

Evaluating the effects of salinity on flocculation and purification mechanism of heavy metals in estuaries

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ABSTRACT

Estuaries are incredibly dynamic systems with their physical, chemical, and biological structure characterized by high spatial and temporal variability. During estuarine mixing, the dissolved metal concentration in the surface waters can be significantly decreased by flocculation and adsorption processes. The present study explores the effect of salinity, pH, dissolved organic carbon and nitrate on the flocculation, adsorption and desorption processes of dissolved metals (Cu, Mn, Ni, Zn, and Pb). The experiment was conducted on a series of mixtures with salinities ranging from 1.1‰ to 7.1‰ during the mixing of fresh water of the Navrood River water with brackish water from the Caspian Sea. The flocculation trend of Cu (74.44%) > Pb (73.92%) > Zn (54.37%) > Ni (52.33%) > Mn (35.36%) at different salinity regimes (1.1‰ to 7.1‰) indicates that Cu and Pb have a non-conservative behavior and Zn, Ni, and Mn have a relatively conservative behavior. Cluster analysis (CA) indicates that Cu and Zn are principally governed by salinity. According to the experiments, Cu, Ni, and Pb are desorbed from suspended particulate matters during estuarine mixing. The outcomes of the three-step chemical partitioning of the suspended particulate matters indicated that Mn and Pb are desorbed from the suspended particulate matters physically, while Ni is adsorbed into the suspended particulate matters chemically. CA indicates Ni, Zn, and Cu are mainly governed by salinity and DOC. According to the mean annual discharge of the Navrood River ($166 \times 10^6 \text{ m}^3/\text{y}$), the annual discharge of dissolved metals (Cu, Mn, Ni, Zn, and Pb) into the Caspian Sea would reduce respectively from 7.01, 5.59, 20.87, 27 and 3.28 to 1.79, 3.61, 9.95, 12.32, and 0.85 tons/y. The results of this study help decision makers in the local and regional levels to make realistic estimations about the pollution load of heavy metals in the Navrood River specifically and the Caspian Sea generally.

Keywords: Estuarine mixing; Cluster analysis; Purification; Geochemical; Metal species; Flocculation

1. Introduction

Substantial components with durable negative impacts on estuary conditions are conveyed by waterways from the landmasses into the oceans [1]. Considered as the interface between the ocean saltness and streams, estuaries are substantial aquatic systems which preserve the coastal biota and are loaded with supplements [2]. Estuaries are also necessary for generating and multiplication of aquatics and

are celebrated for having rich fauna and greenery among the other profitable biological systems in the ocean. As an outcome of the estuarial blend, substantial metals in the dissolvable and insoluble structures are affected essentially by a wide assortment of responses in the waterways; among these responses are flocculation, adsorption, and desorption of metals [3,4].

Flocculation of heavy metals is a process by which dissolved matter and suspended particles come out of the

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suspension to form flocs (cotton-like) or larger particles, happened by estuarial blend in the upper zones of the estuary where salinity variations in space are so large, and highly affected by such factors as ionic power, dissolved organic carbon (DOC), pH, and the measure of suspended particles in estuaries [2,5–7]. Besides, during the flocculation process at the estuary of the streams, a considerable amount of trace metals leave the liquid stage as flocs which keeps up the organic states of the saline water (seas, oceans, and lakes) [8–11]. Most of the estuaries receive a huge input of dissolved metal from industries. Due to the toxicity of heavy metals to aquatic ecosystems and human health and their accumulative behavior metals in sediments of riverbeds, there has been some escalating concern about the inflow of these metals and their compounds into the coastal areas [12]. The dissolved heavy metals carried by a river into the ocean are subjected to removal because brackish water compounds are fairly invariant [13,14]. Dissolved metals are affected by several physical and chemical reactions while passing through saline waters [14]. While entering into the estuarine mixing zone, a portion of dissolved heavy metals convert into flocs and come out of the suspension in this form [6,15]. A large part of the dissolved heavy metals supplied by the river comes into the particulate phase during flocculation processes [16]. Another portion of the flows is the content of suspended particulate matters (SPMs) and are likely to be desorbed from the SPMs and enter the estuary [17]. Heavy metals can generally be linked to sediments and suspended particulate matters via the following five bond types [18]: (1) loose and carbonate bond, (2) iron/manganese oxides and sulfide bond, (3) organic-metallic bond, (4) resistant bond, and (5) within-lattice bond [19].

Although various research has been conducted over the years to find out the controlling mechanisms of flocculation, adsorption and desorption processes, there is a lack of information in this regard during estuarine mixing of freshwaters (from Navrood River) with brackish waters such as the Caspian Sea water [15]. However, DOC has been shown as the main governing reason in the flocculation of trace elements in some studies [2, 20, 21]. In this study, the impact of DOC, saltiness, pH, and NO_3 in removing studied metals (Cu, Zn, Pb, Ni, and Mn) from mixed water during the blend of Navrood River water with the Caspian Sea water is contemplated to review the essential role of flocculation, adsorption and desorption process in self-purging of heavy metals. The necessity of this study can be articulated in this way that Navrood River is a transport agent for the disposal of industrial, agricultural, and urban wastes to the Caspian Sea. So it is of crucial importance to investigate closely the overall geochemical cycle of trace metals and their behavior in the region [22].

2. Materials and methods

2.1. Introduction to study area

The Caspian Sea, the world's largest lake, is located in northern Iran and is bounded on the north by Russia, on the west by Russia and the Republic of Azerbaijan, on the east by the Republic of Turkmenistan and Kazakhstan. The sea is confined to land and is not directly connected to any

of the world's waters. In recent years, the Caspian Sea has been connected to the Black Sea via the Volga-Dan Canal [23]. It is a landlocked sea with semi-saline water, covering an area of about 436,000 km² (one-fourth of Iran's area), a drainage area of 3.5 million km², and a volume of 78,000 km³ and its length is 1,205–1,280 km. The largest lake in the world is 202–554 km wide and its widest area is slightly higher than the southern coast. The salinity of Caspian Seawater varies from 4‰ in the northern parts to 13‰ in the southern parts.

The Navrood River is located on the northern highlands of the Alborz mountain range, in south of the Caspian Sea. The length of the Navrood River is 33 km with a flow rate of 5.15 m³/s. The average annual rainfall is 850 mm/y and its catchment area is 274 km². This river is the main source of irrigation for the agricultural lands, the fish farming industry, the industrial complexes, and tens of cities and villages. Therefore, a large amount of municipal, industrial, and agricultural wastewater containing heavy metals is discharged daily in the Navrood River. In order to investigate the effect of estuarine mixing in the natural elimination of heavy metals, samples were needed to be taken from the Navrood River and the Caspian Sea. Fig. 1 shows the location of the fresh and brackish water samples from the Navrood River and the Caspian Sea, respectively.

2.2. Location of sampling site and collection of sediment samples

On 14 October 2019, a sample of river water and suspended particles in a 25 L pre-prepared polyethylene buckets were taken from the Navrood River (about 16 km upstream). The freshwater sampling location was at the longitude of 48°50'42.42" and latitude of 37°47' 36.60". Sampling was collected at a point where no saline water from the Caspian Sea could penetrate the freshwater. To perform the experiments, fresh water (from Navrood river) was transferred to the laboratory and then filtered using AP and HA Millipore filters (0.45 μm). The filters were then discarded and the filtered water sample was kept for further investigation. Furthermore, a sample of suspended particulates in the Navrood River was dried up for 29 h at 50°C after being transferred to the laboratory [24].

Approximately 1 L of filtered fresh water from the Navrood River was acidified with concentrated nitric acid (HNO_3 , 22 mmol H⁺ L⁻¹) to a pH of 1.8 and was poured into polyethylene bottles before the analysis of heavy soluble metals and stored in a refrigerator at a temperature of less than 4°C. The remaining filtered freshwater sample was stored at 4°C in the refrigerator. It is noteworthy that only 5 g of suspended sediment were used for metal analysis after drying it by the oven. Similarly, on the same day, a sample of salt water from the Caspian Sea was collected about 20 km away from the estuary at a point where no freshwater had been introduced by the river (salinity = 13.6‰). The saline water sample was collected from a point with the coordinates of longitude 49°11'10.51" and latitude 37°54' 27.75".

2.3. Metal analysis

Two laboratory experiments were performed separately to examine heavy metal flocculation and the process of metal adsorption and desorption. In the first experiment

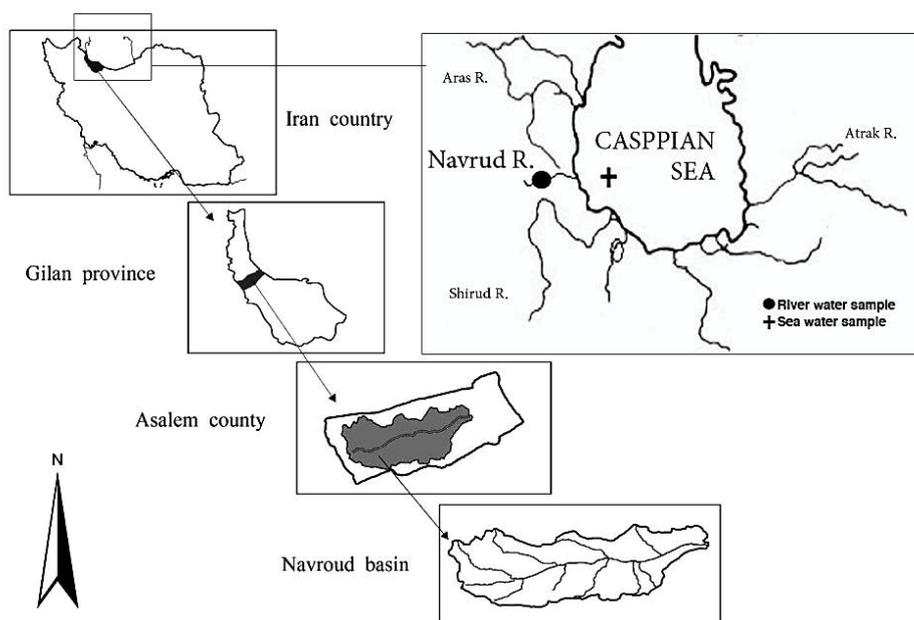


Fig. 1. Location of water and SPM Sample from the Navrood River and Caspian Sea.

of the flocculation process, a certain volume of filtered salt water from the Caspian Sea was added to a constant volume of filtered fresh water from the Navrood River in seven ratios with a salinity function of 1.1‰–7.1‰ at room temperature of 25°C. Seven mixtures were kept for 24 h after preparation at 25°C for the flocculation process. The obtained flocculants at this time were collected in each sample by a Millipore membrane filter with a diameter of 2.5 cm (type HA, 0.45 μm pore size). In the next step, Millipore filters were digested using 5 mL concentrated nitric acid (HNO₃) overnight for total heavy metal analyses. Heavy metal analysis was performed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) in the laboratory to determine the concentration of Cu, Zn, Ni, Pb, and Mn. At the same time, 50 mL of mixed samples with different salinities from each aquarium were taken to ascertain the values of physicochemical parameters such as DOC, NO₃, salinity, and pH.

In the second experiment, for determining the amount of adsorption and desorption of heavy elements in the samples, the constant amount of freshwater (river water) was combined with saline water (Caspian Sea water) to obtain seven mixtures with seven different salinities (1.1‰–7.1‰). After dewatering, suspended sediment samples were placed at 50°C for 24 h to achieve a constant weight. The dehydrated samples were sieved using a no. 230 sieve for using suspended particulate matters (SPMs) smaller than 63 μm in order to eliminate the diluting agents and provide the balanced specific area for the rest of the chemical analyses throughout the experiment. After adding 50 g of the dehydrated suspended sediment to each aquarium, the resulting mixture was constantly stirred for 24 h to allow heavy metals to be absorbed and desorbed from SPMs. After collecting the SPM from each aquarium and drying them, strong acids were used

according to the standard practice of ASTM-D4698-92 (ASTM D2013/D2013M-12 2012) for complete digestion of SPMs. Complete digestion facilitates the determination of heavy metal content values in each of the aquariums.

Subsequently, the three-step sequential chemical extraction method was used to identify the types of heavy metal bonds in the adsorption and desorption process to determine separately the salinity effects on the amount of heavy metals [25]. The sample was filtered and its volume was adjusted to 50 mL using 1 N HCl. 0.1 M hydrochloride hydroxylamine (which was prepared in one of the acetic acid solutions of the previous phase) for establishing the sulfate and iron/manganese species of trace metals. After drying and dehydration, 2 g of sediment samples were placed in an Erlenmeyer flask to detect the values of loose and carbonate bonding in each aquarium. Then 15 mL of acetic acid (25% v/v) was added to the Erlenmeyer flask and the resultant solution was shaken for 30 min. Afterwards, each sample was filtered and their volumes were adjusted to 50 mL using 1 N HCl. Then, according to the mentioned standard, 0.1 M hydrochloride hydroxylamine (which was prepared in the previous step) was applied to create the sulfate and iron/manganese species of heavy metals and to measure this type of bond in sediments and solutions. Approximately 15 mL of this solution were added to 2 g of the dehydrated powdered sample, and the mixture was shaken for 15 min in an Erlenmeyer flask. The solution volume was followingly adjusted to 50 mL using 1N hydrochloric acid (HCl) and each solution was read by the ICP-MS including organic species.

To identify the organic species, 2 g of dehydrated powdered sediment samples were mixed with 10 mL H₂O₂ (30% w/v) and the mixture was continuously heated on a hot water bath. As soon as the volume of oxygen peroxide decreased to about 1 mL, another 5 mL of H₂O₂ was added

to the resulted mixture. It is worth mentioning that during chemical analysis, metal-free AR-grade acids were used. The concentration of heavy metals in the digested samples was read by ICP. Procedural blanks and triples were conducted with the samples in an accurate and same manner. The dilution of single concentrated standards purchased from SPEX Cerprep Company was utilized to calibrate the ICP in determining the concentrations of Cu, Zn, Pb, Ni, Cd, and Mn in the water samples. Certified Reference Materials (CRM) in salinities of 0.28, 4.1, and 7.1 ppm were applied for systematic checking of the method's accuracy and precision. Using sequential extraction procedure, the recovery rates of metals were obtained, and then compared to the sum of three fractions with total metal concentration (Table 1).

In addition, chemical partition experiments were performed for each aquarium to observe the adsorption and desorption processes. In this study, chemical partition experiments were performed in four consecutive stages. The practical abstracts at each stage and the phase of the suspended particulate matters in the sequential extraction method [26] are presented in Table 2.

Dilution of single concentrated standards purchased from SPEX company was used to calibrate and ensure ICP performance. The chemical and physical parameters (pH, NO_3^- , salinity, and DOC) in water/mixture samples were measured using a portable water quality measuring device (BANTE 900) before metal analysis. Cluster analysis was also applied to review the effects of various parameters on trace metal behavior in the estuarine area. Finally, WPG (weighted pair group) method [27] was selected among

existing methods [27–29], and the corresponding results are shown in the form of a dendrogram.

3. Result and discussion

Mixing freshwater and saltwater samples were taken from the Navrood River and the Caspian Sea, and the flocculation process of this mixture may not occur similar to Table 3. Specifically, at the first stages of mixing freshwater and saline water at low salinities, significant amounts of dissolved metals were converted into flocculants [30–32]. However, freshwater may include less flocculates in comparison to its initial contents at the next stages of estuarine mixing. Certain amounts of Navrood river water were mixed with different proportions of salt water in laboratory conditions. The data of studied heavy metals content are summarized in Table 4, which is basically obtained from Table 3 by reducing the concentration of flocculants at each salinity regimen from the sum of the values in the previous steps [33].

As seen in other studies, salinity is a general term that does not express the effect of other components and parameters of saline water on the flocculation of heavy metals in the estuarine mixing samples [3]. Therefore, other parameters such as pH, DOC, and NO_3^- that are studied in this investigation can have considerable effects on the flocculation of the dissolved metals during estuarine mixing. As a result, CA of soluble metal concentrations along with physicochemical parameters in Navrood River water is performed during heavy metals flocculation. Based on Fig. 2, different

Table 1

Recovery rates of metals obtained from sequential extraction (At salinities of 0.28, 4.1 and 7.1 ppm)

Elements	Cu	Mn	Ni	Zn	Pb
Recovery (%) at salinity 0.28 ppm	81.32–91.21	90.1–104.1	91.01–100.33	89.1–101.95	79.24–91.45
Recovery (%) at salinity 4.1 ppm	82.32–93.21	89.87–102.4	90.8–101.02	88.06–101.05	79.24–91.45
Recovery (%) at salinity 7.1 ppm	80.32–92.48	90.87–100.9	89.1–100.88	86.98–100.05	79.24–91.45

Table 2

Methods and apparatus measuring different parameters

Parameter	Method/apparatus of measurement
Mn, Cu, Pb, Zn, Ni	ICP (ULTIMA 2000)
DOC	TOC meter (Shimatzu, TOC-VCSH-3000a)
Salinity	Titration method (APHA, 2005)
Water temperature	Thermometer (accuracy of 1°C)

Chemicals used in each extraction step and the extraction phases of SPM in the sequential extraction procedure

Extraction step	Reagent, concentration, and time	Particulate phase
1	Acetic acid (CH_3COOH), 0.11 mol L, 1–16 h	Acid soluble (exchangeable ions, carbonates)
2	Hydroxylamine hydrochloride (NH_2OHHCl), 0.5 mol L, (pH 2 with HNO_3), 1–16 h	Reducible (iron/manganese oxides and sulfides)
3	Hydrogen peroxide (H_2O_2), 8.8 mol L, 1 h at room temperature + 2 h at 85°C + ammonium acetate ($\text{CH}_3\text{COO NH}_4$), 1.0 mol L, (pH 2 with HNO_3), 1–16 h	Oxidizable (organic substances)

Table 3
Laboratory flocculation of metals during mixing of Navrood River water with Caspian Seawater

Sample	Cu ($\mu\text{g/L}$)	Mn ($\mu\text{g/L}$)	Ni ($\mu\text{g/L}$)	Zn ($\mu\text{g/L}$)	Pb ($\mu\text{g/L}$)	pH	Salinity (%)
River water	42.25 (42.01–42.3)	33.68 (33.2–33.8)	125.7 (124.2–126)	162.68 (161.1–163)	19.75 (19.3–19.9)	8.54	0.28
1	8.31(8.2–8.4) (19.67)	2.12 (2–2.2) (6.29)	47.34 (45.7–49.1) (37.66)	25.4 (24.3–26.6) (15.61)	9.42 (9.1–9.6) (47.7)	8.52	1.1
2	14.03 (13.9–14.1) (33.20)	2.82 (2.7–2.9) (8.37)	65.78 (63.1–67.9) (52.33)	38.24 (37.3–39.9) (23.51)	10.65 (10.5–10.8) (53.92)	8.49	1.8
3	20.31 (19.8–20.7) (48.07)	6.31 (6–6.5) (18.74)	25.76 (25.2–26.7) (20.49)	46.32 (45.1–47) (28.47)	8.43 (8.3–8.6) (42.68)	8.34	2.4
4	28.01 (27.7–28.4) (66.30)	8.80 (8.6–8.9) (26.12)	33.24 (32.1–34.9) (26.44)	75.23 (74.1–77.4) (46.24)	11.02 (10.9–11.2) (55.8)	8.38	3.2
5	31.45 (31.1–31.7) (74.43)	11.91 (11.7–12.1) (35.36)	36.42 (32.1–34.9) (28.97)	78.76 (75.3–80.5) (48.41)	14.6 (14.4–14.9) (73.92)	8.32	4.1
6	24.87 (23.4–25) (58.86)	11.23 (11.1–11.6) (33.34)	38.09 (37.4–39.1) (30.3)	88.45 (87.2–90.3) (54.37)	13.98 (13.7–14.2) (70.78)	8.32	4.6
7	25.22 (24.1–26.2) (59.69)	9.42 (9.2–9.6) (27.97)	39.88 (38.6–41.1) (31.73)	56.54 (53.9–57.9) (34.75)	9.45 (9.3–9.6) (47.85)	8.31	7.1

Values within brackets indicate percentile of removal in comparison with total metal content present in freshwater

Table 4
Actual flocculation of metals during mixing of Navrood River water with Caspian Sea water

Sample	Cu ($\mu\text{g/L}$)	Mn ($\mu\text{g/L}$)	Ni ($\mu\text{g/L}$)	Zn ($\mu\text{g/L}$)	Pb ($\mu\text{g/L}$)	pH	Salinity (‰)	DOC (mg/L)	NO ₃ (mg/L)
River water	42.25	33.68	125.7	162.68	19.75	8.54	0.28	2.87	1.74
1	8.31 (19.67)	2.12 (6.29)	47.34 (37.66)	25.4 (15.61)	9.42 (47.7)	8.52	1.1	4.1	1.42
2	5.72 (13.54)	0.70 (2.08)	18.44 (14.67)	12.84 (7.89)	1.23 (6.23)	8.49	1.8	7.2	1.39
3	6.28 (14.86)	3.49 (10.36)	0.00 (0.00)	8.08 (4.97)	0.00 (0.00)	8.34	2.4	9.1	1.44
4	7.70 (66.30)	2.49 (7.39)	0.00 (0.00)	28.91 (17.77)	0.37 (1.87)	8.38	3.2	18.86	1.21
5	3.44 (8.14)	3.11 (9.23)	0.00 (0.00)	3.53 (2.17)	3.58 (18.12)	8.32	4.1	25.6	1.18
6	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	9.69 (5.96)	0.00 (0.00)	8.32	4.6	29.6	1.08
7	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	8.31	7.1	35.5	0.78
Total	31.45 (74.44)	11.91 (35.36)	65.78 (52.33)	88.45 (54.37)	14.6 (73.92)				

Values within brackets indicate percentile of removal in comparison with total metal content present in freshwater

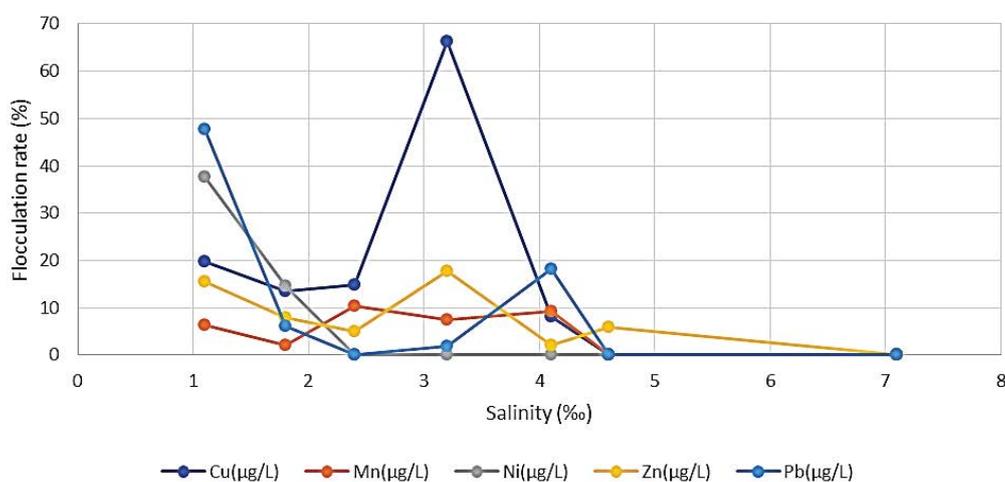


Fig. 2. Flocculation rate of studied metals at various salinities.

values of reduction in metals can be observed in various salinity ranges. Fig. 3 depicts the dendrogram of CA during the flocculation process at different salinities.

As seen in Table 4 and Fig. 2, the highest flocculation rate is related to Cu, which is about 44.74%.

According to the results, the Cu flocculation occurs in salinity 0.28‰–4.1‰, and the highest rate of it occurs in salinity 3.2‰. Mn shows the least tendency to flocculate, and the lowest flocculation belongs to Mn metal. The amount of Mn flocculation does not exceed 31.45% of the total dissolved concentration at salinities of 0.32‰ to 4.1‰. In addition, the process of Zn flocculation is very unique amongst other studied metals (Cu, Mn, Ni, and Pb), due to the fact that the process of flocculation does not stop at low salinities and continues at higher salinities. It is worth mentioning that the total amount of Ni flocculation (approximately 65.78 µg/L) occurs in the earliest stages of salinities or lower salinity. Overall, about 52.33% of the total Ni concentration is condensed during estuarine mixing.

The initial concentration of Pb in the Navrood River water is 19.75 µg/L. 14.6 µg/L or 73.92% of the total Pb concentration was flocculated at the time of mixing fresh water with saline water. It should be noted that the removal of Cu and Mn (similar to Pb) do not continue to salinities above 4.1 and are confined to salinity ranges of 0.28‰ to 4.1‰. The highest rates of Pb and Ni clotting occur in the initial salinity of 1.1‰, whereas the highest amount of Cu and Zn flocculation are found in higher salinities (3.2‰).

In general, the flocculation of studied metals (Mn, Cu, Pb, Ni, and Zn) except for Zn occurs in salinities lower than 4.1‰, and this is in accordance with the obtained results of other researchers [34–36]. The flocculation or clotting rates indicate that the overall dissolved heavy metal pollution loads may be eliminated from about 35% to about more than 70% during estuarine mixing of Navrood River with the Caspian Seawater. The final flocculation values of the studied metals in terms of percentage are as follows:

Cu (74.44%) > Pb (73.92%) > Zn (54.37%) > Ni (52.33%) > Mn (35.36%).

Diagram of CA (Fig. 3) shows that the pH changes control the changes in Ni and Pb concentrations during estuarine mixing. In addition, Cu flocculation is controlled by changes in NO₃ because they join together at a higher similarity coefficient. There is also a relatively high correlation

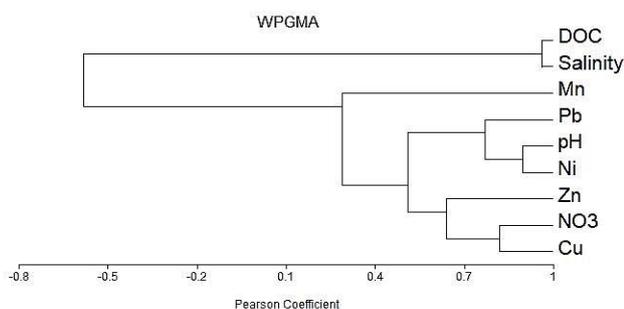


Fig. 3. Dendrogram of cluster analysis amongst studied parameter in the Navrood River.

between Zn and NO₃ changes. This indicates that Zn and Cu changes are mainly governed by NO₃ alterations. It is noteworthy to mention that salinity and DOC changes are inversely related to the studied metals and parameters.

In the second part of the experiment, the adsorption and excretion reactions between the trace metals and the suspended particles in the Navrood River were investigated. Subsequently, the role of sulfate, carbonate, iron/manganese oxide, and organic species were examined separately in the bonds between sediments and heavy metals. According to Table 5 and Fig. 4, as soon as estuarine mixing in the initial salinities happens, a significant amount of Mn and a small amount of Pb are excreted from the suspended particles and enter the liquid phase in the marine environment. As seen in Table 5, the highest amount of metal absorption is related to Cu, which is about 34.4%. The adsorption capacity of dissolved metals due to SPMs during estuarine mixing is in the following orders respectively: Cu (7.25 mg/kg) > Ni (3.22 mg/kg) > Zn (8.52 mg/kg).

Based on Fig. 4a, c, and d, Cu, Zn, and Ni exhibit absorptive behavior, while Pb and Mn exhibit repulsive behavior. Furthermore, 7.25 mg/Kg of the Cu in the marine environment is absorbed by SPMs. Although approximately 3.22 and 8.52 mg/Kg of Ni and Zn are absorbed by SPMs, they show relatively conservative behavior after SPMs entering into the estuarine zone and are exposed to various salinities.

Finally, when the waters of the Caspian Sea and the Navrood river are mixed with salinity of 7.1‰, Cu, Zn and Ni are absorbed into the SPMs in the following order (the percentage values are given in proportion to the initial concentration in the suspended particulate matters): Cu (28.6%) > Ni (9%) > Zn (6.4%).

As shown in Fig. 4b, Mn is significantly excreted as soon as it is exposed to salinity, but at higher salinity levels, this element reacts in very small amounts and exhibits conservative behavior. In total, as soon as SPMs enter the mixing zone, 124.41 mg/kg of Mn is excreted from SPMs.

According to Fig. 4c, the partial excretion of Ni from SPMs with a concentration of 2.39 mg/kg indicates a relatively conservative behavior of this element in the marine environment. Finally, when the waters of the Caspian Sea and the Navrood River are mixed at higher salinities (7.1‰), the Mn and Pb appear to be excreted from the SPM in the following order and enter the aquatic environment (the percentage values are given in proportion to the initial concentration): Mn (28.6%) > Pb (12.1%).

The results of this study are different from the results of a number of previous ones. The possible reason for these differences in the results of the present study and previous cases can be attributed to the difference in the geological unit of the Navrood catchment area with other river catchments. In a study by Marefat [27], the desorption and absorption potentials of the SPMs of Sefidrud river estuary were examined and it was found that due to the mixing of the Caspian Sea brackish water and Sefidrud river fresh water, Zn and Pb are absorbed into the SPMs with the 6% and 20% (the percentage values are given in proportion to the initial concentration), respectively.

On the other hand, Mn and Cu are excreted from the SPMs respectively with 25% and 9%. As mentioned earlier, in the present study, Pb has a repulsive behavior in

Table 5
Trace metal concentrations of suspended particulate matters in the different saline regimes along with physical and chemical parameters in estuarine zone of Caspian Sea

Sample	Cu (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	pH	Salinity (%)	DOC (mg/L)	NO ₃ (mg/L)
River water	25.31 (25.01–25.48)	568.28 (563–572.21)	35.66 (34.98–36.01)	132.46 (131.21–133.09)	19.75 (19.7–19.81)	8.54	0.28	2.87	1.74
1	24.08 (23.99–24.13)	486.88 (479.21–492.6)	35.97 (35.56–36.15)	134.34 (132.34–136.23)	19.55 (19.29–19.73)	8.54	1.1	4.1	1.42
2	28.67 (28.36–28.89)	469.04 (468–470.78)	36.12 (35.98–36.43)	138.67 (137–139.55)	18.97 (18.49–19.43)	8.51	1.8	7.2	1.39
3	29.23 (29.01–29.34)	457.28 (453.31–461.87)	36.16 (35.97–36.27)	139.66 (136.46–141.73)	18.45 (17.98–18.87)	8.48	2.4	9.1	1.44
4	30.00 (29.45–30.54)	451.76 (445.83–460.89)	37.24 (37–37.44)	140.12 (136.46–141.73)	18.04 (17.56–18.39)	8.36	3.2	18.86	1.21
5	29.78 (29.24–30.01)	453.51 (447.98–463.23)	37.25 (37.08–37.55)	140.67 (138.34–142.45)	17.89 (17.27–18.22)	8.37	4.1	25.6	1.18
6	31.67 (29.99–31.98)	446.54 (441–450.34)	37.87 (37.41–38.13)	139.27 (136.34–141.45)	17.78 (17.46–18.03)	8.29	4.6	29.6	1.08
7	32.56 (31.34–33)	443.87 (439.67–447.23)	38.88 (38.28–39.2)	140.98 (137–143.2)	17.36 (17.19–17.48)	8.17	7.1	35.5	0.78
Total adsorption (+)	8.70 (34.3)	1.75 (0.3)	3.22 (9.0)	9.92 (7.4)	0 (0.0)	-	-	-	-
Total desorption (-)	1.45 (5.7)	126.16 (22.2)	0 (0.0)	1.40 (1.0)	2.39 (12.1)	-	-	-	-
Total (%)	+7.25 (28.6)	-124.4 (21.8)	+3.22 (9.0)	+8.52 (6.4)	-2.39 (12.1)	-	-	-	-

the marine environment but in other studies, adsorptive behavior was shown and it was absorbed on suspended sediments. Moreover, Cu was adsorbed by the SPMs in the present research, but in other experiments it was excreted in SPMs and entered the marine environment. Some researchers have reported that the adsorption and desorption process could be governed by pH, DOC, physical properties of particulates and suspended sediments, and the presence and concentration of other metals [37–39].

After analyzing bulk digestion of the suspended particulate matters and identifying trace metal concentration at different salinity regimes, a three-step chemical partitioning was conducted to determine if the process of absorption and excretion of heavy metals is controlled physically or chemically. The role of different metal species and their bonds with sediments in the adsorption and excretion process is presented in Table 6.

As seen in Fig. 5, heavy metals can generally be linked to sediments and suspended particulate matters via the following five bond types: loose and carbonate bond (F1), iron/manganese oxides and sulfide bond (F2), organic-metallic bond (F3), resistant bond (F4), and within-lattice bond (F5). It should be noted that F4 and F5 were not reviewed in this research, which is due to the chemical stability of these bonds and having a neutral role in absorption and desorption.

Cu has the highest absorption rate, which according to Table 6 is mostly absorbed physically and in smaller amounts chemically.

Based on the results of Table 6, it is observed that the removal of Mn from SPMs is more physically and to a lesser extent chemically. As previously reported, while mixing the river, some loose Mn and carbonate species are excreted from suspended sediment [40]. As the name implies, in this type of bond, the bond between the trace metals and the suspended sediments is very weak and can be broken by the slightest change in the physical and chemical properties of the surface water. As mentioned, the behavior of Ni and Zn is conservative and they are absorbed to lower levels than other studied metals into the SPMs. According to Table 6, Ni is chemically and to a lesser extent physically absorbed into SPMs. This indicates the type of bonds with the sediments. In contrast, Mn, Zn, and Pb are linked by physical reactions and to a lesser extent by chemical reactions with sediments. It is worth mentioning that Ni plays a significant role in chemical reactions.

According to Table 6, Zn excretion has only a physical process and bonds with weaker sediments.

The adsorption of Ni and Cu involves both physical and chemical processes, and the bonds between these metals are different from other studied metals. Pb is only physically excreted from the surface of SPMs, but the estuarine mixing zone has a lesser effect on the loose and carbonate Pb species. This might be due to the fact that the initial concentration of the loose and carbonate Pb species is lower than the initial concentration of the loose and carbonate manganese species.

As Saeedi stated in previous studies, the absorption capacity of SPMs was measured in Tajan River and it was concluded that by reducing the initial concentration of trace metals in estuarine environments, the possibility of collision

Table 6

Role of different suspended particulate matter metal species in the absorption and desorption process during estuarine mixing

Metal	Salinity (‰)	Exchangeable ions and carbonates (mg/kg)	Iron/manganese oxides and sulfides (mg/kg)	Organic substances (mg/kg)	Total concentration (mg/kg)
Cu	0.28	2.61 (2.51–2.71)	1.26 (1.22–1.33)	0.65 (0.63–0.67)	25.31
	1.1	3.02 (2.92–3.12)	1.41 (1.41–1.52)	0.23 (0.22–0.24)	24.08
	1.8	3.44 (3.34–3.65)	2.72 (2.71–2.84)	0.63 (0.59–0.64)	28.67
	2.4	3.67 (3.61–3.85)	2.72 (2.62–2.83)	0.56 (0.53–0.58)	29.23
	3.2	4.99 (4.91–5.11)	2.78 (2.69–2.9)	0.53 (0.52–0.55)	30.00
	4.1	4.12 (4.03–4.19)	2.81 (2.79–2.91)	0.53 (0.52–0.54)	29.78
	4.6	6.77 (6.61–6.92)	2.86 (2.79–2.91)	0.52 (0.5–0.55)	31.67
	7.1	7.98 (7.82–8.15)	2.86 (2.72–3)	0.48 (0.46–0.5)	32.56
	Adsorption (%)		21.22	4.70	0
Desorption (%)		0	0	0.67	0.67
Mn	0.28	124.67 (120–127.1)	43.78 (42.87–44.6)	28.65 (28.07–29.1)	568.28
	1.1	92.56 (91.3–93.56)	40.14 (39.22–41.65)	30.25 (28.99–30.71)	486.88
	1.8	87.65 (86–88.9)	45.23 (44.12–46.78)	29.34 (28.68–30.18)	469.04
	2.4	71.34 (70.8–72)	43.56 (43.1–43.9)	28.53 (27.8–29.27)	457.28
	3.2	58.99 (57.4–59.7)	39.20 (38.3–40.08)	31.22 (30.2–32.08)	451.76
	4.1	47.81 (46.9–48.6)	32.20 (31.09–33.54)	32.43 (32.09–33.31)	453.51
	4.6	36.22 (35.5–37.1)	32.90 (31.99–33.48)	32.89 (32.09–33.31)	446.54
	7.1	34.55 (33.6–35.22)	32.29 (31.81–32.33)	33.01 (32.13–33.89)	443.87
	Adsorption (%)		0	0	0.74
Desorption (%)		15.86	1.95	0	17.81
Ni	0.28	4.72 (4.48–4.88)	2.15 (2.08–2.23)	6.1 (5.98–6.33)	35.66
	1.1	4.54 (4.34–4.79)	2.65 (2.54–2.73)	6.18 (5.99–6.34)	35.97
	1.8	4.31 (4.22–4.5)	4.23 (4.13–4.28)	6.19 (6.15–6.25)	36.12
	2.4	4.67 (4.44–4.89)	4.11 (4–4.15)	6.17 (6.11–6.23)	36.16
	3.2	5.02 (4.78–5.18)	4.00 (3.89–4.1)	6.03 (5.98–6.09)	37.24
	4.1	5.58 (5.41–5.68)	4.26 (4.17–4.35)	6.16 (6.11–6.24)	37.25
	4.6	5.67 (5.34–5.77)	4.29 (4.09–4.4)	6.18 (6.09–6.26)	37.87
	7.1	5.59 (5.56–5.63)	4.18 (4.16–4.2)	6.23 (6.18–6.31)	38.88
	Adsorption (%)		2.44	5.69	0.36
Desorption (%)		0	0	0	0
Zn	0.28	23.45 (22.78–24.01)	14.02 (13.9–14.16)	8.54 (8.34–8.7)	132.46
	1.1	24.25 (23.84–24.99)	14.55 (14.43–14.61)	9.02 (8.87–9.12)	134.34
	1.8	24.87 (24.13–25.26)	14.88 (14.68–14.99)	8.34 (8.16–8.44)	138.67
	2.4	25.18 (24.96–25.37)	14.05 (13.99–14.9)	8.30 (7.99–8.45)	139.66
	3.2	28.29 (27.82–28.64)	14.22 (14.18–14.25)	8.12 (8.02–8.23)	140.12
	4.1	32.56 (32.12–33.21)	13.3 (13.01–13.45)	7.88 (7.59–8.03)	140.67
	4.6	32.43 (31.67–33.21)	12.95 (12.82–13.08)	8.25 (8.16–8.3)	139.27
	7.1	31.34 (30.89–32.01)	13.9 (13.56–14.54)	8.45 (8.32–8.52)	140.98
	Adsorption (%)		5.96	0	0
Desorption (%)		0	0.09	0.07	0.16
Pb	0.28	3.45 (3.33–3.54)	2.24 (2.14–2.32)	0.82 (0.81–0.83)	19.75
	1.1	3.69 (3.54–3.77)	2.28 (2.22–2.31)	0.82 (0.82–0.82)	19.55
	1.8	3.3 (3.18–3.44)	2.25 (2.23–2.29)	0.86 (0.85–0.88)	18.97
	2.4	3.25 (3.12–3.34)	2.24 (2.14–2.29)	0.73 (0.73–0.73)	18.45
	3.2	2.59 (2.56–2.65)	2.26 (2.23–2.29)	0.79 (0.76–0.81)	18.04
	4.1	2.03 (1.98–2.06)	2.33 (2.28–2.36)	0.88 (0.85–0.9)	17.89
	4.6	1.55 (1.51–1.59)	2.28 (2.26–2.3)	0.75 (0.74–0.77)	17.78
	7.1	1.36 (1.32–1.39)	2.24 (2.22–2.27)	0.85 (0.84–0.86)	17.36
	Adsorption (%)		0	0	0
Desorption (%)		10.58	0	0	10.58

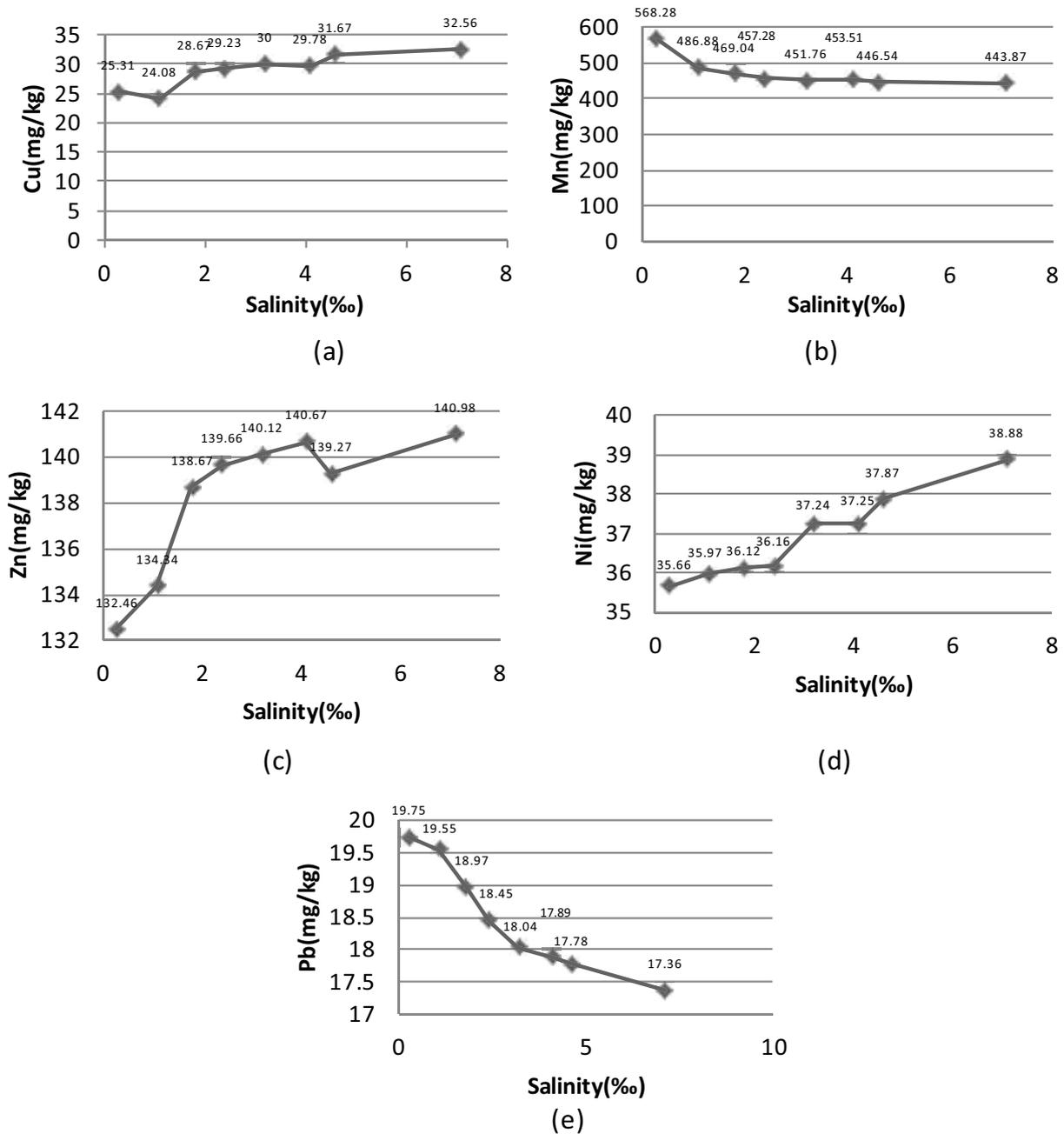


Fig. 4. Changes in metals concentration in SPMs.

and contact decreased, and also the reaction between heavy metals and SPMs reduced [41]. In addition, organic species have little effect on the excretion or absorption of these five metals.

Dendrogram of CA (Fig. 6) indicates that Nitrate (NO_3) and pH control the adsorption process of Mn and Pb during estuarine mixing. It is also shown that Ni is mainly governed by DOC and salinity; there is a high correlation between these parameters. Besides, Zn and Cu are also governed less by DOC and salinity. The CA diagram (Fig. 6) illustrates the fact that nitrate changes (NO_3) and pH changes

control the process of absorption of Mn and Pb when SPMs come into contact with salt water. It further shows that Ni is mainly driven by DOC and salinity changes; in fact, there is a high correlation between these parameters. In addition, Zn and Cu are less controlled by DOC and salinity changes

4. Conclusion

This study investigates the flocculation, adsorption and desorption processes of dissolved heavy metals (Ni, Pb, Cu, Mn, and Zn) during the estuarine mixing of the

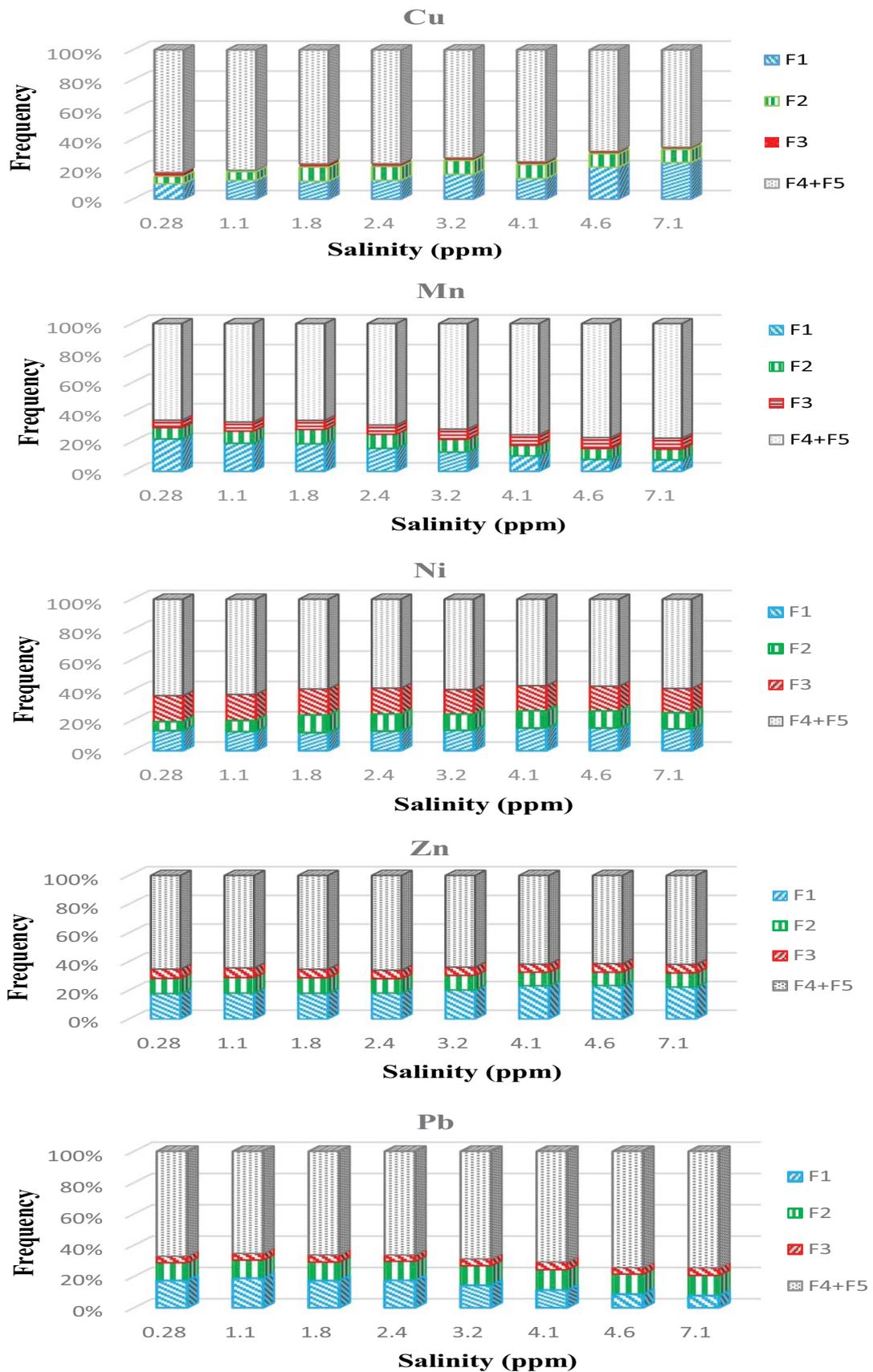


Fig. 5. Heavy metal distributions (%) in various geochemical fractions in the different salinities.

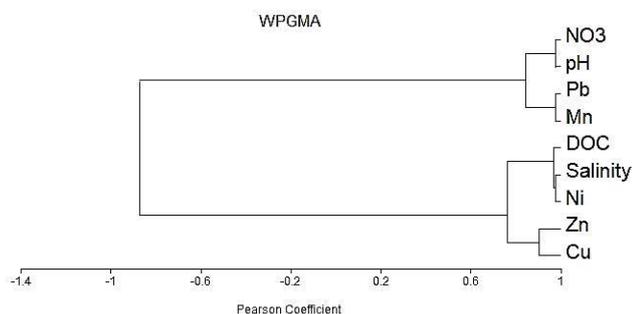


Fig. 6. The dendrogram of cluster analysis of the metals in the adsorption-desorption process.

Navrood River water with Caspian Sea water at various salinity ranges (from 1.1‰ to 7.1‰). The highest percentage of flocculation process is observed for Cu. Furthermore, Cu exhibited the highest desorption behavior from SPMs during estuarine mixing. Among the studied physicochemical parameters of blending samples (pH, DOC, and Nitrate), dissolved organic carbon represents an increasing linear behavior toward salinity changes. The flocculation process of Cu, Zn and, to a lesser extent, Ni and Pb are controlled by Nitrate. Moreover, the adsorption process of Mn and Pb is governed by Nitrate. Desorption rates of the studied metals from suspended particulate matters in the Navrood Estuary are in the following order: Mn (28.6%) > Pb (12.1%). A wide range of research about the variation in the rate of flocculation process of trace elements (Cu, Pb, Mn, and Ni) throughout the year have been conducted in rivers. In this research, the effect of salinity, pH, DOC and NO_3 on the flocculation, adsorption and desorption process of Zn, Mn, Ni, Cu, and Pb is investigated. Based on the CA, the flocculation processes of Pb and Ni are mainly governed by pH. According to the research of chemical partitioning, it is necessary to mention about 81%, 28% and 100% of the concentration of adsorbed Cu, Ni, and Zn are found in carbonate fractions, respectively. Generally, the highest percentage of heavy metal contents is revealed in sulfide and carbonate compounds bound. Based on the rate of flocculation and adsorption for studied heavy metals, total loads of colloidal metal content omitted considerably by different percentiles at various salinity regimes. According to the mean annual discharge of the Navrood River ($166 \times 10^6 \text{ m}^3/\text{y}$), the annual discharge of dissolved Cu, Mn, Ni, Zn and Pb into the Caspian Sea would reduce respectively from 7.01, 5.59, 20.87, 27 and 3.28 to 1.79, 3.61, 9.95, 12.32 and 0.85 ton/y. Navrood River is a transport agent for the disposal of industrial, agricultural, and urban wastes to the Caspian Sea. Therefore, the geochemical cycle of trace metals and their behavior in the region should be closely investigated. The results of this study help decision makers in the local and regional levels to make realistic estimations about the pollution load of heavy metals in Navrood River specifically and the Caspian Sea generally. Besides, the water resources managers and policy makers can benefit from the achievements of this research to guarantee the sustainable development of the region without impinging on the invaluable water bodies in the regional level.

References

- [1] I.C. Potter, B.M. Chuwen, S.D. Hoeksema, M. Elliott, The concept of an estuary: a definition that incorporates systems which can become closed to the ocean and hypersaline, *Estuarine, Estuar. Coast. Shelf Sci.*, 87 (2010) 497–500.
- [2] A.V. Samani, A. Karbassi, M. Fakhraee, M. Heidari, A. Vaezi, Z. Valikhani, Effect of dissolved organic carbon and salinity on flocculation process of heavy metals during mixing of the Navrud River water with Caspian Seawater, *Desal. Water Treat.*, 55 (2015) 926–934.
- [3] A. Karbassi, J. Nouri, G.R.N. Bidhendi, G. Ayaz, Behavior of Cu, Zn, Pb, Ni and Mn during mixing of freshwater with the Caspian Sea water, *Desalination*, 229 (2008) 118–124.
- [4] L.L.H. Roux, S.L. Roux, P. Appriou, Behaviour and speciation of metallic species Cu, Cd, Mn and Fe during estuarine mixing, *Mar. Pollut. Bull.*, 36 (1998) 56–64.
- [5] A. Chowdhury, S.K. Maiti, Assessing the ecological health risk in a conserved mangrove ecosystem due to heavy metal pollution: a case study from Sundarbans Biosphere Reserve, India, *Hum. Ecol. Risk Assess.: Int. J.*, 22 (2016) 1519–1541.
- [6] H. Farajnejad, A. Karbassi, M. Heidari, Fate of toxic metals during estuarine mixing of fresh water with saline water, *Environ. Sci. Pollut. Res.*, 24 (2017) 27430–27435.
- [7] L.M. Mosley, P.S. Liss, Particle aggregation, pH changes and metal behaviour during estuarine mixing: review and integration, *Mar. Freshwater Res.*, 71 (2020) 300–310.
- [8] R.N. Comans, C.P.V. Dijk, Role of complexation processes in cadmium mobilization during estuarine mixing, *Nature*, 336 (1988) 151–154.
- [9] A. Karbassi, M. Heidari, An investigation on role of salinity, pH and DO on heavy metals elimination throughout estuarial mixture, *Global J. Environ. Sci. Manage.*, 1 (2015) 41–46.
- [10] M. Samarghandi, J. Nouri, A. Mesdaghinia, A. Mahvi, S. Nasser, F. Vaezi, Efficiency removal of phenol, lead and cadmium by means of $\text{UV}/\text{TiO}_2/\text{H}_2\text{O}_2$ processes, *Int. J. Environ. Sci. Technol.*, 4 (2007) 19–25.
- [11] E. Sholkovitz, Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater, *Geochim. Cosmochim. Acta*, 40 (1976) 831–845.
- [12] S. Islam, M.A.H. Bhuiyan, T. Rume, M. Mohinuzzaman, Assessing heavy metal contamination in the bottom sediments of Shitalakhya River, Bangladesh; using pollution evaluation indices and geo-spatial analysis, *Pollution*, 2 (2016) 299–312.
- [13] D.W. Pritchard, What is an Estuary: Physical Viewpoint. *Estuaries*, G.H. Lauff, Ed., American Association for the Advancement of Science, Washington DC, 1967, pp. 3–5.
- [14] M. Viswanathan, G. Chakrapani, Laboratory experiments on river-estuary geonanomaterials, *Curr. Sci.*, 99 (2010) 213–215.
- [15] S. Hassani, A. Karbassi, M. Ardestani, Role of estuarine natural flocculation process in removal of Cu, Mn, Ni, Pb and Zn, *Global J. Environ. Sci. Manage.*, 3 (2017) 187–196.
- [16] A. Karbassi, G.N. Bidhendi, M. Saeedi, A. Rastegari, Metals removal during estuarine mixing of Arvand River water with the Persian Gulf water, *Open Geosci.*, 2 (2010) 531–536.
- [17] A. Karbassi, A. Marefat, The impact of increased oxygen conditions on heavy metal flocculation in the Sefidrud estuary, *Mar. Pollut. Bull.*, 121 (2017) 168–175.
- [18] R. Chester, M. Hughes, A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments, *Chem. Geol.*, 2 (1967) 249–262.
- [19] D. Pal, S.K. Maiti, Heavy metal speciation, leaching and toxicity status of a tropical rain-fed river Damodar, India, *Environ. Geochem. Health*, 40 (2018) 2303–2324.
- [20] R. Mantoura, E. Woodward, Conservative behaviour of riverine dissolved organic carbon in the Severn Estuary: chemical and geochemical implications, *Geochim. Cosmochim. Acta*, 47 (1983) 1293–1309.
- [21] J.L. Meyer, C.M. Tate, The effects of watershed disturbance on dissolved organic carbon dynamics of a stream, *Ecology*, 64 (1983) 33–44.

- [22] J. Day, C. Hall, W. Kemp, Y. Arancibia, *Estuarine Ecology*, John Wiley and Sons, Inc., New York, 1989.
- [23] A. Kosarev, E. Yablonskaya, E. Iablonskia, *The Caspian Sea* (Vol. 20), SPB Academic Publishing, The Hague, 1994.
- [24] A. Bayati, F. Moatar, A. Karbasi, A. Hasani, Role of saline water in removal of heavy elements from industrial wastewaters, *Int. J. Environ. Res.*, 3 (2010) 177–182.
- [25] J. Morillo, J. Usero, I. Gracia, Heavy metal distribution in marine sediments from the southwest coast of Spain, *Chemosphere*, 55 (2004) 431–442.
- [26] J. Morillo, J. Usero, I. Gracia, Partitioning of metals in sediments from the Odiel River (Spain), *Environ. Int.*, 28 (2002) 263–271.
- [27] A. Marefat, A. Karbassi, T. Nasrabadi, The role of the estuarine zone on the river particulate toxicity, *Environ. Sci. Pollut. Res.*, 26 (2019) 5038–5053.
- [28] A. Anderson, Numeric examination of multivariate soil samples, *J. Int. Assn. Math. Geol.*, 3 (1971) 1–14.
- [29] G. Lance, W. Williams, A generalized sorting strategy for computer classifications, *Nature*, 212 (1966) 218–218.
- [30] A. Biati, A.R. Karbassi, Flocculation of metals during mixing of Siyahrud River water with Caspian Sea water, *Environ. Monit. Assess.*, 184 (2012) 6903–6911.
- [31] M. Saeedi, A. Karbassi, N. Mehrdadi, Flocculation of dissolved Mn, Zn, Ni and Cu during the mixing of Tadjan River water with Caspian Sea water, *Int. J. Environ. Stud.*, 60 (2003) 575–580.
- [32] L. Zhiqing, Z. Jianhu, C. Jinsi, Flocculation of dissolved Fe, Al, Mn, Si, Cu, Pb and Zn during estuarine mixing, *Acta. Oceanol. Sin.*, 6 (1987) 568–576.
- [33] S.S. Chenar, A. Karbassi, N.H. Zaker, F. Ghazban, Electroflocculation of metals during estuarine mixing (Caspian Sea), *J. Coastal Res.*, 29 (2013) 847–854.
- [34] J.M. Bewers, I.D. Macaulay, B. Sundby, Trace metals in the waters of the Gulf of St. Lawrence, *Can. J. Earth Sci.*, 11 (1974) 939–950.
- [35] J. Burton, *Basic Properties and Processes in Estuarine Chemistry*, Estuarine Chemistry, Academic Press, London, 1976, pp. 1–36.
- [36] J. Duinker, R. Nolting, Distribution model for particulate trace metals in the Rhine estuary, Southern Bight and Dutch Wadden Sea, *Neth. J. Sea Res.*, 10 (1976) 71–102.
- [37] B. Alloway, D. Ayres, Chemical principles of environmental pollution, B.J. Alloway and D.C. Ayres, *Water Air Soil Pollut.*, 102 (1998) 216–218.
- [38] U. Förstner, *Inorganic Pollutants, Particularly Heavy Metals in Estuaries*, Chemistry and Biochemistry of Estuaries (E. Olausson, I. Cato, Eds.), John Wiley & Sons Ltd., Chichester, 1980, pp. 307–348.
- [39] S. Lukman, M. Essa, N.D.M. Azu, A. Bukhari, C. Basheer, Adsorption and desorption of heavy metals onto natural clay material: influence of initial pH, *Int. J. Environ. Sci. Technol.*, 6 (2013) 1–15.
- [40] M. Saeedi, L. Li, A. Karbassi, A. Zanjani, Sorbed metals fractionation and risk assessment of release in river sediment and particulate matter, *Environ. Monit. Assess.*, 185 (2013) 1737–1754.
- [41] M. Saeedi, S. Daneshvar, A. Karbassi, Role of riverine sediment and particulate matter in adsorption of heavy metals, *Int. J. Environ. Sci. Technol.*, 1 (2004) 135–140.