

*Chemistry*

DISTRIBUTION AND MIGRATION OF LEAD IN THE WATER–BOTTOM  
SEDIMENT SYSTEM OF THE HRAZDAN RIVER

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Migration and distribution of lead in the water–bottom sediment system of the Hrazdan River has been investigated. In order to evaluate migration magnitude of metals and the influence of different parameters on it, linear dependence between partition coefficient of metals and different parameters of environment for 2012–2013 period has been studied.

**Keywords:** lead, migration, heavy metals, bottom sediment, Pearson's correlation coefficient, Hrazdan River.

**Introduction.** Heavy metals among biosphere pollutants arose great interest. Physiological effects of metals on human and animals are very different and depend on metal nature, type of compounds present in the environment, as well as concentration.

Possible sources of natural environment heavy metal pollution are aerosol wastes of ferrous and nonferrous metallurgy (polluting the atmosphere), industrial wastewaters (polluting water surface), mechanical engineering (galvanic kits for metals), battery recycling factories, automobile transport etc.

Besides anthropogenic sources of environment heavy metal pollution, there are also natural sources such as volcanic eruptions (it is found cadmium in the eruption materials of the Etna volcano, which is located in the Sicily Island of the Mediterranean Sea). On the surface of some lakes the increment of toxic metal concentrations can be occurred due to acid rains, which can cause solution of minerals and rocks rinsing by lake water. All of these sources of pollution cause an increase of toxic metals quantity in the biosphere and its components (air, water, soil, living organisms) compared to background levels [1].

Lead is a component of natural environment, such as soil, atmospheric air and water. Approximately 27 t of lead is released into the atmosphere as a result of natural emissions annually, but the main part is emitted into the environment due to human activity. As lead is widespread in the environment, it is contained in all types of food [2].

The rivers and lakes can be polluted by lead both from anthropogenic and natural sources. Natural sources of lead are lead containing ores (Galena (PbS),

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anglesite ( $\text{PbSO}_4$ ), cerussite ( $\text{PbCO}_3$ )), and anthropogenic sources are coal burning, usage of tetraethyl lead in fuel, wastes of processing plants, wastewaters of mining drill holes and metallurgical plants. Sedimentation of lead containing compounds and its adsorption on various rocks is a natural way of its content reduction in solutions. Hydrobionts are biological factors of lead content reduction in solutions [3].

Lead is very dangerous even in low concentrations and can become a reason of intoxication. Lead can appear in human body by respiratory and digestion systems. Its removal from the organism occurs very slowly, and it can be accumulated in the kidneys, liver and bones [4, 5].

Quantity of dissolved lead on water surface depends on pH of water and content of dissolved salts. The balance calculations showed that at  $\text{pH} > 5.4$  lead dissolution is approximately  $30 \text{ mg/L}$  in hard water and approximately  $500 \text{ mg/L}$  in soft water. Sulfate ions present in soft water limit lead concentration in the solutions by creating lead sulfate. At  $\text{pH} > 5.4$  the lead carbonates ( $\text{PbCO}_3$  and  $\text{Pb}_2(\text{OH})_2\text{CO}_3$ ) limit the quantity of dissolved lead. The concentration of carbonates depends on partial pressure of carbon dioxide, pH and temperature [6].

Descriptions of studied object and sampling points are reported in [7].

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

pH and dissolved oxygen have been measured by YSI Environmental 556 MPS directly in field conditions [8]. Appropriate calibration of the device has been implemented before each day measurement.

For bottom sediment (BS) samples preparation microwave digestion equipment Berghoff MWS-3<sup>+</sup> has been used [9], in accordance with US EPA 3052 method. For samples digestion the mixture of ultrapure concentric nitric and fluoric acid (with 9 : 3 ratio) has been used [10].

Analyses of heavy metals have been implemented by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) ELAN 9000 (“Perkin Elmer”, USA) [11]. Before analyses water samples have been filtered to remove solid particles. All samples have been conserved by concentric nitric acid in order to ensure stability of samples and compatibility with standards. In one experiment Perkin Elmer Multi-Element Calibration standard solution 3 and Instrument Calibration Standard 2 are used, as the matrix solution distilled nitric acid 2% has been used. Water has been deionized by Easypure II ( $18.2 \text{ M}\Omega/\text{cm}$ ), purity of argon is 99.998% [11, 12].

The contents of sulfate and nitrate ions have been determined by Dionex ICS-1000 ion chromatography system [13]. The content of phosphate ion has been determined by spectrophotometric method, using Shimadzu 1650 spectrophotometer [14].

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

$$K_p = \frac{[\text{sorbed metal}], \text{ g / kg}}{[\text{dissolved metal}], \text{ mg / L}}$$

During transportation of metals in soils and surface water systems, metal sorption to the solid matrix results as a reduction in the dissolved concentration of metal, which affects the overall rate of metal transport [15]:

In Tab. 1 the data of samples analysis for period 2012–2013 is presented. Particularly, the results of field measurements of dissolved oxygen content, pH values, as well as analyses results for sulfate, nitrate and phosphate ions are shown [16].

*Table 1*

*The content of sulfate, nitrate, phosphate ions and DO, and pH values*

Sampling point	Date	pH	Dissolved oxygen, mg/L	Nitrate ion, mg/L	Sulfate ion, mg/L	Phosphate ion, mg/L
1	07. 2012	7.74	6.65	2.5719	20.0173	0.902
	08. 2012	8.08	8.89	10.4258	34.6854	1.159
	09. 2012	8.23	5.57	10.0198	28.6994	–
	02. 2013	8.42	13.48	12.758	38.75	1.513
	05. 2013	8	7.53	4.404	13.7	0.083
	07. 2013	8	11.78	6.681	36.369	0.12
2	07. 2012	7.81	8.96	3.0714	9.9398	1.136
	08. 2012	8.54	9.75	4.4722	14.442	0.035
	09. 2012	8.76	6.37	4.7728	16.8082	–
	02. 2013	8.54	13.77	2.733	19.05	1.408
	05. 2013	7.4	8.26	0.86	5.46	0.941
	07. 2013	8.2	11.08	3.146	9.254	0.02
3	07. 2012	7.08	8.56	6.5208	23.0141	0.386
	08. 2012	7.9	14.74	13.0979	48.5094	0.047
	09. 2012	8.28	9.77	12.2562	45.0914	0.023
	07. 2013	8	10.12	5.605	17.388	0.28
4	07. 2012	8.22	9.3	8.4919	30.5876	0.433
	08. 2012	8.15	12.5	13.4337	54.3735	0.199
	09. 2012	8.19	10.76	13.4883	51.3727	0.012
	05. 2013	5.9	8.48	2.032	9.36	0.229
	07. 2013	7.8	11.52	7.095	26.268	0.18
5	07. 2012	8.92	8.02	0.7779	29.7491	0.902
	08. 2012	8.59	10.12	1.2004	29.6294	0.012
	09. 2012	8.61	8.98	4.2044	28.873	–
	02. 2013	8.52	15.2	9.28	36.11	2.094
	05. 2013	7.7	8.01	1.778	9.49	0.242
	07. 2013	8.4	9.02	0.241	26.544	0.02
6	07. 2012	8.26	–	0.5544	28.8876	0.773
	08. 2012	7.94	4.25	0.6874	30.3053	0.035
	09. 2012	8.12	6.25	1.1115	31.3597	–
	02. 2013	7.99	7.69	7.279	36.66	2.133
	05. 2013	7.7	1.91	0.541	13.43	0.255
	07. 2013	7.5	1.89	0.117	27.812	0.08

In Tab. 2 the concentration of lead both in water and in sediment samples is shown as well as the partition coefficients.

In order to evaluate the influences of different parameters on migration and distribution of lead in water–BS system, Pearson's correlation coefficient has been used, particularly linear dependence between partition coefficients and studied parameters.

Table 2

*Concentration of lead in water and bottom sediment samples and partition coefficients*

Sampling point	Date	[Pb] H <sub>2</sub> O, mg/L	[Pb] BS, g/kg	$K_p$
1	07. 2012	–	0.1721	–
	08. 2012	0.02507	0.0124	0.49458
	09. 2012	0.00201	0.03355	16.6669
	02. 2013	0.00104	0.02508	24.0789
	05. 2013	0.00036	0.01776	49.2746
	07. 2013	0.00021	0.02544	121.467
2	07. 2012	0.00015	0.0153	102.727
	08. 2012	0.0016	0.02024	12.6511
	09. 2012	0.00013	0.01496	113.428
	02. 2013	0.00038	0.01821	47.765
	05. 2013	0.00015	0.01057	71.3801
	07. 2013	0.000037	0.01831	496.089
3	07. 2012	0.00042	0.01198	28.6732
	08. 2012	0.00023	0.02444	106.128
	09. 2012	0.00025	0.02331	92.8697
	07. 2013	0.00038	0.00849	22.4573
4	07. 2012	0.00028	0.01868	66.2756
	08. 2012	0.00041	0.01256	30.6226
	09. 2012	0.00019	0.01174	61.585
	05. 2013	0.00011	0.01299	114.063
	07. 2013	0.00118	0.01764	15.0006
5	07. 2012	0.00019	0.01975	105.533
	08. 2012	0.00015	0.01957	130.23
	09. 2012	0.00018	0.01761	95.8373
	02. 2013	0.0005	0.00899	18.0114
	05. 2013	0.0002	0.01135	56.8212
	07. 2013	0.00038	0.01539	40.9123
6	07. 2012	0.00031	0.01358	43.8611
	08. 2012	0.00012	0.01716	140.634
	09. 2012	0.000036	0.02349	652.511
	02. 2013	0.00026	0.01327	50.8517
	05. 2013	0.00033	0.00984	29.9954
	07. 2013	0.00387	0.00924	2.38524

If two variables have high linear dependence in positive direction, the value of  $R$  should be positive and, therefore, greater than 0. If the linear dependence has negative direction, then growth on one variable implies a reduction of other

variable. In this case  $R < 0$ . Possible range of  $R$  is from  $-1$  to  $+1$ ; if the value is close to  $0$  the dependence between the variables is very small [17].

Correlation coefficient has been calculated using Free Statistics Software [16, 18].

Correlation coefficient determines the strength of correlation and can be demonstrated by the following: low correlation  $0 < |R| < 0.3$ , medium correlation  $0.3 < |R| < 0.7$ , high correlation  $|R| > 0.7$  [19].

**Results and Discussion.** In Tab. 3 Pearson’s correlation coefficients between corresponding partition coefficient and pH, dissolved oxygen, sulfate, nitrate, phosphate ions is presented.

Table 3

*Pearson’s correlation coefficients*

Parameter	Correlation coefficients (for Samp. Point)					
	1	2	3	4	5	6
pH	-0.49616	-0.04378	0.529125	-0.73574	0.420506	0.421548
DO	0.363162	0.143769	0.694698	-0.8878	-0.52004	0.453178
Sulfate ion	0.035671	-0.33772	0.995424	-0.55158	0.042547	0.256137
Nitrate ion	-0.58864	-0.01164	0.998609	-0.57116	-0.52638	-0.1011
Phosphate ion	-0.74137	-0.5013	-0.9377	0.165437	-0.49329	-0.11103

pH has medium influence on migration of lead within water–BS system in the 1<sup>st</sup>, 3<sup>rd</sup>, 5<sup>th</sup> and 6<sup>th</sup> sampling points. In the 1<sup>st</sup> sampling point with increment of pH value the migration of lead is going from BS to water. In the 3<sup>rd</sup>, 5<sup>th</sup> and 6<sup>th</sup> sampling points the migration of lead is right the opposite, with increment of pH value it is going from water to BS. pH has high influence on migration of lead in the 4<sup>th</sup> sampling point and the correlation has negative direction, it means that with increment of pH value Pb is transferring from water to BS. In the 2<sup>nd</sup> sampling point influence of pH on migration of lead is insignificant.

As in case of pH the influence of dissolved oxygen is the same on all sampling points in aspect of effect’s strength, that is medium effect in the 1<sup>st</sup>, 3<sup>rd</sup>, 5<sup>th</sup> and 6<sup>th</sup> sampling points, high in the 4<sup>th</sup> and low in the 2<sup>nd</sup> sampling point. But in the 1<sup>st</sup>, 3<sup>rd</sup> and 6<sup>th</sup> sampling points with increment of dissolved oxygen the migration of lead is going from water to BS and in the 4<sup>th</sup> as well as in the 5<sup>th</sup> sampling point migration is going from BS to water.

In the 3<sup>rd</sup> sampling point the influence of sulfate, nitrate and phosphate ions content is very high. With increment of sulfate and nitrate ions content in water, migration of lead is going from water to BS, and with increment of phosphate ion concentration the migration of lead is going from BS to water. The influence of phosphate ion is also high in the 1<sup>st</sup> sampling point, and it has negative direction.

In the 6<sup>th</sup> sampling point the influence of sulfate, nitrate and phosphate ions content is very low and the effect is insignificant. Sulfate ion content also has insignificant influence on migration of lead in the 1<sup>st</sup> and 5<sup>th</sup> sampling points, nitrate ion in the 2<sup>nd</sup> sampling point, and phosphate ion in the 4<sup>th</sup> sampling point.

Sulfate ion has medium influence on migration of lead in the 2<sup>nd</sup> and 4<sup>th</sup> sampling points, nitrate ion has medium influence on migration of lead in the 1<sup>st</sup>, 4<sup>th</sup> and 5<sup>th</sup> sampling points, phosphate ion has medium influence on migration

of lead in the 2<sup>nd</sup> and 5<sup>th</sup> sampling points and the direction is negative for all these cases.

**Conclusion.** All studied parameters mostly have medium influence on migration of lead in the water–BS system of the Hrazdan River. In the 3<sup>rd</sup> sampling point the influence of these parameters is strongly expressed. In the 5<sup>th</sup> and 6<sup>th</sup> sampling points (after reservoir) environmental conditions of water are changed and that is why all these parameters mainly have medium or low influence on lead migration. Thus high influences are observed in sampling points which are located before reservoir.

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