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ORIGINAL ARTICLE

Flocculation of heavy metals during mixing of freshwater with Caspian Sea water

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Abstract Flocculation of colloidal size fraction for Cu, Zn, Pb, Ni and Mn was investigated on a series of mixtures with water salinities ranging from 1.5 to 9.5‰ during mixing of Haraz River with the Caspian Sea water. The flocculation trend of Zn (85.5%) > Mn (55.2%) > Cu (39.6%) > Pb (33.7%) > Ni (11.3%) indicates that Cu, Zn, Pb and Mn have non-conservative behavior and Ni has relatively conservative behavior during estuarine mixing. Highest flocculation of heavy metals occurs between salinities of 1.5 and 4.5‰. Statistical analysis indicates that the flocculation of Cu, Zn and Ni is governed by pH and total nitrogen.

Keywords Flocculation · Heavy metals · Saline water · Estuary · Caspian Sea

Introduction

Rivers are considered as major transporting agents of dissolved and particulate matter from the continents (Meybeck 1988). During estuarine mixing, dissolved metals come into the particulate phase due to flocculation processes (Eckert and Sholkovitz 1976; Sholkovitz et al. 1977; Boyle et al. 1977). Therefore, flocculation of dissolved metals during estuarine mixing can significantly influence the chemical mass balance between rivers and seas or lakes. 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 (Karbassi and Nadjafpour 1996; Saeedi et al. 2003; Karbassi et al. 2007). This investigation seem to be one of the only three such studies carried out in the southern coasts of the largest lake in the world—the Caspian Sea. Moreover, other researchers have mainly focused on colloidal stability, surface properties, humic acids, salinity and pH (Zhiqing et al. 1987; Hunter 1983; Featherstone and O'Grady 1997; Karbassi 1989; Shankar and Karbassi 1992). In the present study, flocculation of Cu, Mn, Ni, Zn and Pb during mixing of Haraz river waters with the Caspian Sea waters in relation to the parameters such as electrical conductivity (Ec), pH, salinity, total organic carbon (TOC), NO_3, PO_4, SO_4 and total hardness (TH) is investigated. Though a few research works are carried out in the same geographic area, the present work considers more physical and chemical parameters of mixed fresh and saline waters than the previous works.

The Caspian Sea covers an area of about 371,000 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.

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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 agents for disposal of industrial, agricultural and urban wastes. Haraz River has a length of 185 km with a discharge of 940×10^6 m^3/y. The width of river ranges from 50 to 500 m at different locations. The catchments area of river is about 4,060 Km^2 with average precipitation of 832 mm/y. It lies between longitude of 35°52′ and 45°5′ and latitude of 35°45′ and 36°15′. 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.

Materials and methods

Freshwater samples were collected from the Haraz River (ca. 16 km upstream) in a 25 l clean polyethylene bucket from the surface on 26th November 2005. On the same day it was filtered through 0.45 μm Millipore AP and HA filters. About 1 l 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 water was also kept in a 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 equipments were acid washed with a mixture of HNO_3 and HCl. Rinsing was done with running Milli-Q water. Filtered river water and seawater were mixed together at room temperature in various proportions yielding salinities from 1.5 to 9.5‰. They were kept for 24 h 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 inner standards for determination were obtained by dilution of single concentrated standards purchased from Merck Company. The accuracy of analysis was about ±4% for all elements in dissolved and flocculant phases. Salinity, pH and Ec of water samples were measured by Siemens multi-channel portable apparatus. Nitrates, phosphates 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). TH was determined titrimetrically. Of the existing clustering techniques (Lance and William 1966; Anderson 1971; 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 and discussions

The base metal (Cu, Zn, Pb, Ni and Mn) concentrations found in flocculants at various salinities as well as fresh river water are presented in Table 1. Other parameters of freshwater and 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 11% 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) sharply decrease at salinity of 5.5‰.

The concentration of total DOC) in the river water is about 2.1 mg/l that increases to 52.4 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), SO_4 and TH 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; Zobrist and Stumm 1981). In the present investigation we have tried to understand the relationship amongst nutrients and flocculation of colloidal metals during estuarine mixing through cluster analysis that will be discussed later (Fig. 1).

Anyway, 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

Table 1 Heavy metals concentrations and physico-chemical parameters in Haraz River water and experimental aquariums containing Caspian Seawater

Sample[a]	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)	PO_4 (mg/l)	SO_4 (mg/l)	TH (mg/l)
River water	36	25	45	95	25	811	9.05	0.23	2.1	0.208	0.16	165	195
1	3.68 (10.2)	2.5 (10.0)	2.85(6.3)	33.7 (35.5)	0.92 (3.38)	9,632	8.88	1.50	5.64	2.175	0.08	560	1,400
2	6.53 (18.1)	3.7 (10.3)	1.76 (3.9)	48.3 (50.8)	1.84 (7.36)	11,424	8.83	2.50	9.34	1.032	0.09	345	1,750
3	12.42 (3.4)	4.65 (12.7)	4.16 (9.2)	68.5 (61.6)	3.73 (14.9)	12,181	8.81	3.50	27.1	0.983	0.04	330	2,400
4	13.9 (38.6)	9.60 (36.7)	3.31 (7.3)	46.2 (48.6)	1.09 (4.36)	12,972	8.77	4.50	28.6	0.629	0.06	400	2,150
5	12.5 (34.7)	12.3 (3.33)	2.21 (4.9)	19.8 (20.8)	0.95 (0.0)	13,509	8.74	5.50	29.7	0.589	0.05	365	2,400
6	10.08 (28.0)	6.25 (25.0)	4.84 (10.7)	71.8 (75.6)	7.98 (31.9)	14,084	8.70	6.50	30.7	0.478	0.11	385	2,400
7	14.25 (39.6)	6.89 (19.1)	5.07 (11.3)	69.2 (72.8)	3.85 (15.4)	14,652	8.60	7.50	33.9	0.377	0.03	325	2,400
8	8.95 (24.68)	9.44 (26.2)	3.51 (7.8)	79.3 (83.5)	6.21 (24.8)	15,227	8.65	8.50	45.9	0.350	0.10	420	2,050
9	6.87 (19.0)	13.8 (55.2)	3.95 (8.8)	81.3 (85.5)	8.42 (33.7)	15,434	8.61	9.50	52.4	0.478	0.05	550	2,300

[a] Sample 1–9 refers to aquariums with salinities 1.5–9.5; percentile of removal is given within parentheses

colloidal 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 are formed (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 data shown in Table 2, the maximal removal of Cu and Mn occurs between salinities of 1.0–4.5‰ while Ni, Zn and Pb removal is confined to salinity ranges from 1.5 to 3.5‰. 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 metals in the mixing zone could be depleted due to aggregation and settlement. The flocculation rates of studied metals in Haraz River are in the following order:

$$\mathrm{Zn}(85.5\%) > \mathrm{Mn}(55.2\%) > \mathrm{Cu}(39.6\%) > \mathrm{Pb}(33.7\%) > \mathrm{Ni}(11.3\%)$$

Thus, rapid flocculation in the earlier stages of mixing freshwater with lake water (salinity of 1.5–4.5‰) occurs that is in accordance with the findings of other researchers (Duinker and Nolting 1976; Bewers et al. 1974), though at relatively higher salinities. A near conservative behavior of Ni is in conflict with the nearby estuaries (Saeedi et al. 2003). The discrepancy is probably due to the lower concentrations of DOC in nearby estuaries. In general except for Ni and to lower extent Zn, the results are in agreement with those found in estuarine mixing of river 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 DOC represents a dynamic component in the interaction between geosphere, 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 from 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 (Table 1) that is indicative of non-terrigenous DOC. Aquatic fulvic acids account for 50–80% 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 TH with salinity of Caspian Sea water is observed (Fig. 2) that is indicative of influence of seawater

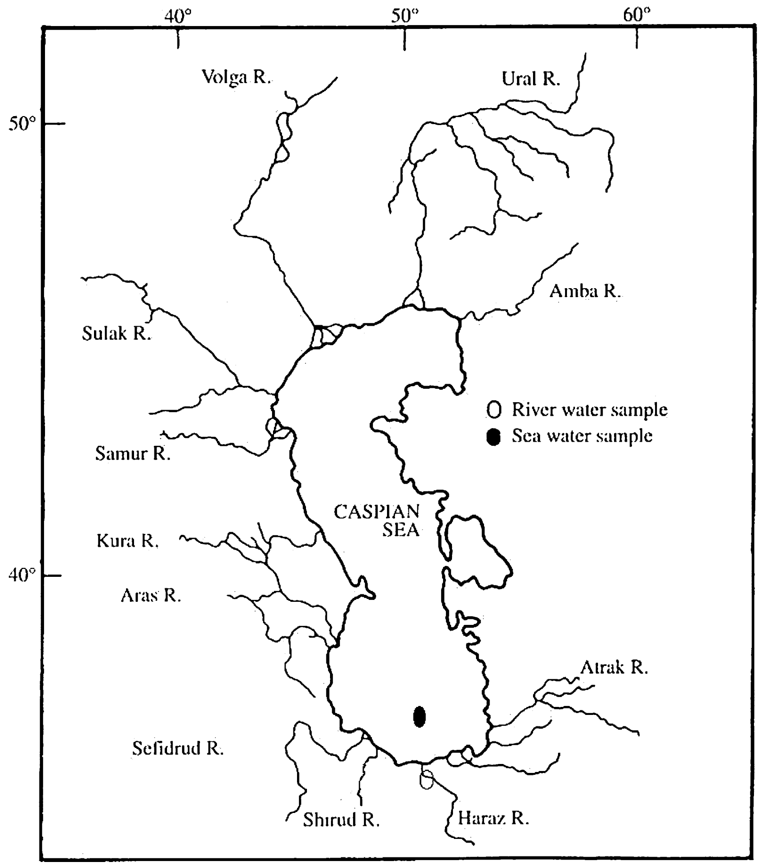

Fig. 1 Locations of water samples from Haraz River and Caspian Sea

as a controlling mechanism for these parameters in the estuarine zone. Cluster ''B'' shows that flocculation of Zn, Ni and Cu is mainly controlled by pH and total nitrogen. Thus neither salinity 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. 1977; Sholkovitz 1976). However, Aston and Chester (1973) have mentioned about metal destabilization in saline waters. Manganese and Pb are grouped with SO_4 and PO_4 in clusters ''C'' and ''D'', respectively (Fig. 2), at very low similarity coefficients. Further investigations are needed to know as which seawater constituents have more effect on the flocculation processes of these two metals. The fact that four clusters (A, B, C and D) join each other at very insignificant similarity coefficients is indicative of different controlling mechanisms amongst studied metals. The processes that are responsible for removing dissolved PO_4 at high concentrations encountered in Haraz estuary include precipitation of apatite (calcium phosphate), vivianite (ferrous phosphate) and magnesium–ammonium phosphate are theoretically possible, but have not been identified in situ or in laboratory experiments simulating estuarine conditions (Meybeck 1982; Deck 1981). Finally, considering the concentrations of dissolved metals in Haraz river water [Cu(36 μg/l), Zn(95 μg/l), Pb(25 μg/l), Ni(45 μg/l) and Mn(25 μg/l)] and mean discharge of river (940×10^6 m^3/y), the mean annual discharge of dissolved Cu, Zn, Pb, Ni and Mn into the Caspian sea via this river would be 33.84, 89.30, 23.50, 42.30 and 23.50 tons/y, respectively. However, results of present study show that 39.6, 85.5, 33.7, 11.3 and 55.2% 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 Haraz River into the Caspian Sea would reduce from 33.84 to 20.44, 89.30 to 12.95, 23.50 to 15.58, 42.30 to 37.52 and 23.50 to 10.53 tons/y, respectively.

Conclusion

The flocculation processes of colloidal Cu, Zn, Pb, Ni and Mn during estuarine mixing of Haraz river water with Caspian Sea water were investigated. The results showed that Cu, Zn, Pb, Ni and Mn flocculate at salinities of 1.5 – 9.5‰. Though the maximum removal is at lower salinities (1.5 to 4.5‰), none of the studied metals flocculate due to salinity of water. Besides, DOC, TH, electrical conductivity, SO_4 and PO_4 do not play any role in flocculation processes of Cu, Zn, Pb, Ni and Mn. Flocculation of Zn, Ni and

Table 2 Actual metal concentrations in flocculants of mixed waters of Haraz 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)	PO_4 (mg/l)	SO_4 (mg/l)	TH (mg/l)
River water	36	25	45	95	25	811	9.05	0.23	2.1	0.208	0.16	165	195
1	3.68 (10.2)	2.5 (10.0)	2.85 (6.30)	33.75 (35.5)	0.92 (3.68)	9,632	8.88	1.50	5.64	2.175	0.08	560	1,400
2	2.85 (7.91)	1.2 (4.80)	0.0 (0.0)	14.55 (15.3)	0.92 (3.68)	11,424	8.83	2.50	9.34	1.032	0.09	345	1,750
3	5.89 (16.36)	0.95 (3.80)	1.31 (2.91)	20.2 (21.26)	1.89 (7.56)	12,181	8.81	3.50	27.1	0.983	0.04	330	2,400
4	1.48 (4.11)	4.95 (19.8)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	12,972	8.77	4.50	28.6	0.629	0.06	400	2,150
5	0.0 (0.0)	2.70 (10.8)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	13,509	8.74	5.50	29.7	0.589	0.05	365	2,400
6	0.0 (0.0)	0.0 (0.0)	0.68 (1.15)	3.30 (3.47)	4.25 (17.0)	14,084	8.70	6.50	30.8	0.478	0.11	385	2,400
7	0.35 (0.97)	0.0 (0.0)	0.23 (0.50)	0.0 (0.0)	0.0 (0.0)	14,652	8.68	7.50	33.9	0.377	0.03	325	2,400
8	0.0 (0.0)	1.50 (6.0)	0.0 (0.0)	7.50 (7.89)	0.0 (0.0)	15,227	8.65	8.50	45.9	0.350	0.10	420	2,050
9	0.0 (0.0)	13.8 (55.2)	0.0 (0.0)	1.99 (2.09)	0.44 (1.76)	15,434	8.61	9.50	52.4	0.478	0.05	550	2,300
Total	14.25 (39.6)	13.8 (55.2)	5.07 (11.3)	81.29 (85.5)	8.42 (33.7)								

Sample 1– 9 refers to aquariums with salinities 1.5–9.5, percentile of removal is given within parentheses

[a] The values presented for Cu, Zn, Pb, Ni and Mn 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

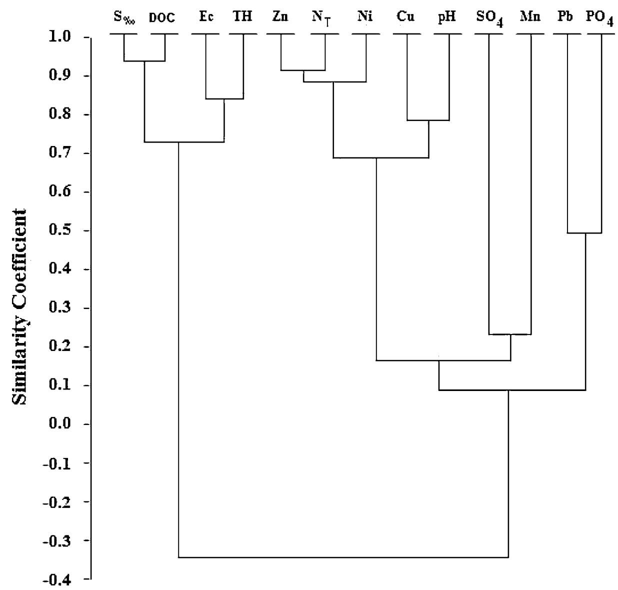

Fig. 2 Dendrogram of cluster analysis for metals and other physico-chemical characteristics of Haraz River and Caspian Sea waters

Cu is controlled by pH and total nitrogen. Many researchers have reported about variation in the rate of flocculation of trace metals throughout the year in a specific river or from river to river. In all such studies, salinity of seawater has been almost constant. Therefore, other constituents of seawater (than salinity) that are variable throughout the year should have been involved in flocculation processes. The 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 colloidal metal pollution loads can be reduced by various percentiles (ranging from as low as 10‰ to as high as 85%); during estuarine mixing of the Haraz river water with the Caspian Sea water. This statement not only proves the important role of the flocculation processes of colloidal metals in natural self-purification of estuarine zone, but also points out the ecological importance of estuarine processes. In the present investigation, the processes of flocculation are mainly inferred through statistical analysis and therefore further chemical analysis is suggested for future investigations.

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