DETERMINATION OF HEAVY METAL CONTENTS IN SURFACE WATER BY INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY: A CASE STUDY OF IALOMITA RIVER, ROMANIA

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Abstract. Heavy metals are among the most significant surface water pollutants being extremely harmful to the environment and human health, in high concentrations. The aim of this study is to determine the heavy metals content (*e.g.* Cd, Cr, Pb, Cu, Ni and Fe), in order to establish the level of pollution at the surface waters of Ialomita River, from Romania, tributary of Danube river. A number of 66 water samples were collected from Ialomita River, in two representative points (*i.e*. upstream and downstream of Targoviste City) in four seasons during of the years 2015–2016. The elemental concentrations, in water samples, were obtained by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique using Thermo Scientific iCAP Qc system. A correlation between the heavy metal concentrations determined by ICP-MS spectrometry technique and physicochemical parameters: pH, turbidity, conductivity and salinity, was performed. Investigation has confirmed that high concentration of Pb, Cu and Fe are not appropriate for formation and development of aquatic organisms and may disturb the ecosystem of Ialomita River. Also, the obtained results shown very clearly that the load of analyzed metals (*i.e*. Pb, Fe, Cr, Cu, and Ni), were higher in samples collected from Ialomita River, downstream of Targoviste City.

Key words: Ialomita River, heavy metal, ICP-MS, physicochemical parameter.

1. INTRODUCTION

In the last decades, a special attention to problems which involve the environmental pollution (*i.e.* atmosphere [1–5], water, including surface water [6–10] or groundwater [11], and soil [12–15]) was granted. Rivers have a significant role in water cycle, providing a great habitat and food for a lot of earth's organisms [16]. Also, the rivers play an important role from economical and transportation route point of view. Surface water quality issues influence human and environmental health, and this can be a reason that the pollution monitoring must offer the full information about main water quality indicators. Among the well-known water pollutants are heavy metals. The heavy metals content in water bodies has increased due to natural processes (*e.g.* soil or rocks erosion, volcanic eruptions, mineral weathering, etc.) and anthropogenic activities (*e.g.* industrial or agricultural activities, fuel combustion, etc.) [17–18]. It is very well known their toxicity and persistence in the environment, as well as the tendency to bio-accumulate in living tissues. The metals accumulation in river water is dependent on several physicochemical parameters, including pH, conductivity, turbidity, TDS, salinity, dissolved oxygen, ions, and anthropogenic inputs, as well. Thus, the aim of this work is to determine the heavy metals content (*i.e.* Cd, Cr, Ni, Pb, Cu and Fe) and the physicochemical parameters (*i.e.* pH, turbidity, conductivity, and salinity) in water samples collected from Ialomita River (upstream and downstream of Targoviste City), in order to assess the quality class of surface water according with Romanian Regulation [19]. Ialomita River (tributary of Danube River) passes across Targoviste City from Northwest to Southeast. Upstream of Targoviste, the main identified pollution sources are represented by the cement factory, thermal power plant, paint and varnish factory, and brick factory. Also, the industrial area of the city represents another pollution source of Ialomita River.

2. MATERIALS AND METHODS

A number of 66 water samples were collected from Ialomita River, in two representative points (*i.e.* upstream and downstream of Targoviste City) in four seasons during of the years 2015–2016. Sampling was carried out for 11 months, 3 days/month, morning between 7^{30}–8^{00} in upstream (Teis: 44º56'34.58 "N and 25º26'43.79" E) and downstream (Nisipuri: 44º54'53.66 "N and 25º32'12.46 ") of Targoviste City (Figures 1 and 2), in spring, summer, autumn, winter of 2015–2016.

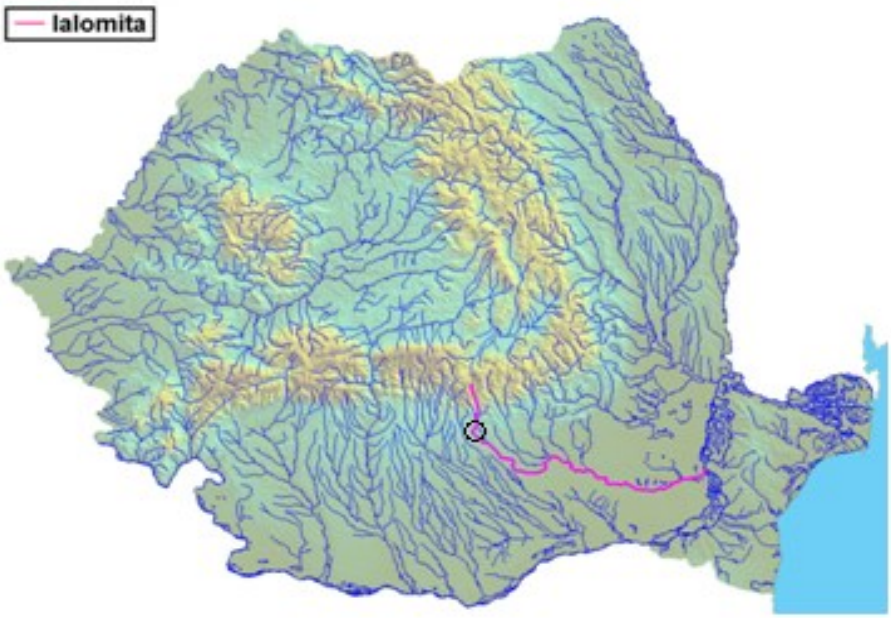


Fig. 1 – Ialomita River, from source to estuary, (pink line) and the sampling area (black circle).

Fig. 2 – Sampling points (*i.e.* upstream and downstream of Targoviste City).

Samples collected from Ialomita River were analyzed by ICP-MS spectrometry technique. Thus, for each fresh sample collected from the geographical chosen points, a series of physicochemical indicators (*i.e.* pH, conductivity, salinity and turbidity) were performed. In order to determine the metals content, the collected samples were mineralized using microwave digestion system, TOPwave (Analytik Jena) under extreme conditions of pressure and temperature. Sample (15 mL) was introduced to the digestion vessel, and then, 2.5 mL of nitric acid 67% high purity (Merck, Germany) and 7.5 mL of hydrochloric acid 37% high purity (Merck, Germany) were added. After stirring (20 minutes) and digestion (25 minutes), the vessels were cooled at room temperature and then, each solution was transferred to volumetric flask (25 mL). Heavy metals content in surface water samples were determined by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) using Thermo Scientific iCAP Qc system. All quantitative measurements in triplicates, in standard mode (STD), were performed using the instruments software Qtegra; *relative standard deviation* (RSD) values were calculated, being less than 10%. Several well-known isobaric interferences were automatic corrected [20–21].

3. RESULTS AND DISCUSSION

The results showed that (Tables 1 and 2), the experimental mean values of pH, for samples collected in upstream of Targoviste City was in the range of (7.08–7.66) and in downstream was in the range (7.14–7.83) respectively. The pH values show that investigated water samples are moderately basic (Fig. 3a).

Table 1

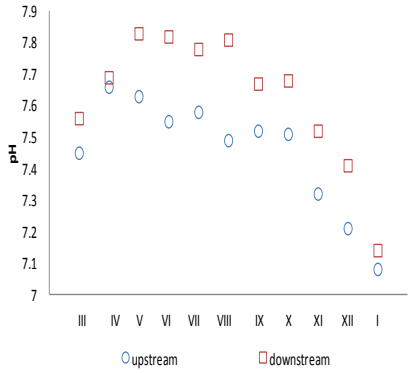
Physico-chemical parameters for water samples upstream of the Ialomita River

		Temperature [°C]	**pH**	**Turbidity [NTU]**	**Conductivity [µS/cm]**	**Salinity [‰]**
Spring	III	7.45	7.45	12.5	360	0.2
	IV	10	7.66	15.7	346	0.2
	V	10.2	7.63	15.1	459	0.3
Summer	VI	14.8	7.55	21.5	572	0.3
	VII	13.8	7.58	28.4	549	0.3
	VIII	13.1	7.49	29.8	561	0.3
Autumn	IX	12.9	7.52	29.8	477	0.3
	X	10.1	7.51	17.9	438	0.2
	XI	9.8	7.32	16.4	336	0.2
Winter	XII	5.9	7.21	11.5	253	0.2
	I	4.1	7.08	9.6	241	0.2

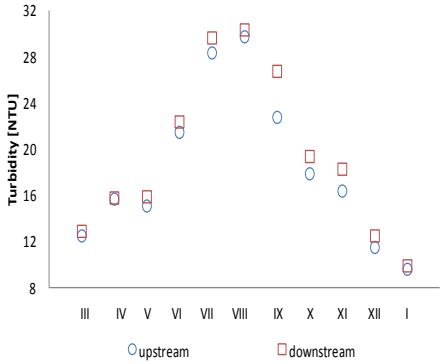
Table 2

Physico-chemical parameters for water samples downstream of the Ialomita River

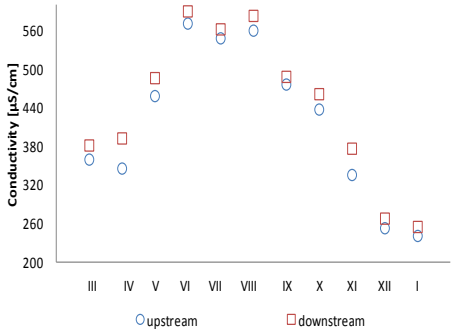
		Temperature [°C]	pH	Turbidity [NTU]	Conductivity [µS/cm]	Salinity [‰]
Spring	III	10.3	7.56	12.9	382	0.2
	IV	10.1	7.69	15.8	393	0.2
	V	10.4	7.83	15.9	487	0.3
Summer	VI	15.1	7.82	22.4	591	0.3
	VII	15.2	7.78	29.7	563	0.3
	VIII	14.6	7.81	30.4	584	0.3
Autumn	IX	13.1	7.67	26.8	489	0.3
	X	10.6	7.68	19.4	462	0.2
	XI	9.9	7.52	18.3	377	0.2
Winter	XII	6.1	7.41	12.5	268	0.2
	I	4.8	7.14	9.9	255	0.2



(a)



(b)



(c)

Fig. 3 – pH (a), turbidity (b) and conductivity (c) of water river samples collected in four seasons over a year.

The turbidity values of Ialomita River water samples, are in the range of (21.5 NTU–30.4 NTU), in the dry season and in the range (9.6 NTU – 12.5 NTU) in the winter season (Fig. 3b).

The mean conductivity of surface water samples was in the range of (241–572) μS/cm for samples collected in upstream, and in the range of (255–591) μS/cm for samples collected in downstream, respectively (Fig. 3c). In addition, the salinity values were in the range of (0.2 ‰–0.3 ‰) in all collected samples (in upstream and in downstream of Ialomita River respectively).

In Figures 3 a,b,c, it can be observe that in the summer time (*i.e*. June, July, August of the year 2015) all analyzed parameters reached the maximum values, and in the winter time (*i.e.* December, 2015 and January, 2016) were recorded minimum values. As expected, the values recorded in downstream of Targoviste are higher than the upstream values. This increase of pollution could be attributed to industrial enterprises from the city.

Heavy metals concentrations in water samples (66 samples) collected from Ialomita River in two representative points (Fig. 2), upstream and downstream, were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique using Thermo Scientific iCAP Qc system and were determinated the concentrations of Cd, Cr, Ni, Pb, Cu and Fe. The mean concentration values of these elements are given in Tables 3 and 4. Their distributions are represented in Fig. 4 a,b.

Table 3

The mean heavy metals content in water samples collected upstream of Ialomita River of Targoviste City

Month	**Metals content [μg/L]**					
	Cd	**Cr**	**Ni**	**Pb**	**Cu**	**Fe**
March	0.03	0.18	2.09	1.93	14.3	621.3
April	0.28	0.19	2.48	2.03	11.4	308.9
May	0.38	1.02	7.45	5.68	32.8	789.2
June	0.42	3.4	5.19	4.96	24.7	772.1
July	0.51	1.52	3.02	3.61	20.7	913.7
August	0.65	1.62	3.23	5.78	21.3	1092.1
September	0.31	1.23	1.94	4.43	12.5	746.4
October	0.24	1.19	1.02	3.03	12.9	543.8
November	0.14	1.15	1.00	2.54	11.6	471.3
December	0.09	1.11	0.97	2.13	10.2	421.9
January	0.03	0.55	0.64	2.02	10.43	356.8
RSD %	0.05–0.1	0.2–0.4	0.2–5.5	0.5–5.6	1.5–7.5	1.1–7.7
Quality Class*	I–II	I	I	I–II	I–II	II–IV

** According with Order 161/2006*

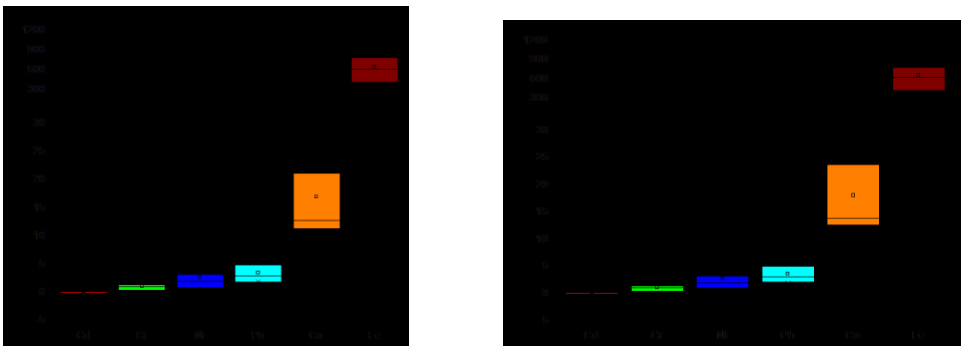
Table 4

The mean heavy metals content in water samples collected downstream of Ialomita River of Targoviste City

Month	Heavy metals content [µg/L]					
	Cd	Cr	Ni	Pb	Cu	Fe
March	0.07	0.22	2.17	1.98	15.1	642.3
April	0.39	0.34	2.58	2.32	12.7	319.4
May	0.43	1.33	7.69	5.97	34.5	792.7
June	0.49	3.4	5.31	5.14	25.2	785.5
July	0.57	1.52	3.24	3.78	22.4	946.2
August	0.68	1.62	3.31	5.82	23.9	1102.5
September	0.35	1.23	1.98	4.54	13.9	776.3
October	0.29	1.19	1.19	3.26	13.1	553.1
November	0.16	1.15	1.02	2.60	11.9	482.2
December	0.11	1.11	0.99	2.28	10.8	431.2
January	0.08	0.55	0.72	2.19	10.1	367.2
RSD %	0.08–0.1	0.2–0.7	0.3–4.1	0.9–4.2	1.8–6.2	1.0–8.1
Quality Class*	I–II	I	I	I–II	I–II	II–IV

** According with Order 161/2006*

The water quality classification is in accordance with Order 161/2006 (Romanian Regulation) [19]. The data obtained were compared with regulated values, thus establishing the quality class of the Ialomita River, which was monitored, each month for two consecutive years (2015–2016). The experimental results given above showed that (Tables 1–4), Ialomita River was classified as quality Class IV in August 2015, Class III in March, May, June, July, September and October 2015 and Class II in April and December 2015, and January 2016. These classes are available as both upstream and downstream. It follows that, Ialomita River water quality can be well described in every season of the year.



(a) (b)

Fig. 4 – The mean content of Cd, Cr, Ni, Pb, Cu and Fe in surface water samples collected from Ialomita River of Targoviste City, in upstream (a) and in downstream (b); (March 2015–January 2016).

The highest concentration level of Ni and Pb, was observed in May, from all eleven months monitored. During the months of June-July the levels of heavy metals are decreasing and in August are increasing.

This behavior is explained by the reduced amount of rainfall during this period of the year. Since September, with the beginning of autumn when the rainfall increased, the concentrations of heavy metals decreased steadily until the last month of monitoring.

4. CONCLUSIONS

Our investigations were carried out over a long period of time, March to December 2015 and January 2016. The physico-chemical parameters and heavy metal concentrations that exceed the reference values lead to a change in water quality with negative influences on self-purification processes of the river due to the reduction of biological activity:

– measured values were just momentary values and characterize the singular contamination level related to the period and locations of the research campaign;

– high concentrations of heavy metals (*i.e*. Fe, Pb and Cu) determined in water samples are not suitable for the formation and development of aquatic organisms and may disturb the ecosystem;

– the analysis of results show very clearly that the content of elements (*e.g*. Pb, Fe, Cr, Cu and Ni), is higher on downstream of Targoviste City, Nisipuri area. This may be, also, due to the influence of wastewater from industrial area.

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