

Evaluation of heavy metals contamination in sediments and hydrogeochemical characteristics of water in Mashalak River, North Iran.

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Abstract:

The present study was conducted aimed to determine the concentration of heavy metals for environmental assessment of water and surface sediment samples taken from the Mashalak River in northern Iran. Sediment and water samples were analyzed by ICP-MS and the concentration of conventional cations and anions was also measured. Results showed that V, Cr, Zn, Ni, Cu, Pb, Co, and Mo had the highest concentration of heavy metals. The geo-accumulation index indicated low-moderate pollution and the ecological risk assessment showed low ecological risk in the study area. There was a positive and significant relationship between metals, indicating a common origin and similar geochemical behavior. The results of the hydrogeochemical assessment showed that the water of the Mashalak River is in the inappropriate quality range only in terms of residual sodium carbonate (RSC). At the stations near the wastewater, the concentration of As and Cr is high, and the water of these stations is not suitable for drinking. The changes in the pattern of heavy metals along the river showed an increase in these pollutants next to the wastewater station. Based on the classification of drinking water by metal concentration and pH, the water of Mashalak River is in the class of near neutral at a low concentration, which is not an environmental concern.

Keywords: Pollution; Heavy metals; Hydrogeochemical assessment; Mashalak river; Iran

1. Introduction

Rivers are important sources of fresh water for agriculture, drinking, and industry. However, the location of urban and rural areas and industrial centers around rivers can cause various pollutants to enter them. If the amount of these pollutants exceeds the river's self-purification capacity, environmental problems may arise. The growth of population and development of residential, commercial, industrial, and agricultural centers have increased the amount of human sewage and wastewater, leading to environmental pollution in different environments, including rivers. Heavy metals are among the most important environmental pollutants in different ecosystems due to their toxicity, Residence time, indestructibility, and bioaccumulation (Hou et al., 2019; Jehangir Khan et al., 2021; Jooybari et al., 2022). Heavy metals not

only reduce the quality of the atmosphere, water sources, and food products but also endanger animals and humans' health (Chen et al., 2019; Fang et al., 2019). The main anthropogenic sources of heavy metals consisted of industrial areas, mining activities pollution, disposal of waste containing high amounts of metal, gasoline, and paint containing lead, use of chemical fertilizers, animal manure, sewage sludge, pesticides, irrigation with wastewater, coal combustion residues, leakage of petrochemical products and atmospheric deposits from different sources (Rezapour Tabari and Yazdi, 2014; Abdullahi et al., 2021). Geogenic pollution is also directly related to the composition of bedrock, mineralogy, and physicochemical conditions governing the river (Khosaravi et al., 2020; Dill et al., 2021). Meanwhile, river sediments and river water with the ability to carry and store heavy metals are also considered indicators of river

pollution (Yazdi et al., 2015; Dabiri et al., 2017; Gayathri et al., 2021). Water quality characteristics are one of the components that are necessary to be considered in the plans related to water resources management, as well as watershed health assessment to ultimately leading to management changes (Akhtar et al., 2021). Inappropriate water consumption for drinking, irrigation, and agricultural uses not only causes health problems in the cycle and human food chain, as well as some problems for irrigation systems, but it also destroys the physical characteristics of the soil and eventually barren the land (Egbueri et al., 2021). To address environmental concerns and human health risks related to environmental pollution in river ecosystems, it is important to monitor the concentration of elements, salts, and pollution in these ecosystems. The Mashalak river is important for north of Iran, passing through forest lands, agricultural lands, and residential areas before ultimately ending in the Caspian Sea. Despite its importance, no comprehensive study has been conducted on the sediment and water pollution of this river. Therefore, the purpose of this study is to investigate the heavy metal contamination of the surface sediments of this river and evaluate the hydrogeochemistry of its waters. This will help predict risks and diseases caused by pollution and determine quality standards for the river's water and sediment.

2. Geological and hydrological setting

The studied area is geographically located in the north of Iran and in Mazandaran province. Mashalak river basin is geologically located in Alborz structural zone. The sedimentary formations of this basin are generally limestone, shale and sometimes sand. The source of the Mashalak river starts from a spring located in the Cretaceous marly limestone and after passing through the Tizkough limestone formation, it enters the deposits of the alluvial plain. In the studied area, large and long faults have caused the formation of the complex morphology of this area and have contributed the most role in guiding the path of the Mashalak River to the Caspian Sea. The general trend of the formations in the studied area is the function of the fault system of the area with a northwest to southeast trend. Considering that the main lithology of Mashalak area is Tizkough formation, Orbitolina limestone is actually the base rock of the area. The Mashalak River is about 66 kilometers long in Mazandaran province in the north of Iran and passes through the port city of Nowshahr and ends in the Caspian Sea. This river originates at a height of 2310 meters and leaves the basin at a height of 60 meters. The flow rate of this river in the high water season is 40 and in the low water season is 39 m³/s. There are a number of villages, sand mines and sewage stations on the route of this river. Branches and seasonal branches also lead to this river from Tizkough limestone formations and marl formations (Upper Cretaceous), sandstone and silty (Middle and Late Miocene). The deposits of the Mashalak River are mainly in the size of gravel and sand. The abundance of gravel particles and the low presence of clay particles in the deposits of the Mashalak River indicate the proximity of these deposits to the source. The morphology of this area is strongly influenced by the regional

constructions and the lithological nature of the outcrops. The height difference from south to north in the region is very large. The northern part (between the foothills and the sea) includes the alluvial plain of the river and Quaternary sediments, and the southern part (heights with medium to high slopes) are more or less parallel due to the presence of large and abundant faults, which generally due to the type and resistance of the rock, mountains and valleys are seen one after the other. Along with the function of faults in the area, the existence of a relatively wide area of alluvial sediments and alluvial fans in the basin indicates strong erosion in the area. Due to the strong erosion factors in the region and the operation of numerous faults in addition to the rainy climate of the region, and on the other hand due to the presence of the young mountain belt of Alborz, it is possible to imagine the existence of steep rivers with high erosion power in this region.

3. Materials and methods

In this research, 25 surface sediment samples were randomly collected from the sediments of this river (Fig. 1). Samples of the Mashalak river were collected using a shovel and transferred to sampling bags, labeled, and transported to the laboratory. To determine the concentration of heavy metals in the collected samples, ICP-MSS analysis was performed on 25 samples below 63 microns at the Zarazma laboratory. River water samples were collected according to standard (ISO 1985) using polyethylene containers that were previously washed with 10% nitric acid and distilled water. 25 samples were taken from the river water for analysis. The hydrogeochemistry of the water was investigated by measuring the concentrations of cations and anions in the Arya Chemistry Laboratory. The concentration of elements was calculated in the Zarazma Laboratory.

3.1 Studies on sediments

3.1.1 Contamination factor (Cf)

The CF measures the value of elements relative to their natural value and indicates the amount of soil contamination. It is calculated using the formula $CF = C_n/B_n$, where CF is the contamination factor, C_n is the element concentration in the contaminated sample, and B_n is the concentration of the same element in the standard soil sample or the geogenic concentration of the area. According to Hakanson (1980) classification of heavy metal pollution, a contamination factor value greater than one indicates moderate to very high pollution. The classification is shown in Table 1 below.

3.1.2 Geo-accumulation index (I_{geo})

A common method for estimating soil contamination with heavy metals is to obtain the concentration of heavy metals in the soil from the metal background concentration using the I_{geo} index presented by Muller (Muller, 1969). In this relation ($I_{geo} = \log_2(C_i/1.5C_{ri})$), I_{geo} is the geochemical accumulation index or contamination intensity index, C_i is the heavy metal concentration in the soil, and C_{ri} is the background concentration. The coefficient of 1.5 is a correction coefficient that has been applied to minimize the effect of a

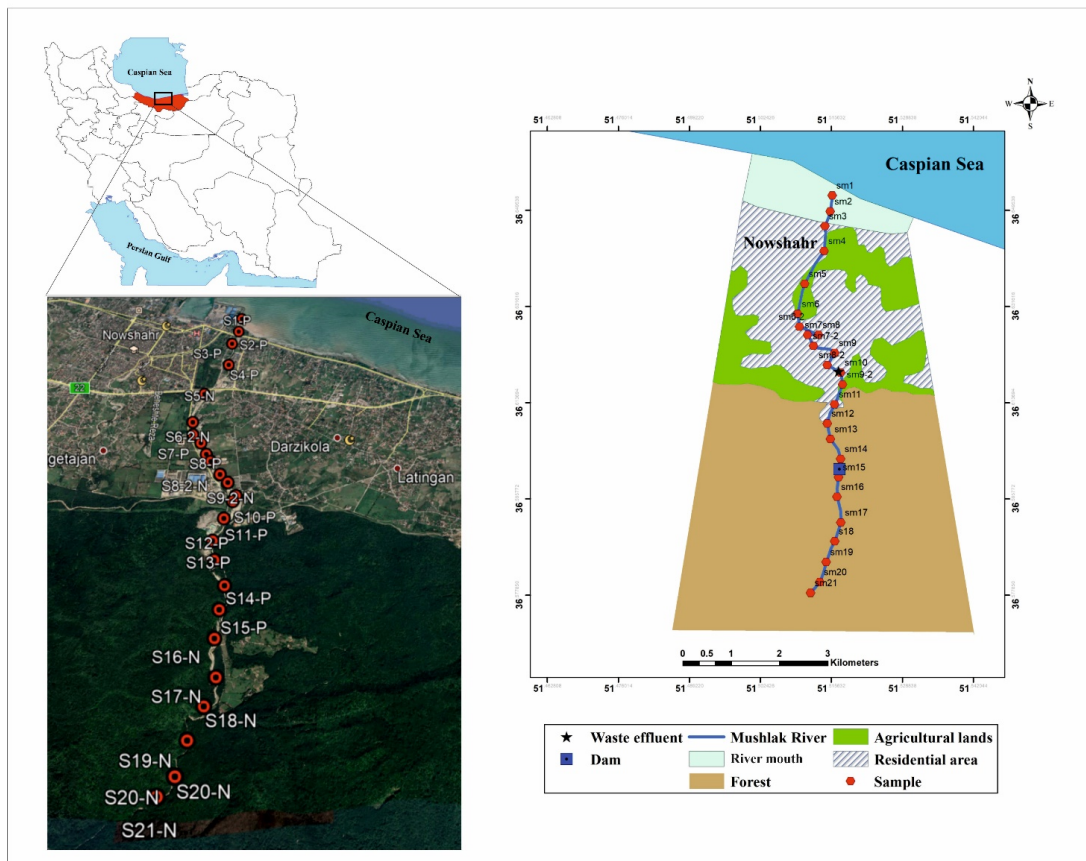


Figure 1. Location of Mashlak river and sampling stations.

Table 1. Contamination Factor (CF) classification of sediments (Hakanson, 1980)

Soil pollution	Value of CF	Class
Low contamination	$CF < 1$	1
Moderate contamination	$3 < CF \leq 1$	2
Considerable contamination	$6 < CF \leq 3$	3
Very high contamination	$CF \geq 6$	4

possible change in the background concentrations generally attributed to soil lithology changes and the impact of human factors. Many researchers considered the concentration of heavy metals in the upper crust as the background value, and aluminum was used as the base metal because it has the lowest level of contamination (Chandrasekaran et al., 2015). Muller (1969) introduced 7 different categories for this index, and the values of the elements in the highest category are at least 100 times the reference values (Table 2).

3.1.3 Enrichment factor (EF)

The enrichment coefficient is a suitable method to separate the geogenic and anthropogenic origins of pollution (Hou et al., 2019). For specifying this index, an element is considered as a reference that must be immobile and not affected by human activities, such as Al, Li, Sc, Fe, Ti, and Zr. The enrichment factor is calculated from (Relation: $EF = (C_x/C_{ref})_{Sample} / (C_x/C_{ref})_{Background}$). If the EF is

less than one, the target element has a geogenic origin. If its EF is between 1 and 10, the element has both geogenic and anthropogenic origins, and if it is greater than 10, the source of element contamination is mainly anthropogenic. The higher the value of the enrichment factor, the greater the contribution of human factors in increasing the contamination of the desired metal in the soil of the region. The classification is presented in Table 2.

3.1.4 Ecological risk factor (E^r)

Although this factor was previously used to control water quality, it is also used to evaluate the quality of sediments and soils in terms of heavy elements nowadays. In this equation (Relation: $E_r^i = T_r^i \times PI_i$), T_r^i is the intensity of pollution and PI_i is the pollution index. Table 2 shows the classification of pollution based on the ecological risk factor.

Table 2. Categories of enrichment factor (EF) (Luo et al. (2012)), and index of geo-accumulation (I_{geo}) (Muller (1969)), and ecological risk (Er) and potential index (RI), (Hakanson (1980))

ER		RI		EF		I_{geo}	
Er<40	Low	RI<150	Low	EF<2	deficiency to minimal enrichment	$I_{geo} \leq 0$	No pollution
40≤Er<80	Moderate	150≤RI<300	Moderate	2≤EF<5	Moderate	0< I_{geo} ≤1	Low to moderate
80≤Er<160	High	300≤RI<600	High	20≤EF<40	Very high	2< I_{geo} ≤3 3< I_{geo} ≤4	Median Heavy
Er≥320	Severe			40≤EF	extremely high	4< I_{geo} ≤5 5< I_{geo}	Serious Extreme

3.1.5 Potential ecological risk (RI)

Potential ecological risk (RI) is an indicator to evaluate the level of ecological risk caused by the concentration of heavy metals in water, air, and soil. This index was first presented by Hakanson (1980), and it is calculated by using this equation (Relation 5: $RI = \sum_{i=1}^n E_r^i$), it is the number of heavy metals and E_r^i is the ecological risk index. Soil quality is classified into four classes based on potential ecological risk (Table 2).

3.2 Studies on water samples

To evaluate the water quality of the Mashalak river, the indicators of electrical conductivity, total hardness, and total dissolved solids have been used. Electrical conductivity is a measurement of the amount of dissolved ions, which is an indirect measurement of dissolved solids in water and a function of water temperature and TDS (Adimalla et al., 2018). The EC of water is the result of the presence of dissolved mineral solids such as sodium, magnesium, calcium, and chloride anions (Fattah et al., 2020). The standard classification of this index for agricultural uses is based on Table 3. Hardness is mainly measured based on the two metals, magnesium and calcium. In general, cations are considered the hardness factors (Fattah et al., 2020).

The qualitative classification of this index is presented in Table 4. Total dissolved solids have been an important factor in water quality and have had a great effect on the transfer, chemical transformation, and ionization of cations and anions (Wafula et al., 2018). This index is divided into 5 parts in terms of salinity and is presented in Table 4.

3.2.1 Qualitative indices and hydro geochemical charts

To examine the water quality of the Mashalak river, qualitative indicators including percent of sodium soluble, sodium adsorption ratio, residual sodium carbonate, sodium bicarbonate, salinity potential, permeability index, magnesium hazard, and overall ratio were used, whose relationships and standard ranges are shown in Tables 5 and 6.

3.2.2 Water Quality Index (WQI)

A WQI is the overall effect of chemical compounds on the quality characteristics of water for human consumption (Aly et al., 2015; Ewaid et al., 2018). This index was widely used by researchers to assess the quality of water resources (Aly et al., 2015; Chung et al., 2015). WQI is attributed to various weighted parameters specifying water quality. It also reduces the negative effects of one or more variables by combining multiple equations (Tiwari and Mishra, 1985; Simoes et al., 2008). The water quality index pa-

Table 3. Water quality classification based on electrical conductivity ((Balachandar et al., 2010).

Classification Ec	Low salt	Brackish	Salt	Very salty	Infinitely salty
	700-2500	2500-8000	8000-12000	12000-20000	>20000

Table 4. Qualitative classification of water hardness (mg/liter calcium carbonate) (Tyagi and Sarma (2020)) and qualitative classification of total dissolved solids (mg/liter) ((Rajesh et al., 2019)).

Concentration mg l⁻¹	Degree of hardness	TDS	Quality
0-50	Soft	<300	soft
soft	Moderate soft	600-300	Moderate soft
100-150	Slightly hard	900-600	Slightly hard
150-200	Moderately hard	1200-900	Moderately hard
200-300	Hard	>1200	Hard
>300	Excessively hard		Excessively hard

Table 5. Water quality indices and their relationships.

Parameter	index	equation	Reference
Percentage of sodium soluble	SSP(Na%)		(Taylor and Todd, 1995)
Sodium adsorption ratio	SAR(meq/l)		(Abdel-Satar et al., 2017)
Residual Sodium Carbonate	RSC($\frac{meq}{l}$)		(Gupta, 1983)
Residual Sodium Sodium Bicarbonate	RSBC		(Piper, 2019)
Salinity potential	PS		(Vasu et al., 2015)
Permeability index	PI		(Gupta, 1983)
Magnesium hazard	MH		(Egbueri et al., 2019)
Kelly ratio	KR		(Kelley, n.d.)

Table 6. Classification of sodium percentage(Abdel-Satar et al., 2017), sodium absorption ratio (Richards, 1954; Abdel-Satar et al., 2017), residual sodium carbonate (Piper, 2019), residual sodium bicarbonate (Gupta, 1983), salinity potential (Vasu et al., 2015), permeability index (Gupta, 1983), magnesium risk (Egbueri et al., 2019) and kelly ratio (Kelley, n.d.).

Parameter	Limit	Classification
SSP (%Na)	<10	Excellent
	20-40	Good
	40-80	permissible
	>26	poor
SAR (meq/l)	<10	Excellent
	10-18	Good
	18-26	Suspicious
	>26	Inappropriate
RSC (meq/l)	<1.25	Good
	1.25-25	Fair
	>2.5	Poor-inappropriate
RSBC (meq/l)	<5	Safe
	5-10	Border limit
	>10	Undesirable
PS	<3	Appropriate
	3>	Inappropriate
PI	<60%	good and appropriate
	>60%	Poor and inadequate
MH (%)	<50%	Appropriate
	>50%	Inappropriate (harmful to soil)
KR (meq/l)	<1	Appropriate
	>1	Surplus rate

Parameters are weighted based on their relative importance in specifying water quality for human use according to the definition provided by the World Health Organization (WHO, 2004),(Houatmia et al., 2016). The calculation of this index consists of three consecutive steps (Simoes et al., 2008). The first step is "weighting," in which a specific weight is given to each parameter according to its relative importance (Table 7). In the next step, the relative weight is calculated using the equation 1,

$$w_i = \frac{w_i}{\sum_{i=1}^n w_i} \tag{1}$$

The third step is to calculate the quality rate scale. This q_i is calculated by dividing the concentration of each parameter in each water sample by the standard value of that parameter.

n is considered the weight of each parameter, and W_i is the number of parameters. In this equation. Equation 2:

$$q_i = \frac{C_i}{S_i} \times 100 \tag{2}$$

C_i is the concentration and S_i is the standard of each chemical parameter in the water sample in milligrams per liter (mg/L). Then, to estimate the WQI, the SI (sub-index of the n^{th} parameter) is determined for each chemical parameter with the equation (below):Equation 3:

$$SI_i = w_i \times q_i WQI = \sum SI_i \tag{3}$$

and then water quality is classified based on the WQI index Table 8

Table 7. Relative weight of physicochemical parameters (Lateef).

Relative weight	weight	WHO	Index
0.090909091	3	6.5-8.5	pH
0.060606061	2	500	TH
0.121212121	4	1500	TDS
0.060606061	2	200	Ca ²⁺
0.060606061	2	150	Mg ²⁺
0.060606061	2	12	K ⁺
0.060606061	2	50	Na ⁺
0.0909090912	3	250	Cl ⁻
0.0909090912	3	250	SO ₄ ²⁻
0.151515152	5	10	NO ₃ ⁻
0.848484848	28	-	Total

Table 8. Water quality classification based on the WQI index (Ketata-Rokbani et al., 2011)

Water quality status	Excellent water	Good water	Poor water	Very poor water	Unsuitable water
Water quality index value(WQI)	<50	50-100	100-200	200-300	>300

3.3 Statistical analyses

All statistical analyses were done with SPSS20 software. In addition, the K-S test was run to test the normality status of the data. The P value was considered above 0.05 Kelepertzis (2014) to accept the hypothesis of normality. The Log relationship was employed to normalize the data (Li et al., 2013). A statistical clustering test was used to evaluate the relationship between different sediment and water pollutants (Luo et al., 2012);(Kelepertzis, 2014; Iordache et al., 2022). The cluster analysis test is one of the most widely used statistical tests in determining the pollution and origin of heavy metals used by many researchers (Batbold et al., 2021);(Linnik et al., 2022).

4. Discussion and results

4.1 Discussion and results of sediment

4.1.1 The Concentration of heavy metals in sediments

The statistical characteristics of the concentration of heavy metals in the studied samples are presented in Table 9. The metals V, Cr, Zn, Ni, Cu, Pb, and Co account for the majority of the average concentration of heavy metals in Mashalak river deposits. Regarding the distribution map of metal concentration in (Fig. 2), the concentration of heavy metals

along the Mashalak river shows clear changes. The stations located immediately after the dam show a decrease in the concentration of heavy metals. This can be due to the presence of more mud particles in the sediments behind the dam than after the dam, which has caused more accumulation of metals behind the dam. On the other hand, due to the presence of forest lands upstream and the entry of different materials such as coarse and sometimes rock-like gravel or tree leaves into the river sediment and the multi-year accumulation of sediments behind the dam, technical and construction operations behind the dam have been carried out to reduce the volume of these sediments and extract these sediments. In addition, the role of anthropogenic pollutants related to this technical building can also be mentioned. Along the river route, an increase in the concentration of metals can be seen below the wastewater effluent station along the Mashalak river, which is directly related to the sewage of this sewage station or further down in connection with domestic sewage and sewage related to the industrial town of this area. There are many changes in the concentration of heavy metals among wastewater stations, i.e., S10 to S5, in addition to municipal and domestic sewage in connection with water drainage channels from agricultural lands, which impose a direct impact on the pro-

Table 9. Concentration of heavy metals and statistical parameters of heavy metals in sediments of Mashalak river (in micrograms/kg).

Element	Co	Cr	Cu	Al	Ni	Pb	Zn
Average	7.30	48.40	13.64	31280.88	18.72	9.40	48.32
Maximum	10.60	77	23	44182	25	28	65
Minimum	3.50	25	7.00	17794	13	2	32
Standard deviation	1.93	12.28	4.49	7377.82	3.54	5.23	10.49

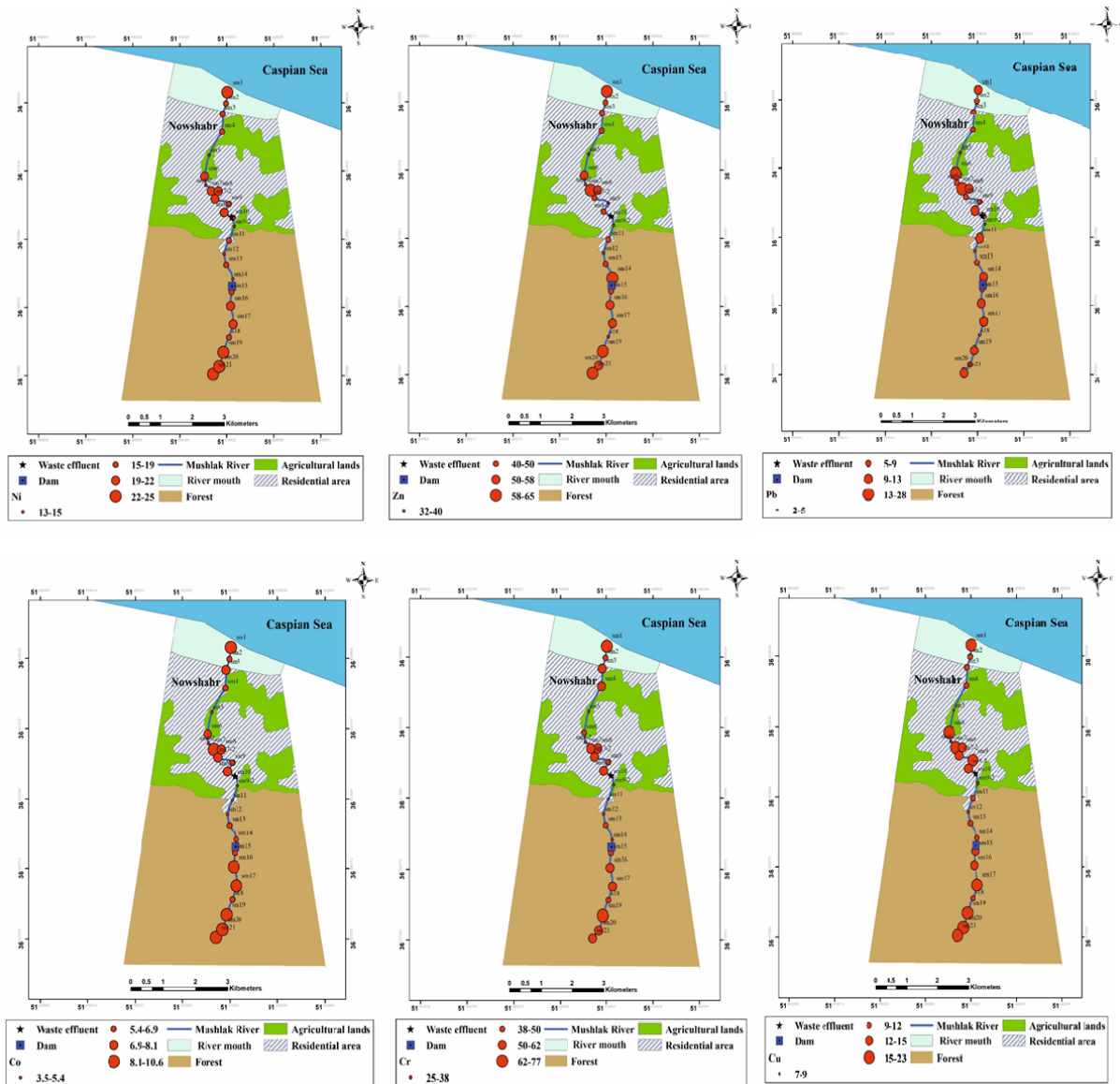


Figure 2. Distribution of heavy metal concentration in Mashlak river sediments.

cess of changes in the concentration of metals. At the end of the river, an increase in metal concentration is evident due to pollution related to loading at the wharf. Paint compounds, transportation, and urban and industrial wastewaters cause an increase in the amount of Pb metal in the soil (Sharma et al., 2020); (Wu et al., 2022); and the high concentration of nickel metal is also related to vehicle traffic and urban and industrial sewage (Zwolak et al., 2019); (Kabir et al., 2021). The concentration of Zn and Cu metals is generally caused by industrial activities and traffic pollution (Liu et al., 2020); (Jooybari et al., 2022).

4.1.2 Enrichment index

The enrichment index of heavy metals in Mashlak river sediment is presented in a box plot (Fig. 3). The highest enrichment index belongs to Cr, Zn, Mo, Cu, Pb, V, and Co. Chromium and nickel have an average contamination level of 2 to 5 in all samples. Other metals like V and Cu have low enrichment and contamination levels. Pb has low

enrichment and pollution in all samples, with moderate contamination levels only in some stations. Mo metal, another heavy metal in the deposits of the Mashlak river in stations S5, S6-2, S9, S9-2, S10, S11, and S12, has medium enrichment, and in other samples, it has low enrichment. Copper metal also has low enrichment in all studied stations and medium enrichment only in the S9 station.

4.1.3 Geo-accumulation index

The land accumulation index shows that only chrome metal has an average index greater than one, indicating low to moderate pollution (Fig. 4). The average geo-accumulation index of other metals in the Mashlak river deposits is in the "no pollution" class. The highest geo-accumulation index of chrome metal is in several stations along the river.

4.1.4 Contamination factor

The results of the contamination factor of Mashlak river deposits are presented in (Fig 5). The contamination fac-

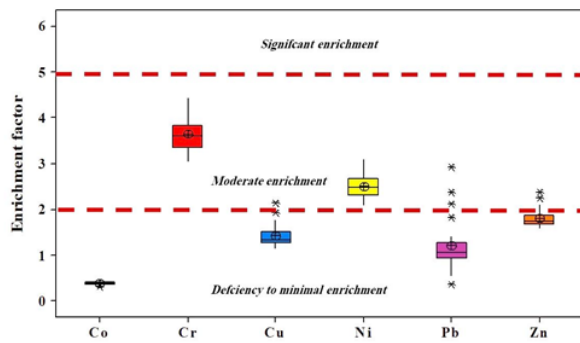


Figure 3. Box plot of the enrichment index of surface deposits of the Mashalak river.

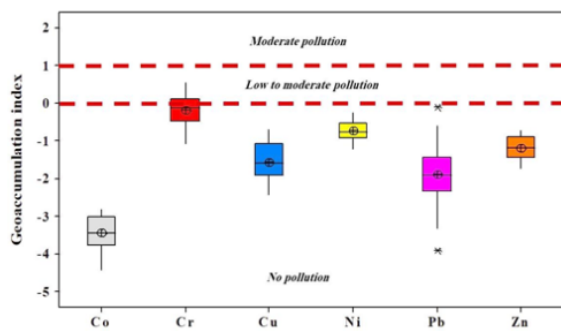


Figure 4. Box plot of the geo-accumulation index of the surface deposits of the Mashalak river.

tor results show that chromium, nickel, zinc, copper, lead, and cobalt are present in Mashalak river sediments, with chromium having the highest average contamination factor. Chromium is moderately polluted in all stations, with S6-2, S9-2, S10, and S12 showing moderate contamination. Nickel has low to moderate contamination in several stations along the river. Lead is lowly contaminated in all stations except for S7, which shows low to moderate contamination. Other metals have low contamination factors.

4.1.5 Ecological risk

Examining the ecological risk of heavy metals in the deposits of the Mashalak river indicates that this deposit is not polluted and indicates the low ecological risk of the studied area (Fig. 6). The average potential ecological risk (RI) in the studied area is 11.54, indicating a low health risk in the area. However, in a linear trend from the upstream of the river to the downstream of the river, this index has an increasing trend, and this could be due to the presence and increase of pollution along the river route(Fig. 7).

4.1.6 Statistical analyses

In order to accurately check the relationship between the concentration of metals and the percentage of particle size, Pearson’s correlation test was performed on the samples, and the results are presented in Table 10. Investigations show that there is a highly positive and significant relationship between all metals separately and with aluminum, and

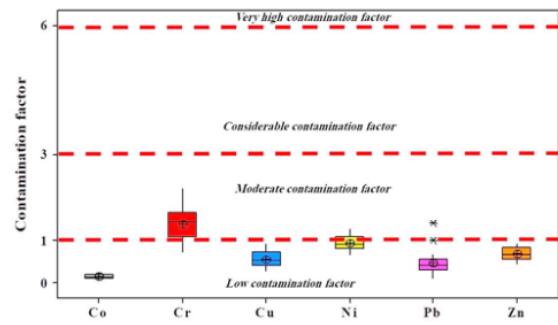


Figure 5. Box diagram of contamination factor of surface deposits of Mashalak river.

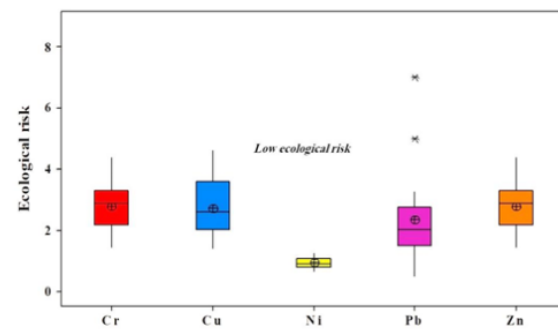


Figure 6. Box diagram of the ecological risk index of surface deposits of the Mashalak river.

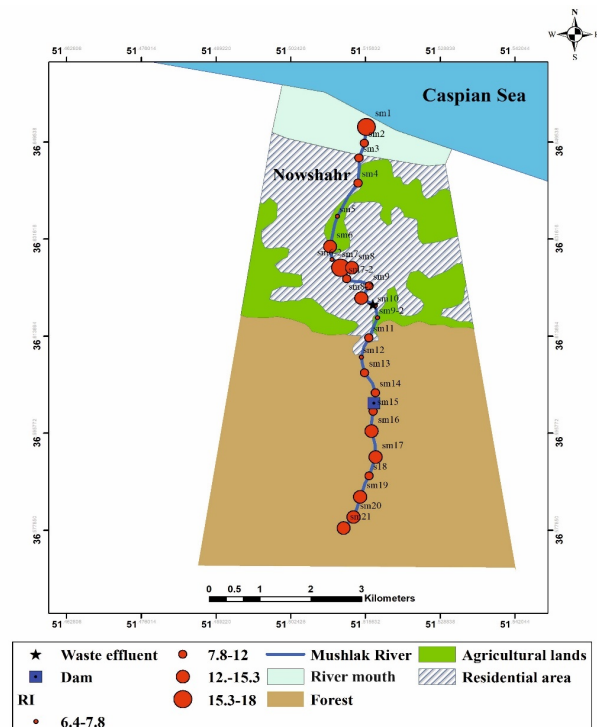


Figure 7. Distribution of potential ecological risk in the sediments of the Mashalak River.

this is an important sign of the common origin and similar geochemical behavior of these metals. The high correlation of heavy metals with Al metal indicates the geogenic origin

Table 10. Pearson correlation analysis between the concentration of elements in the sediments of the Mashalak River.

	Co	Cr	Cu	Ni	Pb	Zn	Al
Co	1						
Cr	.898**	1					
Cu	.872**	.766**	1				
Ni	.926**	.910**	.848**	1			
Pb	.573**	.409*	.687**	.541**	1		
Zn	.925**	.785**	.832**	.819**	.710**	1	
Al	.989**	.907**	.875**	.931**	.543**	.907**	1

*Significant at the 0.05 level **Correlation coefficient is significant at the 0.01 level

of these metals. The results of the clustering test (Fig. 8) also led to the identification of 2 clusters in the range of 0 to 5. The C1 cluster includes Al metal and the C2 branch also includes heavy metals such as Cr, Pb, Co, Zn, Cu, and Ni. The results of this test also confirm the correlation results of metals. In this test, all heavy metals are located in one cluster due to similar geochemical behavior or common origin.

4.2 Discussion and results of water

The statistical parameters of cations, anions, and indices calculated for Mashalak river water samples are presented in Table 11. The average electrical conductivity of Mashalak river water samples is 244 mic/cm, which is in the no salin-

ity category and suitable for watering all plants. However, investigations show an increasing trend in electrical conductivity from upstream to downstream. Samples from forest areas had low electrical conductivity, while those after the wastewater station and with agricultural use had moderate electrical conductivity. This indicates a negative impact of the wastewater station and agricultural waste on the river’s water quality index. Agricultural fertilizers containing various macronutrients can affect the electrical conductivity and control the water quality index. The average total hardness of Mashalak river water samples is 187 mg/liter of calcium carbonate, which is slightly hard. Samples after the dam have less hardness than upstream, while the total hardness increases as the river enters agricultural and residential lands. This indicates the direct impact of human activities on the hydrogeochemical properties of Mashalak river water. The average TDS of Mashalak river water samples is 216.3 mg/liter, which is in the high salinity risk class. The trend of TDS changes along the river shows an increasing trend from upstream to downstream, with the maximum at the wastewater effluent station. Samples from agricultural and residential lands have higher TDS than upstream samples, which may be related to agricultural effluents containing variable concentrations of cations and anions. However, the water quality of the river based on TDS is in the soft to moderate soft class, indicating good water quality compared to the TDS index. Since the quality of the river water based on TDS seems to be a formation composition resistant to

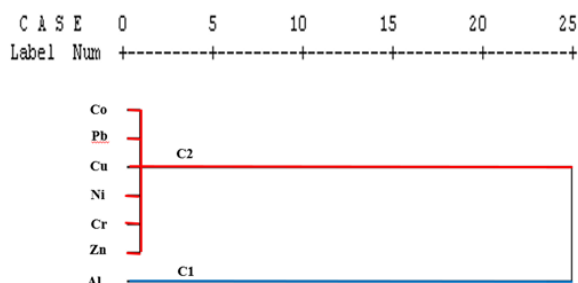


Figure 8. Cluster diagram of surface deposits of Mashalak River.

Table 11. Pearson correlation analysis between the concentration of elements in the sediments of the Mashalak River.

Parameter	Co3	CL	NO3	PO4	SO4	Ca2+	mg2+	Na+	K+	Hco3	T.H
Unite	ppm	ppm	ppm	ppm	ppm	mg/l	mg/l	mg/l	mg/l	ppm	Mg/l
MAX	311	23.2	55.6	73	52.4	100	33.12	368	267	5	182.3
MIN	169.87	2.16	4.29	4.27	4.27	30.61	14.26	20.9	1.29	137.92	
STV	31.4	6.54	15.16	20.3	14.5	16.75	4.5	88.83	71.39	0.96	59.85
CV	0.14	0.842	0.83	0.74	0.92	0.38	0.25	1.72	3.12	0.34	0.32
Parameter	%Na	SAR	RSC	MH	PI	KR	RSBC	PS	PH	EC	T.D.S
Unite	(%)	(meq/l)	(meq/l)	(%)	(meq/l)	(meq/l)	(meq/l)	(meq/l)	-	μmhos/cm	Mg/l
AVE	2.86	1.43	3.65	0.41	32.85	0.47	-2.17	0.38	7.02	339.44	214.51
MAX	75.21	8.25	7.52	0.45	69	2.12	-1.53	1.2	7.34	535.38	348
MIN	20.54	0.67	0.36	0.34	21.77	0.25	-5	0.11	6.56	263.51	174.02
STV	13.54	1.91	1.33	0.026	11.08	0.46	0.83	0.32	0.16	50.11	34.4
CV	0.45	1.33	0.36	0.06	0.33	0.98	-0.38	0.85	0.02	0.14	0.16

erosion in the study area and also the absence of high pollution along the route of the river, the water of this river is in a good condition compared to the TDS index.

4.2.1 Quality indices

The average amount of sodium percentage in the studied samples is 37.2%, which is in the good quality class. The average sodium percentage in the Mashalak river samples is good, and all samples are excellent for the sodium absorption ratio. The RSC index is poor and inappropriate, but the residual sodium bicarbonate index and salinity index are within the safe range and appropriate class, respectively. The permeability index and magnesium risk value are also appropriate. The overall index is within the appropriate quality range. Samples from forest areas have better quality indicators than those from agricultural and residential areas, which may be related to the area's structural composition, bedrock type, and erosion. Downstream samples passing through residential and agricultural areas have more sewage and waste, reducing these quality indices.

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4.2.3 Water quality factor

The average quality of this index in the Mashalak river water is 566, which is in the 5th rank and an inappropriate class for drinking Table 12. The lowest value of this index is at station 21 upstream of the Mashalak river, whose quality index value is 238. It is in the 4th rank and the quality class is very poor. The highest values of the quality index are in SW10 and SW9-2 stations, which are 3140 and 2806,

respectively, and they rank 5th in terms of quality and are unsuitable for drinking. These two stations are located next to the wastewater effluent station, and it is clear that the pollution caused by the wastewater of these stations has an extremely negative effect on the water quality of the Mashalak river. In a longitudinal trend along the river, the quality of the Mashalak river in the stations above the waste effluent station has a quality index below 300 and is in a very poor-quality class. In addition, the stations after the waste effluent have a quality index above 300 and are unsuitable for drinking; this is an indicator of the role of the wastewater station and the pollution caused by this station on the water quality of the Mashalak river.

4.2.4 Changes in heavy metals

Heavy metals are one of the oldest and most important toxic and dangerous environmental pollutants known to mankind, which are important due to properties such as high toxicity, carcinogenicity, non-degradability, and mutagenicity. The pattern of changes in the concentration of heavy metals in the Mashalak river shows that chromium, nickel, arsenic, cobalt, and zinc have the highest average concentrations, respectively (Table 13). The concentration of lead and vanadium metals in the Mashalak river water samples was below the detection limit. The concentration of arsenic metal in all studied stations was less than the standard concentration of rivers, but in two wastewater stations, the amount of this metal is 40 times the standard amount of drinking water, indicating the presence of arsenic metal pollution in the water near these stations. The concentration of cobalt metal was below the detection limit in all stations, and the concentration of this metal is less than the standard of river and drinking water, so it does not cause any environmental pollution in Mashalak river water. The concentration of chromium metal in all samples is below the standard limit of river water, but compared to drinking water, one wastewater station has a higher concentration than this standard. The concentration of nickel metal in the river is lower than the standard of drinking water. Zinc metal is free of environmental pollution and danger. The concentration of molybdenum metal is also lower than standard concentrations and is free of pollution. (Fig.9).

In order to accurately check the concentration of these metals in Mashalak river water, the relationship of Ficklin et al. (1992), modified by Caboi et al. (1999), was used. Fig. 10 shows the total concentration of heavy metals

Table 12. Water quality index in the studied stations of Mashalak river.

S.N	WQI	S.N	WQI	S.N	WQI	S.N	WQI
SW1	524	SW10	3140	SW6-2	407	SW16	264
SW2	540	SW11	268	SW7	307	SW17	269
SW3	569	SW12	255	SW7-2	301	SW18	271
SW4	581	SW13	256	SW8	330	SW19	262
SW5	583	SW14	255	SW8-2	335	SW20	249
SW6	526	SW15	263	SW9	368	SW21	238
				SW9-2	2806	Mean	566

Table 13. Changes in the concentration of heavy metals in the Mashalak river and the standards of river and drinking water (ppb).

Element	As	Co	Cr	Ni	Zn
Ave	3.476	2.374	11.4808	5.6336	2.3232
Max	40.95	18.7	106.15	63.76	26.77
min	0.1	1	2.69	0.1	1
SD	11.05	4.66	26.68	16.7	5.19
Upper limit of river standard	40	15	30	0	330
Lower limit of river standard	11	0	120	0	1030
Drinking	0.1	33	5	7	300

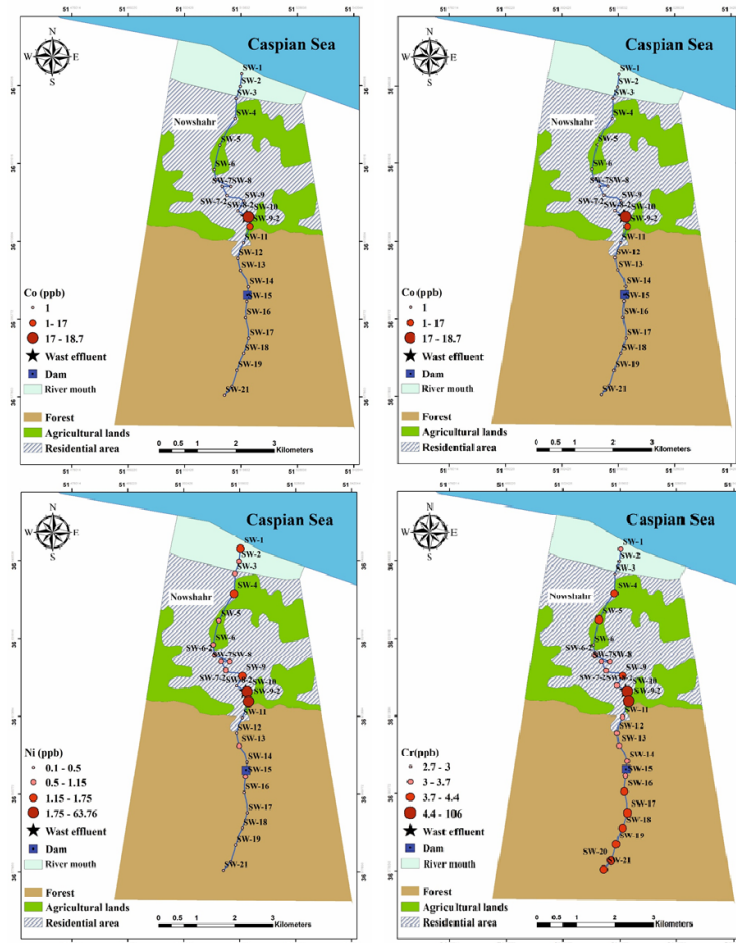


Figure 9. Changes in the concentration of heavy metals in water samples of the Mashalak river.

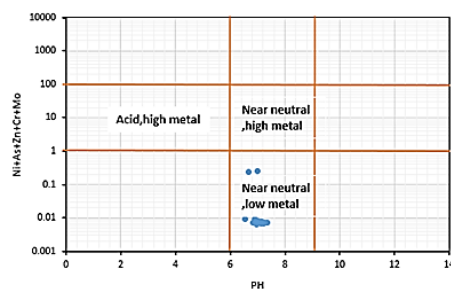


Figure 10. Classification of Mashalak river water based on pH and metal load (Ficklin et al., 1992)

against pH. Based on this classification, the water of the Mashalak river is in the near-neutral category with a low metal load, and in this sense, it is free of pollution.

5. Conclusion

The investigation of metal concentration in the Mashalak river sediments showed that chromium, zinc, nickel, copper, lead, and cobalt have the highest concentrations. Chromium metal concentration exceeds the average concentration of heavy metals in the upper crust, indicating potential pollution. Changes in concentration along the river show three clear peaks related to the dam, waste disposal station, and river estuary. Heavy metal concentration downstream of the dam decreases due to mud particle size, while downstream of the wastewater station and river estuary increases due to human intervention. Heavy metal concentration in the sediments has not increased much compared to international standards, with no health risks. Pollution is generally related to agricultural activities, traffic, and urban sewage. The water Mashalak river is not suitable for drinking due to the presence of wastewater effluent station and sewage from residential and urban areas. The concentration of heavy metals in the water is not warning levels except for arsenic and chromium near the wastewater station. The pollution may decrease the quality of this river in the long term for drinking, irrigation, and agricultural activities.

Authors Contributions

All authors have contributed equally to prepare the paper.

Availability of Data and Materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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