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Effect of dissolved organic carbon and salinity on flocculation process of heavy metals during mixing of the Navrud River water with Caspian Seawater

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ABSTRACT

Behavior of dissolved metals during estuarine mixing can significantly influence the chemical mass balance between fresh water and saline water. The flocculation of dissolved metals has an important role in self-purification of heavy metals during estuarine mixing. Most studies in the field of flocculation of dissolved metals have only focused on effects of salinity on flocculation of heavy metals. The aim of this study was to evaluate and validate effect of dissolved organic carbon (DOC); and salinity on flocculation of dissolved metals (Cu, Mn, Ni, Zn, and Pb) was investigated on a series of mixtures with salinities ranging from 0.6 to 2.7 ppt at various DOC values (3.2, 7.2, and 10.3 mg/L) during mixing of Navrud River water with Caspian Seawater. The results of mixing of a filtered seawater sample (0.45 μm) with a filtered water sample taken from the Navrud River at constant salinity regimes (0.6‰) and at different DOC (3.2, 7.2, and 10.3 mg/L) indicates that Ni, Zn, and Pb have non-conservative behavior and Cu and Mn have conservative behavior [Ni (79.05) > Pb(75.14) > Zn(38.45) > Cu(24.82) > Mn(17.97)]. Also, increasing DOC values (3.2–10.4 mg/L) at constant salinities, lead to increment of maximum flocculation rate of copper. The flocculation trends at constant salinity regimes (1.1 and 2.1 ppt) at various DOCs (DOC = 7.3, 10.4 mg/L) indicate that Mn, Ni, Zn, and Pb have non-conservative behavior and Cu has conservative behavior. It is also important to note that Ni has maximum rate of flocculation at various DOCs and at constant salinity of 2.7 ppt. According to the mean annual discharge of the Navrud River (166 × 10^6 m^3/year), the annual discharge of dissolved Cu, Mn, Ni, Zn,and Pb into the Caspian Sea would reduce from 6.20, 4.88, 12.31, 23.78, 2.69 to 4.37, 3.06, 1.45, 4.92, 0.41 tons/year, respectively.

Keywords: Flocculation; Salinity; DOC; Micro nutrients; Caspian Sea

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1. Introduction

Estuaries are the meeting place of freshwater from river and saltwater from the sea where salinity variations in space are so large [1]. These dynamic eco tones are very important aquatic systems by preserving the costal biota [2–4] and import/export large amount of organic and inorganic materials from natural and anthropogenic sources [5,6]. The majority of estuaries receive a high heavy-metal input from industries. There has been growing concern about the inflow of heavy metals and their compounds to the coastal areas because they can be toxic to aquatic ecosystems and human health. Since saline water composition is fairly constant, the dissolved material that gets carried by river to the sea must be subjected to removal processes [1,7]. During estuarine mixing, considerable amount of the dissolved metals supplied by the river come into the particulate phase due to flocculation processes [8–11]. The flocculation of dissolved elements especially in the upper part of the estuary, where lower salinity regimes are found is a consequence of estuarine mixing [12–14]. Therefore, the flocculation of dissolved elements can affect elemental composition of the sea water [15–19]. Although many investigations have been performed over the years to find out controlling mechanisms of flocculation process, there is not a great deal of information on recognition of dissolved metals flocculation processes during estuarine mixing of river waters with saline waters such as the Caspian Seawater [20–22]. Most studies in the field of flocculation processes have only focused on colloidal stability, surface properties, salinity, and pH [23–25]. It should be pointed out that some studies showed DOC as the main governing reason in flocculation of trace elements [26–28]. Such studies have focused the role of heavy metals on the initial steps of flocculation (especially of the riverine hydrophobic humic component) across an estuarine salinity gradient. Much of this humic material was made up of humic acids [9,28–30]. Spectral absorption and other optical techniques for measuring the chromophoric component of estuarine dissolved organic carbon have been used to assess DOC sources and behavior in estuaries [31–34]. In a global analysis of river DOC, [6] reported that DOC concentrations typically range from as low of 1–3 mg/L in river of arid and semiarid regions to high of 7–9 mg/L typical of rivers from the taiga and wet tropics. This paper critically has discussed effects of salinity and DOC on flocculation of dissolved metals during estuarine mixing. In addition, the efficiency of DOC in removing studied metals from mixed water under different amount of humic acids was investigated.

2. Materials and Methods

The Caspian Sea, the largest island water body on earth, is surrounded by the states of Azerbaijan, Federation of Russia, Iran, Kazakhstan, and Turkmenistan [35]. It is a landlocked sea with semi-saline water, covering an area of about 436,000 km^2, a drainage area of 3.5 million km^2, and a volume of 78,000 km^3. The Caspian Sea water salinity varies from 4 ppt in the northern parts to 13 ppt in the southern parts.

The Navrud River, located on the north highlands of the Alborz mountain range, has a length of 33 km with a discharge of 5.24 m^3/s. Its average annual rate of precipitation discharge is 850 mm/year and its watershed covers an area of 274 km^2. The river acts as a main irrigation source for lands, industrial units, and fish farming projects as well as tens of cities and villages [36]. The huge amount of municipal, industrial, and agricultural wastewater containing heavy metals discharges into the Navrud River [36]. Freshwater sample was collected from the surface of the Navrud River in pre-labeled and 25-L polyethylene buckets (Ca. 16 km upstream). Fig. 1 shows the location of the freshwater sample from the Navrud River and the Caspian Sea.

On the same day, freshwater sample from the Navrud River upstream was filtered through 0.45 μm Millipore AP and HA filters. Freshwater samples were supplemented with calibrated dissolved metal concentrations. About 1 L of filtered water was acidified with concentrated nitric acid (HNO_3) to a pH of approximately 1.8 stored in high-density polyethylene bottles in a refrigerator prior to the analysis of dissolved heavy metals (Ni, Cu, Zn, Pb, Mn). Similarly, on the same day, the saline water sample was collected approximately 20 km away from the shore to ensure that the sample was not diluted by freshwater of the river (seawater salinity = 12.5‰). All equipment must be maintained scrupulously clean and should be sanitized and acidified (acid washed) with aqua regia (mixture of HNO_3 and HCl) in order to prevent the contamination of the samples and then was washed with Milli-Q water. Filtered river water and sea water were mixed in 15 different aquariums at room temperature (25 ℃) in various proportions yielding salinities from 0.6 to 2.7‰ (44, 88, 132, 176, and 220 mL of seawater per 1000 mL of fresh water) with three series of DOCs (DOC = 3.2, 7.3, and 10.4 mg/L) as shown in Fig. 2. Humic acid was used in order to manipulate the DOC in each and every one of the 15 aquariums with various salinities. Then, the samples were stirred occasionally during the first hour as the flocculates started to form. Subsequently, the mixture of two waters was left for 24 h to ensure

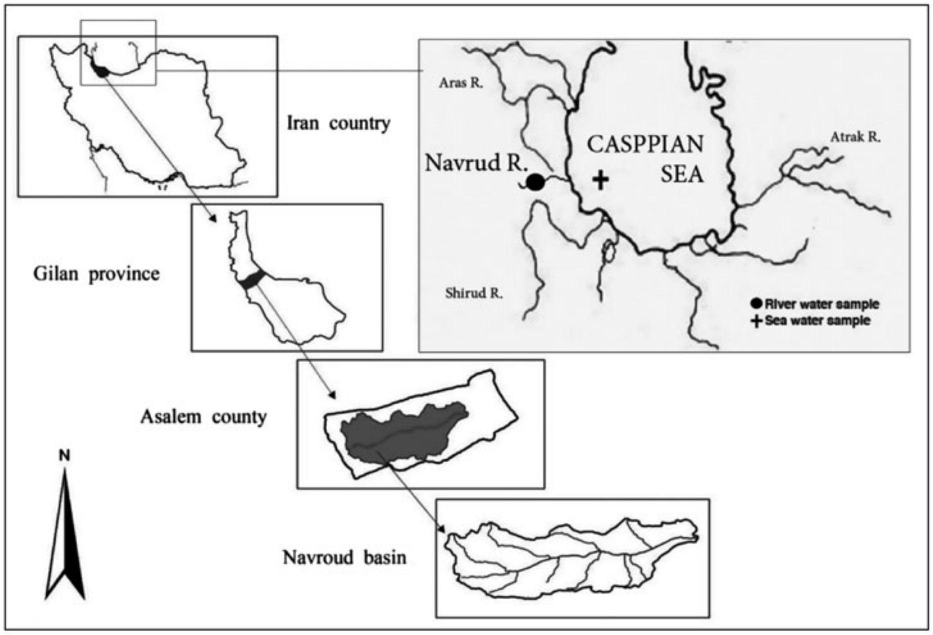

Fig. 1. Sampling location from Navrud River and Caspian Sea.

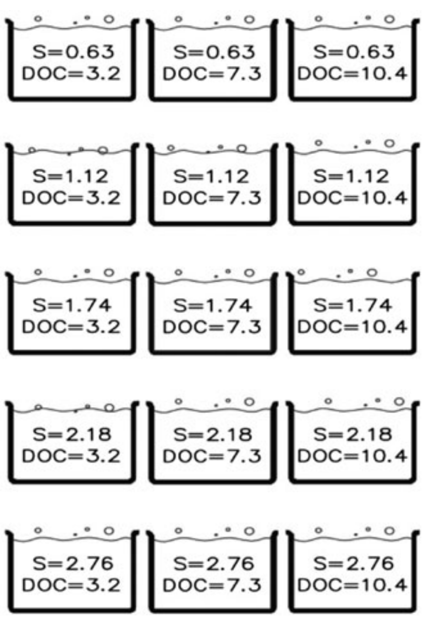

Fig. 2. DOCs (mg/L) and salinities (‰) adjusted in aquariums.

complete flocculation. After 24 h, 50 mL of the mixed samples from each aquarium was taken to measure the physicochemical parameters such as temperature, salinity, and DOC of aliquots.

The resulting flocculated elements (colloidal metals that are bonded to each other) were collected from each aquarium on 2.5-cm diameter Millipore membrane filters (type HA, pore size 0.45 μm). Millipore filters were digested using 5 mL of concentrated nitric acid (HNO_3) overnight. Finally, the concentrations of heavy metals (Cu, Mn, Ni, Zn, Pb) in the samples were determined by inductively coupled plasma-atomic emission spectroscopy (ULTIMA 2000). Procedural blanks and duplicates were analyzed with the samples in a similar way. The ICP was calibrated with commercially available standards purchased from $SPEX_{cerprep}$ Company. The value of the analysis accuracy was approximately ±5% for all elements in the dissolved and flocculent phases. Table 1 shows summary of methods and apparatuses used in this investigation for assessment of different parameters.

3. Results and Discussions

As mentioned in the previous section, following the mixing of freshwater with seawater, the concentrations of metals at various salinities (0.6–2.7 ppt) and various DOCs values (DOC = 3.2, 7.1, and 10.4 mg/L) were measured and recorded in laboratory as shown in Tables 2 and 3.

However, The mixing of river water with seawater in natural estuary and flocculation process, may not occur as shown in Tables 2 and 3, actually at the very initial stage of the mixing of the river water with saline water, high levels of dissolved metals ooze out of the freshwater in the form of flocculants [37–40].

Table 1
Methods and apparatus used for 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)

Table 2
Laboratory flocculation of metals during mixing of Navrud River water with Caspian Seawater [at constant salinities (‰)]

Sample	Cu (μg/L)	Mn (μg/L)	Ni (μg/L)	Zn (μg/L)	Pb (μg/L)	DOC (mg/L)	Salinity (‰)
River water	37.47	29.55	74.50	143.90	16.29	3.20	0.24
1	9.30 (24.82)	5.31 (17.97)	26.52 (35.60)	0.00 (00.00)	6.12 (37.57)	3.20	0.63
2	8.70 (23.22)	4.16 (14.06)	58.89 (79.05)	76.23 (52.97)	12.24 (75.14)	7.32	0.63
3	9.15 (24.42)	4.01 (13.55)	48.81 (65.52)	110.67 (76.91)	6.17 (37.85)	10.41	0.63
1	8.10 (21.62)	5.39 (18.22)	29.58 (39.70)	29.40 (20.43)	6.09 (37.38)	3.20	1.12
2	8.46 (22.58)	8.25 (27.92)	37.20 (49.93)	54.56 (37.91)	13.55 (83.15)	7.32	1.12
3	9.51 (25.38)	6.00 (20.30)	42.60 (57.18)	37.02 (25.73)	6.19 (38.03)	10.41	1.12
1	9.60 (25.62)	7.74 (26.19)	46.89 (62.94)	24.45 (16.99)	15.02 (92.17)	3.20	1.74
2	15.45 (41.23)	8.76 (29.64)	50.52 (67.81)	52.20 (36.28)	9.56 (58.66)	7.32	1.74
3	18.90 (50.44)	9.72 (32.89)	44.06 (59.13)	54.30 (37.73)	12.38 (75.97)	10.41	1.74
1	9.60 (25.62)	13.52 (45.74)	63.15 (84.77)	109.8 (76.30)	14.01 (86.00)	3.20	2.18
2	6.41 (17.09)	15.47 (52.34)	48.84 (65.56)	42.15 (29.29)	12.72 (78.08)	7.32	2.18
3	8.70 (23.22)	17.1 (57.87)	57.39 (77.03)	50.10 (34.82)	13.82 (84.81)	10.41	2.18
1	11.04 (29.46)	8.04 (27.21)	65.70 (88.19)	21.00 (14.59)	12.41 (76.15)	3.20	2.76
2	12.45 (33.23)	18.79 (63.60)	69.30 (93.02)	139.88 (97.20)	4.64 (28.45)	7.32	2.76
3	21.84 (58.29)	3.24 (10.96)	72.75 (97.65)	0.00 (0.00)	15.05 (92.36)	10.41	2.76

Note: Values within brackets indicate % removal in comparison with total metal content present in freshwater.

Table 3
Laboratory flocculation of metals during mixing of Navrud River water with Caspian Seawater [at constant DOCs]

Sample	Cu (μg/L)	Mn (μg/L)	Ni (μg/L)	Zn (μg/L)	Pb (μg/L)	Salinity (‰)	DOC (mg/L)
River water	37.47	29.55	74.50	143.90	16.29	0.24	3.20
1	9.30 (24.82)	5.31 (17.97)	26.52 (35.60)	0.00 (0.00)	6.12 (37.57)	0.63	3.20
2	8.10 (21.62)	5.39 (18.22)	29.58 (39.70)	29.40 (20.43)	6.09 (37.38)	1.12	3.20
3	9.60 (25.62)	7.74 (26.19)	46.89 (62.94)	24.45 (16.99)	15.02 (92.17)	1.74	3.20
4	9.61 (25.62)	13.52 (45.74)	63.15 (84.77)	109.80 (76.30)	14.01 (86.00)	2.18	3.20
5	11.04 (29.46)	8.04 (27.21)	65.70 (88.19)	21.00 (14.59)	12.41 (76.15)	2.76	3.20
1	8.70 (23.22)	4.16 (14.06)	58.89 (79.05)	38.12 (26.49)	12.24 (75.14)	0.63	7.32
2	8.46 (22.58)	8.25 (27.92)	55.80 (74.90)	54.56 (37.91)	13.55 (83.15)	1.12	7.32
3	15.45 (41.23)	8.76 (29.64)	50.52 (67.81)	52.20 (36.28)	9.56 (58.66)	1.74	7.32
4	6.36 (16.97)	15.47 (52.34)	48.84 (65.56)	42.15 (29.29)	12.72 (78.08)	2.18	7.32
5	12.45 (33.23)	18.79 (63.60)	69.30 (93.02)	139.88 (97.20)	4.64 (28.45)	2.76	7.32
1	9.15 (24.42)	4.01 (13.55)	48.81 (65.52)	55.34 (38.45)	6.17 (37.85)	0.63	10.41
2	9.51 (25.38)	6.00 (20.30)	42.60 (57.18)	37.02 (25.73)	6.19 (38.03)	1.12	10.41
3	18.90 (50.44)	9.72 (32.89)	44.06 (59.13)	54.30 (37.73)	12.38 (75.97)	1.74	10.41
4	8.70 (23.22)	17.10 (57.87)	57.39 (77.03)	50.10 (34.82)	13.82 (84.81)	2.18	10.41
5	21.84 (58.29)	3.24 (10.96)	72.75 (97.65)	0.00 (0.00)	15.00 (92.08)	2.76	10.41

Note: Values within brackets indicate % removal in comparison with total metal content present in freshwater.

Eventually, freshwater may include less flocculates in contrast with its initial contents at the later stages of estuarine mixing. During laboratory conditions, some certain amount of river water was mixed with various proportions of saline water. In this way, the flocculate quantity is not calibrated to the very first concentrations of the metals in the river water. The data of elemental content are also summarized in Tables 4 and 5 that are actually derived from Tables 2 and 3 by subtracting the concentration of flocculates at each salinity regime from the sum of previous stages [13,21,25,38].

A number of studies have found that "salinity" is a general term which does not state the effect of other components of saline water on the colloidal metal flocculation process in estuarine mixing [5,13]. Therefore, other parameters such as DOC, DO, EC, and Eh can play significant roles on the flocculation process of elements during the mixing of freshwater with seawater [13,38]. According to the data shown in Tables 4 and 5, the maximal mean removal of studied metal (73.60%) occurs at salinity = 2.7 ppt with various DOCs (mg/L). Also, it should be added that at DOC = 7.3 mg/L with various salinity regimes recorded high mean removal of studied metals. The mean removal of all studied metals in Navrud River at constant salinity regimes with various DOCs and at constant DOC values with different salinity regimes are in the following orders, respectively, salinity = 2.7 ppt (73.60%) > 2.1 ppt (66.20%) > 1.7 ppt (56.21%) > 1.1 ppt (48.20%) > 0.6 ppt (47.09%), DOC = 7.3 mg/L (75.64%) > 10.4 mg/L (72.25%) > 3.20 mg/L (63.83%). Based on the above results, increasing salinity ranges lead to increment of mean removal of studied metals. The variation in the maximal removal of the elements studied may be due to destabilization dissolved elements, corresponding to the different stages of mixing with seawater and a decrease in their negative net charge [41].

Previous studies have reported that Pb and Ni have minimum flocculation rates in contrast with those of Cu, Zn, and Mn in the northern part of Iran [4,5]. The results of this study indicate that Ni undergoes maximum flocculation at various salinity regimes (0.6–2.7 ppt) and different DOC values. This might be due to higher initial metal contents in Navrud River water than in other northern rivers of Iran.

Biati and karbassi [37] suggested that further researches need to be carried out to find out the governing factor of Zn and Ni. In the issue currently under discussion, flocculation rate of Ni is governed by salinity with constant DOCs values. As mentioned above, the mean removal of studied metals is raising by increasing salinity ranges. Salinity play role in the flocculation of studied metals which is in accordance with the finding of some researchers [8,30,37,38]. De facto, increasing

Table 4
Actual flocculation of metals during mixing of Navrud River water with Caspian Seawater (at constant salinities ‰)

Sample	Cu (μg/L)	Mn (μg/L)	Ni (μg/L)	Zn (μg/L)	Pb (μg/L)	DOC (mg/L)	Salinity (‰)
River water	37.47	29.55	74.50	143.90	16.29	3.20	0.24
1	6.20 (24.82)	5.31 (17.97)	26.52 (35.60)	0.00 (0.00)	6.12 (37.57)	3.20	0.63
2	0.00 (0.00)	0.00 (0.00)	32.37 (43.45)	38.12 (26.49)	6.12 (37.57)	7.32	0.63
3	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	17.22 (11.97)	0.00 (0.00)	10.41	0.63
Total	6.20 (24.82)	5.31 (17.97)	58.89 (79.05)	55.34 (38.45)	12.24 (75.14)		
1	8.10 (21.62)	5.39 (18.22)	29.58 (39.70)	29.4 (20.43)	6.09 (37.38)	3.20	1.12
2	0.36 (0.96)	2.87 (9.70)	26.22 (35.19)	25.16 (17.48)	6.11 (37.48)	7.32	1.12
3	1.05 (2.80)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	10.41	1.12
Total	9.51 (25.38)	8.25 (27.92)	55.80 (74.90)	54.56 (37.91)	12.20 (74.86)		
1	9.60 (25.62)	7.74 (26.19)	46.89 (62.94)	24.45 (16.99)	15.02 (92.17)	3.20	1.74
2	5.85 (15.61)	1.02 (3.45)	3.63 (4.87)	27.75 (19.28)	0.00 (0.00)	7.32	1.74
3	3.45 (9.21)	0.96 (3.25)	0.00 (0.00)	2.10 (1.46)	0.00 (0.00)	10.41	1.74
Total	18.90 (50.44)	9.72 (32.89)	50.52 (67.81)	54.30 (37.73)	15.02 (92.17)		
1	9.60 (25.62)	13.52 (45.74)	63.15 (84.77)	109.80 (76.30)	14.01 (86.00)	3.20	2.18
2	0.00 (0.00)	1.95 (6.60)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	7.32	2.18
3	0.00 (0.00)	1.64 (5.53)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	10.41	2.18
Total	9.60 (25.62)	17.10 (57.87)	63.15 (84.77)	109.80 (76.30)	14.01 (86.00)		
1	11.04 (29.46)	8.04 (27.21)	65.7 (88.19)	21.00 (14.59)	12.41 (76.15)	3.20	2.76
2	1.41 (3.76)	10.76 (36.40)	3.60 (4.83)	118.88 (82.61)	0.00 (0.00)	7.32	2.76
3	9.39 (25.06)	0.00 (0.00)	3.45 (4.63)	0.00 (0.00)	2.64 (16.21)	10.41	2.76
Total	21.84 (58.29)	18.80 (63.60)	72.75 (97.65)	139.88 (97.20)	15.05 (92.36)		

Note: Values within brackets indicate % removal in comparison with total metal content present in freshwater.

Table 5
Actual flocculation of metals during mixing of Navrud River water with Caspian Seawater [at constant DOCs (mg/L)]

Sample	Cu (μg/L)	Mn (μg/L)	Ni (μg/L)	Zn (μg/L)	Pb (μg/L)	Salinity (‰)	DOC (mg/L)
River water	33	16	16	230	10	0.24	3.20
1	9.30 (24.82)	9.30 (31.47)	26.52 (35.60)	0.00 (0.00)	6.12 (37.57)	0.63	3.20
2	0.00 (0.00)	0.00 (0.00)	3.06 (4.11)	29.40 (20.43)	0.00 (0.00)	1.12	3.20
3	0.30 (0.80)	0.30 (1.02)	17.31 (23.23)	0.00 (0.00)	7.69 (47.24)	1.74	3.20
4	0.00 (0.00)	0.00 (0.00)	16.26 (21.83)	80.40 (55.87)	0.00 (0.00)	2.18	3.20
5	1.44 (3.84)	1.44 (4.87)	2.55 (3.42)	0.00 (0.00)	0.00 (0.00)	2.76	3.20
Total	11.04 (29.46)	11.04 (37.36)	62.70 (88.19)	109.80 (79.30)	13.82 (84.81)		
1	8.70 (23.22)	4.16 (14.06)	58.89 (79.05)	38.12 (26.49)	12.24 (75.14)	0.63	7.32
2	0.00 (0.00)	4.10 (13.86)	0.00 (0.00)	16.44 (11.42)	1.31 (8.01)	1.12	7.32
3	6.75 (18.01)	0.51 (1.73)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	1.74	7.32
4	0.00 (0.00)	6.71 (22.69)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	2.18	7.32
5	0.00 (0.00)	3.33 (11.27)	10.41 (13.97)	85.32 (59.29)	0.00 (0.00)	2.76	7.32
Total	15.45 (41.23)	18.80 (63.60)	69.30 (93.02)	139.88 (97.20)	13.55 (83.15)		
1	9.15 (24.42)	4.01 (13.55)	48.81 (65.52)	55.34 (38.45)	6.17 (37.85)	0.63	10.41
2	0.36 (0.96)	2.00 (6.75)	0.00 (0.00)	0.00 (0.00)	0.03 (0.18)	1.12	10.41
3	9.39 (25.06)	3.72 (12.59)	0.00 (0.00)	0.00 (0.00)	6.18 (37.94)	1.74	10.41
4	0.00 (0.00)	7.38 (24.97)	8.58 (11.52)	0.00 (0.00)	1.44 (8.84)	2.18	10.41
5	2.94 (7.85)	0.00 (0.00)	15.36 (20.62)	0.00 (0.00)	1.19 (7.27)	2.76	10.41
Total	21.84 (58.29)	17.10 (57.87)	72.75 (97.65)	55.34 (38.45)	15.00 (92.08)		

Note: Values within brackets indicate % removal in comparison with total metal content present in freshwater.

saline's values (0.6–2.7 mg/L) lead to increase of total flocculation rate of Ni [Constant DOC = 10.4 mg/L (97.65%) > 7.3 mg/L (93.02%) > 62.70 mg/L (88.19)]. It is also important to note that the minimum of flocculation of Ni occurs at salinity of 1.7 ppt, and under various DOC (DOC = 3.2, 7.3, and 10.4 mg/L) and at DOC of 10.4 mg/L along with various salinity ranges (0.6–2.7 ppt).

According to the data shown in Table 5, the flocculation of studied metals except for Zn occurs in salinity lower than 2.1 ppt and this is in accordance with other researchers [40]. In the most cases maximal removal of heavy metals occur at constant salinities and at DOCs of 3.2 mg/L. It is important to note that flocculation of all studied metals sharply decrease at constant salinities at DOCs of 10.4 mg/L.

The mean annual discharge of Navrud River is 5.24 m^3/s. The natural flocculation of heavy metals in Navrud River estuary occur at DOC of 3.2 mg/L and various salinity, the flocculation rates reveal that dissolved Ni pollution load (74.50 μg/L) would be reduced from 12.31 to 1.45 ton/year.

Considering the concentration of dissolved copper in the Navrud River [Cu(37.47 μg/L)] and the mean discharge of the river (5.24 m^3/s), the mean annual inputs of dissolved Cu into the Caspian Sea via this river would be 6.20 ton/year. The results of the present study (Table 5) indicate that 29.46% of dissolved concentration of Cu flocculated during estuarine mixing. Therefore, the mean annual discharge of dissolved Cu from Navrud River into the Caspian Sea would be reduce from 6.20 to 4.37 ton/year. It is important to note that maximal removal of Cu (29.46%) and Ni (88.19%) occur at constant salinity of 2.7 ppt and DOC of 3.2 mg/L.

At constant salinities, increasing DOC values (3.2–10.4 mg/L) lead to increment of maximum flocculation rate of copper [Constant salinity = 2.7 ppt (29.46%) > 2.1 ppt (25.62%) > 1.7 ppt (25.62%) > 1.1 ppt (21.62%)]. The result shows that copper is controlled by dissolved organic carbon (DOC) at constant salinity ranges and different DOC values.

The maximum flocculation rate of Mn(45.74%) occurs in DOC of 3.2 mg/L and constant salinity of 2.1 ppt, whereas the highest flocculation of Mn (63.60%) occur at constant salinities of 2.7 ppt and various DOC ranges and at constant DOC of 7.32 mg/L and salinity of 2.1 ppt also. Increasing DOC values (3.2–10.4 mg/L) lead to increment of flocculation rate of Manganese [constant salinity = 2.7 ppt (63.60%) > 2.1 ppt (57.87%) > 1.7(32.89%) > 1.1 ppt (27.92%) > 0.6 ppt (17.97%)]. Above results indicate that the flocculation process of Mn is mainly controlled by DOC at constant salinity values.

The concentration of Mn is 29.55 μg/L in Navrud River. In addition, the mean annual inputs of dissolved Mn into the Caspian Sea via this river would

Table 6
Order of metal flocculation rate during the mixing of the Navrud River with Caspian Sea (% of total metal content)

S = 0.6‰ & DOC = 3.2, 7.3, 10.4 mg/L	Ni(79.05) > Pb(75.14) > Zn(38.45) > Cu(24.82) > Mn(17.97)
S = 1.1‰ & DOC = 3.2, 7.3, 10.4 mg/L	Ni(74.90) > Pb(74.86) > Zn(37.92) > Mn(27.92) > Cu(25.38)
S = 1.7‰ & DOC = 3.2, 7.3, 10.4 mg/L	Pb(92.17) > Ni(67.81) > Cu(50.44) > Zn(37.73) > Mn(32.89)
S = 2.1‰ & DOC = 3.2, 7.3, 10.4 mg/L	Pb(86.00) > Ni(84.77) > Zn(76.30) > Mn(57.87) > Cu(25.62)
S = 2.7‰ & DOC = 3.2, 7.3, 10.4 mg/L	Ni(97.65) > Zn(92.20) > Pb(92.36) > Mn(63.60) > Cu(21.84)

Table 7
Order of metal flocculation rate during the mixing of the Navrud River with Caspian Sea (% of total metal content)

DOC = 3.2 mg/L & S = 0.63–2.76‰	Ni(88.19) > Pb(84.81) > Zn(79.30) > Mn(37.36) > Cu(29.46)
DOC = 7.3 mg/L & S = 0.63–2.76‰	Zn(97.21) > Ni(93.02) > Pb(83.15) > Mn(63.60) > Cu(41.23)
DOC = 10.4 mg/L & S = 0.63–2.76‰	Ni(97.65) > Pb(92.08) > Cu(58.29) > Mn(57.87) > Zn(55.34)

be 4.88 ton/year. The results of the present study (Table 5) indicate that 37.36% of dissolved concentration of Mn flocculated during estuarine mixing. Therefore, the mean annual discharge of dissolved Mn from Navrud River into the Caspian Sea would be reduced from 4.88 to 3.06 ton/year. It is interesting to note that Mn shows minimum flocculation rate (Mn = 17.97%) at salinity of 0.6 ppt and at various DOC (DOC = 3.2, 7.3, and 10.4).

About 79.3% of total Zn content flocculates during estuarine mixing, equal to 6 μg/L. The flocculation rates of Zn (37.73%, 76.3%, 97.2) have substantial boosts at constant salinity ranges (from 1.7 to 2.7 ppt) and at various DOCs. The initial concentration of Pb in Navrud water is 16.29 μg/L, and only 13.82 μg/L of Pb flocculates during estuarine mixing (about 85% of total Pb concentration). Interestingly, maximum flocculation rates of Pb (37.57, 37.38, 92.17, 86, and 76.15%) occur at constant salinities (0.6–2.7) and DOC of 3.2 mg/L. As mentioned above, the flocculation process of Pb is mainly controlled by salinity at constant DOC values.

In the present study, Ni has maximum rate of flocculation at various DOCs and at constant salinities of 2.7 ppt. The most interesting finding is that the maximum flocculation rate (Zn, Mn, Cu, Pb, and Ni) occurs at the salinities of 0.6–1.7 which is compatible with the finding of other investigation in northern Iranian estuaries [37,39,40]. Based on most investigations, maximum iron removal occurs at salinity ranges of 0–5‰ [9]. Percentages of metal removal at low salinity regimes (0.6–2.7 ppt) with constant pH values (DOC = 3.2, 7.3, and 10.4 mg/L) are shown in Tables 6 and 7.

The present investigation shows higher flocculation rates in the earlier stages of an estuarine mixing process that is in agreement with the some previous works [42–44]. Flocculation mechanisms of metals may vary at various estuarine regions. Though some studies have shown that flocculation process is pH dependent [45], it is found that in the present investigation, DOC can also govern the flocculation of metals effectively. As a matter of fact, diverse mechanism has been suggested for flocculation of metals during estuarine processes [46].

4. Conclusion

The aim of this study was to evaluate and validate the effect of DOC and salinity on flocculation process of heavy metals during mixing of Navrud River water with Caspian Sea. The maximum flocculation rate at different salinities (0.6–2.7‰) and with DOC of 3.2, 7.3, and 10.4 mg/L was recorded for Ni except for the DOC of 7.3 mg/L and different salinity regimes (0.6–2.7‰). The maximal metal removal (Zn, Mn, Cu, Pb, and Ni) occurred at the first stage of estuarine mixing. DOC could play a significant role in flocculation of dissolved Ni, Pb, and Cu at different salinity (0.6–2.7‰) with constant DOC values (DOC = 3.2, 7.3, and 10.4). The result showed that, the lowest percentage of flocculation belongs to Mn (Mn = 17.97%) at constant salinity (S = 0.64 ppt) with different DOCs (DOC = 3.2, 7.3, and 10.4). The flocculation process of Pb is just mainly controlled by salinity at DOC of 3.2. Also, flocculation rates of Ni governed by salinity. The lowest flocculation rates of Mn (17.97%) and Cu (24.82%) are recorded at constant salinity (S = 0.6 ppt) with various DOC values (DOC = 3.2, 7.3, and 10.4 mg/L). In present study, flocculation rates of metals shown that the overall colloidal metal pollution loads could be reduced by different percentages (ranging from Mn = 17.97 and Ni = 97.65%) during the mixing of the Navrud River with Caspian Seawater. The maximum mean removal of all studied metals (75.64%) recorded at constant DOC = 7.3 mg/L with various salinities. Also, it should be pointed out that minimum mean removal of studied metals occurs at constant salinity = 0.6 ppt with various DOCs. Many investigations have been carried out about variation in the rate of flocculation of heavy elements throughout the year in a specific river or from river to river. In all such investigations salinity of brackish water is known as a constant parameter. Therefore, other constituents of sea water (than salinity) that are variable throughout the year should have been taken into the consideration. Considering the mean annual discharge of Navrud River (5.24 m^3/s) and concentration of dissolved elements in Navrud River water, the mean annual discharge of dissolved metals (Cu, Mn, Ni, Zn, and Pb) into the Caspian Sea via this river would be reduced from 6.20, 4.88, 12.31, 23.78, 2.69 to 4.37, 3.06, 1.45, 4.92, 0.41 tons/year, respectively. This statement not only proved the significant role of the flocculation processes of dissolved elements in the natural self-purification of estuarine zone, but also shown the ecological noticeable role of the estuarine processes. Further studies on the current topic are therefore recommended.

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