019	0.089	–	–	–	0.004	–	–	0.0115

Continuation of Table 2

Water(mg/l)	Ca	K	Na	B	P
8. 3. 2013					
M1	49.62	1.90	5.30	0.018	0.030
M2	41.78	1.28	4.80	<0,01	0.023
M3	64.60	1.41	7.20	0.022	<0,01
M4	58.64	1.39	6.40	0.012	0.006
M5	68.11	2.57	16.62	<0,01	0.121
M6	62.49	1.34	7.30	0.013	0.017
M7	74.29	1.43	7.70	0.017	<0,01
M8	70.53	1.54	8.50	0.014	0.078
M9	65.72	1.42	8.20	0.012	0.018
Mean	61.76	1.59	8.00	0.015	0.035
Med	64.60	1.42	7.30	0.013	0.018
Min	41.78	1.28	4.80	0.010	0.006
Max	74.29	2.57	16.62	0.022	0.121
SD	10.34	0.41	3.46	0.004	0.039

Water(mg/l)	Ca	K	Na	B	P
26. 3. 2013					
M1	35.176	1.49	5.1	<0,01	0.074
M2	41.583	1.44	5.2	<0,01	0.051
M3	43.693	1.49	5.7	<0,01	<0,01
M4	38.642	1.32	5.4	<0,01	0.165
M5	36.890	2.12	7.8	<0,01	0.141
M6	38.207	1.39	5.6	<0,01	0.038
M7	32.758	1.16	4.2	<0,01	0.022
M8	36.301	1.36	6.0	<0,01	0.091
M9	30.777	1.62	7.0	<0,01	0.076
Mean	37.12	1.49	5.78	0.010	0.075
Med	36.89	1.44	5.60	0.010	0.074
Min	30.78	1.17	4.25	0.010	0.010
Max	43.70	2.12	7.83	0.010	0.166
SD	4.04	0.269	1.06	0.000	0.053
12. 4. 2013					
M1	32.980	1.49	4.1	<0,01	0.014
M2	36.724	1.48	4.7	<0,01	<0,01
M3	40.632	1.44	5.1	<0,01	<0,01
M4	37.891	1.47	4.9	<0,01	0.023
M5	33.655	1.86	25.5	<0,01	0.044
M6	35.333	1.57	5.0	<0,01	<0,01
M7	34.453	1.59	5.1	<0,01	0.024
M8	32.018	1.39	4.8	<0,01	0.042
M9	35.149	1.32	4.7	<0,01	<0,01
Mean	35.43	1.52	7.10	0.010	0.021
Med	35.15	1.48	4.90	0.010	0.014
Min	32.02	1.33	4.10	0.010	0.010
Max	40.64	1.86	25.50	0.010	0.045
SD	2.67	0.155	6.91	0.000	0.014
29. 4. 2013					
M1	34.833	1.27	4.5	<0,01	0.111
M2	42.069	1.55	5.7	<0,01	<0,01
M3	51.762	1.54	6.1	0.015	0.018
M4	44.524	1.44	5.5	<0,01	0.024
M5	65.548	3.89	22.2	0.014	0.267
M6	41.199	1.46	5.3	<0,01	0.017
M7	39.409	1.38	5.6	<0,01	<0,01
M8	39.869	1.46	6.3	<0,01	0.039
M9	44.959	1.68	7.3	<0,01	0.083

Water(mg/l)	Ca	K	Na	B	P
Mean	44.91	1.75	7.62	0.011	0.065
Med	42.07	1.46	5.70	0.010	0.024
Min	34.84	1.28	4.50	0.010	0.010
Max	65.55	3.89	22.20	0.015	0.267
SD	9.03	0.82	5.53	0.002	0.084
17. 5. 2013					
M1	29.420	1.07	3.1	<0,01	<0,01
M2	28.110	1.16	3.0	<0,01	0.020
M3	37.297	1.42	4.7	<0,01	<0,01
M4	35.497	1.20	4.0	<0,01	0.016
M5	51.292	3.01	12.5	<0,01	0.229
M6	35.681	1.33	4.1	<0,01	0.047
M7	31.097	1.34	4.2	<0,01	0.045
M8	30.545	1.40	4.9	<0,01	0.108
M9	49.950	1.34	5.2	<0,01	1.167
Mean	36.55	1.48	5.08	0.010	0.184
Med	35.50	1.34	4.20	0.010	0.045
Min	28.12	1.07	3.04	0.010	0.010
Max	51.30	3.02	12.51	0.010	1.167
SD	8.57	0.589	2.89	0.000	0.376
MAC Mak I–V class	200▲	12*	200*	0.2–0.75	0.004–0.05
Dutch (TG–MAC)	–	–	–	–	–
ANZECC	–	–	180	4	–
Average values for harmful and hazardous substances in the Vardar river and its tributaries on the territory of the city –Treska river and Lepenec river [Source: Study on wastewater management 2007 – LEAP 2 Skopje City – 2011]					
Saraj	–	–	–	–	–
Vlae	–	–	–	–	–
Kamen	–	–	–	–	–
Saem	–	–	–	–	–
Ohis	–	–	–	–	–
Trubarevo	–	–	–	–	–
Treska	–	–	–	–	–
Lepenec	–	–	–	–	–

▲ MAC – Maksimum Allowable Concentration in drinking water in extraordinary circumstances following Rules for water safety, Official Gazette RM, No.46 / 08

* MDK – Maximum Permissible Concentration by Rules on water safety, Official Gazette No.46 / 08

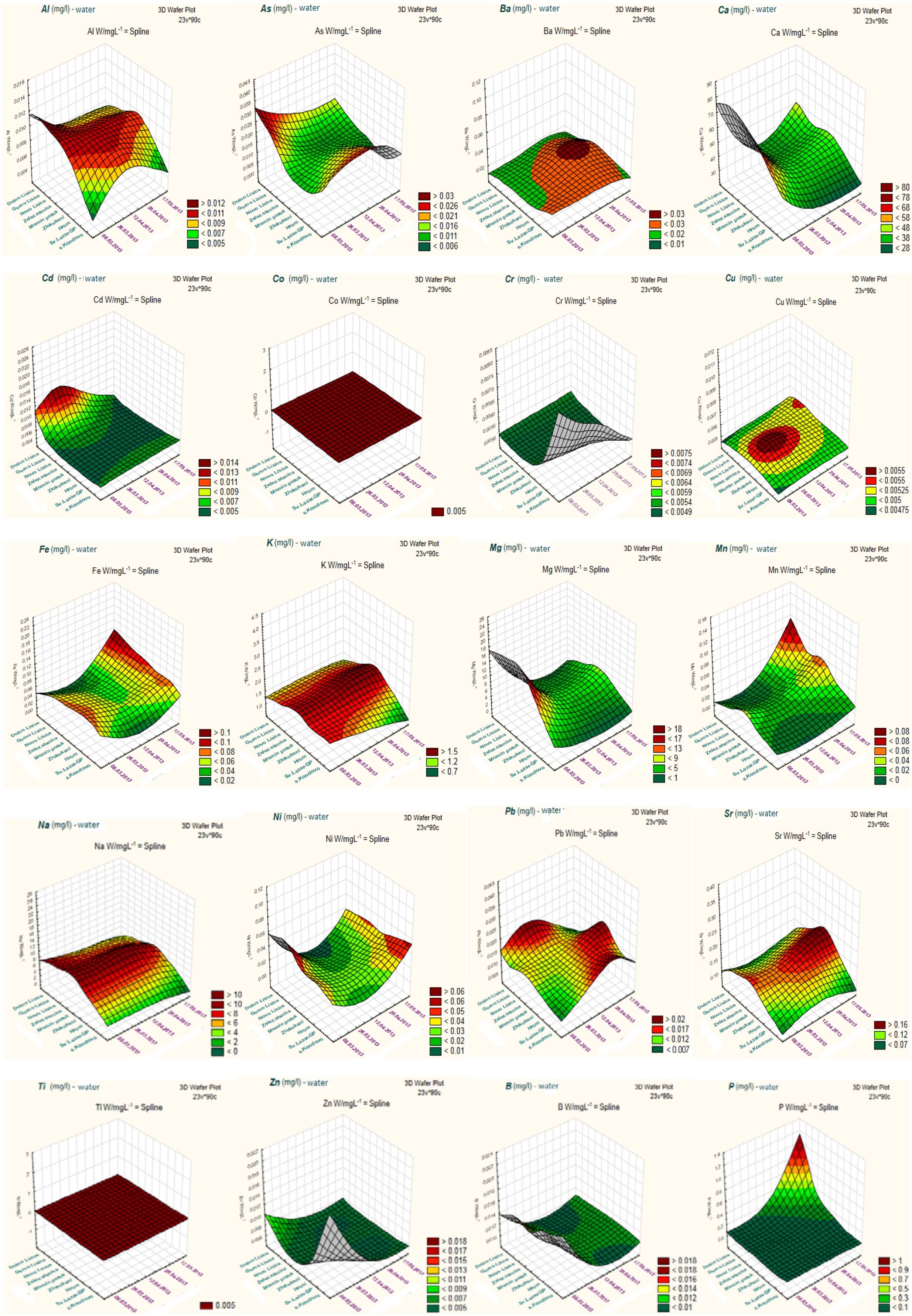

Fig. 2. Distribution of elements-measuring locations and date of sampling-water

River sediments

The distribution of heavy metals is not equal in sediments along the river (Table 3 and Figure 3). Varying the concentration of heavy metals is due to differences in the sources of heavy metals, physic-chemical conditions and complex reactions, such as absorption, precipitation and redox conditions prevailing in the sediments. The results for the measured concentrations of heavy metals and some non-metals in river sediments of Vardar are given in Table 3 and have been compared with Macedonian recommended, maximum permissible concentrations of heavy metals in soils and sediments (*Godišen izveštaj za obraboteni podatoci za kvalitet na životna sredina vo RM za 2006 – Annual report on the processed data for Quality Environment in Macedonia for 2006 – MZHSPRM),* the Dutch standards for soil and sediment (target – TG values, and intervention – IntV values) and the American Standards for sediments – EPA for region III and V (EPA).

Compared with Macedonian recommended MAC for heavy metals in soil and sediments (*Godišen izveštaj za obraboteni podatoci za kvalitet na životna sredina vo RM za 2006 – Annual report on the processed data for Quality Environment in Macedonia for 2006 – MZHSPRM*), in sediments of the Vardar river within the allowed values are the presence of Cd, Co, Cu, Mn and Pb. Comparing these concentrations with the Study of pollution of the topsoil horizon in Skopje (Study on waste water management 2007 – LEAP 2 Skopje City – 2011) shows that in the sediments of the Vardar river, Cd and Co are with slightly reduced values and Pb with the much smaller values, compared to 2007. There is variation in the content of As, so the M6 and M9 is noted incidentally elevated and on 26. 3. 2013, in all measurement locations there is contamination with As, but this pollution is smaller than the pollution of soil, as it was measured by the 2007 Study. Sediments in Vardar suffer more intense pollution with Cr and Ni, all the way, for the entire period of study. In the 2007 study, there was higher pollution with Cr and Ni. Heavy metals for which, there are no recommended MAC, are compared with Dutch standards for soil and sediment and it was found that observed value of Ba in the course of the river is higher. The amount of Fe is analyzed relative to the reference value for sediments in fresh water for the EPA Region III and V (USA). In all measurement locations in the period from 8. 3. 2013 to 17. 5. 2013, Fe is with higher value. There is extremely pollution of Fe in the measuring location M9 (Dolno Lisiče) on 17. 5. 2013, where is a large source of Fe-pollution, although in the water, at the same period, in M9 is not observed contamination. This only indicates that the sediments accumulate larger concentrations of heavy metals. Mo, compared to the Dutch list, is with low values in sediments and V is with values that are below the intervention value, but above optimal according to this list.

T a b l e 3

Concentrations of heavy metals and non-metals in river sediments of Vardar

Sediment mg/kg	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni	Pb	Sr
8. 3. 2013														
M1	75427	42	187	<0.25	16	129	30	51991	27495	889	1.1	80	11	154
M2	72555	17	154	<0.25	20	330	29	71836	31162	1048	1.1	99	12	242
M3	65213	21	158	<0.25	15	143	24	51007	29855	853	1.0	80	12	179
M4	69314	18	228	<0.25	15	136	27	51620	30895	884	1.0	81	12	154
M5	79112	6.8	352	0.89	19	134	84	38826	30477	1014	1.4	107	39	168
M6	54274	31	171	0.35	15	128	33	34844	34930	778	0.9	89	21	173
M7	56795	17	174	0.24	16	128	30	36693	39548	784	0.9	106	15	190
M8	56195	7.2	195	<0.25	15	120	32	35058	46138	791	1.0	91	22	151
M9	59894	2.5	183	<0.25	13	98	34	36436	49202	754	1.0	84	21	138

Sediment mg/kg	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni	Pb	Sr
Mean	65420	18.1	200.1	0.34	16.00	149.56	35.89	45368	35523	866	1.05	90.8	18.34	172.2
Med	65214	18.40	183	0.25	15	129	30	38826	31162	853	1.00	89	15	168
Min	54274	2.5	154	0.24	13	98	24	34844	27494	754	0.9	80	11	138
Max	79112	42	352	0.89	20	330	84	71836	49202	1048	1.4	107	39	242
SD	9138	12.47	61.01	0.21	2.32	68.84	18.30	12401	7737	106	0.16	10.84	8.95	30.69
26. 3. 2013														
M1	77158	45	275	<0.25	18	123	32	59215	28710	928	1.1	83	17	171
M2	72340	51	212	<0.25	17	119	32	55667	27485	818	1.0	71	13	184
M3	65455	28	198	<0.25	17	140	38	50709	29335	778	0.9	86	9	173
M4	67686	49	205	<0.25	16	116	38	51285	28520	821	1.0	82	10	164
M5	65492	27	286	0.96	16	94	53	44796	31961	692	1.0	80	26	122
M6	60772	53	195	<0.25	19	147	51	57934	35366	935	0.8	89	17	141
M7	60623	32	193	<0.25	14	96	30	43452	39446	646	0.8	85	14	129
M8	49958	16	157	<0.25	13	99	23	37004	38739	591	0.7	67	15	118
M9	52016	41	153	<0.25	12	76	21	33573	53431	536	0.7	61	10	124
Mean	63500	37.91	208.2	0.33	15.78	112.23	35.34	48181.5	34777	749.4	0.89	78.23	14.56	147.34
Med	65455	40.75	198	0.25	16	116	32	50709	31961	778	0.9	82	14	141
Min	49958	16	153	0.25	12	76	21	33573	27485	536	0.7	61	9	118
Max	77158	53	286	0.96	19	147	53	59215	53431	935	1.1	89	26	184
SD	8811	12.91	45.65	0.24	2.34	23.03	11.07	9090	8310.35	142.14	0.15	9.61	5.23	25.66
12. 4. 2013														
M1	56682	39	280	<0.25	18	131	34	54664	37069	1027	1.3	82	15	203
M2	54879	44	205	<0.25	19	176	30	55817	34786	1019	1.2	79	11	240
M3	47056	25	216	<0.25	18	188	23	52666	37290	971	1.0	84	20	220
M4	49302	14	227	<0.25	16	134	27	50271	35664	736	1.1	79	11	211
M5	50524	29	342	<0.25	18	164	39	43682	35524	893	1.2	116	26	156
M6	36927	8	186	<0.25	13	101	24	24940	38999	657	0.8	67	17	147
M7	41834	37	201	<0.25	15	112	23	32766	42796	754	0.9	85	14	165
M8	39753	26	185	<0.25	16	134	23	32119	41574	811	0.9	77	79	186
M9	38727	30	240	<0.25	13	96	26	24454	50995	674	0.9	75	18	170
Mean	46188	27.94	231.19	0.25	16.22	137.34	27.67	41265	39411	837.88	1.04	82.67	23.45	189
Med	47057	29.12	216	0.25	16	134	26	43682	37290	811	1.00	79	17	186
Min	36927	8	185	0.25	13	96	23	24454	34786	657	0.8	67	11	147
Max	56683	44	342	0.25	19	188	39	55817	50995	1027	1.3	116	79	240
SD	7218	11.50	50.93	0.00	2.23	32.61	5.66	12812	5136	144.45	0.18	13.62	21.35	31.70

Sediment mg/kg	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni	Pb	Sr
29. 4. 2013														
M1	63312	32	213	<0.25	19	129	28	39971	18669	923	1.6	73	18	183
M2	65712	27	214	<0.25	16	130	34	42146	19424	1037	1.7	72	20	156
M3	53091	22	154	<0.25	17	127	17	37798	19950	774	1.3	71	33	175
M4	58858	20	183	<0.25	17	118	30	37211	20722	788	1.4	71	16	165
M5	59678	9.4	220	<0.25	18	145	31	39280	24090	803	1.5	95	21	140
M6	49820	11	229	<0.25	18	138	34	37220	24025	833	1.4	101	22	126
M7	48074	18	141	<0.25	14	109	21	38011	36698	622	1.2	73	11	141
M8	45223	6.96	175	<0.25	15	124	25	28677	24293	638	1.3	77	18	136
M9	58579	44	216	<0.25	15	117	26	38628	32248	717	1.4	83	19	125
Mean	55817	20.98	193.8	0.25	16.56	126.36	27.33	37661	24458	792.78	1.43	79.56	19.78	149.67
Med	58579	19.53	213	0.25	17	127	28	38011	24025	788	1.4	73	19	141
Min	45223	6.96	141	0.25	14	109	17	28677	18669	622	1.2	71	11	125
Max	65712	44	229	0.25	19	145	34	42146	36698	1037	1.7	101	33	183
SD	7084	11.72	31.78	0.00	1.67	11	5.75	3712	6165	131.14	0.16	11.22	5.92	21.08
17. 5. 2013														
M1	–	18	289	<0.25	21	118	47	37582	32638	1196	1.2	90	19	144
M2	–	4.7	226	<0.25	20	140	46	–	–	1001	1.1	103	13	177
M3	67886	33	172	<0.25	17	115	20	43305	39196	813	0.9	83	19	161
M4	51420	15	196	<0.25	19	140	30	33848	37816	843	1.0	97	12	164
M5	59989	12	215	<0.25	17	120	42	41262	41700	758	1.0	103	21	124
M6	54920	32	157	<0.25	15	161	28	15439	41471	648	0.6	79	20	121
M7	45153	10	175	<0.25	17	107	27	27062	44427	779	0.9	84	16	142
M8	51525	19	238	<0.25	21	161	31	34464	47905	923	1.1	112	28	187
M9	–	44	222	<0.25	21	132	30	2919404	–	899	1.1	99	19	165
Mean	55149	21.0	210	0.25	18.67	133	33.45	394046	40737	874	0.99	94.45	18.56	154
Med	53223	17.52	215	0.25	19	132	30	36023	41471	843	1.00	97	19	161
Min	45153	4.7	157	0.25	15	107	20	15439	32638	648	0.6	79	12	121
Max	67886	44	289	0.25	21	161	47	2919404	47905	1196	1.2	112	28	187
SD	7908	13	41	0.00	2.24	19.56	9.33	1020437	4882	158.54	0.18	11.07	4.72	23
MAC Mak	–	30	–	1-3	50	100	100	–	–	2300	–	70	100	–
Dutch (TG-MAC)	–	29-55	200-625	0.8-12	9-240	100-380	36-190	–	–	–	0.5-200	35-210	85-530	–
EPA-III Vreg	–	9.8	–	0.99	50	43.4	31.6	20000	–	460	–	22.7	35.8	–
Contamination of the topsoil horizon with heavy metals in Skopje [Study on waste water management 2007 – LEAP 2 Skopje City – 2011]														
Minimum	–	<3.0	–	<0.4	4.26	42.0	7.28	–	–	–	–	24.39	1.00	–
Maximum	–	70.1	–	1.3	22.53	345.8	592.1	–	–	–	–	304.47	608.5	–
Average	–	15.24	–	0.57	12.71	108.7	57.26	–	–	–	–	95.36	134.7	–

Continuation of Table 3.

Sediment mg/kg	Ti	V	Zn	Ca	K	Na	B	P
8. 3. 2013								
M1	4542	176	81	66082	14596	21152	229	1366
M2	6275	213	63	70013	13799	18628	311	1423
M3	4693	151	67	87493	13946	19715	537	1185
M4	4118	201	75	91390	15088	18724	253	1244
M5	4164	196	224	128690	17389	11930	862	2150
M6	4161	148	96	128409	11776	14119	486	1275
M7	4171	147	79	132388	10581	15404	440	1164
M8	3685	176	100	148314	14541	12626	467	1344
M9	3168	99	91	161467	14204	12753	595	1210
Mean	4331	167.4	97.34	112694	13991	16117	464.3	1374
Med	4164	176	81	128409	14204	15404	467	1275
Min	3168	99	63	66082	10581	11930	229	1164
Max	6275	213	224	161467	17389	21152	862	2150
SD	856	35.21	49.11	34680	1938	3481	195.27	303.93
26. 3. 2013								
M1	4042	154	76	69917	14110	20628	61	1395
M2	4442	163	66	76822	11704	21698	50	1289
M3	4445	135	64	96674	10311	17430	142	1053
M4	4191	148	75	79566	10992	19624	67	1174
M5	3382	120	131	125906	12799	11564	131	1433
M6	5029	81	78	93762	10021	14435	73	976
M7	3389	97	59	132751	13161	15796	799	828
M8	3094	96	60	136088	10411	12716	41	806
M9	3673	187	51	165290	10709	13653	81	745
Mean	3966	131.3	73.34	108530.7	11579.8	16393.6	160.6	1077.67
Med	4042	135	66	96674	10992	15796	73	1053
Min	3094	81	51	69917	10021	11564	41	745
Max	5029	187	131	165290	14110	21698	799	1433
SD	628.75	35.35	23.40	32717.60	1454.03	3642.30	241.65	259.55
12. 4. 2013								
M1	4002	184	88	45119	15210	18386	16	1541
M2	4354	172	80	43486	12773	18230	15	1475
M3	4762	167	73	52488	11382	15146	28	1338
M4	4496	157	77	50421	11868	15694	18	1364
M5	3923	165	108	56118	15120	12060	17	1276
M6	3306	133	67	80480	11013	10407	12	966
M7	3444	174	64	72306	11465	12663	18	1041
M8	4364	174	71	70796	10528	12543	20	1073
M9	3357	187	76	73422	11683	10512	16	1024

Mean	4001	168.2	78.23	60515	12338	13961	17.78	1234
Med	4002	172	76	56118	11683	12663	17	1276
Min	3306	133	64	43486	10528	10407	12	966
Max	4762	187	108	80480	15210	18386	28	1541
SD	536	16.06	13.23	13796	1716	3043	4.44	213
29. 4. 2013								
M1	4595	129	86	38634	15907	17189	13	1613
M2	4936	128	96	39675	14954	16558	31	1566
M3	5478	119	79	52463	12305	15230	47	1254
M4	4450	126	80	51550	13443	17183	11	1370
M5	4387	110	94	57773	15974	14046	44	1337
M6	4432	126	103	64793	15463	10933	12	1166
M7	3897	121	60	92408	12382	14373	9	990
M8	4092	108	79	51093	11492	10761	75	1149
M9	3878	102	86	74110	16200	12804	10	1101
Mean	4460.56	118.78	84.78	58056	14236	14342	28	1283
Med	4432	121	86	52463	14954	14373	13	1254
Min	3878	102	60	38634	11492	10761	9	990
Max	5478	129	103	92408	16200	17189	75	1613
SD	509.72	9.84	12.50	17031	1838	2470	23.16	209.45
17. 5. 2013								
M1	4394	118	103	37350	15891	24242	144	1413
M2	4968	129	84	–	–	–	273	1393
M3	4883	106	76	44243	16862	25870	194	1183
M4	4790	130	80	54058	10705	22595	301	1163
M5	4064	106	99	56814	13769	26220	19	1159
M6	3138	46	89	63528	14276	19587	15	813
M7	4214	129	67	79114	10434	17374	17	1015
M8	4941	128	101	71657	13703	22243	397	1252
M9	4723	123	93	–	–	–	23	1167
Mean	4458	112.78	87.9	58110	13663	22591	154	1174
Med	4723	123	89	56814	13769	22595	144	1167
Min	3138	46	67	37350	10434	17374	15	813
Max	4968	130	103	79114	16862	26220	397	1413
SD	593.27	26.79	12.28	14694	2407.02	3241	145.8	183
MAC Mak	–	–	200	–	–	–	–	–
Dutch (TG–MAC)	–	42–250	140–720	–	–	–	–	–
EPA–III I Vreg	–	–	121	–	–	–	–	–
Contamination of the topsoil horizon with heavy metals in Skopje [Study on waste water management 2007 – LEAP 2 Skopje City – 2011]								
Minimum	–	–	23.08	–	–	–	–	–
Maximum	–	–	366.25	–	–	–	–	–
Average	–	–	101.71	–	–	–	–	–

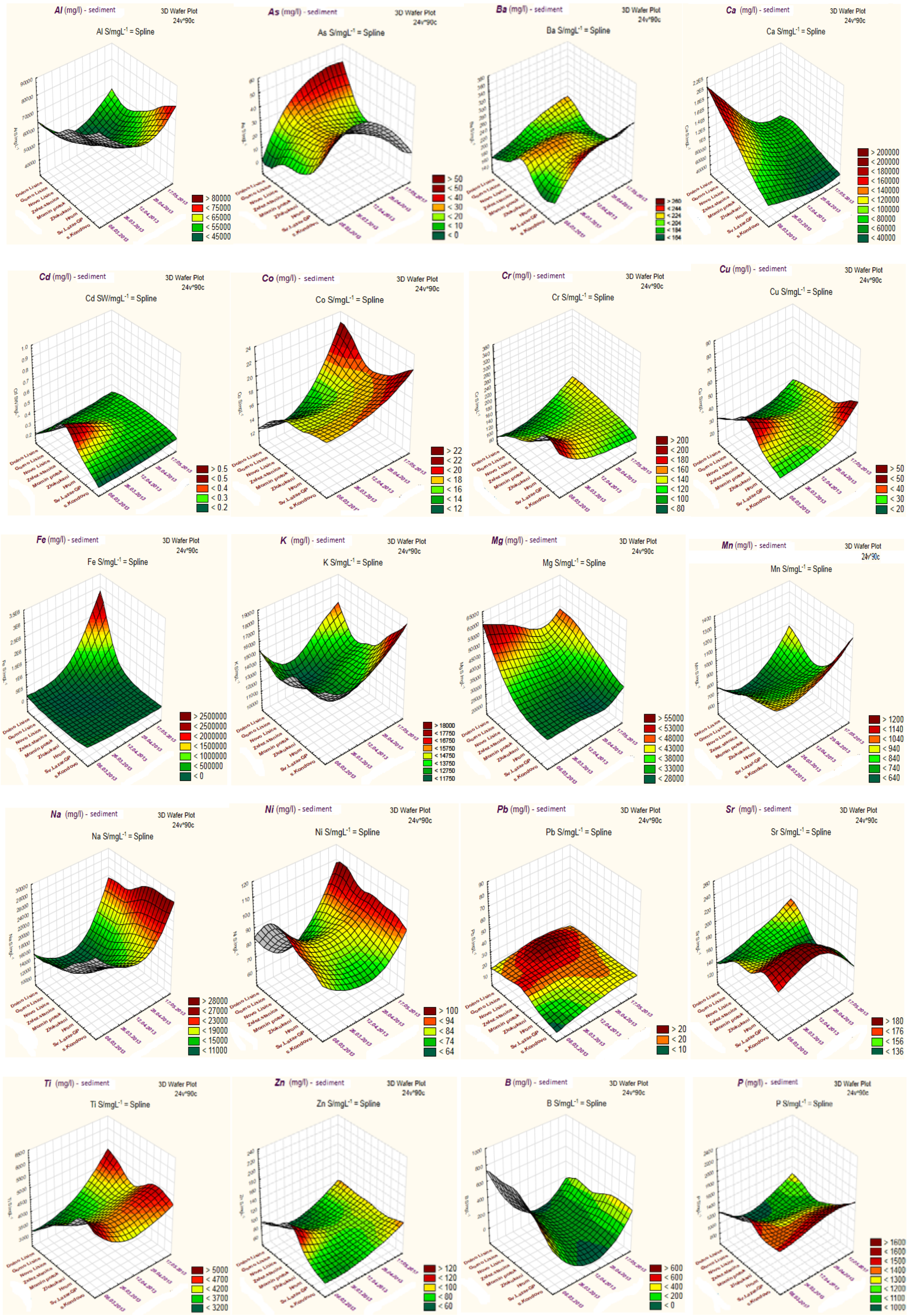

Fig. 3. Distribution of elements-measuring locations and date of sampling-sediments

Correlation analysis for heavy metals in water and sediments

In the following Table 4 is given correlation matrix for heavy metals and some non-metals in sediments in relation to these elements in the waters of Vardar river.

It is notable, that there is a significant positive correlation between the Cu in river water and Cd of river sediment under that water, then between the Mg from water and Cu, Zn, Ca and B of river sediments, between Na from water and Ba, Ni and Zn from sediments and between Ca from the waters and B of sediments and between Mn from the water and Zn from sediment. If the observed correlations are between the same metal contents in water and sediments, we can observe positive and significant correlation only between forms of Cu, Ca, K and B in water and sediments, because of their transformation and mobilization of water in the solid phase and vice versa.

T a b l e 4

Correlation between metals and some non-metals in water and sediments

Correlations, Marked correlations are significant at p < .05000N=42

Metals water & sediment	Al S/mgkg^{-1}	As	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sr	Ti	Zn	Ca	K	Na	B	P
Al W/mgL^{-1}	0.1401	-0.1977	0.3459	0.1852	0.1086	-0.0240	0.3279	0.1564	0.0006	0.1328	0.3058	0.0528	0.1015	-0.1454	0.3049	0.1024	0.1355	0.0138	0.0938	0.3016
As	0.0503	0.0992	-0.0751	-0.1788	0.0672	-0.0419	-0.0904	0.0491	-0.0393	0.1809	-0.1232	-0.1429	0.3008	0.0800	-0.0388	-0.0004	-0.0177	0.0630	0.0133	0.1944
Ba	-0.0098	-0.1470	0.1105	-0.0477	0.2172	0.0176	0.0553	-0.0370	-0.4463	0.1431	0.1620	0.0607	-0.1799	0.1632	0.2029	-0.3306	0.3554	-0.1073	-0.2682	0.1662
Cd	-0.0805	0.1813	-0.1807	-0.0371	-0.3290	-0.2279	-0.1465	-0.1152	0.3399	-0.3377	-0.2941	-0.1262	-0.1962	-0.1300	-0.1905	0.3809	-0.1827	-0.0991	-0.0597	-0.2967
Cr	0.1874	0.2513	0.1335	-0.0531	0.0695	-0.0102	0.0146	0.2405	-0.0647	0.2637	-0.0590	-0.1209	0.1182	0.0212	0.0068	-0.1695	0.2026	0.1963	-0.0438	0.2073
Cu	0.1067	0.0058	0.2872	0.7182	0.0312	-0.1331	0.3056	0.0283	-0.0110	-0.1201	0.0045	0.1160	-0.1836	-0.1693	0.2897	0.1922	-0.0129	-0.1397	0.0023	0.1339
Fe	0.3942	0.0600	-0.0700	0.0943	0.0404	0.0099	0.2793	0.1430	-0.2732	0.0897	0.1104	-0.1603	-0.3002	0.1913	0.0699	0.1185	0.0263	0.1642	0.2081	-0.0326
Mg	0.3625	-0.3981	0.2421	0.4497	-0.0598	-0.0433	0.5593	0.0045	0.0763	0.1124	0.3851	0.1083	-0.0555	-0.1258	0.6051	0.5550	0.2917	-0.1396	0.6626	0.4130
Mn	0.2179	-0.2951	0.3248	0.3922	0.2098	-0.0265	0.4632	-0.0660	-0.1080	0.0481	0.3485	0.1805	-0.2624	-0.0391	0.5134	-0.0418	0.3625	0.0868	0.0448	0.3109
Ni	0.2888	-0.1004	-0.2223	-0.1088	0.0646	0.1426	0.0557	0.0659	-0.1393	0.2425	0.1056	-0.1634	0.1068	0.2282	0.0381	0.0206	0.0789	0.2125	0.1590	0.1408
Pb	-0.1284	-0.0330	-0.0936	-0.1005	0.0024	-0.1250	-0.1150	-0.1818	-0.0682	-0.1249	-0.0789	0.2209	-0.1147	0.1031	0.0034	-0.1187	0.0648	0.0586	-0.2278	-0.0340
Sr	0.0795	-0.2871	0.3316	0.1823	0.2927	0.0321	0.3477	-0.0609	-0.1007	0.1447	0.3922	0.1835	-0.0783	0.0124	0.4362	-0.2195	0.3361	0.1228	-0.0702	0.3225
Zn	0.2876	0.0410	-0.0789	-0.0622	-0.0733	-0.0385	0.0064	0.1176	-0.0892	0.0628	-0.0095	-0.1044	-0.1036	0.0061	0.0052	0.0474	0.1729	0.1121	0.1238	0.0915
Ca	0.3441	-0.4039	-0.0304	0.1683	-0.0868	0.0171	0.2656	0.0296	-0.1369	0.1100	0.2912	0.0176	-0.0094	0.0393	0.3710	0.3920	0.2851	-0.0818	0.5561	0.3377
K	0.1942	-0.2392	0.3570	0.3308	0.1565	-0.0411	0.3995	-0.0142	-0.1496	0.0385	0.3138	0.1543	-0.2434	-0.0509	0.4648	-0.0459	0.3711	-0.0210	-0.0229	0.3014
Na	0.1167	-0.2507	0.5170	0.2558	0.1382	0.0500	0.4226	-0.0280	-0.0857	0.0836	0.5221	0.1940	-0.1966	-0.0938	0.5049	0.0788	0.3840	-0.2230	0.1228	0.2789
B	0.2119	-0.1224	-0.2643	-0.0885	-0.1377	-0.0002	-0.1471	0.0816	-0.1435	0.0487	0.0582	-0.0769	0.0670	0.1530	-0.0474	0.1745	0.0974	0.0903	0.3724	0.0601
P	0.2244	-0.0746	0.2719	0.2898	0.1782	-0.1057	0.3617	-0.0393	-0.0758	-0.0679	0.2425	0.1391	-0.3196	-0.1121	0.3510	0.0443	0.2292	0.1049	-0.0637	0.1606

Other physico-chemical parameters

Apart from the content of heavy metals in water and sediments of Vardar river, some other parameters, such as pH, temperature, turbidity, COD, alkalinity and organic matter, were also determined,. The distribution of measured physical-chemical parameters of the tested waters and sediments are presented with box&whisker plots for all 5 sampling (Figure 4). Then it is observed elevated values for turbidity, COD and alkalinity over the limit for Macedonian MAC values (*Uredba za klasifikacija na vodite* – Sl. vesnik br.18/99 – Decree for classification of waters – Official Gazette No.18/99), downstream, in the water of the Vardar river. The content of organic matter in sediments is in satisfactory frame, compared to a value of Australian soil, after which it should be in the range 2.58 to 3.44%. These parameters are important because of their impact to the forms in which different metals can be found in water and sediments, their balance and, on the other hand, toxicological impact of metals depends on these parameters.

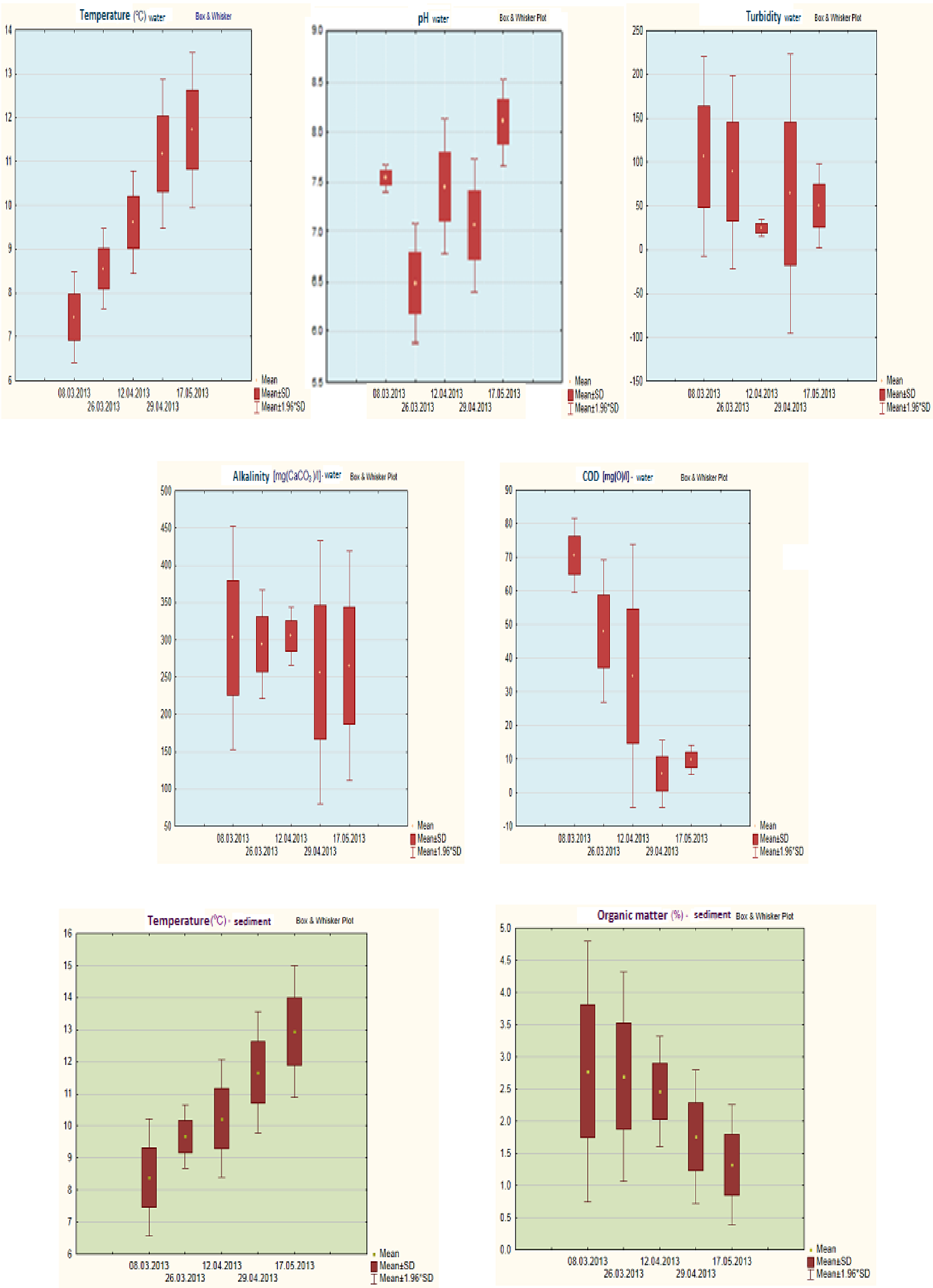

Fig. 4. Box & Whisker plots for the distribution of the measured parameters in water and sediments of Vardar river, by the date of sampling

Correlation analysis for heavy metals in relation to the other examined parameters

The influence of various physico-chemical parameters on metals in water and sediments can be analyzed using the correlation matrix for the parameters and metals. As is evident from the Table 5, there is a significant positive correlation between pH of water present and Mg and Ni-forms in sediments. The presence of B-forms in water is positively correlated with the river water turbidity, in which they are located, and in this respect there is a relationship between turbidity of river water and Al in sediments, from the same sampling area, which is also significantly positively correlated. Significant, positive correlation exists in the relationship between the chemical oxygen demand in river water and Ca, B, Fe and Al from sediments, and the B, Ca and Mg in the water. There is a strong link between oxygen and Ca and B, because their positive correlation exists for forms, in the waters and also in sediments. Unlike these elements, which are positively correlated with COD, Ba from river waters has a significant negative correlation with COD of water.

T a b l e 5

Correlations between parameters of water and metals and some non-metals in water and sediments of Vardar

Metals	Correlations, Marked correlations are significant at p < .05000N=42 temperature water (oC)	temperature sediment (oC)	pH water	turbidity (NTU)	HPK (mgO2/l)	alkalinity (mg C-CO3/l)	Organic matter- OM (%)
Al W/mgL-1	-0.16	-0.11	-0.05	-0.19	0.16	**0.66**	0.26
As	-0.07	-0.12	-0.16	0.08	0.15	-0.16	0.03
Ba	0.27	0.23	-0.02	0.10	**-0.36**	-0.04	-0.18
Cd	-0.05	0.01	-0.09	-0.16	0.07	0.07	-0.04
Cr	-0.14	-0.28	-0.05	0.24	0.21	-0.21	0.23
Cu	0.00	0.03	-0.18	0.30	0.00	0.04	**0.40**
Fe	0.07	0.03	-0.30	0.27	0.00	-0.14	0.06
Mg	**-0.48**	**-0.39**	0.16	0.05	**0.50**	**0.62**	**0.43**
Mn	0.21	0.22	0.15	-0.10	-0.21	**0.59**	0.14
Ni	-0.04	-0.10	0.03	0.07	0.11	-0.05	-0.19
Pb	0.23	0.19	0.03	0.08	-0.27	0.20	-0.19
Sr	0.24	0.23	0.22	-0.21	-0.24	**0.64**	0.02
Zn	-0.26	-0.24	0.05	**0.36**	0.21	-0.07	0.20
Ca	**-0.43**	**-0.39**	0.13	0.24	**0.41**	**0.46**	0.21
K	0.10	0.12	0.09	-0.06	-0.15	**0.62**	0.20
Na	-0.01	0.04	0.16	-0.13	0.03	**0.57**	0.28
B	**-0.40**	**-0.42**	0.13	**0.50**	**0.40**	0.09	0.01
P	0.22	0.27	-0.06	-0.14	-0.15	**0.45**	0.13
Al S/mgkg-1	**-0.47**	**-0.51**	**-0.39**	**0.48**	**0.39**	-0.12	**0.36**
As	-0.09	-0.19	**-0.49**	0.15	0.09	**-0.32**	0.11
Ba	-0.05	-0.06	-0.09	-0.07	0.05	0.18	**0.62**
Cd	-0.21	-0.19	-0.10	0.24	0.18	0.24	**0.62**
Co	0.14	0.04	-0.01	0.14	-0.15	-0.26	-0.10
Cr	-0.13	-0.21	0.12	0.12	0.15	-0.26	-0.17
Cu	-0.22	-0.19	-0.13	0.12	0.28	0.29	**0.62**
Fe	**-0.53**	**-0.63**	**-0.50**	**0.32**	**0.43**	-0.17	**0.31**
Mg	0.03	0.20	**0.49**	**-0.40**	0.11	**0.34**	0.03
Mn	-0.17	**-0.35**	-0.09	0.17	0.18	-0.29	0.21
Ni	0.03	0.11	**0.41**	-0.06	0.07	0.24	0.06
Pb	0.14	0.16	0.18	-0.01	-0.20	0.14	0.10
Sr	-0.29	**-0.43**	-0.06	0.05	0.24	-0.23	-0.02
Ti	-0.05	-0.17	-0.05	**0.35**	-0.06	**-0.41**	**-0.31**
Zn	-0.03	-0.03	0.13	0.08	0.07	0.27	**0.52**
Ca	**-0.48**	-0.30	-0.09	0.06	**0.55**	**0.39**	**0.40**
K	0.08	0.01	0.12	0.03	-0.08	-0.03	0.20
Na	0.05	0.00	0.11	0.18	-0.04	-0.22	-0.30
B	**-0.49**	**-0.40**	0.17	0.18	**0.56**	0.21	0.30
P	-0.21	**-0.35**	-0.14	0.18	0.15	-0.07	**0.45**

Alkalinity of water has the most impact on present heavy metals in river waters. Affect Al, Mg, Sr, K, Mn and Na of water, but on the other hand is significantly negatively correlated to Ti and As from sediments. Organic matter present in sediments binds especially Ba, Cd, Cu and Zn from sediments and its presence is greatly influential on the content of metals in sediments – a high positive correlation. Organic matter of sediments is positively correlated to Cu and Mg of river waters. The only significant negative correlation has organic matter from the sediments with Ti.

Geo-accumulation index (I_{geo}) and enrichment factor (EF)

Geo-accumulation index – I_{geo}, proposed by Müller (1979; Müller & Forstner, 1981), were used to compare the accumulation of each metal in sediment fraction. He quantifies individual metals pollution, and is calculated by formula:

$$I_{geo} = \log_2 [C_n / 1.5 \times B_n],$$

where C_n – measured concentration, B_n – natural concentration [concentration of geochemical origin, where, what is taken into account, is average shale value (Turekian & Wedepohl, 1961) and 1.5 is correlation matrix factor. Depending on the value of I_{geo} (Müller. 1981), proposed several levels of pollution, $I_{geo} \leq 0$ uncontaminated, $0 < I_{geo} < 1$ uncontaminated to moderately contaminated, $1 < I_{geo} < 2$ moderately contaminated, $2 < I_{geo} < 3$ moderately to heavily contaminated, $3 < I_{geo} < 4$ heavily contaminated, $4 < I_{geo} < 5$ heavily to extremely contaminated and $5 < I_{geo}$ extremely contaminated. In this study were considered maximum values (maximum on all measurement locations) of individual metals found in surface sediments of the Vardar river for the class of I_{geo} Mean values for I_{geo} by date of sampling are presented in the graph shown in Figure 5.

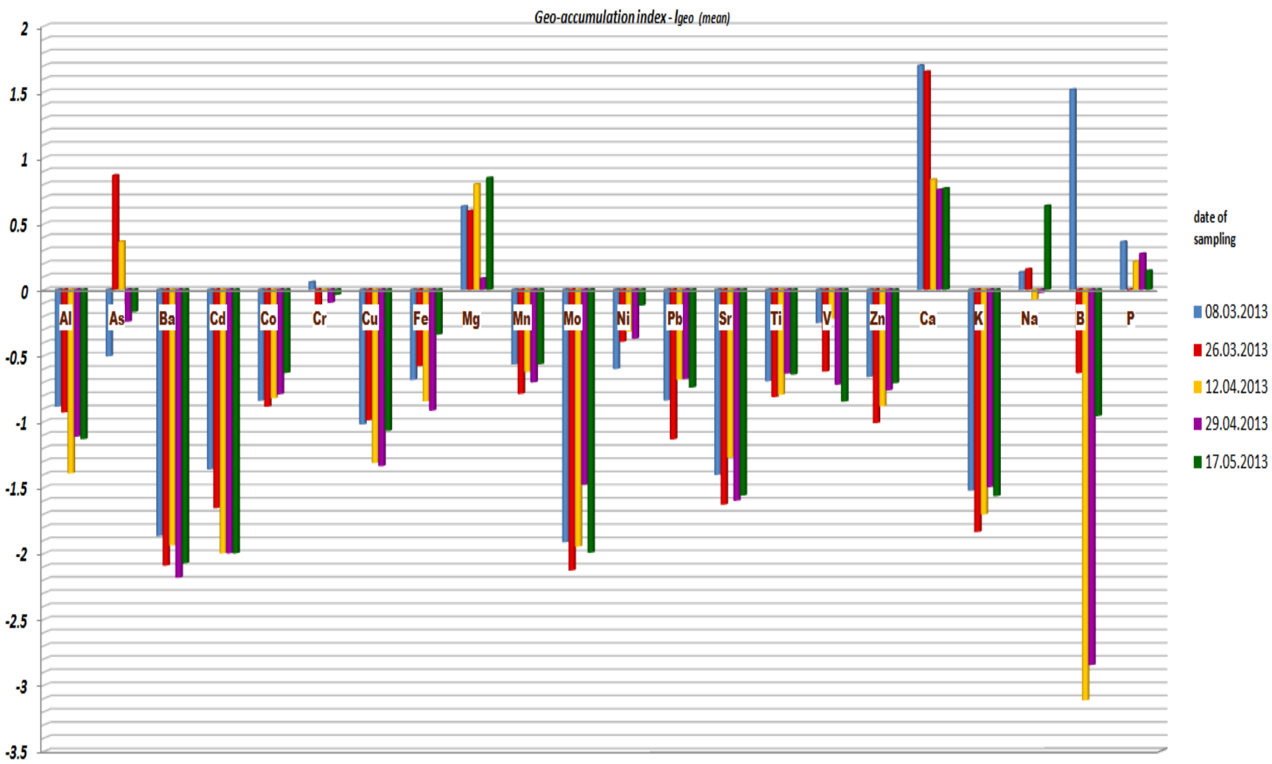

Fig. 5. Mean values of Geo-accumulation index (Igeo) for the cations in river sediments, by the date of sampling

From aspect of Geo-accumulation index, we can consider river uncontaminated with: Al, Co, Mn, Mo, Sr, Ti and K, because within research, through its whole course, I_{geo} for these metals have a value ≤ 0. Small to moderate contamination in terms of Ba, Cu, Ni, V, Zn and Na, was found. Contamination with As, Cr, Mg and P is higher, but moderately. Pollutions with Ca and B are strongly expressed in Vardar, all the way downstream in Skopje, but the most extreme pollution is with Fe at only one measurement location M9 (Dolno Lisiče), on 17. 5. 2013, which is the result of incidentally anthropogenic pollution.

In natural systems, metals, and other substances appear in the relative proportions in relation to each other. These proportions depend on many processes that make up geochemical cycle of substances and can be modified as a result of the input materials, from anthropogenic activities. Enrichment factor (EF) is index which considers the input of metals – pollutants from anthropogenic sources. Enrichment factor for each element is calculated by the formula

$$EF = [C_n / C_{\text{ref}}]_{\text{samp.}} / [C_n / C_{\text{ref}}]_{\text{backgr.}}$$

where $C_{n\ \text{samp}}$ is the concentration of the element in the sample, and $C_{\text{ref.samp}}$ is the concentration of the reference element, which is taken as a standard for normalization in the sample. $C_{\text{n.backgr.}}$ is the natural concentration [concentration of geochemical origin, which is taken into account – average shale value, Turekian & Wedepohl (1961)], of element, while $C_{\text{ref backgr.}}$ is the natural concentration of geochemical origin – average shale value, Turekian & Wedepohl (1961) of the reference element. As reference element can be Fe, Al (the most commonly used for this purpose), then TI, Si, K, Sr and others. The reference element is usually the element which shows small variations in the presence and quantity and because of this, in this study as the reference element is taken Ti. The obtained values are compared with the EF scale, which determines the degree of pollution. On this scale if EF< 1, there is no enrichment in terms of a metal from anthropogenic sources. With EF< 3, there is minor enrichment, EF at 3–5 appears moderate enrichment, value of 5–10 has moderate to intense enrichment and 10–25 intensive enrichment. Very intense enrichment EF shows with the values 25–50, and over 50 extreme, intense enrichment (after Chen – 2007). Enrichment of Vardar, in the urban center, for most metals is minor to moderate with few exceptions, where is no enrichment or where enrichment is intense and extremely intensive. Moderate enrichment there is with As, Cd and all the way with Mg. Intensive enrichment is found with Ca and B, but the most extreme enrichment from anthropological source occurs with Fe, with a value of 60.237 for EF in M9 (Dolno Lisiče), on 17. 5. 2013. More intense enrichment of Vardar is going on, till 12. 4. 2013, except for the enrichment of Fe, on 17. 5. 2013. There is noticeable and often greater enrichment with different metals from anthropological sources in measurement point M5 (Momin Potok). Mean values for Enrichment factor, by date of sampling are presented in the graph shown in Figure 6.

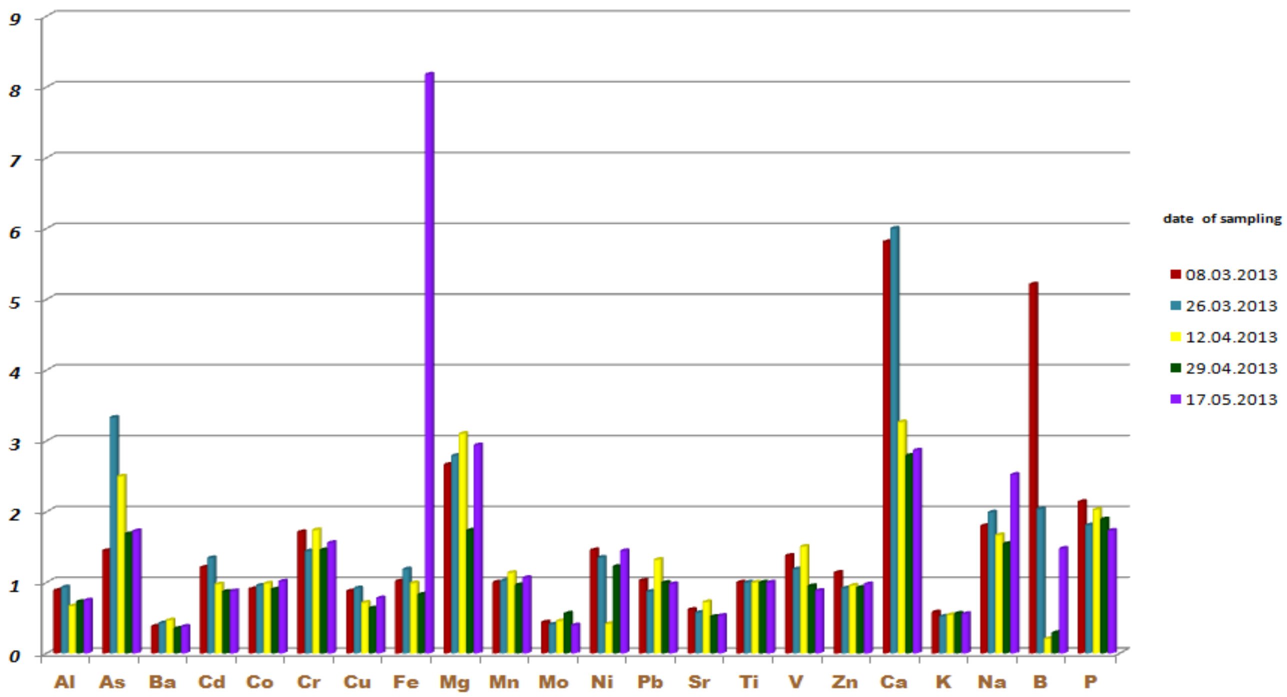

Fig. 6. Mean values of Enrichment factor – EF, for the cations in river sediments, by the date of sampling

CONCLUSIONS

Observing the overall condition of the Vardar river, compared with the measured values for heavy and toxic metals in water and sediments, we can say that the pollution in the Vardar river happens, incidentally, mostly in small-scale except for Pb, which throughout downstream and throughout the duration of the study is somewhat elevated. This situation is a result of urbanization, increased traffic, and untreated industrial water coming into the Vardar river. Also on the entire course of the river appears increased content of P and at some measurement locations, over the content of the V class waters, suggesting the alarming state with eutrophication in the river. The situation should be greatly enhanced with the planned construction of water treatment plants, main in v. Trubarevo and others as they in Saraj and Kondovo. The pollution of the Vardar river, is more visible in the river sediments. During the research and measurement in most locations is noticeably small pollution with As, Cr, Ni and especially pollution with Fe, from anthropogenic sources. Pollution of Fe is particularly extreme in the last measurement location Dolno Lisiče. This pollution is not measured in the river water, but due to the binding of metals to sediments, they were found in new, surface sediments, leading to the conclusion that if only water of the river is examined, that can not give a true picture of the state of its pollution. Analysis of I_{geo} and EF indicate that all these pollution originating from anthropogenic sources. It is noticeable that in the Vardar river, the largest pollution coming from the tributaries Lepenec and especially Serava, who coming into the measuring locations in M4 and M5 and bring larger quantities of pollutants in Vardar, as a result of industrial zones and major arable agricultural land through which they flow. Dilution of pollution mainly happens with river of Treska`s flows, because it brings cleaner water to Vardar river.

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ТЕШКИ И ТОКСИЧНИ МЕТАЛИ ВО ВОДАТА И СЕДИМЕНТИТЕ НА РЕКАТА ВАРДАР ВО СКОПЈЕ

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Клучни зборови: тешки метали; река Вардар; загадување; води; седименти

Беа анализирани деведесет, композитни примероци (45 примероци површинска вода и 45 примероци речни седименти) беа собрани од изворот на реката Вардар и во урбаниот дел на Скопската Котлина – градот, во периодот од 8. 3. 2013 до 17. 5. 2013 за да се одреди и дискутира загадувањето на реката Вардар. Беа проучувани концентрациите на тешките метали (Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, Ti и Zn), некои неметали (B и P), анјони и повеќе физичко-хемиски параметри на водата и седиментите во реката Вардар по течението на реката низ урбаната област. Покрај водата беа анализирани и речните седименти како резервоари на најголем дел од контаминентите, исто така со користење на методот на Индекс на геоакумулација (I_{geo}) и фактор на збогатување (EF).