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ASSESSMENT OF METAL POLLUTION IN WATER AND SURFACE SEDIMENTS OF GORANCHAY RIVER

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Abstract: *Concentration of metals in water and sediment samples from Goranchay River was examined to obtain information about metal pollution. Also, 6 surface sediments and water samples were collected from sampling points and analyzed for metals (Na, K, Mg, Ca, Al, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Cd, Sr, Ba, Pb) using Varian model Spectra AA 220 FS atomic absorption spectrometer. The average concentration of examined metals at the same sampling locations was in line with the order of Ca>Fe>Mg>K>Na>Mn>V>Zn>Ni>Cr>Cu>Co>Pb in sediment samples. Single element pollution index values, including geo-accumulation index (Igeo), contamination factor (CF) and enrichment factor (EF), were used to evaluate contamination with metals in the examined sediment samples.*

Keywords: *Goranchay river, water, sediment, metals, pollution*
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Introduction

Heavy metals are considered to be serious pollutants of aquatic ecosystems due to their environmental persistence, toxicity, and ability to be incorporated into food chain [1].Heavy metal pollution in the natural environment is a worldwide problem because they are not removed from water due to the self-purification; however, they can get accumulated in reservoirs by means of biological and geochemical mechanisms and join the biological chain [2]. There are two main sources for lauding heavy metals into the environment: lithogenic and anthropogenic. Lithogenic is the natural process, such as weathering of rocks and volcanic activities that plays a noticeable role in enriching the water of reservoirs with heavy metals [3]. Anthropogenic sources arise from human activities, such as industry, agriculture, mining and construction of urban development that can transport pollutants to marine waters by rivers and outlets [4,5].

Goranchay is the North Caucasus River located in Azerbaijan. It flows through regions of Goygol and Goranboy and after joining with Kurakchay flows further to Kura. Length of the River is 81 km. It starts from a mountain area (height-3100 m) between Gamishdagh and Murovdagh. Goranchay is divided into two parts: Garachay and Goranchay near the village of Meshali in Goranboy region. Garachay and Goranchay flows parallel to each other up to Garachinar village. Main water sources of the Goranchay are snow, rains and underground waters. Water of the Goranchay is widely used as drinking water and for watering plantations in Goranboy region. Mean annual water usage of the river is 1.96 m^3/s. During the period of intensive watering (July-August) 20% of the annual current is used. Spring flood of the river starts in March and continues till the end of July. Note that the River water is considered as moderately mineralized (300-500 mg/L) and known to have high amount of hydrocarbonates and calcium.

Materials and Methods

6 sampling points along Goranchay were estimated to examine heavy metal content in the study. Both water and sediment samples were collected from the same area. Note that pH, salinity, total dissolved solids, conductivity, temperature parameters of river water were measured at sampling points. Water samples were collected by means of a standard polyethylene water sampler which was rinsed a few times with river water from the sampling point before representative sampling from 15-30 cm below water surface. Two hundred millilitres of water was filtered through a 0.45 μm membrane filter using a plastic filtration assembly without pump. A few drops of high-purity nitric acid were added to the filtrate to adjust to pH < 2. The sample was stored at 4 °C during transportations to the laboratory. Between each sampling, the water sampler was soaked with10% v/v nitric acid and rinsed with ultrapure water. All plastic-ware sample bottles, pipette tips, filtration unit and flasks were soaked in 10% v/v HNO_3 for 24 h and rinsed with ultra pure water before being used. Ultra pure water collected from Milli-Q apparatus (resistivity 18.2 MΩ·cm, pH (5.5-6.5)) was used throughout in all laboratory operations.Sediment samples from sampling points were collected by stainless-steel Van Veen grabs. Approximately 200 g of the sample was taken from the surface oxic layer of sediment at each station. Labeled samples stored in a frozen on the way back to the laboratory. Geographical locations of examined stations and measured water parameters(pH, conductivity (COND), total dissolved solids(TDS), salinity(SAL), dissolved oxygen(DO)) of Goranchay are given in Table 1.

Table 1. GPS coordinates of sampling points and water parameters of Goranchay at the location

N/N	Point description	Coordinate	pH	COND	TDS	SAL	DO	DO
				msm/cm	*mg/L*	*%*	*%*	*mg/L*
G1	YukhariAgcakand	40.406800° 46.522500°	7.12	146	85	0.01	86.8	8.89
G2	AshagiAgcakand	40.418596° 46.573495°	6.95	168	97	0.01	86.9	8.89
G3	Meshali	40.436619° 46.615070°	7.16	221	122	0.01	88.1	8.71
G4	Shafaq	40.453792° 46.641328°	7.52	331	191	0.02	89.4	8.68
G5	Shafibayli	40.483823° 46.713179°	7.71	404	233	0.02	91.1	8.45
G7	Goran	40.648798° 46.822691°	7.65	750	433	0.04	27.3	2.26

Collected sediment samples air were dried in the laboratory, disaggregated with a mortar and pestle and passed through a 2 mm sieve. Particles with a bigger diameter than 2 mm were discarded. Dried, disaggregated and sieved particles (<2 mm) were mixed well and kept in labeled plastic containers for further analysis. To determine analytical and handling errors, two sub-samples were taken from each of these sediment samples, each undergoing an independent digestion procedure. Solutions were prepared using deionized water (from a Milli-Q apparatus (Millipore). Aliquots of approximately 0.5 g of sediment samples were weighed and added into the acid-cleaned TFM vessels and digested with a 9 ml of nitric and 3 ml of hydrochloric acid mixture in a microwave oven (Milestone Ethos 1 with HPR –1000/10S high pressure rotor). Samples transferred to 50 ml plastic vessels and diluted for analysis. Varian SpectrAA 220FS atomic absorption spectrometer system was used to determine heavy metal concentrations in samples to evaluate contamination levels in samples.

Results and discussion

The measured concentration of metals in water and sediment samples are given in Table 2 and Table 3 respectively. According to Table 2, concentrations of the analyzed elements in water samples of river Goranchay were as following: As: <0.5 mkg/L in all samples; Ba: ranged between 9-17 mkg/L; Cd: <0.1 mkg/L in all samples; Co: <0.7mkg/L in all samples; Cr: <0.5 mg/L in all samples; Cu: ranged between 0.60-2.26mkg/L; Fe: ranged between 6.64-33.05 mkg/L; Ni: ranged between 0.7-0.88mkg/L; Pb:<0.7 mkg/L in all samples; Mn: ranged between 0.357-4.257 mkg/L; Zn: ranged between 3.95-23.43mkg/L; Na: ranged between 3.78-18.59 mg/L; K: ranged between 0.49-1.49 mg/L; Mg: ranged between 2.98-13.35 mg/L, Ca ranged between 18.46-52.04 mg/L; Al: ranged between 11.15-29.85 mkg/L; Sr: ranged between 98-327.2 mg/L.

Table 2. Measured concentration of investigated metals in water samples

Element	Unit	G1 w	G2 w	G3 w	G4 w	G5 w	WHO
Na	mg/L	3.78	5.53	7.31	13.19	18.59	50
K	mg/L	0.49	0.75	0.83	0.98	1.49	100
Mg	mg/L	2.98	3.65	4.69	8.92	13.35	30
Ca	mg/L	18.46	22.96	26.58	45.16	52.04	75
Al	ug/L	26.27	29.85	16.56	11.15	12.90	200
Cr	ug/L	<0.5	<0.5	<0.5	<0.5	<0.5	50
Mn	ug/L	0.637	4.257	0.503	0.357	0.512	100
Fe	ug/L	20.69	33.05	9.26	8.83	6.64	300
Ni	ug/L	0.700	0.810	0.720	0.840	0.880	70
Co	ug/L	<0.7	<0.7	<0.7	<0.7	<0.7	-
Cu	ug/L	2.26	2.20	0.60	2.20	1.24	2000
Zn	ug/L	13.79	22.76	3.95	9.09	23.43	5000
As	ug/L	<0.5	<0.5	<0.5	<0.5	<0.5	10
Cd	ug/L	<0.1	<0.1	<0.1	<0.1	<0.1	5
Sr	ug/L	98.00	131.2	156.8	313.5	327.2	-
Ba	ug/L	9.00	9.05	11.90	12.30	17.00	700
Pb	ug/L	<0.7	<0.7	<0.7	<0.7	<0.7	10

Comparison between measured concentrations of investigated metal in water samples and limit values presented for the drinking water by World Health Organization (Table 2) shows that water of Goranchay is not polluted with metals and can be used for drinking purposes (with due regard for measured parameters in this study, further analysis is required for total evaluation). According to Table 3, measured parameters (examined metal concentrations) of sediment samples were as follows: Na: ranged between 543.52-3027.65 mg/kg, average concentration - 1601,13 mg/kg; Ca: ranged between 27872.34-84006.77 mg/kg, average concentration - 56609.01 mg/kg; Zn:ranged between 54.92-89.33 mg/kg, average concentration -69.18 mg/kg; Mg: ranged between 15031.37-20263.06 mg/kg, average concentration -17523.41 mg/kg; K: ranged between 900.48-4483.56 mg/kg, average concentration -1857.87 mg/kg ; Mn: ranged between 464.89-864.92 mg/kg, average concentration -695.04 mg/kg; Fe: ranged between 37714.38-61459.77 mg/kg, average concentration -43019.55 mg/kg; Co: ranged between 8.41-18.30 mg/kg, average concentration -14.02 mg/kg; Ni: ranged between 40.51-78.12 mg/kg, average concentration -57.06 mg/kg; Cu: ranged between 23.97-46.05 mg/kg, average concentration -32.49 mg/kg; Pb: ranged between 2.89-7.31 mg/kg, average concentration -5.16 mg/kg; Cr: ranged between 28.52-112.27 mg/kg, average concentration -54.53 mg/kg ; V: ranged between 83.56-283.78 mg/kg, average concentration -140.71 mg/kg.

Table 3. Measured concentration of metals in sediment samples

	G1 sed	**G2 sed**	**G3 sed**	**G4 sed**	**G5 sed**	**G7 sed**
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Na	3027.66	1302.80	1782.16	1349.16	1282.10	543.52
Ca	84006.77	57917.42	64287.16	42527.93	58860.16	27872.34
Zn	61.69	89.33	61.38	85.91	55.64	75.41
Mg	1878662	15031.37	16443.30	18436.59	17268.90	20263.06
K	1743.63	1133.55	1410.66	1961.17	900.48	4483.56
Mn	691.76	864.92	694.56	627.65	826.13	464.89
Fe	37731.18	61459.77	39896.80	43642.46	40305.39	40386.85
Co	14.21	18.30	13.46	12.91	17.48	13.35
Ni	40.51	43.10	58.42	78.02	71.91	58.03
Cu	31.51	46.05	29.88	32.56	23.97	29.30
Pb	6.04	7.31	4.64	4.67	2.89	4.67
Cr	28.52	34.83	38.41	59.36	112.27	67.39
V	129.51	283.78	134.25	132.18	97.76	83.56

Sediments are capable of recording the history and indicating the degree of pollution. To assess the degree of pollution of the heavy metal, it is necessary to compare the pollutant metal concentration with an unpolluted reference material (geochemical background)[6-13]. Absence of background values of metal concentrations in Azerbaijan estuarine systems made us to use the reference material. The reference material represents a benchmark to which the metal concentrations in the polluted samples are compared and measured. Many authors used average shale values or average crustal abundance data as reference baselines [14]. In this work, average shale values are used as a reference material for background values [14]. Single element pollution indexes which give information of how an individual element is concentrated at a site of interest relative to the background were used to evaluate metal contamination. These include geo-accumulation index (I_{geo}), contamination factor (C*f*) and enrichment factor (Ef).

Geo-Accumulation Index (I_{geo})

A common criterion to evaluate the heavy metal pollution in sediments is the geo-accumulation index. The geo-accumulation index (I_{geo}) has been used since the late 1969s, and widely employed in European trace metal studies. Geo-accumulation index was proposed by Muller [15] to determine metal contamination in sediments by comparing current concentrations with pre-industrial levels. It can be calculated using the following formula:

$$I_{geo} = \log_2[(C_n)/(1.5B_n)] \quad (1)$$

where C_n is the concentration of element "n," and B_n is the geochemical background value of the element n in average crust (average upper crustal concentration was given by Turekian K.K. Wedepohl, K.H) [14]. The factor 1.5 is incorporated in the relationship to account for possible variation in background data due to lithogenic effect. The geo-accumulation index (I_{geo}) scale consists of seven grades (0 - 6) ranging from unpolluted to highly polluted. Class 1 (uncontaminated to moderately contaminated): 0 <Igeo<1; Class 2 (moderately contaminated): 1<Igeo<2; Class 3 (moderately to heavily contaminated): 2<Igeo<3; Class 4 (heavily contaminated): 3<Igeo<4; Class 5 (heavily to extremely contaminated): 4<Igeo<5; and Class 6 (extremely contaminated): 5>Igeo. Calculated Igeo values of metals are given in Table 4. As it can be seen from Table, Igeo values of Cr, Mn, Co, Zn and Pb are less than 0 in all sampling points. This indicates that investigated sediment samples can be categorized as practically unpolluted with mentioned heavy metals. Igeo values of V, Fe and Cu in sampling point 2, Ni in sampling points 4 and 5 are in the range of 0<Igeo<1 indicating uncontaminated to moderately contaminated level of pollution.

Table 4. Calculated I_{geo} values of metals in sediment samples

V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	
-0.16797	-2.27445	-0.74888	-0.64006	-0.86839	-0.79931	-0.41465	-0.70408	-2.07762	**G1 sed**
0.963762	-1.98614	-0.42659	0.063826	-0.50372	-0.70998	0.132829	-0.17004	-1.80332	**G2 sed**
-0.11614	-1.84522	-0.74306	-0.55954	-0.94701	-0.2712	-0.4911	-0.71136	-2.4571	**G3 sed**
-0.13853	-1.21703	-0.88919	-0.43008	-1.0078	0.146161	-0.36747	-0.22636	-2.44953	**G4 sed**
-0.57377	-0.29771	-0.49279	-0.54484	-0.56976	0.028504	-0.80922	-0.8531	-3.14117	**G5 sed**
-0.80015	-1.03409	-1.32226	-0.54193	-0.9593	-0.2809	-0.51931	-0.41444	-2.45013	**G7 sed**

Contamination Factor

The level of metal contamination can be expressed by the contamination factor (CF). CF is the ratio between the metal content in the sediment and the background value of the metal. The contamination factor is used to determine the contamination status of the sediment in the present study. Contamination factor is calculated according to the equation given by D. C. Thomilson, D. J. Wilson, C. R. Harris and D. W. Jeffrey [16].

$$CF = \frac{Cs}{Cb} \quad (2),$$

where Cs and Cb: are the heavy metal contents in sample and background reference, respectively. According to Hakanson [17] CF<1 indicates low contamination; 1<CF<3 indicates moderate contamination; 3<CF<6 indicates considerable degree of contamination; and CF>6 indicates very high contamination. Calculated CF values of heavy metals in the analyzed samples are given in Table 5.Cf values of Cr in sampling points 1,2,3,4,7; Mn in sampling points 1,3,4,7; Fe in sampling point 1; Co in sampling points 1,3,4,7; Ni in sampling points 1 and 2; Cu in sampling point 5; Zn in sampling points 1,3,5; Pb in all sampling points are lower than 1 indicating low contamination of sediments with mentioned heavy metals. CF values of V in sampling points 1-5; Cr in sampling point 5; Mn in sampling points 2 and 5; Fe in sampling points 2-7; Co in sampling points 2 and 5; Ni in sampling points 3-7; Cu in sampling points 1,2,3,4,7; Zn in sampling points 2,4,7 are in the range of 1<CF<3 which can be classified as moderately contaminated.

Table 5. CF values of metals in investigated samples

	CF								
	V	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Pb**
G1 sed	1.335139	0.310037	0.8926	0.96253	0.821638	0.861934	1.125302	0.92075	0.355359
G2 sed	2.925583	0.378621	1.116031	1.567851	1.057927	0.916991	1.644662	1.333228	0.42977
G3 sed	1.383976	0.417469	0.896206	1.017776	0.778061	1.242945	1.067222	0.916115	0.273168
G4 sed	1.362668	0.645251	0.809876	1.113328	0.745955	1.659931	1.162709	1.282185	0.274606
G5 sed	1.00779	1.22031	1.065973	1.028199	1.01059	1.529931	0.856033	0.83039	0.170022
G7 sed	0.861433	0.732487	0.599863	1.030277	0.771458	1.234619	1.04656	1.125466	0.274491

Enrichment Factor

The concept of enrichment factor (EF) was developed in the 1970s to evaluate the anthropogenic contribution. The enrichment factor (EF) is based on the standardization of a tested element against a reference one. The obtained result is described as an enrichment factor (EF) given by the following equation [18].

$$EF = \frac{(Cs/Cr)}{(Csb/Crb)} \qquad (3),$$

where Cs and Cr are the content of the target element and reference element in the examined sediment, respectively and C_{sb} and C_{rb} are the content of the target element and reference element in the average shale. To identify anomalous metal concentration, geochemical normalization of the heavy metals data was used for the investigated element. The behavior of a given element in sediment established by comparing the concentration of certain heavy metal with the reference element. Because Al is one of the most abundant elements on the earth and usually has no pollution concerns, it is commonly used for normalization purpose [10,19,20]. In enrichment factor (EF) calculations, Fe is also widely used [21-23] as a reference element. In this study, we used Fe as a reference element to differentiate natural and anthropogenic components. The world average shale and world average rock element concentrations are widely used as background concentrations in most of the studies [15]. EF<2 indicates that the source of a metal is crust materials or natural processes; whereas EF >2 indicates anthropogenic sources [24-26]. EF<2 indicates minimal enrichment, 2–5 indicates moderate enrichment, 5–20 indicates significant enrichment, 20–40 indicates very high enrichment and EF > 40 indicates extremely high enrichment. EF values of elements were calculated using Equation (3). Results are given in Table 6. Results shows that EF values of all heavy metals in all sampling points are less than 2. This means that sources of the analyzed metals in sediment samples are crust materials or natural processes.

Table 6. EF values of metals in sediment samples

V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	
1.387114	0.322107	0.927347	1	0.849268	0.895487	1.169108	0.956593	0.369192	**G1 sed**
1.865983	0.24149	0.711822	1	0.67132	0.584871	1.048991	0.850353	0.274114	**G2 sed**
1.359804	0.410178	0.880554	1	0.760572	1.221236	1.048583	0.900115	0.268397	**G3sed**
1.223959	0.57957	0.727437	1	0.666605	1.490963	1.044355	1.151669	0.246653	**G4 sed**
0.980151	1.186843	1.036738	1	0.97786	1.487972	0.832556	0.807616	0.165359	**G5 sed**
0.836118	0.710961	0.582235	1	0.744967	1.198337	1.015805	1.092391	0.266424	**G7 sed**

Conclusions

Metal concentrations (Na, K, Mg, Ca, Al, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Cd, Sr, Ba,Pb) of water samples and surface sediments from Goranchay River were measured. Comparison between measured concentration of heavy metal in water samples and limit values presented for the drinking water by World Health Organization (Table 2) shows that water of Goranchay is not polluted with heavy metals and can be used for drinking purposes (with due regard for measured parameters in this study, further analysis is needed for total evaluation).To investigate the contamination degree of heavy metals in sediments, geo-accumulation index (Igeo),enrichment factor (EF) andcontamination factor (CF) were calculated. Calculated Igeo values of Cr, Mn, Co, Zn and Pb are less than 0 in all sampling points. This indicates that investigated sediment samples can be categorized as practically unpolluted with mentioned heavy metals. Igeo values of V, Fe and Cu in sampling point 2, Ni in sampling points 4 and 5 are in the range of 0<Igeo<1 indicating uncontaminated to moderately contaminated level of pollution. CF values of heavy metals shows low or moderate contamination in all sediments from investigated sampling points. Calculation results showed that EF values of heavy metals in all sampling points are less than 2. This means that sources of the analyzed metals in sediment samples are crust materials or natural processes. According to the calculated single element pollution index values, it can be said that anthropogenic effect on sediments of Goranchay is considerably low and contamination level of sediments of the river is ranging from low to moderate.

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GORANÇAYDAN GÖTÜRÜLƏN SU VƏ DİB ÇÖKÜNTÜSÜ NÜMUNƏLƏRİNDƏ METALLARLA ÇİRKLƏNMƏNİN QİYMƏTLƏNDİRİLMƏSİ

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Xülasə: *Gorançaydan götürülən su və dib çöküntüsü nümunələrində metallarla çirklənməylə bağlı informasiya toplamaq məqsədilə metalların konsentrasiyaları tədqiq olunmuşdur. 6 səth dib çöküntüsü və su nümunəsi nümunə götürmə nöqtələrindən toplanmış və Varian SpectrAA 220FS atom absorbsiya spektrometri vasitəsilə metallara (Na, K, Mg, Ca, Al, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Cd, Sr, Ba, Pb) görə analiz olunmuşdur. Dib çöküntüsü nümunələrində eyni nümunə götürmə nöqtəsində ağır metalların orta konsentrasiyalarının azalma ardıcıllığı belədir Fe>Mn>V>Zn>Ni>Cr>Cu>Co>Pb. Geo-akkumulyasiya indeksi, çirklənmə faktoru, zənginləşmə faktoru daxil olmaqla tək elementli çirklənmə indeksi qiymətlərindən dib çöküntüsü nümunələrində ağır metallarla çirklənməni qiymətləndirmək üçün istifadə olunmuşdur.*
Açar sözlər: *Goran çayı, su, dib çöküntüsü, ağır metallar, çirklənmə*

ОЦЕНКА ЗАГРЯЗНЕНИЯ ВОДЫ И ПОВЕРХНОСТНЫХ ОТЛОЖЕНИЙ РЕКИ ГОРАНЧАЯ МЕТАЛЛАМИ

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Для получения информации о загрязнении металлами были определены концентрации металлов в воде и образцах донных отложений реки Горанчай. 6 проб отложений и воды были собраны в точках отбора проб и проанализированы на содержание металлов (Na, K, Mg, Ca, Al, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Cd, Sr, Ba, Pb) с помощью атомно-абсорбционного спектрометра Varian SpectrAA 220 FS. Средняя *концентрация исследованных металлов в тех же местах отбора проб следовала порядку Ca>Fe>Mg>K>Na>Mn>V>Zn>Ni>Cr>Cu>Co>Pb в пробах отложений. Значения индекса загрязнения одним элементом, включая индекс геоаккумуляции (Игео), коэффициент загрязнения (КЗ) и коэффициент обогащения (КО), использовались для оценки загрязнения тяжелыми металлами в исследованных пробах отложений.*

***Ключевые слова**: Река Горанчай, вода, отложения, тяжелые металлы, загрязнение.*