PROCEEDINGS OF THE YEREVAN STATE UNIVERSITY

Chemistry and Biology 2014, № 3, p. 51–54

COMMUNICATIONS

Chemistry

STUDY OF CONTENT OF Cr, As, Cd, Pb ELEMENTS IN SOME RIVERS OF ARMENIA

Sh. L. MARABYAN [1*], L. A. MARGARYAN [2], G. P. PIRUMYAN [1]

[1,3] *Chair of Ecological Chemistry YSU, Armenia*
[2] *Armenian Branch of Mendez England & Associates, Armenia*

The content of Cr, As, Cd, Pb elements was studied in water samples of the Debed, the Gargar, the Shnogh, the Akhtala, the Voghji, the Artsvanik Rivers during 2008–2013 years.

Keywords: heavy metals, contamination, rivers, sampling point.

Introduction. Among the pollutants greater concern is attached to heavy metals involved in the prime group of pollution agents, the control of which is essential for any environment. There are no self-purification mechanisms for heavy metals, they simply redistribute, moving from one reservoir to another, interacting with different kinds of living organisms, leaving their visible and invisible undesirable consequences [1, 2].

Emission of heavy metals in the atmosphere, water, entrails of the earth, flora and fauna occur via their industrial use. Most of the metals are carcinogenic for humans and animals. The hazardous metal toxic impact is especially dangerous for infant organisms. Different chemical forms of arsenic, chrome(VI) compounds are known as carcinogenic agents for humans, and cadmium compounds are known as potential ones. It is supposed that the element manifests itself as carcinogenic agent while its ions interact with cell DNA. Metal toxicity can manifest itself by the dysfunction of different organs and their systems. So, the influence of cadmium ions damage the kidney tissues [3].

In the ground waters arsenic background level depends on its content in the aquifers ranging within 0.1–200 *mg*/*L*. In natural waters As occurs in the areas, where there are similar deposits in the rock. At this, about 5–10% of arsenic amount moves from the soils into the aquatic environment. As a rule, the arsenic content in the surface waters makes up 0.01 *mg*/*L*. Subject to the As content in the water its consumption can result either in organism fermentative process activation (in case of its low concentrations), or hyperkeratosis and hyperpigmentation induced by As poisoning (in case of high concentrations) [4].

In water reservoirs and rivers the concentration of cadmium ranges within 200–400 *mg*/*L*. This element is accumulated in the aquatic plants and fish tissues

[*] E-mail: sh-marabyan@mail.ru

(not in the skeleton). The harder the water the less is Cd poisoning probability. A long time is required for Cd release from the organism – for about 30 years [5].

We studied the water samples taken from different water sampling points on the Debed, the Gargar, the Shnogh, the Akhtala Rivers in 2008–2013 and the ones that were sampled from the Voghji and the Artsvanik Rivers during 2008–2012.

Table 1

The location of sampling points of rivers water quality monitoring

The name of the river	№ obs. post	The place of sampling point
Debed	5	0.5 *km* below from the spill point of the Marciget River
	6	0.5 *km* above from the Ayrum Town
	7	sector near the border
Akhtala	14	estuary of the river
Shnox	343	estuary of the river
Gargar	210	estuary of the river
	342	near the river source
Voghchi	91	1,7 *km* above from the Qajaran Town
	92	1,8 *km* below from the Qajaran Town
	93	0,8 *km* above from the Kapan City
	94	6,8 *km* below from the Kapan City
	321	near the airoport of Kapan
Artsvan	95	0,5 *km* above from tailings dams
	96	estuary of the river

The Debed River is the biggest river of the Kur River watershed and the deeper mountain river in Armenia. It is the confluent of the Zoraget and the Pambak Rivers, which join at 2 *km* northward from Tumanyan Railway Station, and then flows into the Kharam River. The Debed length, starting from the Pambak River head, makes up 178 *km*, 152 *km* of which is on the territory of Armenia, the rest of it is on Georgia area. The watershed surface area is 4080 km^2, 3790 km^2 of which is on the territory of Armenia. It has mixed feeding, unsteady regime, rises in spring up to 1 *m*. The Debed is of great importance considering its hydro energy and irrigation water potential [6, 7].

The Voghji River by its length is the second river in Zangezur after the Vorotan River. It starts from the Kaputjugh Mountain slope of the Zangezur Mountain Range. The total length of the river is 82 *km*, 43 *km* of which is on the Republic area, the total surface area of the water shed is 1175 km^2, 788 km^2 of which is on the Republic territory.

The Gargar River starts from the prong of the Spitak Mountain and down Kurtan village it joins the Dzoraget River. Its total length is 28 *km*.

The Shnogh River length is 19 *km*, it starts from the slopes of the Gugarats Mountains and in the northern part of v. Snogh joints the Debed River.

The Artsvanik River is the left tributary of the Voghj River (the RA Syunik Marz). It starts from the Bagrushat mountain range south slopes, near Kapan City falls into the Voghji River The total length is 17 *km*, the watershed surface area is 44 km^2 [8]. The MAC (maximum allowable concentration) for Cr, As, Cd and Pb are 0.001, 0.05, 0.005 and 0.1 *mg*/*L* respectively.

Materials and Methods. Tests are performed on ELAN 9000 mass-spectrometer. The method determines almost all elements of the periodic system within 1–100 *ng*/*L* concentrations. The base of this method are atomization, separation and detection of ions by the detector, which reports the number of pulses by the argon plasma. Indium solution (10 *mg*/*L*) is used as an internal standard, and solution of 1% nitric acid and deionized water in ratio 1:50 is used as background medium. Special purity argon as leading gas is used [9].

Results and Discussion. At 91, 92, 93, 94, 95, 96, 210, 321, 342, 343 water sampling point among the studied metals only Cr concentration exceeded the MAC. The concentrations of As, Cd and Pb were within the MAC.

Table 2

Content of Cr and Cd during 2008–2013 years at 5, 6, 7 and 14 sampling points

Year	№ obs. post	Metal	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2008	5	Cr	0.006	0.007	0.007	0.010	0.004	0.000	0.004	0.004	0.004	0.003	0.004	0.005
		Cd	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.003	0.003	0.002	0.003
	6	Cr	0.006	0.011	0.007	0.10	0.005	0.000	0.003	0.005	0.005	0.003	0.005	0.006
		Cd	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.003	0.003	0.003	0.003
	7	Cr	0.005	0.007	0.007	0.009	0.004	0.000	0.003	0.006	0.005	0.003	0.006	0.007
		Cd	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.003	0.003	0.003	0.003
	14	Cr	0.005	0.005	0.008	0.008	0.006	0.000	0.003	0.004	0.004	0.004	0.005	0.006
		Cd	0.036	0.035	0.005	0.012	0.005	0.005	0.031	0.053	0.023	0.012	0.015	0.003
2009	5	Cr	0.001	0.003	0.001	0.001	0.000	0.001	0.000	0.000	0.002	0.000	0.001	0.001
	6	Cr	0.001	0.003	0.001	0.001	0.000	0.001	0.000	0.001	0.002	0.000	0.001	0.004
	7	Cr	0.007	0.007	0.000	0.001	0.001	0.001	0.000	0.001	0.001	0.000	0.001	0.003
	14	Cr	0.000	0.003	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.001
		Cd	0.020	0.020	0.031	0.014	0.010	0.006	0.005	0.019	0.034	0.026	0.007	0.021
2010	5	Cr	0.002	0.002	0.010	0.001	0.000	–	0.001	0.002	0.002	0.001	0.002	0.001
	6	Cr	0.002	0.003	0.007	0.001	0.000	–	0.001	0.002	0.001	0.001	0.002	–
	7	Cr	0.003	0.003	0.004	0.001	0.000	–	0.001	0.001	0.002	0.001	0.002	–
	14	Cr	0.001	0.002	0.016	0.001	0.000	–	0.000	0.000	0.026	0.000	0.000	0.000
		Cd	0.015	0.002	0.011	0.014	0.009	–	0.026	0.052	0.038	0.019	0.028	0.044
2011	5	Cr	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.002
	6	Cr	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.003	0.003	0.002	0.002
	7	Cr	0.000	0.000	0.003	0.001	0.001	0.001	0.002	0.001	0.001	–	–	–
	14	Cd	0.018	0.022	0.009	0.010	0.012	0.006	0.023	0.031	0.026	0.071	0.040	0.034
2012	5	Cr	0.001	0.001	0.001	0.001	0.009	0.001	0.012	0.003	0.001	0.006	0.002	0.001
	6	Cr	0.001	0.004	0.002	0.002	–	0.001	0.021	–	0.001	–	0.003	0.001
	7	Cr	–	0.003	0.002	0.001	0.013	0.001	0.033	0.001	0.001	0.001	0.002	0.001
	14	Cr	0.001	0.001	0.001	0.001	–	0.002	0.001	–	0.001	–	–	–
		Cd	0.050	0.016	0.031	0.029	–	0.024	0.044	–	0.044	–	–	–
2013	5	Cr	0.001	0.001	0.002	0.001	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.001
	6	Cr	0.001	0.001	0.002	–	0.001	0.000	0.001	0.001	0.001	0.001	0.001	–
	7	Cr	0.001	0.002	0.016	0.001	0.000	–	0.000	0.000	0.026	0.000	0.000	0.000

At the sampling point 91 in 2009 the content of Cr exceeded the MAC in May and September, in 2010 in May and in 2012 in May, July and December. At the sampling point 92 the excess of Cr concentration over the MAC was observed in 2009 in April, May and September; in 2010 in May, in 2011 in February and in 2012 in February, March, May, July, August and December.

At the sampling point 93 the Cr concentration exceeded the MAC in 2008 in April and May, in 2010 in May and in 2012 in February, May, July and October. At the sampling point 94 the concentration of Cr exceeded the MAC in 2008 in

April, in 2009 in March and April, and in 2011 in October. At the sampling point 321 the excess of Cr concentration over the MAC was observed in 2008 in March, April and July, in 2009 in April and August and in 2012 in March, May, June, July and September. At the sampling point 95 in 2008 the concentration of Cr exceeded the MAC in April and June, in 2009 in April and in 2010 in May. At the sampling point 96 Cr content exceeded the MAC in 2008 in June, in 2009 in July and August and in 2010 in May. At the sampling point 210 the tests were performed during 2010–2013, the results showed that Cr content exceeded the MAC in 2010 in February and in 2012 in April. At the sampling point 342 and 343 the tests were performed in 2009–2013, during which at the inspection hole 342 Cr content exceeded the MAC in 2011 in October, in 2012 in April and in 2013 in May and August, while at the inspection hole 343 in 2009 in September and December, in 2010 in February, March, April, July, November and December, in 2011 in March, April, May, July and September, in 2012 in April, June, September, November, and in 2013 in February, March, May and September. At 5, 6, 7 and 14 water sampling points concentration of Cr exceeded the MAC. And also was observed Cd content exceeded the MAC at water 5, 6, 7 sampling points in 2008, and at 14 water sampling point during 2008–2014.

The results obtained in the Tab. 2, where high contents underlined. Data shows that in water of the Debed River max concentration of Cr observed at 7 sampling point in May 2012 was 0.033 *mg*/*L* (33 times exceeded MAC), and max concentration of Cd at 6 sampling point in August 2008 was 0.012 *mg*/*L* (2.4 times exceeded MAC). In water of the Akhtala River max concentration of Cr observed in March 2010 was 0.016 *mg*/*L* (16 times exceeded MAC), and max concentration of Cd in November 2011 was 0.071 *mg*/*L* (14.2 times exceeded MAC). In water of the Shnogh River max concentration of Cr observed in March 2010 was 0.04 *mg*/*L* (4 times exceeded MAC). In water of the Gargar River max concentration of Cr observed at 342 sampling point in August 2013 was 0.003 *mg*/*L* (3 times exceeded MAC). In water of the Voghji River max concentration of Cr observed at 93 sampling point in April 2008 was 0.033 *mg*/*L* (33 times exceeded MAC). In water of the Artsvanik River max Cr concentration observed at 96 sampling point in July 2009 was 0.033 *mg*/*L* (33 times exceeded MAC).

Received 10.10.2014

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