Chemistry

INFLUENCE OF pH ON MIGRATION OF IRON IN WATER–SEDIMENT SYSTEM

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It has been investigated the influence of pH on iron migration in water–bottom sediment system in the Hrazdan River based on 2012–2013 hydrological investigations. Obtained results show that in some sampling points the iron concentration exceeded the maximum permissible concentration. It has been observed particularly in August 2012. Correlation coefficients are given based on data analysis results. 66 samples of water and bottom sediment have been taken from six sampling points.

***Keywords*:** bottom sediment, iron, migration, pH, correlation coefficient.

Introduction. The quantity of iron in natural water reservoirs is higher compared to other metals. Infiltration of iron into water can occur from natural as well as from anthropogenic sources [1]. Iron's status in rivers and lakes waters depends on solution content, pH value and partially on temperature.

The role of oxidation processes, both chemical and biochemical (iron bacteria) [2, 3], is very important for investigation of iron compounds transformation in aquatic systems. The maximum permissible concentration for iron in fishery waters is 0.3 *mg*/*L* [4].

The Hrazdan River is one of the biggest and the most important rivers in Armenia, it is the left tributary of the Araks River. The Hrazdan River starts from Lake Sevan, flows to South-West and falls into the Araks.

Sampling points description: I point – down from the Hrazdan hydroelectric station, up to the mixing point with the Marmarik River; II point – river-mouth of the Marmarik River; III point – down from the mixing point with the Marmarik River; IV point – before flowing to "Akhpar Lich" reservoir; V point – after flowing to "Akhpar Lich" reservoir; VI point ‒ 1 *km* down from "Akhpar Lich" reservoir.

The reason of great interest to this area is the possibility of iron mine opening there.

Materials and Methods. The linear dependence of iron content in water-bottom sediment system from pH value has been investigated.

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Inductively Coupled Plasma Mass Spectrometry ELAN 9000 ("PerkinElmer", US) has been used for determination of iron concentration in samples. For sample preparation Berghoff microwave digestion equipment MWS 3+ has been used. pH has been determined by the YSI 556 MPI equipment.

In Tab. 1 aqua-chemical analysis results of the samples taken from 6 different sampling points of the Hrazdan River are presented, particularly the iron content in the water and bottom sediment for July–September 2012 and in February, May and July 2013. pH values are also presented.

Table 1

Iron content in water and bottom sediment (BS) of the Hrazdan River, pH values

Date	Parameter	I point	II point	III point	IV point	V point	VI point
July 2012	pH	7.74	7.81	7.08	8.22	8.92	8.26
	[Fe] water, *mg/mL*	0.0561	0.2721	0.0261	0.2271	0.1079	0.0975
	[Fe] BS, *g/kg*	40.9185	32.1092	33.5536	50.8141	38.7357	39.8905
	[Fe] water/[Fe]BS	0.0014	0.0085	0.0008	0.0045	0.0028	0.0024
August 2012	pH	8.08	8.54	7.90	8.15	8.59	7.94
	[Fe] water, *mg/mL*	0.4421	0.8598	0.0627	0.0652	0.4099	0.4446
	[Fe] BS, *g/kg*	24.9135	44.1892	33.1086	32.2953	28.2878	32.8817
	[Fe] water/[Fe]BS	0.0177	0.0195	0.0019	0.0020	0.0145	0.0135
September 2012	pH	8.23	8.76	8.28	8.19	8.61	8.12
	[Fe] water, *mg/mL*	0.1853	0.1923	0.1642	0.1405	0.1803	0.1555
	[Fe] BS, *g/kg*	36.7586	26.6468	30.9269	22.4175	25.1660	24.8808
	[Fe] water/[Fe]BS	0.0050	0.0072	0.0053	0.0063	0.0072	0.0063
February 2013	pH	8.42	8.54	–	–	8.52	7.99
	[Fe] water, *mg/mL*	0.2049	0.4287	–	–	0.1178	0.1122
	[Fe] BS, *g/kg*	34.5521	42.1684	–	–	30.9732	34.7405
	[Fe] water/[Fe]BS	0.0059	0.0102	–	–	0.0038	0.0032
May 2013	pH	8.0	7.4	–	5.9	7.7	7.7
	[Fe] water, *mg/mL*	0.2938	0.0655	–	0.0766	0.1622	0.2422
	[Fe] BS, *g/kg*	34.6422	33.8324	–	27.3095	22.9251	22.0354
	[Fe] water/[Fe]BS	0.0085	0.0019	–	0.0028	0.0071	0.0110
July 2013	pH	8.0	8.2	8.0	7.8	8.4	7.5
	[Fe] water, *mg/mL*	0.1092	0.1570	0.1407	0.1829	0.2908	0.7924
	[Fe] BS, *g/kg*	31.5779	37.6174	43.0335	34.7602	25.7644	17.4030
	[Fe] water/[Fe]BS	0.0035	0.0042	0.0033	0.0053	0.0113	0.0455

Results and Discussion. The correlation coefficients (R) have been determined by the following formula:

$$S_{xx} = \sum x^2 - \left(\sum x\right)^2 \big/ n, \quad S_{yy} = \sum y^2 - \left(\sum y\right)^2 \big/ n, \quad S_{xy} = \sum xy - \left(\sum x\right)\left(\sum y\right) \big/ n,$$
$$R = S_{xy} \big/ \sqrt{S_{xx} S_{yy}},$$

where x and y are the variables, n is data amount.

In the case when $|R| < 0.1$ there is no correlation, in the case when $|R| > 0.1$ there is a correlation, and the correlation increases when $|R| \to 1$.

In the case when $R > 0.1$ metal migration is more intensive from bottom sediment to water (water $\leftarrow$ bottom sediment), and metal migration is more intensive from water to bottom sediment (water $\rightarrow$ bottom sediment) when $R \leq -0.1$.

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

Table 2

Correlation coefficients between iron content and pH value in the samples of I–VI sampling points

Parameter	Correlation coefficients					
	I point	II point	III point	IV point	V point	VI point
pH	0.213121	0.559768	0.88207	0.400802	−0.1575	−0.8368

During the months of the iron investigation content in sampling points exceeded maximum permissible concentration in the samples taken from I, II, V and VI sampling points in August 2012, as well as taken from II and VI sampling points in February and July 2013 respectively.

In I–IV sampling points the migration of iron toward water presumably is caused by anthropogenic factors, as well as by weakly expressed bifacial property of Fe^{3+} ions. In V and VI sampling points with the increment of pH value there is migration of iron from water to bottom sediment. The presence of the reservoir increases the duration of pH exposure. Unlike the rapid stream, the water in reservoir is in relatively standing condition, which increases pH exposure duration on iron migration. Therefore, there is a decrement of iron content in the water with the increase of pH value in the relatively standing aquatic environment.

Conclusion. During the investigation months and sampling points the iron content exceeded maximum permissible concentration in the samples taken in August 2012, as well as in February and July 2013.

In I–IV sampling points an intensive migration of iron from bottom sediment to the water is observed. And in V and VI sampling points it is just the opposite: the migration of iron is more intensive from water to bottom sediment.

pH value has direct influence on iron migration. In I–IV sampling points, parallel with pH value, increment the migration of iron increases toward water, and in V and VI sampling points the migration of iron increases toward bottom sediment.

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