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Analytical Studies on the Pollution of Arges River

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ABSTRACT: The Arges River arises from the ice lake Capra, which is situated in the Fagaras mountains, and is flows into the Danube River near Oltenita city. During this “trip” it collects, more or less cleaned, industrial or home-originated wastewater and other waste materials. Some of these are deposited on the river bed, others are transported downstream by water or fish.

Among antropogenic compounds, heavy metal ions may be the most harmful pollutants. While many other compounds are more or less biodegradable, heavy metal ions could be retained in the ecosystem, indefinitely. The water samples were collected between Cumpana and Oltenita from 12 sites placed in the middle of the stream. Heavy metal ions concentration in the samples were quantified by Atomic Absorption Spectrometry and by Inductively Coupled Plasma Atomic Emission Spectrometry. The values were compared with Anodic Stripping Voltammetry delivered results (Cu, Cd, Zn, Pb), which provided a good agreement. The values determined within our work represent singular cases. Considering the obtained values for the water elements — loading related to reference limit values, the Arges River is, with few exceptions, a clean river.

KEY WORDS: environmental analysis, metal ions, water.

I. INTRODUCTION

The existence of pollutants in the environment is an important national and world problem. It was not generally recognized until 1960. Today, many people consider pollution as a problem that will not go away, but one that could get worse in the future. The general effects of pollution produce a deterioration on the environment quality. Pollution started at the time when man began to use the natural sources of the environment for his own use. Pollution of the water affects the lives of a great many people throughout the world, especially those living in heavy industrialized areas. The hydrodynamic properties of the water may be a major factor influencing site and selection. In the case of the river, it is important to specify the exact location of the measurement site. Depending on the flow characteristics and the extent of lateral and vertical mixing at any given location, it may be necessary to define each site in terms of depth from surface and distance from either bank. Climatic conditions, such as

temperature, evaporation, precipitation, dust fall, and wind speed and direction, may have profound effects of water quality. The selection of site and frequency of measurement make us having in mind these variables.

For this study the Arges River was chosen. Arges River arises from the ice lake Capra, which is situated in the Fagaras mountains, and it flows into the Danube River near Oltenita city. In length, 340 km, Arges is the fifth river from Romania after Siret, Mures, Olt, and Someș, and lengthways the riverbeds are located in four cities, Curtea de Arges, Pitesti, Gaesti, and Oltenita, and many other localities (countryside and commune).¹

II. EXPERIMENTAL

The water samples were collected between the Cumpana and Oltenita from 12 sites, (1) Cumpana (Poienari), (2) Albesti, (3) Curtea de Arges, (4) Manicesti, (5) Borlesti, (6) Pitesti, (7) Cateasca, (8) Stoenesti, (9) 1 Decembrie, (10)

Negoiesti, (11) Mitreni, (12) Oltenita, placed in the middle of the stream. A second effort, the first sampling site was Poienari, was necessary because it was raining and there was a storm. The samples were collected into the polyethylene containers, and they were filtered before analysis.

For the determination of the metal ions concentration in Arges River Atomic Absorption Spectrometry for sodium, potassium, and magnesium was used; Direct Coupled Plasma Atomic Emission Spectrometry for calcium; Inductively Coupled Plasma Atomic Emission Spectrometry for copper, cadmium, zinc, aluminium, lead, titanium, zirconium, chromium, molybdenum, manganese, iron, and nickel. The determination was carried out by means of an atomic emission spectrometer with inductively coupled plasma, SPECTROFLAME-P (SPECTRO-Analytical Instruments, Germany). The instrument has 30 fixed spectral channels that can simultaneously be monitored by the three polychromators and allow one to carry out the background correction, application of internal standard method, and other facilities.

The argon utilized was of spectral purity (99.998 %), the cooling flow rate $12 \text{ L}\cdot\text{min}^{-1}$, the auxiliary flow rate $0.8 \text{ L}\cdot\text{min}^{-1}$ and nebulizer flow rate $1 \text{ L}\cdot\text{min}^{-1}$ all of them are functions of plasma power and some of them were automatically controlled. The consumption rate of the liquid sample was about $2 \text{ mL}\cdot\text{min}^{-1}$. The observation height is adjustable; it is usually 12 mm.

For copper, cadmium, zinc, and lead, two methods were chosen, with the same detection limit, but with the different principle, Inductively Coupled Plasma Atomic Emission Spectrometry and Anodic Stripping Voltammetry, and the results were comparable. Boron, phosphorus, and silicon were also determined by ICP-AES.

An electrochemical system EG&G 273 A Model Princeton Applied Research Potentiostat coupled with a Static Mercury Drop Electrode (SMDE) 303 A Model and a Stirrer 305 Model was used. Electrochemical cell contains a working electrode, hanging mercury drop electrode (HMDE), a reference electrode, Ag/AgCl and an auxiliary electrode, platinum wire. The deposition of copper, cadmium, zinc, and lead on the mercury electrode was achieved using a fast stir-

ring rate and a medium size drop. The solutions were deaerated with analytical grade argon at the start of each experiment, and a flow of argon was maintained over the solution during the experiment to prevent oxygen interference. All experiments were performed at a constant temperature of 25°C .

III. RESULTS AND DISCUSSION

Table 1 presents the comparative results obtained for copper, cadmium, zinc, and lead by Inductively Coupled Plasma Atomic Emission Spectrometry and Anodic Stripping Voltammetry. Table 2 presents the maximum allowable concentration values in natural waters (Romanian standards) and experimental values obtained within the present work for some elements with pollution potential. The variation of the metal ions concentration and the variation of the boron, silicon, and phosphorus concentration, depending on the location is observed.

In the samples the concentration of major elements like sodium, potassium, calcium, and magnesium increase when the Arges joins with the Dâmbovită, and for the other elements the concentrations increase in the industrial areas. The low concentration of metal ions observed in the second sampling of the samples is due to rainy weather. In the mountain regions the Arges' water is clean, but in the city areas there are many possible pollution sources, industrial and/or home-originated wastewater and other waste materials.

Pitești is a big industrial center, with a chemical industry, food industry, a nonferrous metallurgical industry, etc. The vegetation on the bank consists mainly of trees (mainly forest) and bushes. The erosion of the bank caused by the river can also be responsible for the presence in the water of aluminium, iron, titanium, and zirconium.

The effluents from Râul Doamnei and Sabar flow into the Arges discharging wastewater and suspensions. After it joins with the Dâmbovită River (which flows through Bucharest) the water of Arges becomes dirty and metal ions concentration increases.

Among the anthropogenic compounds, heavy metal ions may be the most harmful pollutants.

TABLE 1
Comparative Study of Copper, Cadmium, Lead, and Zinc Concentration by ICP-AES and ASV Methods

Sample	Copper µg/L			Cadmium µg/L			Lead µg/L			Zinc µg/L					
	April 1999		May 1999	April 1999		May 1999	April 1999		May 1999	April 1999		May 1999			
	ICP-AES	ASV	ICP-AES	ASV	ICP-AES	ASV	ICP-AES	ASV	ICP-AES	ASV	ICP-AES	ASV			
1	32.90 (1.0%)	17.00 (1.2%)	0.20 (3.0%)	0.23 (3.0%)	0.40 (1.5%)	0.30 (1.3%)	5.60 (1.0%)	4.33 (1.2%)	1.00 (1.5%)	0.88 (2.0%)	26.00 (1.0%)	23.40 (1.2%)	0.21 (2.4%)	0.50 (2.3%)	0.23 (2.1%)
2	9.70 (2.0%)	9.90 (1.7%)	0.20 (3.1%)	0.160 (3.5%)	6.70 (1.0%)	5.5 (1.2%)	5.60 (1.3%)	4.40 (1.5%)	1.00 (2.0%)	0.76 (2.4%)	1.00 (2.0%)	0.58 (2.6%)	0.15 (2.2%)	0.50 (2.0%)	0.41 (1.8%)
3	9.40 (2.1%)	8.20 (1.9%)	0.20 (3.0%)	0.180 (2.0%)	-	-	7.30 (1.0%)	7.08 (1.0%)	31.80 (1.1%)	36.00 (1.0%)	1.00 (2.0%)	0.48 (3.0%)	0.19 (2.3%)	0.50 (2.0%)	0.39 (2.3%)
4	6.20 (2.5%)	8.20 (1.8%)	0.20 (2.5%)	0.160 (2.3%)	-	-	9.40 (1.0%)	7.60 (1.2%)	42.90 (1.0%)	38.30 (1.4%)	1.00 (1.7%)	0.43 (2.0%)	0.18 (2.0%)	0.50 (2.1%)	0.35 (2.5%)
5	3.30 (3.0%)	5.30 (2.1%)	0.20 (3.0%)	0.150 (2.7%)	-	-	1.30 (2.7%)	0.72 (3.0%)	1.00 (2.0%)	0.83 (2.4%)	1.00 (1.3%)	1.04 (1.0%)	0.27 (2.4%)	15.70 (1.1%)	14.60 (1.3%)
6	3.70 (2.8%)	6.00 (2.0%)	1.00 (1.7%)	1.65 (1.0%)	4.90 (1.1%)	5.01 (1.5%)	3.00 (2.0%)	1.93 (2.3%)	1.00 (1.5%)	0.86 (1.0%)	1.00 (1.8%)	0.65 (2.0%)	0.22 (2.6%)	46.00 (1.0%)	57.23 (1.0%)
7	6.30 (2.3%)	8.00 (1.5%)	0.50 (2.0%)	0.46 (2.0%)	-	-	1.70 (1.8%)	1.60 (2.0%)	1.00 (1.2%)	0.79 (1.3%)	16.40 (1.0%)	13.70 (1.1%)	4.60 (1.1%)	66.10 (1.5%)	58.77 (1.4%)
8	7.40 (2.0%)	9.00 (1.3%)	0.20 (2.2%)	0.150 (2.4%)	-	-	6.00 (1.2%)	4.82 (1.6%)	1.00 (2.0%)	0.84 (1.8%)	2.70 (1.6%)	1.85 (1.5%)	7.92 (1.0%)	95.20 (1.0%)	90.30 (1.0%)
9	3.70 (3.0%)	2.90 (3.0%)	0.50 (2.5%)	0.41 (1.7%)	1.30 (2.0%)	0.80 (2.1%)	6.80 (1.0%)	5.50 (1.3%)	1.00 (1.0%)	1.12 (1.1%)	1.00 (2.0%)	0.59 (2.2%)	0.35 (2.2%)	126.10 (1.2%)	120.80 (1.0%)
10	4.20 (2.6%)	3.70 (2.8%)	0.20 (3.0%)	0.160 (3.0%)	8.9 (1.1%)	7.22 (1.0%)	3.40 (2.0%)	2.80 (2.2%)	1.00 (2.0%)	0.90 (2.2%)	1.00 (1.0%)	0.63 (1.5%)	15.00 (1.1%)	164.80 (1.5%)	159.00 (1.3%)
11	6.40 (2.0%)	6.55 (2.0%)	0.70 (1.8%)	0.63 (1.3%)	7.10 (1.0%)	5.40 (1.3%)	4.30 (1.2%)	3.72 (1.6%)	1.00 (1.0%)	0.89 (1.1%)	1.00 (2.0%)	0.71 (2.2%)	40.10 (1.0%)	207.30 (1.4%)	201.20 (1.0%)
12	6.20 (2.2%)	5.20 (2.0%)	0.20 (3.3%)	0.160 (1.8%)	0.40 (2.5%)	0.50 (2.2%)	3.80 (1.5%)	3.45 (1.7%)	2.80 (1.5%)	1.90 (2.0%)	1.00 (1.7%)	0.64 (1.6%)	28.40 (1.0%)	240.70 (1.7%)	236.00 (1.0%)

*Results are presented as mean of five determinations and, in brackets, relative standard deviations (%) are also given.

TABLE 2
Elements Concentration in Surface water: Reference and Experimental Data

<i>Trace elements</i>	STAS* 4706/88 $\mu\text{g/L}$	<i>Concentration found within this work</i> $\mu\text{g/L}$			
		<i>maximum</i>		<i>minimum</i>	
		April 1999	May 1999	April 1999	May 1999
Aluminium	—	4326	531	5	42.7
Copper	50	32.9	1	3.3	0.2
Cadmium	3	8.9	9.4	0.4	1.7
Zinc	30	43.9	240.7	0.5	0.5
Lead	50	42.9	26	1.0	1.0
Titanium	—	201.1	16.2	0.4	0.1
Chromium	500	8.3	1.2	0.3	0
Molybdenum	50	1.0	4	0.1	0.1
Manganese	100 300, 800	74.2	118.1	0	0.2
Iron	300 1000	3129	362.7	10.4	9.8
Nickel	100 100	10.1	5.2	0.1	0.1

*STAS: Romanian official norms.

While many other compounds are more or less biodegradable, heavy metal ions could be retained in the ecosystem, indefinitely. Very small quantities or traces of metal ions are required for normal growth and metabolism, for example, copper, iron, nickel, and zinc. Metal ions produce physiological poisoning by becoming attached or adsorbed on the cellular enzymes, causing inhibition of enzymatic control of respiration, photosynthesis, and growth.

One of the most significant effects is the accumulation of various metal ions in the aquatic organisms.

Lead and cadmium can displace calcium from bones and cause them to become brittle; lead, cadmium, and chromium can concentrate in the liver and kidneys, causing damage and malfunctioning of these organs. The nervous system is susceptible to concentrations of lead and copper, and the effects vary from brain damage (encephalopathy) to damage to the peripheral nerves, caus-

ing uncoordinated muscular control and poor eyesight. Specific toxic effects in humans vary according to the ion type, multi-ion combinations, tissue concentrations, the frequency of dosage, and the age of the individual.

IV. CONCLUSION

We can conclude, after the examination of the experimental results obtained by different techniques, that, in general, the Arges River has a limited degree of pollution.

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