

Determination of Toxic Heavy Metals Present in Jiu River Water using ICP-MS

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Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. As trace elements, some heavy metals (copper, zinc, selenium), are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metals poisoning could result from drinking-water contamination (for instance, lead pipes), high ambient air concentrations near emission sources, or intake *via* the food chain. This paper presents a study of some of the toxic heavy metals distribution on the Jiu river course, an important river in Romania. The most pollutants heavy metals from Jiu river course are lead, mercury and arsenic. The concentration of metals was determined by inductively coupled plasma mass spectrometry.

Key Words: Environment, Heavy metals, Inductively coupled plasma mass spectrometry, Jiu river.

INTRODUCTION

The Jiu river is an important river in Romania, with a total length of 339 km. The Jiu river has two sources *i.e.*, the Eastern Jiu, which springs from the Parang mountains and the Western Jiu, which springs from the Retezat mountains. The two branches of the Jiu River join in the Petrosani Depression.

The domestic pollution is dependent on the number of people from the inhabited areas¹. The overcharge of the organics and minerals pollutants of the domestic liquid residues is extremely big, reaching 10 L mud/inhabitant/day or 50 kg of solid dry meter/inhabitant/year (values taken from the Annual Report of World Health Organization-WHO, 2005). Concerning the industrial pollution, it is much more difficult to establish the quantity

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of the pollutants. Most frequently sources are detergents, solvents, heavy metals, organic acids, washing agents, ammonia. The most toxic inorganic products are arsenic, zinc, cadmium, selenium, mercury *etc.*². The zoo-technic pollution proceeds from animal residues, erosion products of the soil, natural or synthetic fertilizers, inorganic salts, mineral substances resulted from irrigations, herbicides and pesticides, bio-stimulators, antibiotics, *etc.*

Heavy metals, such as iron, chromium, copper, zinc, selenium are indispensable for the biochemical processes in the human body, but in small quantities³. When they overtake a certain concentration, they become dangerous for human's life.

The contamination of the sediments in the Jiu river with heavy metals has bad effects for different forms of life. Some pollutants were released many years ago, having a cumulative effect; other pollutants are released every day. Their origins are very varied, from industrials and domestic offal, industrial activities which generate pollutants, agricultural industries which use biodegradable compounds².

To determine the content of heavy metals in the samples of water taken from several points of the Jiu River, an analytical method inductively coupled plasma mass spectrometry (ICP-MS) has been used.

EXPERIMENTAL

The samples have been taken in three months, representing the summer, the autumn and the winter, from nine different points of the Jiu river. These points were: (1) Campu' lui Neag (The West Jiu) (2) Lupeni (The West Jiu) (3) Iscroni (The West Jiu) (4) Livezeni (The East Jiu) (5) upstream the confluence with Sadu (6) Balteni (7) Podari (8) Malu Mare and (9) Zaval, the point where the Jiu river flows into the Danube.

The aspect of the Jiu river was different during the three seasons, being under the influence of the meteorological conditions. The results of the analysis can be influenced by defective harvesting or by the improper preparation of the material. Thus, the two steps of the analysis, the harvesting of the samples and the preparation of the material are very important in the process of analyzing the containing of heavy metals, because the samples have to be representative and mustn't introduce modifications in the composition and quality of water⁴.

Liquids can be analyzed directly, sometimes with prior dilution. Water samples were collected manually into polyethylene bottles. Prior to use, all bottles were cleaned with 10 % HNO₃, rinsed with distilled water and after that, with the water to be analyzed⁵. The distance from the river side⁶ is about 2.00-2.50 meters and the depth was about 0.20-0.50 meters.

The analysis of water was made by using inductively coupled plasma mass spectrometry. The method has quickly become popular in many analytical laboratories because of its precision and accuracy and determination of heavy metals at trace level (ppb-ppm) and even at a ultra trace level (ppq-ppb)⁷. In ICP-MS, a plasma or gas consisting of ions, electrons and neutral particles is formed from argon gas. The plasma is used to atomize and ionize the elements in a sample⁸. The resulting ions are then passed through a series of apertures (cones) into the high vacuum mass analyzer. The isotopes of the elements are identified by their mass-to-charge ratio (m/e) and the intensity of a specific peak in the mass spectrum is proportional to the amount of that isotope (element) in the original sample. In this research, an ICP-MS-Quadrupole Mass Analyzer, AGILENT 7500 (Fig. 1) was used. This analyzer consists of four cylindrical rods onto which is applied both RF and DC electric fields. The four rods are arranged such that they form two pairs, one pair in the X plane and one in the Y.

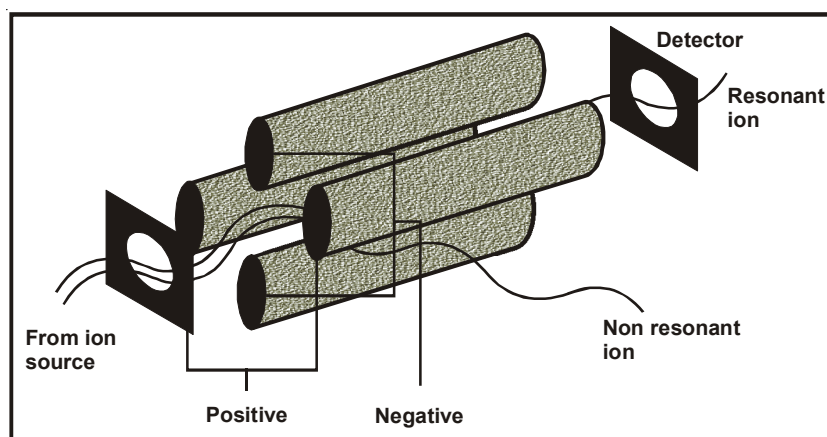


Fig. 1. Quadrupole scheme

As ions enter the quadrupole, they begin to oscillate in both the X and Y planes. In such a system, the lower m/e ions will be destabilized in the quadrupole whenever the alternating (RF) component of the electric field exceeds the direct (DC) component. In this instance, the lower m/e ions will quickly be thrown out of the quadrupole and will not reach the detector. This mode of operation makes an effective low mass filter. If the direct component exceeds the alternating component then the reverse is true. High m/e ions become unstable while lower m/e ions are stabilized by the presence of the alternating component. This makes an effective high mass filter.

In the quadrupole, the mass analyzer is created by connecting the two pairs of rods in such a way that the X plane acts as a low mass filter and the Y plane acts as a high mass filter. By carefully matching the two fields, only ions of a particular mass are able to resonate at the correct frequency and pass through the quadrupole at any point in time. The quadrupole mass analyzer is a very fast and efficient system.

For the three analyzed heavy metals, As, Pb, and Hg, it can be seen from Table-1, that the used method is the most efficient.

TABLE-1
DETECTION LIMIT FOR THREE ANALYZED IONS IN SOME OF
THE MOST EFFICIENT CHEMICAL METHODS

Metals	Approximate detection limit		
	Neutron activation analysis ($\mu\text{g/g}$)	X-ray fluorescence ($\mu\text{g/g}$)	Inductively coupled plasma mass spectrometry (Pg/g)
Arsenic	0.01	0.5	25
Lead	–	1.0	10
Mercury	1.00	1.0	50

Advantages of quadrupole ICP-MS include^{7,8}:

- The quadrupole mass analyzer is able to scan the mass spectrum from 3-250 very quickly.

- **Sensitivity:** Modern quadrupoles are easily able to detect trace levels of many elements at levels well below a ppb (ng/g).

- **Reliability:** Quadrupole ICP-MS systems are rapidly becoming the workhorse of many analytical laboratories throughout the world.

A disadvantage of quadrupole ICP-MS is a high background noise.

RESULTS AND DISCUSSION

Table-2 presented the highest concentration levels admitted by Romanian standards for different ions of the heavy metals⁹. The quality classes are:

I = very good; II = good; III = moderate; IV = satisfactory; V = week

TABLE-2
THE HIGHEST CONCENTRATIONS ADMITTED BY
ROMANIAN STANDARD

Metals	Measure units	Concentrations values – Romanian standard				
		I	II	III	IV	V
As	$\mu\text{g/L}$	Below the detection limit – b.d.l.	5.0	10.0	25.0	>25.0
Hg	$\mu\text{g/L}$	b.d.l.	0.1	0.2	0.5	>0.5
Pb	$\mu\text{g/L}$	b.d.l.	5.0	10.0	25.0	>25.0

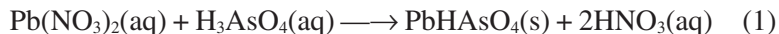
A part of the analyzed metals had normal values in the admitted limits (*e.g.*, mercury), but several metals are over the admitted limit (*e.g.*, arsenic, lead).

Arsenic forms colorless crystalline oxides As_2O_3 and As_2O_5 which are hygroscopic and readily soluble in water to form acidic solutions. Arsenic (V) acid, is a strong acid. Arsenic forms an unstable, gaseous arsine (AsH_3). In subtoxic doses, soluble arsenic compounds act as stimulants and were once popular in small doses as medicinals by people in the mid 18th century. Arsenic compounds were also once used to dope racehorses¹⁰.

Elemental arsenic is found in many solid forms. The yellow form is soft, waxy and unstable and is made of tetrahedral As_4 molecules. The gray, black or 'metallic' forms have somewhat layered crystal structures with bonds extending throughout the crystal. They are brittle semiconductors with a metallic lustre.

The arsenic has been used well into the 20th century, as an insecticide on fruit trees as "Lead hydrogen arsenate". Lead hydrogen arsenate, also called lead arsenate (PbHAsO_4) is an inorganic insecticide used primarily against the potato beetle.

Lead arsenate is the most extensively used arsenical insecticide¹¹ and it is usually produced using the following reaction:



The arsenic was also used as Scheele's Green, a copper arsenate (CuHAsO_3), has even been recorded in the 19th century as a colouring agent in sweets. It is a compound similar to Paris Green, it is a green pigment, of yellowish hue and was used in some paints, but has since fallen out of use due to its toxicity. In the last half century, monosodium methyl arsenate ($\text{CH}_3\text{AsNaO}_3$), (MSMA), a less toxic organic form of arsenic, has replaced lead arsenate's role in agriculture as arsenic-based herbicide and fungicide.

During the 18-20th centuries, a number of arsenic compounds have been used as medicines, including arsphenamine (Fig. 2) (by Paul Ehrlich) and arsenic trioxide (by Thomas Fowler)¹¹. Arsphenamine is a drug that was used to treat syphilis and trypanosomiasis.

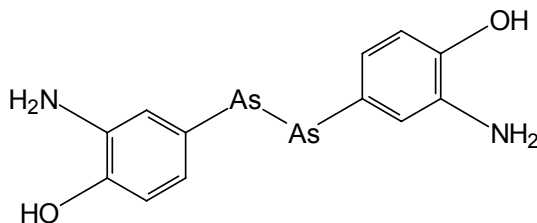


Fig. 2. Structure of arsphenamine

Arsenic trioxide has been used in a variety of ways over the past 200 years, but most commonly in the treatment of cancer. Arsenic trioxide, As_2O_3 , was used as a medicine (Fowler's drink) and tonic in different diseases. Today it is known that it can produce even tumours. Arsenic is known to cause arsenicosis due to its manifestation in drinking water, the most common species being arsenate [HAsO_4^{2-} ; As(V)] and arsenite [H_3AsO_3 ; As(III)]. The ability of arsenic to undergo redox conversion between As(III) and As(V) makes its availability in the environment possible.

Arsenic poisoning can lead to a variety of problems, from skin cancer to keratoses of the feet. Chronic arsenic poisoning results from drinking water with high levels of arsenic over a long period of time.

WHO recommends a limit of 0.01 mg/L of arsenic. It is estimated that *ca.* 57 million people are drinking groundwater with arsenic concentrations elevated above the WHO's standard of 10 parts per billion. It is a significant pollutant which can be found in soils and sediments contaminated with pesticides based on arsenic, in geothermal sources of water and evacuations of the mining industrial points¹². The arsenic in the groundwater is of natural origin and is released from the sediment into the groundwater due to the anoxic conditions of the subsurface. The concentration of the arsenic on the Jiu river course was, in most of the harvesting points, below the detection limit.

Fig. 3 shows the variation of the concentration of the arsenic in the samples taken from the Jiu River during the three seasons.

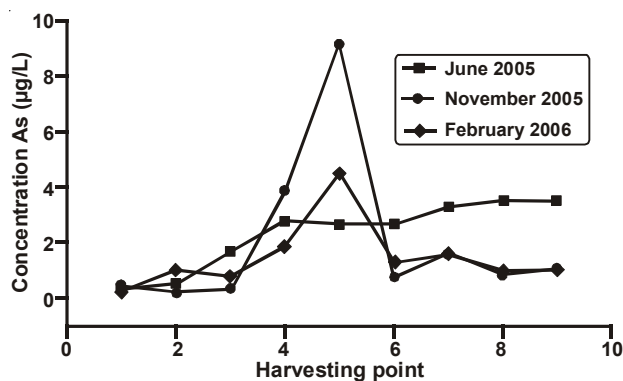


Fig. 3. The variation of the concentration of the arsenic in the samples taken from the Jiu river

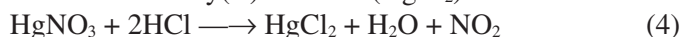
In June 2005, the concentration of the arsenic grows relatively constantly, from the source towards the flowing point. This growth also maintains during November and February, in the point Iscroni, where in November the concentration overtakes the admitted limit and then lowers towards Zaval, a tendency which maintains in both months.

Mercury and its compounds have been used in medicine for centuries, the toxic effects of mercury and its compounds are known.

Mercury(I) chloride (calomel, Hg_2Cl_2) is obtained:



Mercury(I) chloride has traditionally been used as a diuretic, topical disinfectant and laxative. Mercury(II) chloride (HgCl_2) is obtained:



and was once used to treat syphilis, although it is so toxic that sometimes the symptoms of its toxicity were confused with those of the syphilis it was believed to treat; it was also used as a disinfectant. In the early 20th century, mercury was administered to children yearly as a laxative and dewormer and was used in teething powders for infants¹³.

The determinations have shown that, in the Jiu river the concentration of mercury is below the detection limit (the detection limit-0.1 ppb-much lower than the highest concentration admitted-CMA-stipulated by the Romanian standards). The mercury is used in the chemical industry, in metrology and electronics to fabricate thermometers, measure devices and in the industry of plastic masses¹⁴.

Fig. 4 shows the variation of the concentration of the mercury, in the samples taken from the Jiu river during the three seasons.

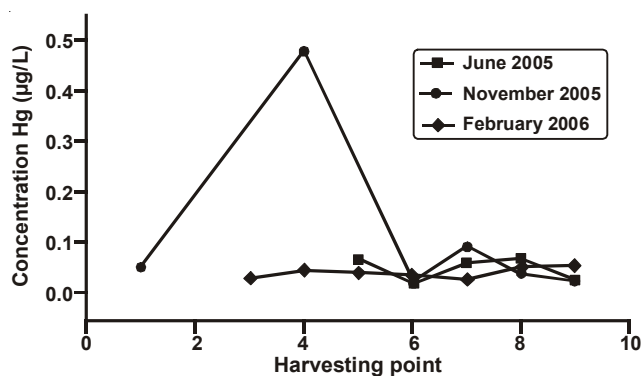


Fig. 4. Variation of the concentration of the mercury, in the samples taken from the Jiu river

The admitted limit for mercury is $\text{Hg} = 1 \mu\text{g/L}$. The mercury is an extremely toxic heavy metal and it can be seen that, during the three seasons, in the Jiu river, the concentrations of mercury in all the harvesting points do not overtake the admitted limit.

In June 2005, the concentration of mercury is under the detection limit in the first four harvesting points on the Jiu river and grows insignificantly

towards the confluence of the Jiu river with the Danube. In November 2005, the concentration of mercury in the samples taken from Lupeni, Livezeni and Iscroni is below the detection limit. The concentration grows towards the flowing point, but remains under the admitted limit. In February 2006, the concentration of mercury at Campu' lui Neag and Lupeni is below the detection limit and remains constant towards the flowing point.

The lead is the most known metallic pollutant. Being strongly absorbed by the sediments and the soil particles, the lead gets to plants and animals. In the aquatic systems, influenced by the temperature, salinity and pH, its solubility can grow. High levels of this metal could be a result of environmental pollution as well as of high levels of mineral contents in soils of production areas¹⁵. It is extremely toxic, it diminishes immunity of the human body, diminishes the capacity of oxygenating the blood and alters the function of the nervous system. Lead is also responsible for the illness known as saturnism. The effects of these illnesses are also obvious at the succeeding generations¹⁶. It is thought that, in the big cities where the pollution with lead is more accented because of the road traffic, the juvenile delinquency is due to the intoxication with lead.

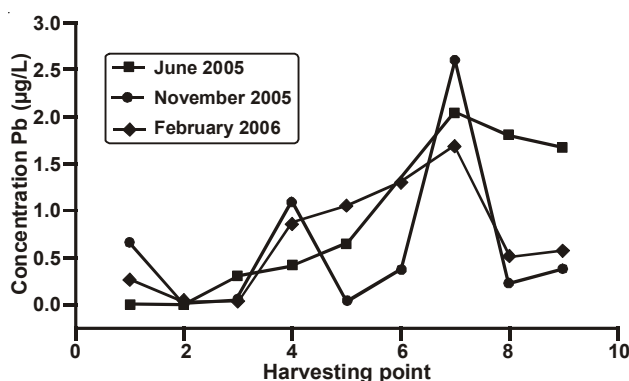


Fig. 5. Variation of the concentration of the lead in the samples taken from the Jiu river

Fig. 5 shows the variation of the concentration of lead in the samples taken from the Jiu river during the three seasons. The admitted limit for lead is $Pb = 1.7 \mu\text{g/L}$.

In June 2005, this concentration isn't reached in any of the harvesting points. In Balteni, the concentration of the lead is under the detection limit, at Podari it grows, and then, towards Zaval, it lowers again. In November 2005, it can be seen that at Podari, the concentration of the lead overtakes the admitted concentration, and then lowers towards the flowing point. In February 2006, the concentration uniformly grows from Livezeni towards

Podari, without reaching concentrations which are over the admitted limit and then suddenly lowers towards Malu Mare.

Conclusion

In 1950-1989, the quality of the waters of the Jiu River has constantly worsened. Because of the restriction of the social-economic activities, after 1990, the situation of the waters of the Jiu River and of the waters in Romania has continually improved. In the same time, in 1990 there is a transfer to a more rigorous management of the environment which also includes legislation according to the international norms.

After 1990, a part of the mines from the Jiu Valley were closed, which had led to a constant lower of the concentration of the heavy metals from the Jiu river. Until then, a part of the chemism of the waters in the area was determined by the excessively mining practiced in these areas.

A detailed analysis of the diagrams shows that, at most of the studied metals, the concentration is higher in summer-June 2005- than in November and February 2006.

Last summer, the Jiu Valley was flooded, in the entire area being registered the most powerful floods in the last 50 years. This may be the reason for which, in the taken samples, the concentrations of heavy metals are higher in summer than in winter and autumn.

High concentrations, which overtake the limit admitted by the Romanian standard, were recorded at the ions of the following metals: arsenic, and lead (at Podari).

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