

Behavior of vanadium in the water-bottom sediment system

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Поведение ванадия в системе «Вода - донные отложения»

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Abstract: in the present study the behavior of vanadium is investigated, especially the influence of pH value, dissolved oxygen, nitrate and sulfate ions content on the migration of vanadium in the water-bottom sediment system of Hrazdan River. The content of vanadium has been determined in 66 samples from the bottom sediments and surface water for 2012-2013 periods.

Аннотация: в настоящей работе исследовано поведение ванадия, особенно влияние pH, растворенного кислорода, содержания нитрат и сульфат ионов на миграцию ванадия в системе «Вода - донные отложения» реки Раздан. Содержание ванадия была определена в 66 пробах из донных отложений и поверхностных вод для периода 2012-2013 годов.

Keywords: vanadium, correlation, heavy metals, migration, bottom sediment.

Ключевые слова: ванадий, корреляция, тяжелые металлы, миграция, донные отложения.

Introduction

Rivers can be polluted by flowing through the industrial polluted areas. They can be also accumulated in the sediment, which affects wildlife and humans.

Migration of the metals may cause an increase of their content in the ground and surface water as well as other ecosystem components, so the pollution of the environment by heavy metals can rise a serious environmental and health risk. Human activities can increase the content of heavy metals in the environment and contaminated sediment can be accumulated in water courses as a result of it. There are many sources of heavy metals to pollute the environment: agrochemicals usage, sewage sludges, irrigation waters, atmospheric deposition and etc [1, 2].

Many factors have an influence on the behavior of metals in natural waters such as substrate and suspended sediment composition, water chemistry. Metals have a high affinity for humic acids, organoclays [3].

Control of pollutants' distribution and their sources have a great importance, especially the identification of migration routes, quantitative description of their distribution size in the environment, mathematical modeling of the mass movement and prediction of pollution level [4].

Vanadium

Vanadium is highly distributed element in the earth's crust with an average concentration of approximately 100 mg/kg [5]. Vanadium is the 22nd most abundant element in the earth's crust [6].

Concentrations of vanadium in drinking-water may range from about 0.2 to more than 100 µg/liter [7]; typical values appear to be between 1 and 6 µg/liter [8].

The concentration of vanadium in drinking-water significantly depends on geographical location. The concentrations of vanadium in coal and crude petroleum oils vary widely (1-1500 mg/kg) [9].

Natural sources of vanadium in water include soil erosion, leaching from rocks and soils [10]. The concentrations of vanadium in coal and petroleum oils are very high (1-1500 mg/kg), from which natural objects can be polluted by vanadium or it can increase natural background concentration of vanadium in surface, ground waters and bottom sediment [9].

Anthropogenic sources of vanadium in water include leaching from the residue of ores and clays, urban sewage sludge, certain fertilizers. All of these are subjected to rain and groundwater drainage, as well as leachate from ash ponds and coal preparation wastes [10].

The migration and distribution of vanadium in water and soil is influenced by pH, redox potential, and by the presence of various compounds. The distribution of vanadium between water and sediment is strongly influenced by the presence of particulate in the water. Vanadium is known to bind strongly to mineral or biogenic surfaces by adsorption or complexing [11]. As an element, vanadium cannot be degraded in the environment, but may undergo various precipitation or ligand exchange reactions. Despite forming complexes with organic matter, it is generally not incorporated into organic compounds. Thus, transformation occurs primarily between various inorganic compounds during its movement through the environment, and biotransformation is not considered to be an important environmental fate process [12].

The dissolved complex compounds of vanadium with organic matter, especially with humic acids have essential role in the migration of vanadium [13].

Study object

Hrazdan River

Hrazdan River is one of the largest and most important rivers in Armenia, left tributary of the Araks River. It originates from Lake Sevan. Many hydroelectric power stations, a series of canals, artificial reservoir «Yerevan Lake» were built on Hrazdan River.

Materials and methods

33 sediment samples and 33 surface water samples were collected from the 6 sampling points along the Hrazdan River.

Sampling points description: **1st samp.point** - down from Hrazdan hydroelectric station, up to the mixing point with Marmarik river; **2nd samp.point** -river-mouth of Marmarik River; **3rdsam.point** - down from the mixing point with Marmarik River; **4thsam.point** - up to the flowing to «Akhpar Lich» reservoir; **5thsam.point** - after flowing to«Akhpar Lich» reservoir; **6th sam.point** - 1 km down from the «Akhpar Lich» reservoir.

In natural media, metal contaminants undergo reactions with ligands in water and with surface sites on the solid materials having contacts with water. Reactions in which the metal is bound to the solid matrix are referred to as sorption reactions, and metal that is bound to the solid is said to be sorbed. The metal partition coefficient (K_p ; also known as the sorption distribution coefficient) is the ratio of sorbed metal concentration (expressed in g metal per kg sorbing material) to the dissolved metal concentration (expressed in mg metal per L of solution) at equilibrium:

$$K_p = \frac{\text{sorbed metal concentration (g/kg)}}{\text{dissolved metal concentration (mg/l)}}$$

During transportation of metals in soils and surface water systems, metal sorption to the solid matrix results in a reduction in the dissolved concentration of metal, which affects the overall rate of metal transport [14].

In order to evaluate the influence of pH value, dissolved oxygen, nitrate and sulfate ions content on migration of vanadium in the water-bottom sediment system, it has been investigated the liner dependence between the partition coefficient and pH value, dissolved oxygen, nitrate and sulfate ions content.

In **Table 1** are presented aqua-chemical analysis results of the samples taken from 6 different sampling points of Hrazdan River, particularly the vanadium content in the water and bottom sediment for July, August & September 2012 and in February, May & July 2013. pH values, dissolved oxygen, sulfate and nitrate ions content are also presented.

Table 1. The content of vanadium, dissolved oxygen, pH values, nitrate and sulfate ion

in River Hrazdan

Sampling point	Date	pH	dissolved oxygen (DO)	[NO ₃], mg/l	[SO ₄ ²⁻], mg/l	[V] H ₂ O, mg/l	[V] BS, g/kg	K _p
1	August, 2012	8.08	8.89	10.4258	34.6854	0.0079	0.0885	11.2025316
	September, 2012	8.23	5.57	10.0198	28.6994	0.0035	0.1720	49.1428571
	February, 2013	8.42	13.48	12.758	38.75	0.0047	0.1282	27.2765957
	May, 2013	8.0	7.53	4.404	13.70	0.0037	0.0997	26.9459459
	July, 2013	8.0	11.78	6.681	36.369	0.0027	0.1184	43.8518519
2	July, 2012	7.81	8.96	3.0714	9.9398	0.0021	0.0781	37.1904762
	August, 2012	8.54	9.75	4.4722	14.4420	0.0047	0.1485	31.5957447
	September, 2012	8.76	6.37	4.7728	16.8082	0.0017	0.0994	58.4705882
	February, 2013	8.54	13.77	2.733	19.05	0.0016	0.1235	77.1875
	May, 2013	7.4	8.26	0.860	5.46	0.0012	0.1176	98
	July, 2013	8.2	11.08	3.146	9.254	0.0016	0.1065	66.5625
3	July, 2012	7.08	8.56	6.5208	23.0141	0.0012	0.0873	72.75
	August, 2012	7.90	14.74	13.0979	48.5094	0.0049	0.1093	22.3061224
	September, 2012	8.28	9.77	12.2562	45.0914	0.0041	0.1152	28.097561
	July, 2013	8.0	10.12	5.605	17.388	0.0020	0.1239	61.95
4	July, 2012	8.22	9.3	8.4919	30.5876	0.0021	0.1269	60.4285714
	August, 2012	8.15	12.5	13.4337	54.3735	0.0099	0.1329	13.4242424
	September, 2012	8.19	10.76	13.4883	51.3727	0.0070	0.0956	13.6571429
	May, 2013	5.9	8.48	2.032	9.36	0.0023	0.0743	32.3043478
	July, 2013	7.8	11.52	7.095	26.268	0.0043	0.0964	22.4186047
5	July, 2012	8.92	8.02	0.7779	29.7491	0.0043	0.1052	24.4651163
	August, 2012	8.59	10.12	1.2004	29.6294	0.0067	0.0940	14.0298507
	September, 2012	8.61	8.98	4.2044	28.8730	0.0071	0.0922	12.9859155
	February, 2013	8.52	15.2	9.280	36.11	0.010	0.1077	10.77
	May, 2013	7.7	8.01	1.778	9.49	0.0039	0.0681	17.4615385
	July, 2013	8.4	9.02	0.241	26.544	0.0052	0.0982	18.8846154
6	July, 2012	8.26	-	0.5544	28.8876	0.0066	0.1123	17.0151515
	August, 2012	7.94	4.25	0.6874	30.3053	0.0027	0.1323	49
	September, 2012	8.12	6.25	1.1115	31.3597	0.0035	0.0899	25.6857143
	February, 2013	7.99	7.69	7.279	36.66	0.0087	0.1284	14.7586207
	May, 2013	7.7	1.91	0.541	13.43	0.0040	0.0789	19.725
	July, 2013	7.5	1.89	0.117	27.812	0.0106	0.0875	8.25471698

The correlation coefficient (R) was determined by formulas which are reported in [15].

Results and discussions

As a result of calculations correlation coefficients are obtained and presented in **Table 2**.

Table 2. Correlation coefficients between partition coefficient and the content of nitrate and sulfate ions, dissolved oxygen and pH values in Hrazdan River

Parameter	Correlation coefficients					
	Samp. point 1	Samp. point 2	Samp. point 3	Samp. point 4	Samp. point 5	Samp. point 6
pH	0.048407	-0.40792	-0.70374	-0.06355	0.15858	0.270818
DO	-0.1896	0.142053	-0.72074	-0.67863	-0.69643	0.118191
SO ₄ ²⁻	-0.00412	-0.28084	-0.94722	-0.49515	-0.27626	0.077469
NO ₃ ⁻	-0.17232	-0.76142	-0.96223	-0.43999	-0.72953	-0.20398

In 1st sampling point pH value and sulfate ion content have a very little influence on migration of vanadium, but mostly directions of migration are from water to bottom sediment and from bottom sediment to water respectively. Dissolved oxygen and nitrate ion content's effect on migration of vanadium are from bottom sediment to water, but these effects are insignificant.

In 2nd sampling point pH value, nitrate and sulfate ions content effect on migration of vanadium and the direction is from bottom sediment to water. And dissolved oxygen affects migration of vanadium, but it goes from water to bottom sediment. However, that effect is also insignificant.

In 3rd sampling point pH value, dissolved oxygen, nitrate and sulfate ions content affect migration of vanadium (vividly expressed impact), and the migration is from bottom sediment to water.

In 4th sampling point pH value, dissolved oxygen, nitrate and sulfate ions content affect migration of vanadium, and the migration is from bottom sediment to water. The influence of pH value is insignificant.

In 5th sampling point dissolved oxygen, nitrate and sulfate ions content effect on migration of vanadium, and the direction is from bottom sediment to water. pH value effects on migration of vanadium, but it goes from water to bottom sediment, but again with very minor effect.

In 6th sampling point pH value, dissolved oxygen and sulfate ion have effect on migration of vanadium and the migration is from water to bottom sediment, but the part of sulfate ions influence is very small. Nitrate ion's content effect on migration of vanadium in the opposite way, migration goes from bottom sediment to water.

Conclusions

Generally the influences of sulfate and nitrate ions on migration of vanadium have similar character in all 6 sampling points. The influence of sulfate and nitrate ions on migration of vanadium are especially expressed in 2-5 observation points. In 1st and 6th points the influence is relatively small. In 3rd sampling point the influence of all 4 parameters (pH, dissolved oxygen, sulfate and nitrate ions content) is vividly expressed. There is no source of vanadium pollution near to the Hrazdan River basin, that is why it can be assumed that the presence of vanadium is conditioned by natural background.

References

1. *Prokop Z., Vangheluwe M. L., Van Sprang P. A., Janssen C. R., Holoubek I.* Mobility and toxicity of metals in sandy sediments deposited on land, *Ecotoxicology and Environmental Safety*, 54, 2003, P. 65–73.
2. *Senesi G. S., Baldassarre G., Senesi N., Radina B.* Trace element inputs into soils by anthropogenic activities and implications for human health, *Chemosphere*, 39, 1999, P. 343–377.
3. *Connell D. W., Miller G. J.* *Chemistry and Ecotoxicology of Pollution*, John Wiley & Sons, New York, 1984, 444 p.
4. *Pirumyan G. P.* *Ecological Chemistry*, Yerevan, 2008, 179 p.
5. *Byerrum R. U.* Vanadium. In: Merian E, ed. *Metals and their compounds in the environment*. Weinheim, Germany: VCH, 1991, P. 1289-1297.
6. *Baroch E F.* Vanadium and vanadium alloys. In: *Kirk-Othmer encyclopedia of chemical technology*. John Wiley & Sons, Inc. 2006.
7. *Davies D. J. A. & Bennett B. G.* Exposure commitment assessments of environmental pollutants. London, University of London Monitoring Assessment and Research Centre, 1983, Vol. 3 (MARC Report No. 30).
8. *Vouk V.* Vanadium. In: Friberg, L. et al., ed. *Handbook on the toxicology of metals*. Amsterdam, Elsevier-North Holland Biomedical Press, 1979, P. 659-674.
9. Committee on Biologic Effects of Atmospheric Pollutants. Vanadium. Washington, DC, National Academy of Sciences, 1974, 117 p.
10. *Van Zinderen Bakker, Jaworski J. F.* Effects of vanadium in the Canadian environment. Ottawa, Canada: National Research Council Canada, Associate Committee Scientific Criteria for Environmental Quality, 1980, 94 p.
11. *Wehrli B, Stumm W.* Vanadyl in natural waters: Adsorption and hydrolysis promote oxygenation, *Geochimica et Cosmochimica Acta* 53 (1), 1989, P. 69-77.
12. *Crans D. C, Amin S. S, Keramidas A. D.* Chemistry of relevance to vanadium in the environment. In: Nriagu JO, ed. *Vanadium in the environment*. Vol. 30. New York, NY: John Wiley & Sons, Inc., 1998, P. 73-95.
13. *Filova V. A. et al.* Hazardous chemical substances. Inorganic compounds of V-VIII groups: L.: «Chemistry», 1989, 592 p.
14. U.S. Environmental Protection Agency, Partition Coefficients For Metals In Surface Water, Soil, And Waste, Jerry D. Allison, Terry L. Allison, July 2005, 93 p.
15. *Petrosyan V. A.* «Influence of pH on Migration of Iron in Water–Sediment System» , *Proceedings of the Yerevan State University, Chemistry & Biology*, № 2, 2015, P. 22–24.