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Flocculation of Trace Metals During Mixing of Talar River Water with Caspian Seawater

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ABSTRACT: In the present investigation flocculation of dissolved Cu, Zn, Pb, Ni and Mn in a series of mixtures with salinities ranging from 1.5 to 9.5% during mixing of Talar river water with the Caspian Sea water was studied. The flocculation trend of Zn (87.22%) >Mn (45.31%) >Pb (39.09%) >Cu (36.58%)>Ni (12.70%) indicates that Cu, Zn, Pb and Mn have non-conservative behavior and Ni has relatively conservative behavior during estuarine mixing. Highest flocculation of metals occurs between salinities of 1.5 to 3.5%. Statistical analysis indicates that the flocculation of studied metals except for Ni is governed by pH and total nitrogen.

Key words: River water, Sea water, Flocculation, Metals, Caspian Sea

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INTRODUCTION

Rivers are the major transporting means for dissolved and particulate matter from the continents into the seas and lakes (Meybeck, 1988). Dissolved metals come into the particulate phase due to flocculation processes during estuarine mixing (Eckert and Sholkovitz, 1976; Sholkovitz, *et al.*, 1977 and Boyle, *et al.*, 1977). Many investigations have been carried out on flocculation of dissolved substances to know about the controlling mechanisms. In wetlands, flocculation is enhanced by increased pH, turbulence, concentration of suspended matters, ionic strength and high algal concentration (Matagi, *et al.*, 1998). However not much information is available on recognition of dissolved metals flocculation processes during estuarine mixing of river waters with brackish lake waters such as the Caspian Sea water (Karbassi and Nadjafpour, 1996 and Saeedi, et al., 2003). These investigations seem to be one of a few studies of the sort carried out in the southern coasts of the largest lake in the world – the Caspian Sea. It should be pointed out that other researchers have mainly focused on colloidal stability, surface properties, humic acids, salinity and pH (Zhiqing, *et al.*, 1987; Hunterm, 1983 Featherstone and O'Grady, 1997; Karbassi, 1989 and Shankar and Karbassi, 1992). In the present study, flocculation of Cu, Mn, Ni, Zn and Pb during mixing of Talar of river waters with the Caspian Sea waters in relation to the various important sea water parameters such as Ec, pH, salinity, total organic carbon, NO_3, and SO_4 is investigated. The Caspian Sea covers an area of about 371000 km^2 that lies between the Caucasus Mountains and northern Iran. The salinity of Caspian Sea waters ranges from 4 ppt in the northern parts to almost 13% in the southern parts. Many of ecologically significant rivers flowing into the Caspian Sea via its southern coast through the northern part of Iran (e.g. Haraz, Sefidrud, Chalus, Talar, Tadjan and Gorganrud rivers) are used as transport means for disposal of industrial, agricultural and urban wastes. In spite of the above mentioned studies, it is obvious that flocculation processes is not well known and thus more investigations are needed. While a part of geochemical cycle of a few heavy metals is quantified in this study; more detailed studies such as sediment water interactions (Day, *et al*., 1989) that have significant influences on the behavior of metals are needed.

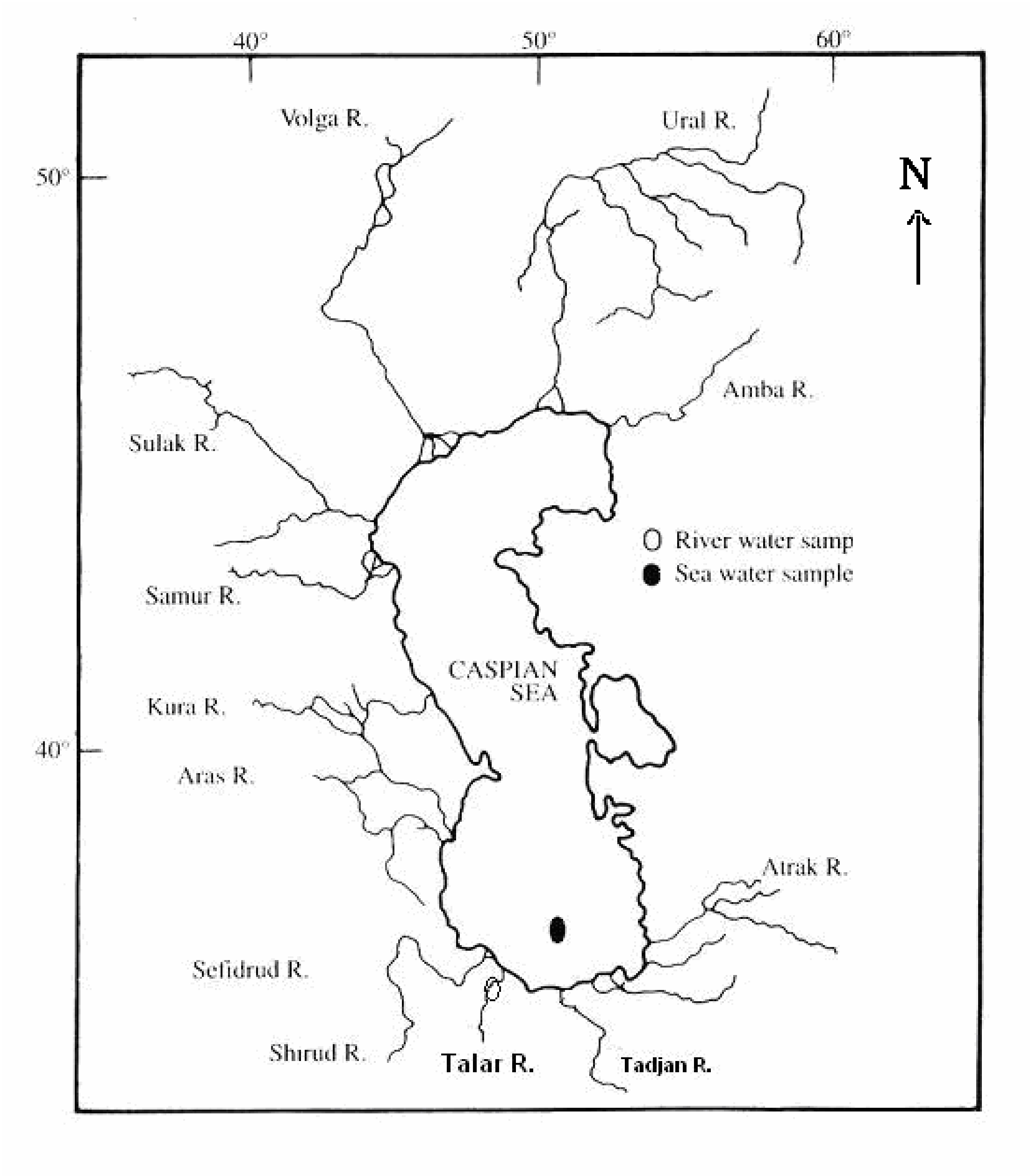

Fig. 1. Locations of water samples from Talar River and Caspian Sea

MATERIALS & METHODS

Freshwater samples were collected from the Talar River (ca. 16 Km upstream; Fig.1) in a 25 liter clean polyethylene bucket from the surface on 24th. Nov. 2005. On the same day it was filtered through 0.45 µm Millipore AP and HA filters. About one liter of filtered water was acidified with concentrated HNO_3 to a pH of approximately 1.8 and stored in polyethylene bottles in a refrigerator prior to the analysis of dissolved metals. The rest of filtered waters were also kept in refrigerator. On the same day, Caspian Sea water was collected approximately 20 Km away from the coast to ensure that the sample was not diluted by river water (salinity=12.5%). In order to prevent the contamination of samples, all equipment was acid washed with a mixture of HNO_3 and HCl. Rinsing was done with running Milli-Q water. Filtered river water and sea water were mixed together in 8 different aquariums at room temperature in various proportions yielding salinities 1.5 to 9.5%. They were kept for 24 hours with occasional stirring. The resulting flocculants were collected on 2.5 Cm diameter Millipore membrane filters (type HA, Pore size: 0.45 µm). Millipore filters were digested by 5 ml concentrated HNO_3 overnight. The concentrations of Cu, Zn, Ni, Pb and Mn were determined by AAS (Philips model PU-9004). Procedural blanks and duplicates were run with the samples in a similar way. The accuracy of analysis was about ±6% for all elements. Salinity, pH and electrical conductivity (Ec) of water samples were measured by Siemens multi-channel portable apparatus. Nitrates and sulfates were measured by photometer (model 8000) in accordance with ASTM procedure (2003). Total Dissolved organic carbon (DOC) of water samples were measured by TOC meter (Shimatzu model TOC-VCSH-3000a). Of the existing clustering techniques (Lance and William, 1966; Anderson, 1971 and Davis, 1973), the Weighted Pair Group (WPG) method (Davis, 1973) was used in this study because of its merits. It uses the linear correlation coefficient as a similarity measure. Highest similarities are clustered/linked first. Two variables are connected only if they are highly correlated. After two variables are clustered, their correlations with all the other variables are averaged. The results of clustering are displayed in the form of a Dendrogram.

RESULTS & DISCUSSIONS

Table 1 shows the base metal (Cu, Zn, Pb, Ni and Mn) concentrations found in flocculants at various salinities as well as in fresh river water. Other parameters of freshwater at different salinity regimes are also shown in Table 1. It can be noticed that Ni and Zn undergo minimum and maximum flocculation at different salinity regimes respectively. It is interesting to note that while most of studied metals (Cu, Pb and Mn) show maximum flocculation at salinities ranging from 4.5 to 9.5%, Zn flocculates at high concentrations even in the lower salinities. Nickel shows minimum flocculation tendency amongst the studied metals and generally its flocculation does not exceed 12.75% of total dissolved concentration at various salinities. Therefore, Ni is showing a rather conservative behavior while other elements (Cu, Zn, Pb and Mn) are non-conservative. It is also important to note that flocculation of all studied metals (except for Cu and Mn) sharply decreases at salinity of 5.5%.

Table 1. Metal concentrations and physico-chemical parameters in Talar River water and experimental aquariums containing Caspian Seawater

Sample	Cu (µg/L)	Mn (µg/L)	Ni (µg/L)	Zn (µg/L)	Pb (µg/L)	Ec (µs/cm)	pH	S (%)	DOC (mg/L)	NO_3 (mg/L	SO_4 (mg/L)
River Water	**41**	**32**	**51**	**90**	**22**	**760**	**8.90**	**0.20**	**2.7**	**0.20**	**155**
1	4.5 (10.98)	3.5(10.93)	3.5 (6.86)	39.0(43.33)	1.5 (6.82)	9600	8.84	1.50	5.60	2.15	590
2	7.2 (17.56)	5.5 (17.19)	2.2 (4.31)	42.5(47.22)	2.3 (10.45)	11500	8.80	2.50	9.50	1.10	370
3	14.5 (35.36)	6.2 (19.37)	5.5 (10.78)	68.5 76.11)	4.5 (20.45)	12100	8.80	3.50	27.0	0.98	340
4	15.0 (36.58)	10.5 (32.80)	3.2 (6.27)	46.5(51.67)	2.2 (9.99)	13000	8.75	4.50	28.0	0.62	410
5	14.0 (34.15)	13.5 (3.33)	3.0 (5.88)	22.2(24.57)	1.2 (5.75)	13500	8.70	5.50	29.0	0.58	375
6	12.5 (30.48)	7.5 (42.18)	5.2 (10.19)	66.5(73.89)	8.5 (38.64)	14000	8.70	6.50	30.0	0.47	385
7	13.5 (32.93)	7.5 (23.43)	6.5 (12.75)	70.3(78.11)	4.2 (19.09)	14600	8.70	7.50	33.0	0.37	315
8	10.5 (25.61)	10.5 (32.81)	5.5 (10.78)	75.8(84.22)	6.5 (29.55)	15300	8.65	8.50	45.0	0.35	435
9	9.50 (23.17)	14.5 (45.31)	6.0 (11.76)	78.5(87.22)	8.6 (39.10)	15400	8.60	9.50	52.0	0.47	565

Sample 1 to 9 refers to aquariums with salinities 1.5 to 9.5; Percentile of removal is given within parentheses

The concentration of total dissolved organic carbon (DOC) in the river water is about 2.7 mg/L that increase to 52 mg/L at salinity of 9.5%. Such an increase is suggestive of marine carbon source in the estuarine zone. Other parameters such as total nitrogen (N_T), and SO_4 show similar trend as DOC does. The increasing trend of SO_4 is mainly due to redox conditions that prevail in the Caspian Sea (Saeedi, *et al*., 2003). The estuarine system is characterized by profound changes in the chemical properties of the water masses and usually by high biological activities, both of which significantly affect the speciation of the elements and transfer to the adjacent coastal zones. This is particularly true in the case of nutrients and organic matter (Wollast and Peters, 1978; Meybeck, 1982 and Zobrist and Stumm, 1981).

In General, during estuarine mixing, flocculation processes may not occur as shown in Table 1. In fact, at the very first stages of mixing of river water with lake water, some of the dissolved metals ooze out of the freshwater in the form of flocculants. Thus, at the later stages of mixing (i.e. higher salinities) freshwater is impoverished in base metals and fewer flocculates form (Table 2). The values presented in Table 2, are actually derived from Table 1 by subtracting the concentrations of flocculates at a specific salinity from the prior steps. In this way, the flocculate quantity is not calibrated to the very first concentration of the metals in the river water (Karbassi and Nadjafpour, 1996). According to Fig. 2, the maximal removal of Cu occurs between salinities of 1.5 to 3.5% while Mn removal stops at 5.5% salinity (Fig. 3). Removal of Ni, Zn and Pb are confined to salinity ranges of 1.5 to 3.5% though they show some scattered removal at other salinities (Figs. 4, 5 & 6). The variation in the maximal removal of the studied metals may be due to destabilization of dissolve metals, corresponding to the different stages of mixing with seawater and a decrease in their negative net charge (Aston and, Chester, 1973). The flocculation rates of studied metals in Talar river are in the following order: Zn(87.22%)>Mn(45.31%)>Pb(39.09%)>Cu(36.58 %)>Ni(12.70%).

Table 2. Actual* metal concentrations in flocculants of mixed waters of Talar river with the Caspian Sea

Sample	Cu (µg/L)	Mn (µg/L)	Ni (µg/L)	Zn (µg/L)	Pb (µg/L)	Ec (µs/cm)	pH	S (%)	DOC (mg/L)	NO_3 (mg/L)	SO_4 (mg/L)
River Water	41	32	51	90	22	760	8.90	0.20	2.7	0.20	155
1	4.50 (10.98)	3.5 (10.94)	3.5 (6.86)	39 (43.33)	1.5 (6.82)	9600	8.84	1.50	5.60	2.15	590
2	2.70 (6.59)	2.0 (6.25)	0.0 (0.0)	3.5 (3.89)	0.8 (3.64)	11500	8.80	2.50	9.50	1.10	370
3	7.30 (17.80)	0.7 (2.19)	2.0 (3.92)	26 (28.89)	2.2 (10.0)	12100	8.80	3.50	27.0	0.98	340
4	0.50 (1.22)	4.3 (13.43)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	13000	8.75	4.50	28.0	0.62	410
5	0.0 (0.0)	3.0 (9.38)	0.0 (0.0)	0.0 (0.0)	0.0 (00)	13500	8.70	5.50	29.0	0.58	375
6	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	4.0 (18.18)	14000	8.70	6.50	30.0	0.47	385
7	0.0 (0.0)	0.0 (0.0)	1.0 (1.96)	1.8 (2.0)	0.0 (0.0)	14600	8.70	7.50	33.0	0.37	315
8	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	5.5 (6.11)	0.0 (0.0)	15300	8.65	8.50	45.0	0.35	435
9	0.0 (0.0)	1.0 (3.13)	0.0 (0.0)	2.7 (3.0)	0.1 (0.45)	15400	8.60	9.50	52.0	0.47	565
Total	**15.0 (36.58)**	**14.5 (45.31)**	**6.5 (12.70)**	**78.5 (87.22)**	**8.6 (39.09)**						

Sample 1 to 9 refers to aquariums with salinities 1.5 to 9.5; Percentile of removal is given within parentheses.
The values presented for Cu, Zn, Pb, Ni & Mn are actually derived from Table 1 by subtracting the concentrations of flocculates at a specific salinity from the prior steps. In this way, the flocculate quantity is not calibrated to the very first concentration of the metals in the river water.

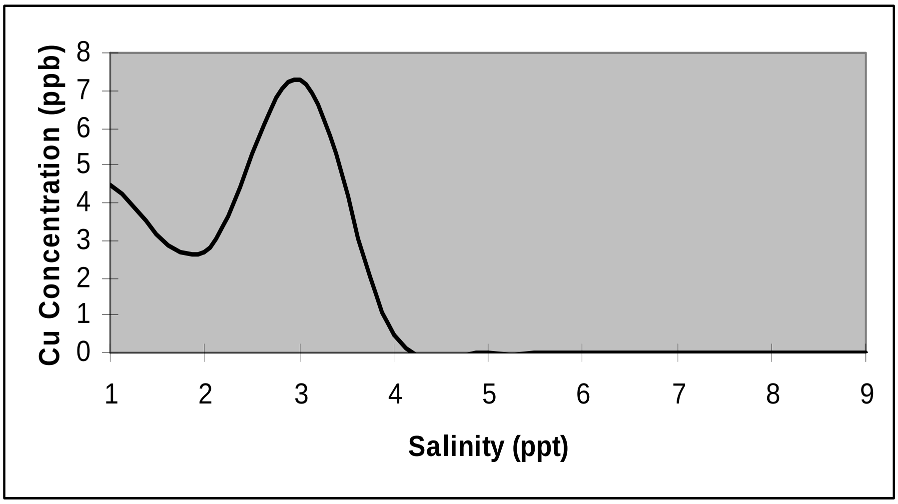

Fig. 2. Flocculation of Cu during estuarine mixing

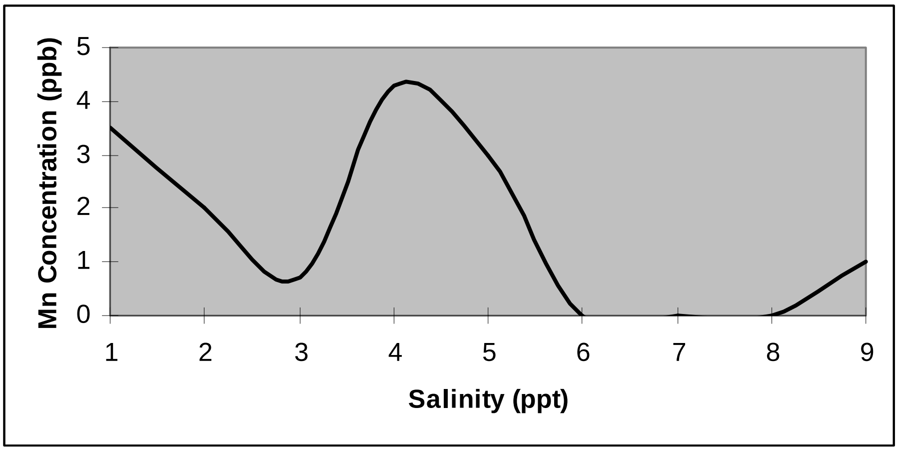

Fig. 3. Flocculation of Mn during estuarine mixing

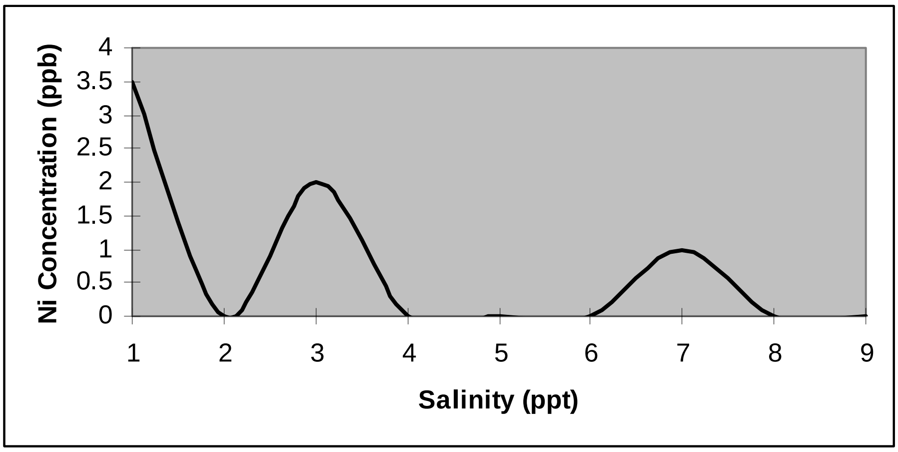

Fig. 4. Flocculation of Ni during estuarine mixing

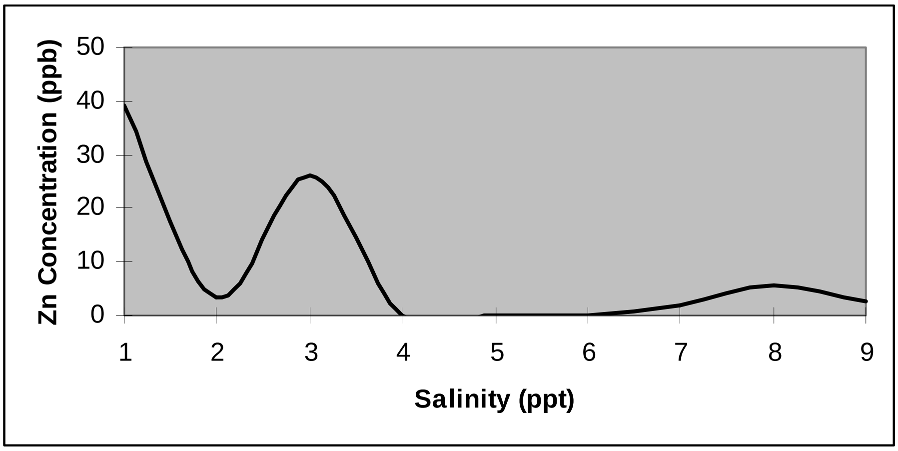

Fig. 5. Flocculation of Zn during estuarine mixing

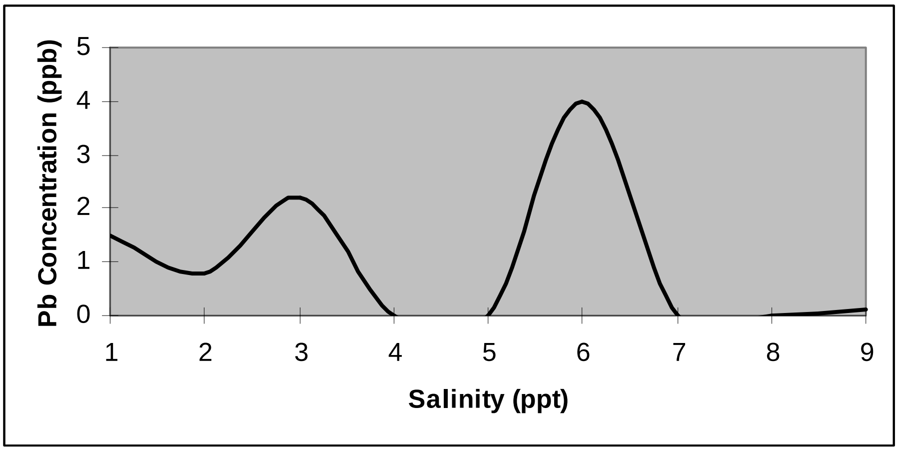

Fig. 6. Flocculation of Pb during estuarine mixing

Thus, rapid flocculation in the earlier stages of mixing freshwater with lake water (salinity of 1.5 to 3.5%) occurs that is in accordance with the findings of other researchers (Duinker and Nolting, 1976 and Bewers, *et al.*, 1974). A near conservative behavior of Ni is in conflict with the nearby estuaries (Saeedi, *et al.*, 2003). As general and except for Ni and to lower extend Zn, the results are in agreement with those found in estuarine mixing of rivers water with the Caspian Sea water in the vicinity of the study area (Karbassi and Nadjafpour, 1996, Bewers, *et al.*, 1974). It is widely accepted that dissolved organic carbon (DOC) represent a dynamic component in the interaction between geo-sphere, biosphere and hydrosphere. Conservative DOC behavior is reported during estuarine mixing in Beaulieu Estuary, England (Moore, *et al.*, 1979). A linear decrease in DOC over salinity range of 17 to 28% is reported for Bristol Channel (Mantoura and Mann, 1979). However, in the present study consistent linear DOC increase with increase in salinity is noticed (Tables 1 and 2) that is indicative of non-terrigenous DOC. Aquatic fulvic acids accounts for 50 to 80% of the total amount of DOC in coastal waters (Krachler, *et al*., 2005). The reasons for such increase in DOC concentration, which may be related to exudation by micro-algae, require further investigation. Interestingly high relationship amongst DOC, Ec and salinity of Caspian Sea water is observed (Fig. 7) that is indicative of influence of sea water as a controlling mechanism for these parameters in the estuarine zone. Cluster “B” shows that flocculation of Zn, Ni and Cu are mainly controlled by pH and total nitrogen. Thus neither salinity and nor DOC do not play any role in the flocculation of studied metals which is in contrast with findings of some researchers (Boyle, *et al*., 1979 and Sholkovitz, 1976). However, Aston and Chester (Aston and Chester, 1973) have mentioned of metal destabilization in saline waters. Manganese and Pb are grouped with SO_4 in clusters “C” (Fig. 7) at very low similarity coefficients. Further investigations are needed to know as what sea water constituents have more effect on the flocculation processes of these two metals. The fact that three clusters (A, B and C) join each other at very insignificant similarity coefficients is indicative of different controlling mechanisms amongst studied metals.

Finally, considering the concentrations of dissolved metals in Talar river water (Cu (36 µg/L), Zn (90µg/l), Pb (22µg/L), Ni (51µg/L) and Mn (32µg/L)) and mean discharge of river ($440x10^6$ m^3/yr.), the mean annual discharge of dissolved Cu, Zn, Pb, Ni and Mn into the Caspian sea via this river would be 18.04, 39.6, 9.68, 22.45 and 14.08 tons/yr., respectively. However, results of present study show that 36.58, 87.22, 39.09, 12.7 and 45.31% of dissolved concentrations of Cu, Zn, Pb, Ni and Mn respectively, flocculates during estuarine mixing. Therefore, the mean annual discharge of dissolved Cu, Zn, Pb, Ni and Mn from Talar River into the Caspian Sea would reduce from 18.04 to 11.44, 39.6 to 5.01, 9.68 to 5.89, 22.45 to 19.59 and 14.08 to 7.70 tons/yr., respectively.

CONCLUSION

The flocculation processes of dissolved Cu, Zn, Pb, Ni and Mn during estuarine mixing of Talar river water with Caspian Sea water was investigated. The results showed that Cu, Zn, Pb, Ni and Mn flocculate at salinities of 1.5 to 9.5%. Though the maximum removal is at lower salinities (1.5 to 3.5%) but none of the studied metals flocculate due to salinity of water. Besides,

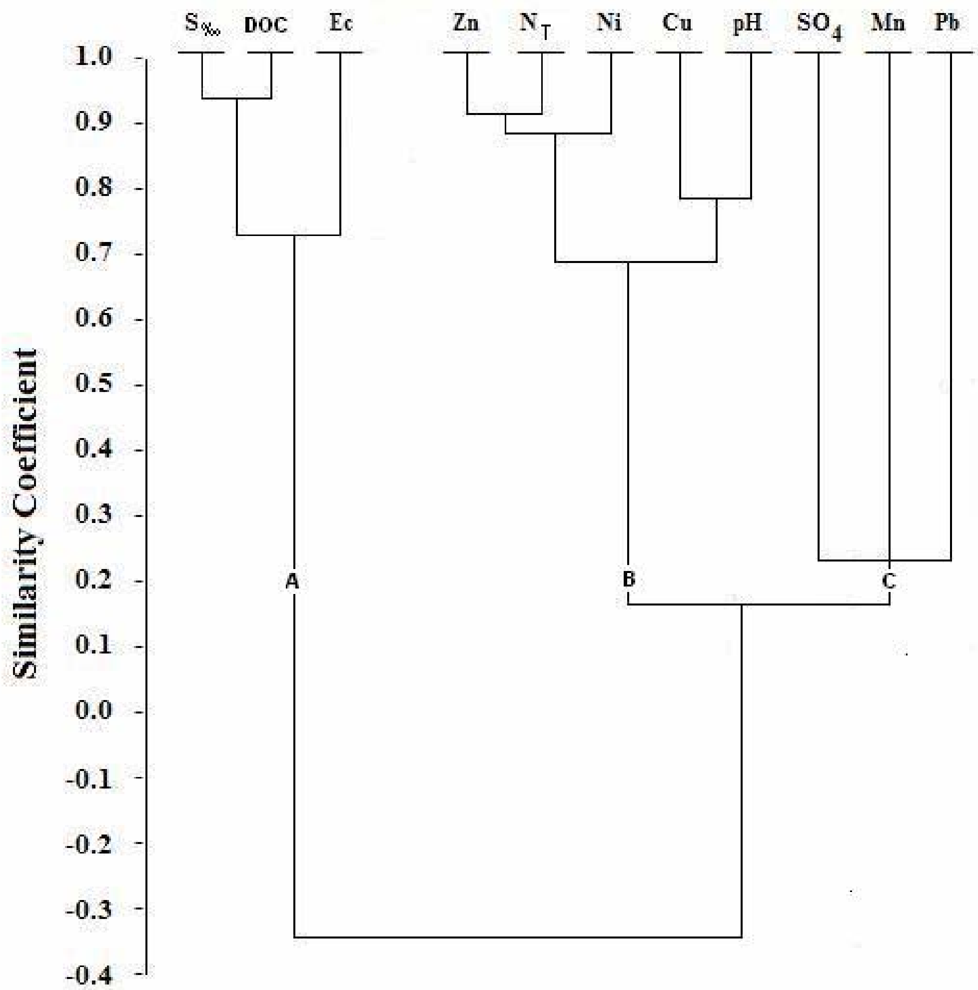

Fig. 7. Dendrogram of cluster analysis for metals and other physico-chemical characteristics of Talar river and Caspian Sea waters

dissolved organic carbon, electrical conductivity, and SO_4 do not play any role in flocculation processes of Cu, Zn, Pb, Ni and Mn. Flocculation of Zn, Ni and Cu is controlled by pH and total nitrogen. Many researchers have reported about variation in the rate of flocculation of trace metals

through out the year in a specific river or from river to river. In all such studies, salinity of seawater has been almost considered as the main source of metal flocculation. However, the term salinity is a very broad term that covers many constituents of seawater. Present investigation brought out the importance of sea-derived total nitrogen that has not been reported earlier. The mechanisms for flocculation of Pb and Mn need further investigation. The flocculation rate of studied metals showed that the overall dissolved metal pollution loads can be reduced by various percentiles (ranging from as low as 12.7 to as high as 87.22%); during estuarine mixing of the Talar river water with the Caspian Sea water. This statement not only proves the important role of the flocculation processes of dissolved metals in natural self purification of estuarine zone, but also points out the ecological importance of estuarine processes.

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