



# Determination of heavy metal background concentration in bottom sediment and risk assessment of sediment pollution by heavy metals in the Hrazdan River (Armenia)

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## Abstract

The purpose of this study is to determine background concentrations of heavy metals in bottom sediments, as well as to characterize potential danger of heavy metals in bottom sediments of the Hrazdan River. Linear regression method was used to determine background concentrations of metals in bottom sediments. While using this method, the linear regression of determining metal with a comparative element was used: The cobalt was chosen as a relative element, which is conditioned by the absence of significant sources of cobalt in this river. Risk assessment index of Hakanson was calculated for evaluation of bottom sediments contamination by heavy metals. It is obtained that in this part of the Hrazdan River basin potential ecological risk caused from bottom sediments contamination by heavy metals is not high.

**Keywords** Bottom sediments · Heavy metals · Background concentration · Linear regression · Risk index

## Introduction

The intensity of human activities during the last centuries causes a significant violation of the existing balance of the nature. Among serious environmental problems, the investigation of increasing pollution of the hydrosphere is particularly important. Moreover, providing the population with clean water has become an actual issue for the entire planet (Albering et al. 2016).

Along with the scientific and technological progress, the scale of the impact on the environment is increasing, which leads to undesirable changes of air, water, and soil physical, chemical, and biological characteristics, and these can have adverse effects on humans, animals, and plant lives (Tchounwou et al. 2012).

Recently, studies of bottom sediments have gained an importance. Adsorption of heavy metals by bottom sediments leads to the so-called hidden pollution, which could turn into a real pollution under external factors (Liang et al. 2015; Ali et al. 2016).

The objectives of this paper are:

- to determine background concentrations of heavy metals in bottom sediments of the river in order to assess the future anthropogenic influence on the ecosystem,
- to characterize potential danger of heavy metals in bottom sediments of the river.

Taking into account the fact that bottom sediments of surface water are not investigated in our country, these kinds of investigations are very important.

## Materials and method

### Site description

The Hrazdan River and its major tributary Marmarik were chosen as objects of the study. Hrazdan is one of the major rivers of Armenia, which flows through the country's central, densely populated section. The water of this river is used for irrigation and energy purposes, and water of Marmarik River is used also for drinking water supply purposes. Hrazdan and Marmarik rivers are polluted mainly by the domestic wastewater of surrounding regions, which, due to the absence of treatment facilities, are dumped into the rivers

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without any treatment. The rivers are polluted with solid household waste, plastic bags, plastic bottles, food waste, construction waste, etc. In Yerevan, the Hrazdan River is also polluted with domestic wastewater and garbage from numerous restaurants situated in the Hrazdan gorge. Wastewater of small- and medium-sized enterprises (leather factories, juice factories, etc.) also flows into the Hrazdan River, contaminating it with various pollutants, including heavy metals, such as chromium, manganese, zinc, and iron. The biggest source of pollution of the Hrazdan River is Yerevan, whose utility-household wastewater is discharged from the “Aeratsiya” clearing station without treatment and spilled into the river near Geghanist village, polluting river water (Margaryan 2009).

### Hydrological characteristics of the Hrazdan and Marmarik rivers

Hrazdan is one of the largest and the most important rivers in Armenia, and it is the left tributary of the Araks River. The river's length is 141 km, and the surface of the basin, without Lake Sevan, is 2650 km<sup>2</sup>. Sevan, Hrazdan, Charentsavan, Lusakert towns, Yerevan city, Arzni resort are on the shores of the Hrazdan River. A recreational zone has been created in the region. The bridges of Haghtanak (1945), Hrazdani Mets (1956), Nurnus (1981), Davtashen (2000) are on the Hrazdan River. The oldest bridge on the river is Red Bridge (1679, Yerevan).

The Marmarik River is the largest tributary of the Hrazdan River. It has 37 km length and 427 km<sup>2</sup> catchment basin. The river flow is formed by the watercourses flowing from Pambak and Tsakhkunyats mountain ranges. It flows into the Hrazdan River 116 km above from the estuary (Chilingaryan et al. 2002; Pirumyan and Babayan 2008; Babayan 2006).

Six sampling points were selected for determining the background concentrations of heavy metals in bottom

sediments of the Hrazdan River. The study was implemented during 2015–2016. Totally, 33 samples of bottom sediments were taken from each sampling point.

The locations of the sampling points are given in Table 1 and Fig. 1.

### Sampling and analysis

Special samplers were used for sampling of the bottom sediments. Collection and handling of sediment samples were conducted in accordance with standard methodology (ISO 5667-12). The latters were transported to the laboratory in special containers at 4 °C. In the laboratory, the samples were dried at room temperature (US EPA 2012).

Microwave digestion system (Speedwave MWS-3, Berghof, GmbH) was used for sample preparation. It is designed for long-term processes up to 230 °C, depending on the autoclaves of the samples, under pressure of up to 100 bar (1450 psi), depending on the autoclave applied.

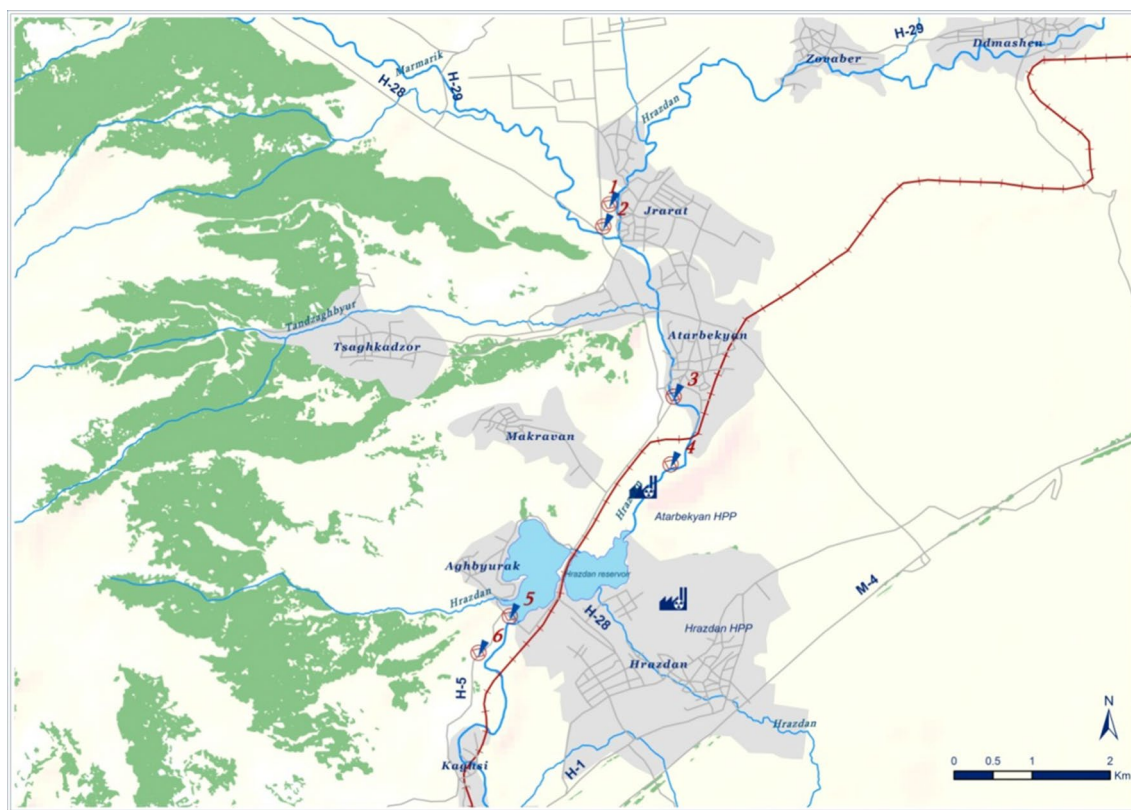
Sample preparation of bottom sediments was carried out according to the US EPA 3052 method, which was first introduced in Berghof (2004). The samples were air-dried to a stable mass at room temperature. The obtained dry mass was weighted and installed in the corresponding containers of MWS-3+ microwave digestion system, a mixture of 12 ml HNO<sub>3</sub>/HF (3:1 v/v) was added, and then, the mass was placed in the device where the breakdown of complex insoluble compounds to soluble is implemented (US EPA 1996; Berghof 2004).

To obtain ultrapure acids for analyses, acid distillation apparatus of GmbH Berghof was used. The double distillation was accomplished under the infrared radiation.

During the analyses, ultrapure deionized water was obtained by EASYpure II deionizer. The conductivity of pre-distilled water was reduced up to 18.2 MOhm/cm<sup>2</sup> by the device.

**Table 1** Locations and coordinates of sampling points

No. sampling point	Location	Coordinates	Absolute height (m)
1	3 km down from Hrazdan hydroelectric station, before the mixing point with the Marmarik River	N 40°32'52.5" E 44°45'19.8"	1720
2	River mouth of the Marmarik River	N 40°32'43.3" E 44°45'16.5"	1714
3	Down from the mixing point with the Marmarik River	N 40°31'32.5" E 44°45'55.0"	1710
4	Before flowing to “Akhpar Lich” reservoir	N 40°31'04.4" E 44°45'53.5"	1708
5	After flowing to “Akhpar Lich” reservoir	N 40°30'1.0" E 44°44'26.2"	1695
6	1 km down from the “Akhpar Lich” reservoir	N 40°29'45.7" E 44°44'09.2"	1690



**Fig. 1** Map of the study area and the locations of sampling points

Inductively coupled plasma mass spectrometry ELAN 9000 (PerkinElmer, USA) was used for determination of metals concentration in bottom sediment samples. Inductively coupled plasma mass spectrometry (ICP-MS) is a complex equipment used to accurately measure more than eighty elements in different types of samples, as well as to measure isotope relations and can serve as an excellent semiquantitative instrument. The equipment allows to identify both rare and trace elements in a wide range up to ng/l. By this method, concentrations of iron, chromium, cadmium, lead, copper, manganese, cobalt, vanadium, zinc, and nickel were determined.

The analyses were performed in the following sequence: blank (zero solution) → standard solution → sample. In order to minimize the memory effect, the capillaries were washed with a concentrated nitric acid solution for about 5–7 min until the intensities corresponding to the zero solution were registered (Thomas 2013).

99.998% pure argon gas was used during the analyses by inductively coupled plasma mass spectrometric method. As an internal calibration solution, 1 ml of 10 mg/l solution of indium was used (Thomas 2013; Taylor 2001).

## Data analysis

### Linear regression method for determination of metal background concentration in bottom sediment

The linear regression method was used to determine the background concentrations of investigated metals in the bottom sediments of the Hrazdan River. While using this method, the linear regression of determining metal with a comparative element was used. The following criteria must be met in the selection process of the comparative element:

1. The comparative element must have a dependency on the background concentration of the element to be determined;
2. Have a little sensitivity to anthropogenic pollution;
3. Have a little sensitivity to changes in the geochemical factors (Luoma 1990).

The Minitab software package provides a statistical calculation of data, taking into account the 95% predictive range. All points which were found out of that range

were considered as non-representative and removed from the calculating system, after which a recalculation was made. The cobalt was chosen as a relative element, which is conditioned by the absence of significant sources of cobalt pollution as well as the higher values of correlation coefficients calculated (Roussiez et al. 2005; Matthai and Birch 2001).

Figures 2, 3, 4, 5, 6, 7, 8, 9 and 10 show graphical images of the linear regression of explored metals. With the dotted line, 95% prediction range is mentioned.

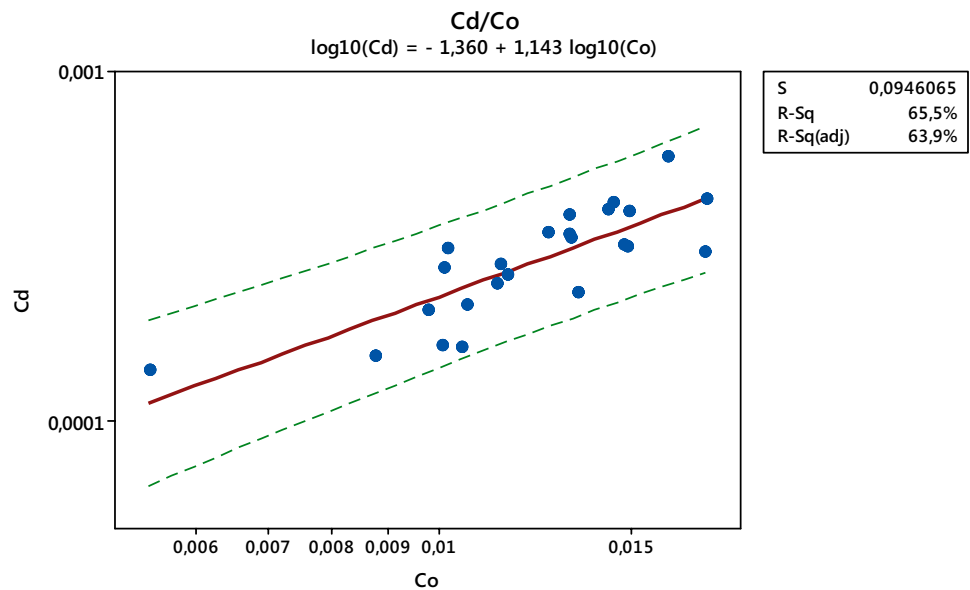
In Table 2, suggested background concentrations for the explored metals are presented.

### Evaluation of bottom sediment contamination by heavy metals and risk assessment

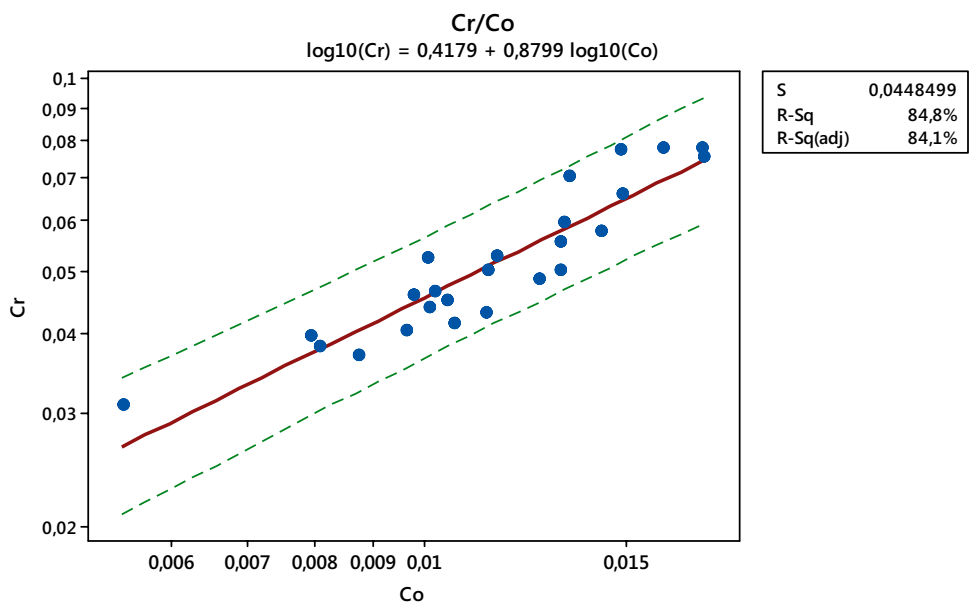
The content of metals in bottom sediments did not provide a complete assessment of the probability of possible consequences due to the metals specified in that section. A risk assessment calculation was performed by the risk assessment index developed by Hakanson.

For the risk assessment, six metals proposed by Hakanson were selected: Cd, Cr, Cu, Pb, Ni, and Zn, each of which is characterized by a specific hazard factor: Cd = 30, Pb = Ni = Cu = 5, Cr = 2, Zn = 1. The calculated risk index is characterized by the likelihood of impact on heavy metal

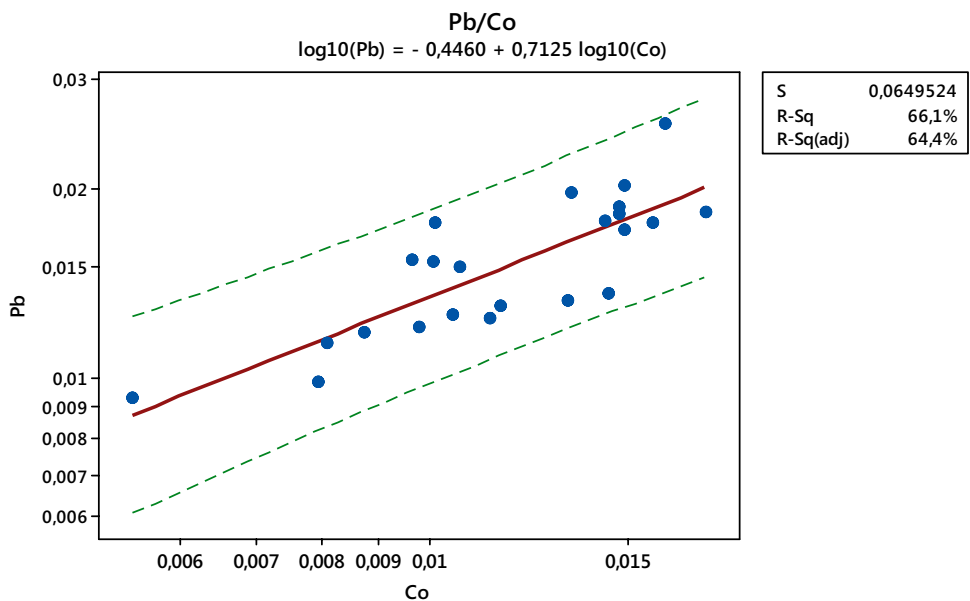
**Fig. 2** Linear regression graph of cadmium background concentration determination ( $R^2 = 65.5\%$ )



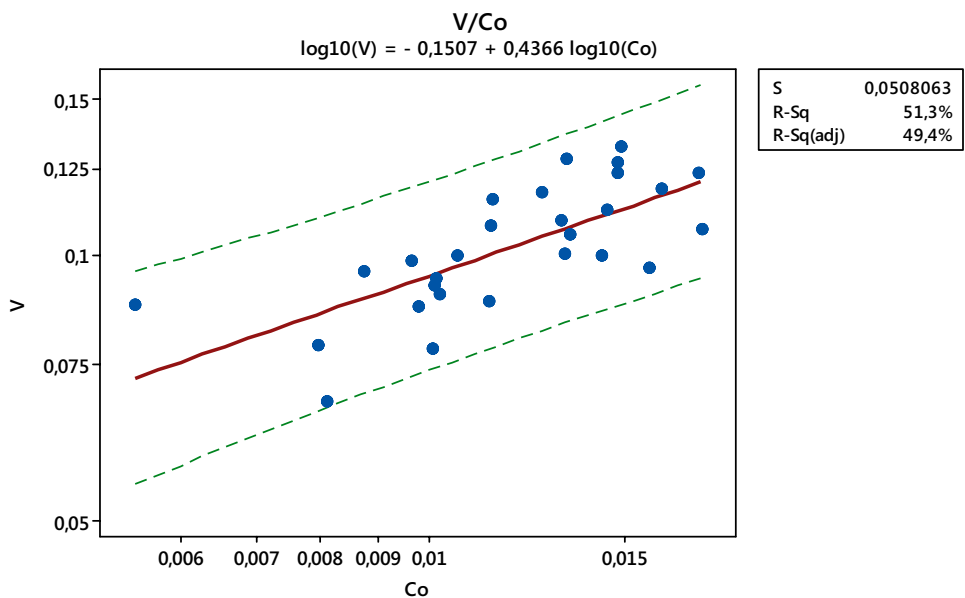
**Fig. 3** Linear regression graph of chromium background concentration determination ( $R^2 = 84.8\%$ )



**Fig. 4** Linear regression graph of lead background concentration determination ( $R^2 = 66.1\%$ )



**Fig. 5** Linear regression graph of vanadium background concentration determination ( $R^2 = 51.3\%$ )



content in bottom sediments, as well as the intensity of anthropogenic impact. The classification of risk index values is given in Table 3.

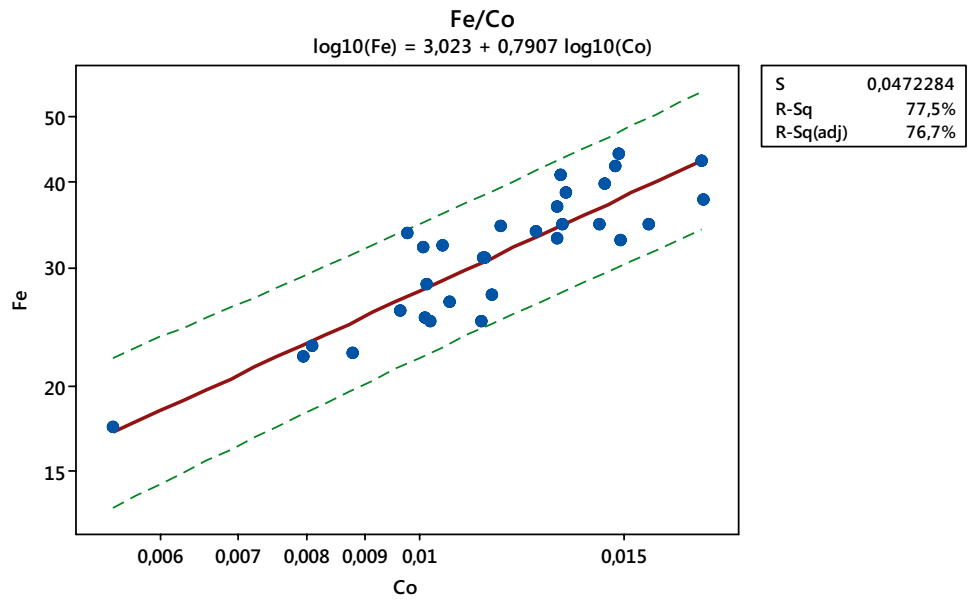
Potential ecological risk index calculated by the following formula:

$$RI = \sum_{i=1}^n \left( T_i \times \frac{C_i}{C_0} \right), \tag{1}$$

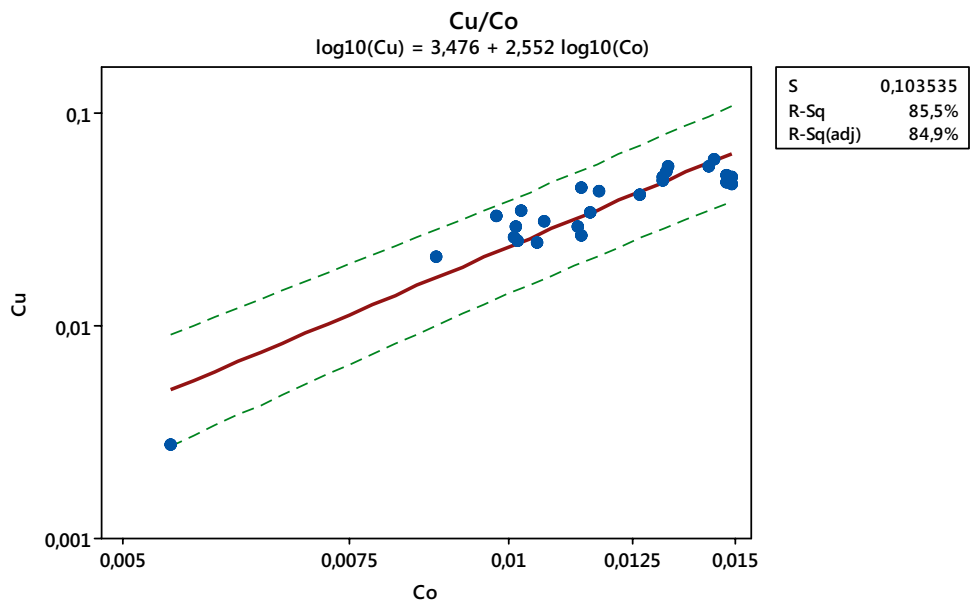
where  $T_i$  is the toxic-response factor for a given substance,  $C_i$  represents metal content in the sediments, and  $C_0$  is the background value of heavy metals in the sediments.

In the explored sampling points, which are located at the upper part of the Hrazdan River, according to the formula (1), the calculated risk index has a value of 49.3. The value of risk index means that the anthropogenic impact does not have a significant influence on the contamination of the bottom sediments and the pollution of sediments with heavy metals is characterized as a low risk (Li 2014; Yin et al. 2011; Hakanson 1980).

**Fig. 6** Linear regression graph of iron background concentration determination ( $R^2 = 77,5\%$ )



**Fig. 7** Linear regression graph of copper background concentration determination ( $R^2 = 85,5\%$ )



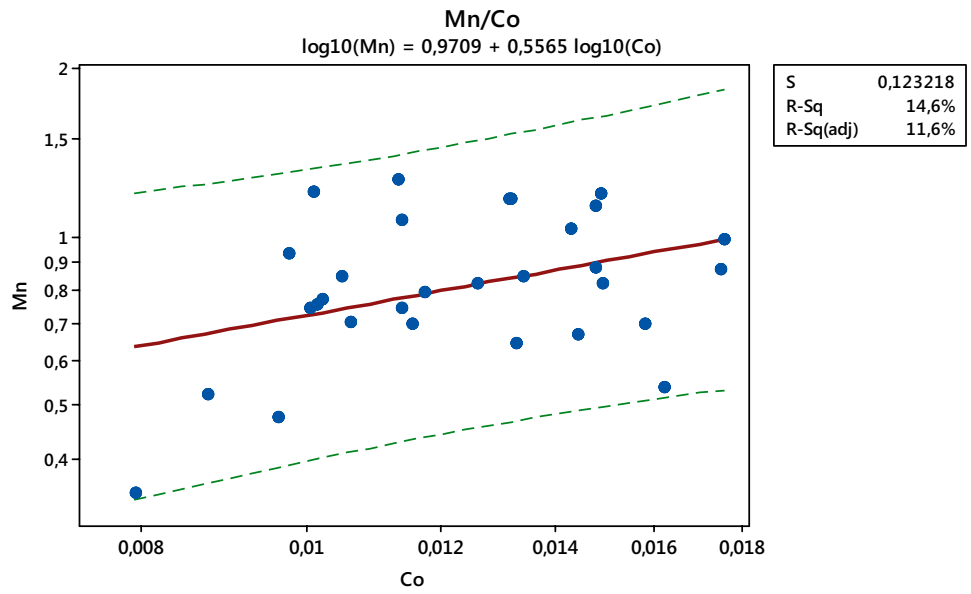
## Results and discussion

Background concentrations calculated by the linear regression method can be used as the background concentrations of heavy metals in the bottom sediment of the Hrazdan and Marmarik rivers. The linear regression model using a comparative element is applicable for the determination of the metal background concentration in the bottom sediments of all river ecosystems.

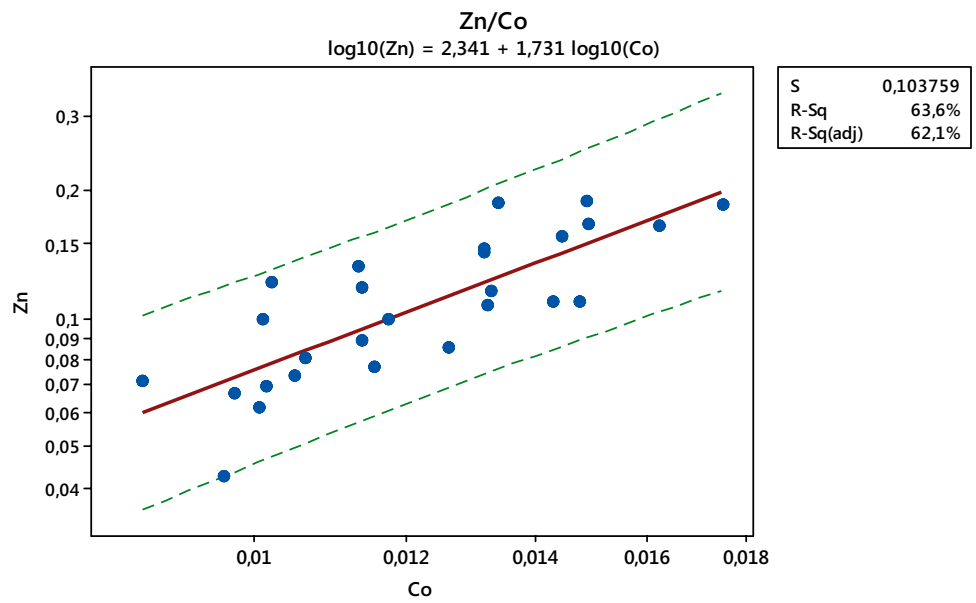
The value of the calculated risk index shows that the level of anthropogenic pollution in the Hrazdan River, as well as in its main tributary Marmarik River, is not high, and the content of heavy metals in bottom sediments is mainly related to the background concentrations of metals.

The above-described linear regression method for calculation of background concentration metals in the bottom sediments can be used for rivers as well as for lakes and reservoirs of Armenia.

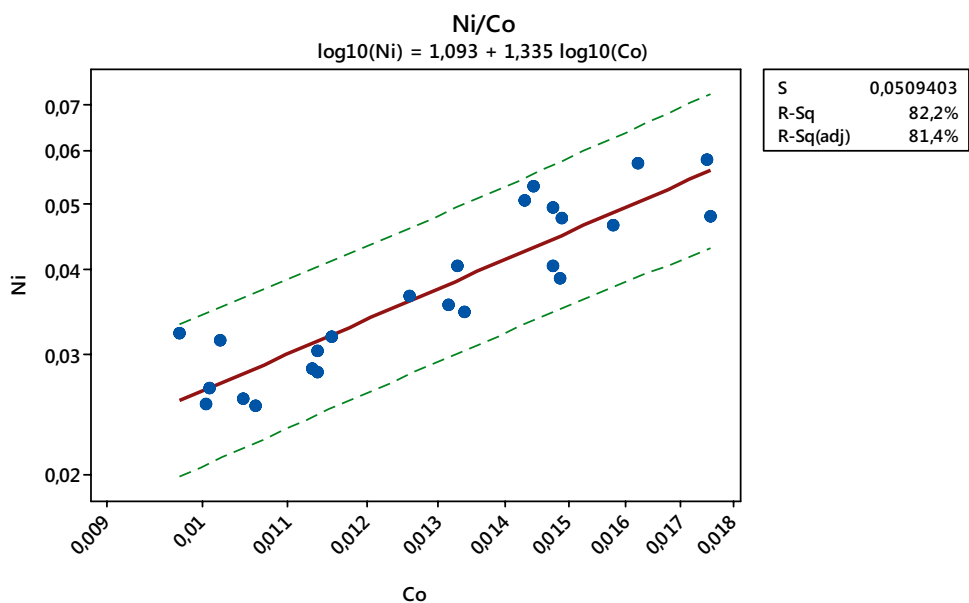
**Fig. 8** Linear regression graph of manganese background concentration determination ( $R^2 = 14.6\%$ )



**Fig. 9** Linear regression graph of zinc background concentration determination ( $R^2 = 63.6\%$ )



**Fig. 10** Linear regression graph of nickel background concentration determination ( $R^2 = 82.2\%$ )



**Table 2** Suggested background concentrations of explored metals

Metal	Cd	Cr	Cu	Fe	Mn <sup>a</sup>	Ni	Pb	V	Zn
Suggested background concentration (mg/kg)	0.298	52.96	38.5	31,917.3	–	38.41	15.45	102.9	113.579
$R^2$ (%)	65.5	84.8	85.5	77.5	14.6	82.2	66.1	51.3	63.6
$R^2_{adj}$ (%)	63.9	84.1	84.9	76.7	11.6	81.4	64.4	49.4	62.1

<sup>a</sup>Background concentration of manganese has not been calculated

**Table 3** Classification of risk index values

Risk index (RI)	Classification
< 150	Low risk
150 < RI < 300	Average risk
300 < RI < 600	Possible high risk
> 600	High risk

**Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflicts of interest regarding the publication of this paper.

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