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Role of metal species in flocculation rate during estuarine mixing

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ABSTRACT: Flocculation can be considered as an effective mechanism in self-purification of metals during estuarine mixing. In the present investigation, flocculation of metals during mixing of Minab River water with the Strait of Hormuz (The Persian Gulf) water is studied for the first time. Flocculation behavior of metals (except for Pb) is governed by dissolved organic carbon. The source of dissolved organic carbon is terrigenous in the estuarine waters of study area. The general pattern of flocculation of studied metals is manganese (180 µg/L) > zinc (88 µg/L)> nickle (73 µg/L)> copper (30 µg/L)> lead (19 µg/L). The results of present study show that metal species are a very important factor in overall flocculation rate. It is found that solids and oxides have the highest and lowest flocculation levels, respectively. Eh-pH diagram indicated that lead is present as lead oxide in Minab River water and the least flocculation rate is attributed to this element. The results also showed that flocculation rate of metal species could be as solids > free ions ≈ hydroxides > oxides. The amount of metal flocculation is about 30.5, 6.6, 25.3, 10.4 and 62.5 ton/y for zinc, Pb, Ni, Cu and Mn, respectively.

Keywords: *Environment; Estuary; Flocculation; Metal; Pollution; River; Species; Water*

INTRODUCTION

Fluxes of materials (dissolved and particulate matters) find their way into lakes and seas through rivers (Meybeck, 1988). Estuaries are the major biogeochemical interfaces between land and sea where terrigenous elements born by river on their way to the sea under go various changes (Sharp *et al.*, 1982; Breuer *et al.*, 1999). Mixing of river and seawater results in flocculation of trace metals especially in the upper part of the estuary where lower salinity regimes are found (Gerringa *et al.*, 2001; Karbassi *et al.*, 2008a; Biati *et al.*, 2010). Due to the flocculation process a large portion of the dissolved metals supplied by the river come into particulate phase (Eckert and Sholkvitz, 1976; Boyle, 1977; Sholkovitz *et al.*, 1977; Karbassi *et al.*, 2008b; c). Thus, estuarine processes can influence elemental composition of the sea water (Sillen, 1961; Mackenzie and Garrels, 1966; Mackenzie, 1975; Troup and Bricker, 1975; Nouri *et al.*, 2008a). The two important mechanisms affecting the concentration and distribution of trace metals during estuarine mixing have been successfully modeled by water-column mixing experiments (Sholkovitz, 1976; Comans and Van Dijk, 1988; Samarghandi *et al.*, 2007). These two counteractive, non biological mechanisms are desorption of metals from resuspension of riverine particles and flocculation of metals-humate from solution (Li *et al.*, 1984). Controlling mechanisms of flocculation process have been investigated intensively. In wetlands, flocculation is enhanced by increased pH, turbulence, concentration of suspended matters, ionic strength and high algal concentration (Matagi *et al.*, 1998; Zvinowanda *et al.*, 2009). Flocculation mechanisms are mainly due to colloidal stability, surface properties, humic acids, salinity and pH (Hunter, 1983; Zhiging, *et al.*, 1987; Featherstone and O'Grady, 1997; Karbassi *et al.*, 2007). Removal of significant amounts of reiverine dissolved organic carbon (DOC) may occur due to flocculation or precipitation reactions that result in the conversion of DOC to particulate organic carbon and their subsequent settlement on to the sediments (Sholkovitz, 1976; Nouri *et al.*, 2008b). Production of autochthonous DOC in estuaries may also occur through several processes (Sharp, 1991; Aliabadi *et al.*, 2006). Although many studies have reported conservative mixing of DOC during estuarine transport (Moor *et al.*, 1979;

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Laane, 1980; Sharp *et al.*, 1982; Mantoura and Woodward, 1983; Aminot *et al.*, 1990), some investigations displayed a relatively dynamic DOC pool (Doering *et al.*, 1994). Redox processes is of major concern for mobilization of trace metals in estuaries where an oxygen gradient exists in addition to the salinity gradient (Gerringa *et al.*, 2001; Abdel-Ghani *et al.*, 2009). A combination of high organic matter content and a long residence time, may result in development of anoxic conditions that may be either restricted to the sediments (Westerlund *et al.*, 1986; Kerner and Wallmann 1992) or can occur in the water column (Zwolsman and Van Eck, 1993; Zwolsman *et al.*, 1997; Shiller and Mao, 1999). Sulfides of elements (e.g. zinc (Zn) and cadmium (Cd)) may precipitate in anoxic conditions (Malakootian *et al.*, 2009). In more saline parts of the estuary, some elements (e.g. Zn and Cd) are released in to the water as a result of oxidation (Sholkovitz, 1976; Duinker and Nolting, 1978; Duinker *et al.*, 1983; Wollast, 1988; Regnier and Wollast, 1993; Chiffoleau *et al.*, 1994; Paucot and Wollast, 1997). Flocculation process has been studied in northern part of Iran (Haraz, Sefidrud, Chalus, Talar, Tadjan and Gorgan rud rivers) (Karbassi and Nadjafpour, 1996; Karbassi *et al.*, 2007, 2008a). Such investigations has not been carried out in southern part of Iran. Present study would fill up such gap for southern coasts of Iran.

MATERIALS AND METHODS

Strait of Hormuz is an important corridor that connects Iran and other oil producing economic countries (OPEC) to the world's open seas. Strait of Hormuz has a width of 50 to 60 Km. Maximum depth of water in strait of Hormuz is 100 m. Minab Rive has a length of 200 Km and its average annual discharge is 10.99 m^3/ s. Minab River is formed by two main branches named Rudan in western part and Jaghin in eastern part. It lies between longitude of 57° 07´ and Latitude of 27 ° 09´. Various municipal and industrial waste water containing heavy metals and organics along with agricultural fertilizers, pesticides and herbicides enter into the Minab River. Fresh and saline water samples were collected in pre-cleaned 25 L polyethylene bucket from the Minab River upstream and Strait of Hormuz (16 Km away from river mouth), respectively (Fig. 1). Water sampling was carried out on 5th. October 2008. On the same day, water samples were filtered through 0.45 µm Millipore AP and HA filters. About one liter of filtered fresh water was acidified with concentrated HNO_3 to a pH of approximately 1.8 and stored in polyethylene bottles in a refrigerator prior to analysis of dissolved metals. Filtered river water and seawater were mixed together at room temperature (ca. 25 °C) in nine proportions yielding salinities of 3.3-29.7. The

Fig. 1: Locations of water samples from Minab River and Strait of Hormuz

Table 1: Methods and apparatus used for measurement of various parameters

Parameter	Method/ apparatus of measurement
Mn, Cu, Pb, Zn, Ni	ICP (JOBINYVON model JY138 ULTARCE
Ca, Mg	AAS (Varian, model Spectraa. 200)
Na	Flame photometer
pH/Eh	pH meter (Metrohm 744)
EC	Conductimeter (CRISON GLP32)
DO	DO meter (Inolab WTW)
DOC	Photo cathalitical oxidation method (ANATOC^{TM} SERIES II)
Chloride	Argentometric method (4500-Cl^{-}) (APHA, 2005)
Sulfate	Turbidimetric method (4500- SO_4^{-2}) (APHA, 2005)
Alkalinity of phenol and methyl	Titration method (2320) (APHA, 2005)
Salinity, carbonate, bicarbonate, total alkalinity	Titration method (APHA, 2005)
Temp. of water	Thermometer (accuracy of 1C°)

Table 2: Flocculants of trace metal contents (laboratory scale) along with pH, Eh, EC, temperature, salinity, DO and DOC – laboratory condition

Parameter aquarium No.	DOC (Mg/L)	DO (mg/L)	Salinity (ppt)	T (C°)	EC (µs/cm)	Eh (m V)	pH	Mn (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
River water	4.31	6.3	0.72	20.85	1900	-89	8.84	259	36	88	50	117
Seawater	3.13	5.3	37.5	23	59500	-60	8.32	75	3	15	3	12
1	4.60	6.6	3.3	22.3	6500	-77	8.67	85	14	55	5	37
2	0.97	6.7	8. 3	22.3	14000	-72	8.63	133	20	56	19	28
3	2.66	6.7	9.1	22.3	15000	-72	8.55	76	26	58	13	46
4	0.21	6.9	11.4	22.3	19000	-67	8.49	175	10	59	6	52
5	2.39	6.9	14.5	22.3	22575	-66	8.47	109	8	73	7	29
6	1.84	6.9	18.5	22.3	29500	-65	8.47	180	5	54	4	50
7	0.48	6.9	26.7	22.3	41500	-68	8.48	170	28	30	4	41
8	1.39	6.9	28.8	22.3	44500	-68	8.52	74	30	18	7	33
9	1.36	6.9	29.9	22.3	46250	-66	8.45	78	30	16	13	88
Total	-	-	-	-	-	-	-	1414	210	522	131	533

samples were kept for 24 h with occasional stirring. The resulting flocculants were collected on 47 mm diameter Millipore membrane filters (type HA, Pore size 0.45 µm) Millipore filters were digested using 5ml concentrated HNO_3 overnight. The concentrations of copper (Cu), zinc (Zn), nickel (Ni), lead (Pb) and manganese (Mn) were determined by ICP (JOBINYVON model JY 138 ULTRACE). Procedural blanks and duplicates were run with the samples in a similar way. Table 1 shows summary of methods used in the present investigation.

RESULTS AND DISCUSSION

The metal contents of flocculants along with pH, Eh, EC, temperature, salinity, DO and DOC are shown in Table 2. It should be pointed out that data on trace metal contents are not the real ones since flocculation processes carried out in laboratory scale does not occur in nature. In other words, at laboratory scale fresh water with its initial trace metal contents is mixed up with saline water. But, in the nature fresh water does not mixes up with saline water in the way it is mixed up. For instance, during the very first collision of fresh water with saline water, some trace metals ooze out of fresh water. Subsequently, in the next movement of fresh water towards sea, the river water will not possess its initial metal contents. Therefore, cumulative summation is used to convert the trace metal values obtained in Table 2 and the actual metal contents that occur in nature are presented in Table 3. Thus, the data in Table 2 will not be discussed further.

About 75% of total Zn contents (117 µg/L) flocculates during estuarine mixing. The highest flocculation of Zn (37 and 36 µg/L) is found at salinities of 3.3 and 29.9, respectively. The other salinities do not play an important role in the flocculation of Zn. It should be noted that amongst studied metals only Zn flocculates at salinity of 29.9.The initial concentration of Pb in Minab Rive water is 50 µg/L and only 19 µg/L of Pb flocculates during estuarine mixing (about 38 % of total Pb content). The flocculation of Pb is rather unique amongst studied metals (Zn, Ni, Cu and Mn) since its flocculation occurs at salinities of 3.3 and 8.3. The majority of Ni flocculation (about 55 µg/L) occurs

Table 3: Flocculants of trace metal contents (natural scale) along with pH, Eh, EC, temperature, salinity, DO and DOC - Natural condition

Parameter Aquarium No.	DOC (Mg/L)	DO (mg/L)	Salinity (ppt)	T (ºC)	EC (µs/cm)	Eh (mV)	pH	Mn (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
River water	4.31	6.3	0.72	20.85	1900	-89	8.84	259	36	88	50	117
Seawater	3.13	5.3	37.5	23	59500	-60	8.32	75	3	15	3	12
1	4.60	6.6	3.3	22.3	6500	-77	8.67	85 (32.8)	14 (38.9)	55 (62.5)	5 (10)	37 (31.6)
2	0.97	6.7	8. 3	22.3	14000	-72	8.63	48 (18.5)	6 (16.7)	1 (1.1)	14 (28)	0 (0)
3	2.66	6.7	9.1	22.3	15000	-72	8.55	0 (0)	6 (16.7)	2 (2.3)	0 (0)	9 (7.7)
4	0.21	6.9	11.4	22.3	19000	-67	8.49	42 (16.2)	0 (0)	1 (1.1)	0 (0)	6 (5.1)
5	2.39	6.9	14.5	22.3	22575	-66	8.47	0 (0)	0 (0)	14 (15.9)	0 (0)	0 (0)
6	1.84	6.9	18.5	22.3	29500	-65	8.47	5 (1.9)	0 (0)	0 (0)	0 (0)	0 (0)
7	0.48	6.9	26.7	22.3	41500	-68	8.48	0 (0)	2 (5.5)	0 (0)	0 (0)	0 (0)
8	1.39	6.9	28.8	22.3	44500	-68	8.52	0 (0)	2 (5.5)	0 (0)	0 (0)	0 (0)
9	1.36	6.9	29.9	22.3	46250	-66	8.45	0 (0)	0 (0)	0 (0)	0 (0)	36 (30.80)
Total	-	-	-	-	-	-	-	180 (69.4)	30 (83.3)	73 (82.9)	19 (38)	88 (75.2)

Table 4: Concentrations of anions and cations in river and Gulf waters along with aquariums

Parameter aquarium No.	SO_4 (mg/L)	HCO_3 (mg/L)	CO_3 (mg/L)	Total alkalinity (mg $CaCO_3$/L)	Cl (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)
River water	274.4	45.14	13.2	59	436.36	33.5	34.69	300
Seawater	1920.8	13.42	4.8	27	22727.27	4161	1288.8	9550
1	760.32	40.26	12	53	2000	228	156	1000
2	1070.16	35.38	12	49	5000	282.8	300	2800
3	1100	34.16	9.6	44	5500	276.1	440.3	3200
4	1350	32. 94	9.6	43	6900	389.9	623.6	3900
5	1262.24	32.94	8.4	41	8795	396	614.7	4600
6	1320	29.28	8.4	38	11230	432	723	4700
7	2003.12	29.28	7.2	36	16181.82	476	800.9	8325
8	1920.8	18.30	6.0	25	17454.54	425	806.2	9250
9	1975.68	24.4	7.2	32	18125	471	1021.4	9360

at 3.3 salinity. Flocculation of Ni ranges from 1 to 2 µg/L at salinities of 8.3 to 11.4 and again raises to 14 µg/L at salinity of 14.5 . Nickle does not flocculates at salinities higher than 14.5. In general, about 83% of total Ni content (88 µg/L) flocculates during estuarine mixing. The over all flocculation of Cu resembles Ni and 83 % of its initial content (36 µg/L) flocculates during estuarine mixing. The higher flocculation rate for Cu occurs at salinity of 3.3 its flocculation can be traced at other salinities (8.3 and 9.1) and to a lower extent at 26.7 and 28.8, as well. Highest flocculation of Mn (about 33 µg/L) occurs at 3.3. However, Mn flocculates at salinities of 8.3 and 11.4. In general, about 70 % of initial content of riverine Mn (259 µg/L) flocculates during estuarine mixing. The general pattern of flocculation of studied metals is Mn (180 µg/L) > Zn (88 µg/L) > Ni (73 µg/L) > Cu (30 µg/L) > Pb (19 µg/L). However, the percentages of flocculation taking into consideration the initial metal contents in river water is Cu (83.3 %) > Ni (82.9 %) > Zn (75.5 %) > Mn (69.4 %) > Pb (38 %). Except for Zn, other studied metals flocculates at higher rates when compared with metal contents of rivers flowing into the Caspian sea in the northern part of Iran (Karbassi *et al.*, 2007; 2008). It should be pointed out that the initial metal contents of rivers flowing into the Caspian Sea are lower than Minab River that discharges into the Strait of Hormuz. Therefore, it can be inferred that higher initial metal contents in river water will result in higher metal flocculation in estuaries. As Karbassi *et al.* (2007; 2008)

stated, salinity is a general term that does not necessarily show the effect of other saline water constituents on the flocculation of metals in the estuarine zone. Therefore, other parameters such as pH, DO, EC, Eh, Ca, DOC, SO_4, Mg, Na, K, CO_3, HCO_3 and Alkalinity were measured (Table 4) in freshwater, seawater and the nine aquariums. Fig. 2 is indicative of a rather good balance among studied anions and caution. However, Fig. 3 shows that a considerable portion of river water falls in SO_4, Cl^- and Na + K classification that is not indicative of suitable potable water. This is more clear in Fig. 4 where piper diagram is used for the classification of Minab River water. Wilcox diagram also classifies the Minab River water as C_3S_2 class that is indicative of high salinity hazard (Fig. 5). The Eh-pH diagrams (Fig. 6) show that Ni and Mn could be present as free ions while Pb could be present as PbO in riverine waters. On the other hand, speciation of Zn and Cu falls within ZnOH and Cu(s) classes, respectively. This may to some extend justify the reason for changes in the rates of flocculation of studied metals. For example, Pb that is less flocculated during estuarine mixing is present as PbO in Minab River water. On the other hand, Cu that is found as Cu(s)shows highest rate of flocculation

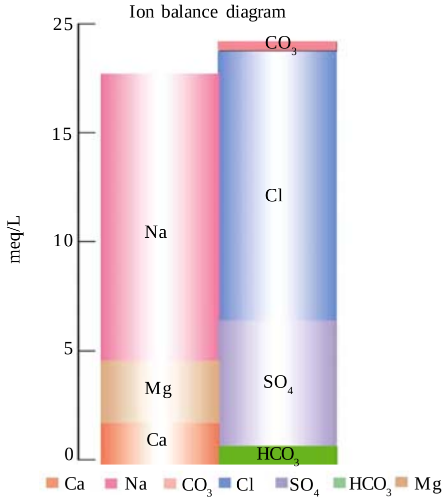

Fig. 2: Diagram of ion balance for Minab river water

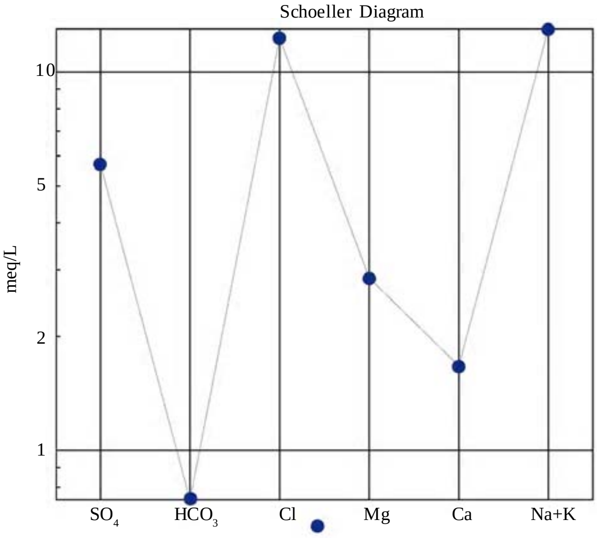

Fig. 3: Schoeller diagram for Minab River water

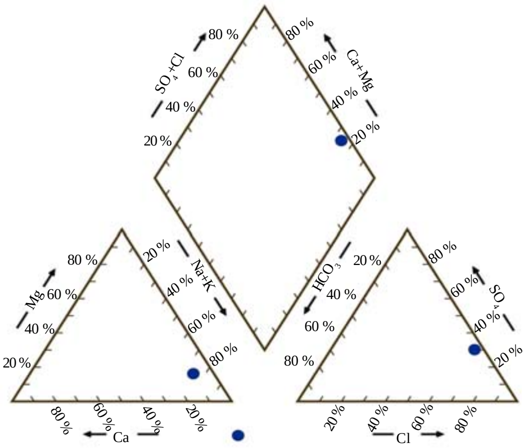

Fig. 4: Piper diagram for Minab River water

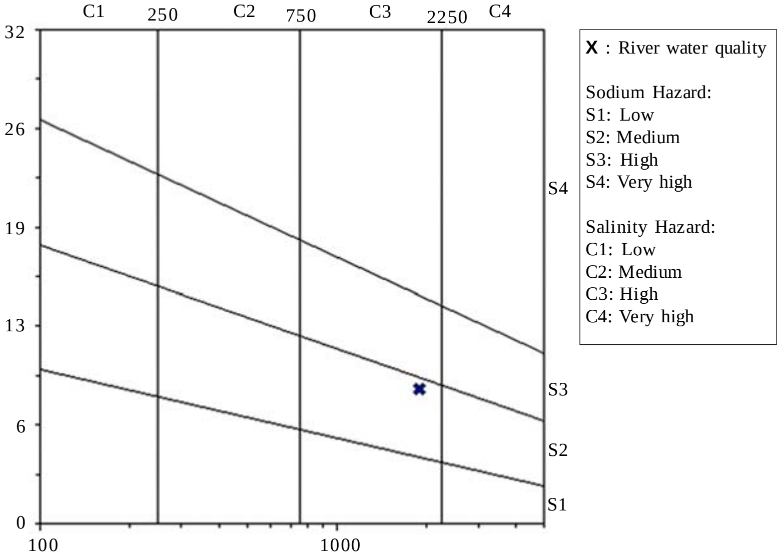

Fig. 5: Wilcox diagram for Minab River water

during estuarine mixing. Free ions such as Ni and Mn and also Zn which could be present as ZnOH have flocculation range closer to solids Cu(s) than oxides (PbO). Therefore, one may suggest the following pattern for the flocculation of metals during estuarine mixing.

solids > free ions » hydroxides > oxides

Finally, considering the concentrations of dissolved metals in Minab Rive water [Zn (117 µg/L), Pb (50 µg/L), Ni (88 µg/L), Cu (36 µg/L) and Mn (259 µg/L)] and the mean discharge of river (347×10^6 m^3/y), the annual discharge of dissolved Zn, Pb, Ni, Cu and Mn into the Strait of Hormuz via Minab River would be 40.6, 17.4, 30.5, 12.5 and 89.9 ton/y, respectively. However, results of present study show 75.2, 38, 82.9, 83.3 and 69.4 % of dissolved concentrations for Zn, Pb, Ni, Cu and Mn, respectively, flocculates during estuarine mixing. Therefore, the mean annual discharge of dissolved Zn, Pb, Ni, Cu and Mn from Minab River into Strait of Hormuz would reduce from 40.6, 17.4, 30.5, 12.5 and 89.9 ton/y to 10.1, 10.8, 5.2, 2.1 and 27.5 ton/y, respectively. Further cluster analysis was carried out to evaluate the intera-relationship amongst metal flocculation and governing factors. Many studies show that salinity and pH are the main governing

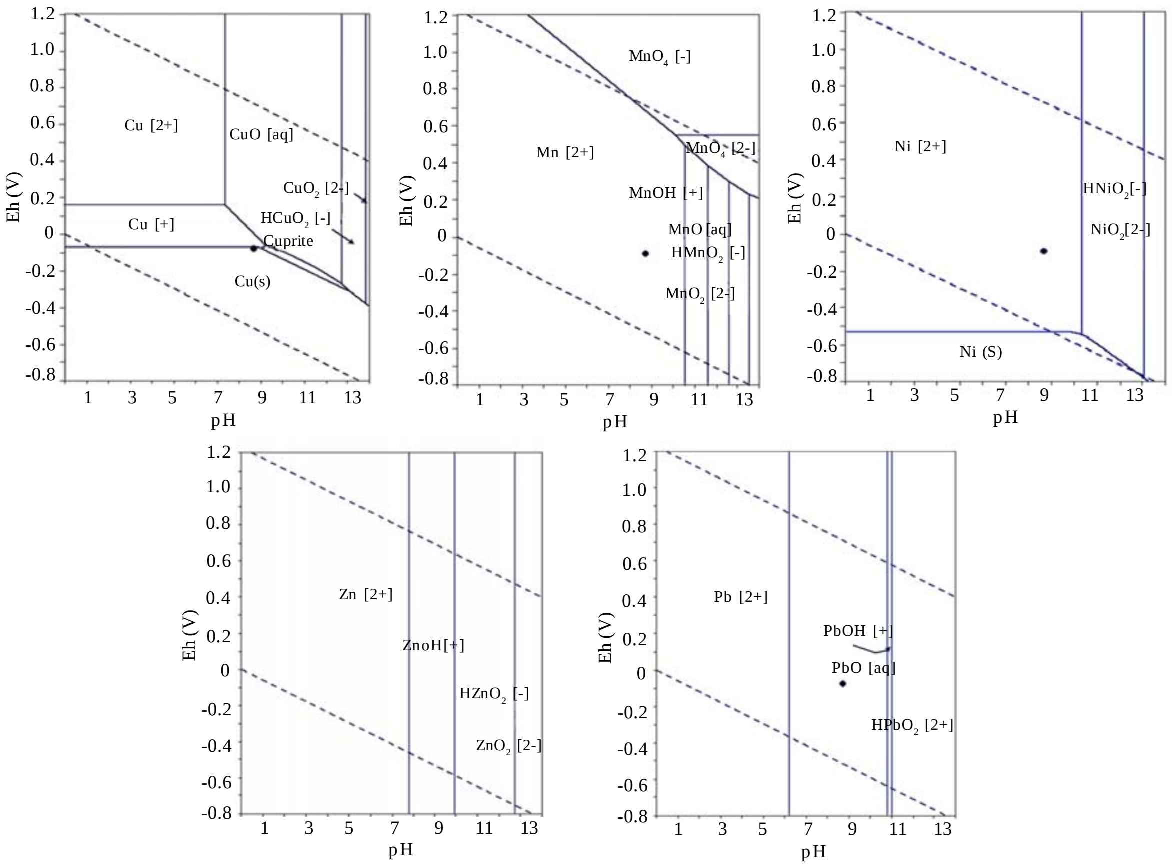

Fig. 6: Eh- pH diagram of Ni, Mn, Cu, Zn and Pb in Minab River water

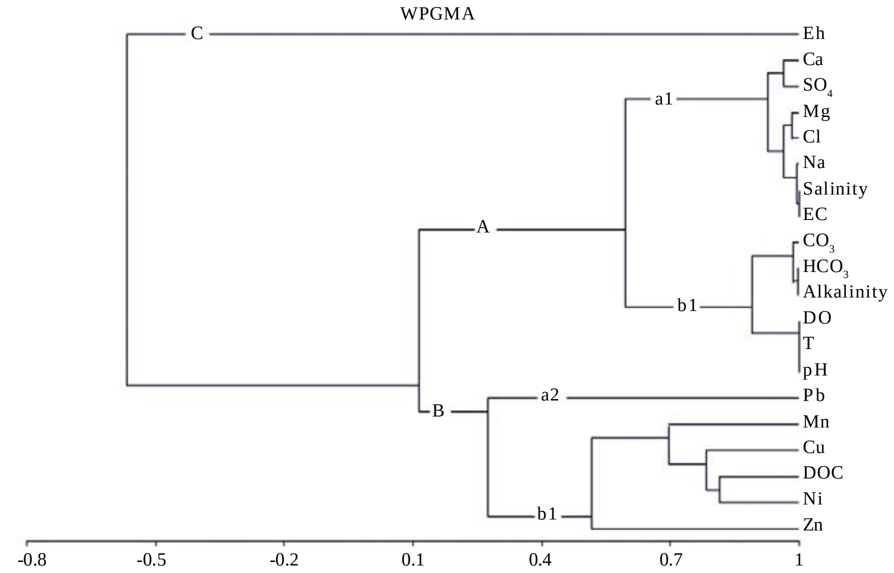

Fig. 7: Dendrogram of cluster analysis amongst studied parameter in Minab Estuarine zone

factors in the flocculation of metals during estuarine mixing (Boyle *et al.*, 1977; Duinker *et al.*, 1983; Hunter 1983; Zhiqing *et al.*, 1987). However, cluster analysis (Fig. 7) shows that DOC is the main governing factor for the flocculation of Zn, Ni, Cu and Mn in the Minab estuary. This finding is in agreement with the studies of Sholkovitz (1976), Mantoura and Woodward (1983), Meyer (1983).

It seems that DOC has a little effect on the flocculation of Pb. Further investigations are required to find out governing factors for the flocculation of Pb during estuarine mixing.

Van der Berg *et al.*, (1987) have clearly showed the effect of dissolved organic complexing ligand on the geochemical cycle of Zn and Cu in Scheldt estuary. They argue that Zn and Cu contents are regulated by DOC. Kozelka and Bruland (1998) showed that organic chelates of Cu, Zn, Pb and Cd are the dominant forms in Narragansett Bay. Zwolsman *et al.*, (1997) showed rapid removal of Cu, Zn and Cd in the very low salinity zone of Scheldt estuary. They argued that flocculation due to formation of organo-metal complexes along with coagulation of colloids and also formation of Fe and Mn hydroxide could likely be involved in removal processes.

Cluster analysis shows that pH, temperature, DO, alkalinity, HCO$_3$, CO$_3$, EC, salinity, Na, Cl, Mg, SO$_4$, Ca and Eh do not have any effect on the flocculation processes during mixing of the Minab River water with the Strait of Hormuz waters during estuarine mixing. Though, DOC shows high similarity coefficients with Cu, Zn, Ni and Mn but its concentration is very low in the Minab River water (4.3 mg/L) and also the Strait of Hormuz waters (3.1 mg/L). Though some studies on Iranian estuaries show that marine carbon source (about 50 mg/L) dominates over riverine (2 mg/L) DOC (Karbassi *et al.*, 2008b), but such difference is not seen for the study area. The DOC content of Minab River (4.3 mg/L) is slightly higher than Strait of Hormuz's water (3.1 mg/L). Though DOC content increases (4.6 mg/L) in the initial stages of mixing freshwater with saline water (3.3), but it decreases at other salinities (8.3 to 29.9). The lowest DOC (0.21 mg/L) is found at salinity of 11.4. Conservative DOC behavior is reported during estuarine mixing in Beaulieu Estuary, England (Moore *et al.*, 1979). In the area of investigation, DOC behavior is non-linear and non-conservative. Karbassi *et al.* (2008a) reported linear DOC increase for the rivers flowing into the Caspian Sea. Mantoura and Mann (1979) reported linear decrease in DOC over salinity range from 17 to 28 for Bristol Channel. In short, it might be inferred that DOC originates from terrigenous source in the study area.

CONCLUSION

The flocculation rate of Zn, Pb, Cu, Ni and Mn during estuarine mixing of Minab River with the Strait of Hormuz water were investigated. The results showed that studied metals flocculates at different salinities; however, except for Zn, the most important salinity regime varies between 3.3 to 11.4. Among common parameters (salinity, EC, pH, DO, temperature and DOC) that are known as governing flocculation factors only DOC play major role in flocculation of metals (except for Pb) during estuarine mixing in the study area. The source of DOC is terrigenous and the Strait of Hormuz waters do not contribute to DOC contents of Minab River estuarine zone. Eh-pH diagram indicated that Pb is present as PbO in Minab River water and the least flocculation rate is attributed to this element. The results also showed that flocculation rate of metal species could be as solids > free ions ≈ hydroxides > oxides. The flocculation rate of studied metals showed that the overall metal pollution load can be reduced by various percentile (ranging from 38 % to 83 %) during estuarine mixing of Minab river water with the Strait of Hormuz water. Therefore, estuarine processes can be considered as effective mechanism in self purification of colloidal metals that are anthropogenically entered into the fresh water eco-system. It is also concluded that higher initial metal contents in river water can lead to higher metal flocculation during estuarine mixing.

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