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# An investigation on role of salinity, pH and DO on heavy metals elimination throughout estuarial mixture

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**ABSTRACT:** One of the most paramount processes that play a considerable role in reducing the concentration of heavy metals during estuarine mixing is flocculation. Not only does such a process cause a huge percentage of metals to come into the particulate phase, but also it provides ample nutrients for the aquatic life. In the present study, impact of such factors as salinity, pH and DO on flocculation of Cu, Zn, Pb, Ni, Cd and Mn throughout mixing of Chaluse River with Caspian Sea is investigated. The trend of flocculation of Pb (24.32%) < Zn (24.38%) < Cd (40.00%) < Cu (64.71%) < Ni (68.00%) < Mn (76.47%) reveals that among the studied elements Mn and lead experience minimum and maximum flocculation at diverse salinity regimes, respectively. Moreover, flocculation rate of studied metals fluctuates between 24.32 and 76.47 percent. It is interesting to note that much of metal flocculation occurs at the very lower (less than 2 ppt) salinity regimes.

**Keywords:** *Dissolved oxygen, Freshwater, Chalus river, Pollution elimination, Diverse salinities*



## INTRODUCTION

Heavy elements which have long lasting detrimental effects on environment are carried from the continents into the seas by rivers (Meybeck, 1988; Karbassi *et al.*, 2007, 2008). Chiefly, as a consequence of the estuarial mixture, heavy metals in the soluble and insoluble forms are influenced by a wide variety of reactions in the river which flocculation of metals is one of these reactions (Boyle *et al.*, 1977; Karbassi *et al.*, 2007, 2008, 2013). Flocculation process is one of the vital physicochemical processes, occurred by estuarial mixture in the upper areas of the estuary where the salinity is low, and strikingly impacted by such factors as ionic power, pH, and the amount of suspended particles in wetlands (Matagi *et al.*, 1998). On account of the occurrence of flocculation process at the estuary of the rivers, a large proportion of heavy metals leave the soluble phase in the form of cotton-like strings as nutrients, on the one hand, and contributes to improve and maintain the biological conditions of the oceans, seas and lakes (Sholkovitz, 1976; Li *et al.*, 1984; Comans and Van Dijk 1988; Samarghandi *et al.*, 2007). Estuaries are one of the coastal points and considered as construed as the interface between the sea salinity and rivers (Pritchard 1967; Viswanathan and Chakrapan, 2010), compatible places for aquatics' spawning and reproduction, areas full of nutrients, and celebrated for possessing diversified fauna and flora among the highly productive ecosystems in the sea (Dobson and Frid, 1998; Currier and Small, 2005; Karbassi *et al.*, 2007). Based on results of comprehensive investigations all around the world, as a result of estuary mixture, various parameters such as electrical conductivity, pH, dissolved oxygen, dissolved organic carbon, etc. change (Eckert and Sholkovitz, 1976; Fox and Wofsy, 1983; Hunter, 1983; Saeedi *et al.*, 2003; Karbassi *et al.*, 2007; Biati *et al.*, 2010a; Biati *et al.*, 2010b; Fazelzadeh *et al.*, 2012; Karbassi *et al.*, 2013; Valikhani Samani *et al.*, 2014). It is believed that owing to poison and threat posed by heavy metals to aquatics as well as the ecological importance of the estuary, paying meticulous attention to the geochemical cycle of the elements is necessary. In the present work, because of the important role of flocculation process in self-purification of heavy metals, the influence of pH, salinity and DO on the flocculation of such soluble metals as Cu, Zn, Pb, Ni, Cd and Mn

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during the mixture of Chalus River with the Caspian Sea is studied.

## MATERIALS AND METHODS

Fig. 1 illustrates the sampling location from freshwater and saline water samples which were taken from the Chalus River (Ca. 16 km upstream) and Caspian Sea (20 Km away from the coast) in 25-liter pre-labeled buckets respectively.

The freshwater's samples obtained from the Chalus River at 36° 24' latitude and the 52° 26' longitude and Caspian Sea at 36° 45' atitude and the 52° 30' longitude were filtered through 0.45 ìm Millipore AP and HA filters on the same day. About 1L of water sample that passed through filter was acidified with $HNO_3$ (pH = 1.8) and kept in polyethylene bottles in a refrigerator prior to determine the concentrations of the studied heavy metals (Cu, Zn, Pb, Ni, Cd & Mn) by ICP. Subsequently, filtered water of Chalus River and Caspian Sea were mixed in 5 various aquariums at the ambient temperature (25°C) in a wide variety of proportions producing salinities ranging from 1.5 to 9.5 ppt. Afterward, the mixed water samples were stirred throughout the first hour as the flocculates form. The mixture of freshwater and saline water was, then, left for 24 hours to assure thorough flocculation process. About 50 mL of the mixed freshwater and saline water from various aquariums (the number of aquariums was 5) was taken to measure physicochemical parameters such as salinity (Titration method (APHA, 2005)), temperature (Thermometer (accuracy of 1º C)), dissolved oxygen (DO meter (Inolab WTW)), and pH (pH meter (Metrohm 744)) of aliquots. The dissolved metals that came to the particulate phase were collected from each aquarium by a 2.5 cm diameter Millipore membrane filters (type HA, pore size 0.45 µm). In the present investigation, About 5 mL of concentrated nitric acid (HNO3), ICP (ULTIMA 2000) and weighted pair group (WPG) method (Davis, 1973), as one of the existing clustering techniques (Anderson, 1971; Davis, 1973) were used

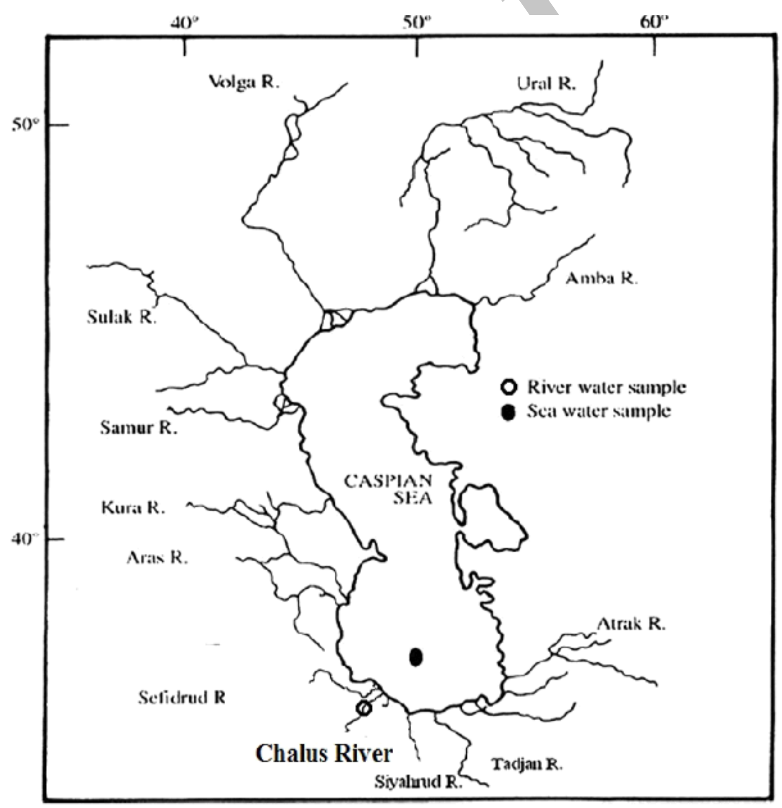


Fig.1: Sampling location from Chalus River and Caspian Sea

to digest Millipore filters overnight, determine the concentrations of studied elements and found the relationship between physicochemical parameters and studied metals respectively. Procedural blanks and duplicates 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. The accuracy of the analysis was ±5% for mentioned elements (Cu, Zn, Pb, Ni, Cd and Mn) in the dissolved and flocculent phases approximately.

## RESULTS AND DISCUSSION

Caspian Sea is the largest enclosed body all across the world where encompass three basins with divers feathers and the salinity of this sea changes from 4 ppt in the northern parts to about 12.5 ppt in the southern parts. The length of Caspian Sea is about 1030 km, the width of the lake ranges from 196 to 435 km and the area is 371,000 $km^2$. Chalus River with 80km length grafts to Caspian Sea on Chalus city. The average discharge of such a river is 53.30 × $10^6$ $m^3$/year. Table 1 including the concentration of such elements as cadmium, copper, manganese, nickel, zinc, and lead occurring in the flocculates in varied salinity regimes (1.5, 3.5, 5.5, 7.5 & 9.5 ppt), pHs (pH = 8.71, 8.55, 8.57, 8.6 & 8.62) and DO ( DO = 8.36, 8.12, 7.1, 6.41 & 5.9) does not illustrate the actual conditions throughout the mixture of freshwater and saline water; and at every stage, as the salinity increases, part of the flocculate produced during the prior stage mixes with the flocculate produced at the next stage; thus, the amount of the flocculate produced at each stage should be deducted from that of the prior stage in establishing the natural position of estuarial mixture (Table 2) (Zhiqing *et al.*, 1987; Saeedi *et al.*, 2003; Karbassi *et al.*, 2008a; Biati *et al.*, 2010b; Shamkhali Chenar *et al.*, 2013; Karbassi *et al.*, 2014).

According to Table 2, Mn and Pb demonstrate the maximum and minimum removal at various salinity regimes (1.5 to 9.5 ppt), pHs (pH = 8.71, 8.55, 8.57, 8.6 & 8.62) and DO (DO = 8.36, 7.78, 7.1, 6.41 & 5.9 mg/L) respectively which is disagreement with other studies (Saeedi *et al.*, 2003; Karbassi *et al.*, 2007; Karbassi *et al.*, 2008). Moreover, Cu, Ni, Cd and Mn show non-conservative behavior. On the other hand, Zn and Pb relatively reveal a conservative behavior. Fig. 2 shows all studied elements undergo their highest flocculation rate at low salinity regimes which acknowledges the results of other researches (Biati and Karbassi, 2012; Karbassi *et al.*, 2013, 2014). Based on gained results, it

Table 1: Laboratory flocculation of metals during mixing of Chalus River water with Caspian Sea water

| Sample | Cu(µg/L) | Zn(µg/L) | Pb(µg/L) | Ni(µg/L) | Cd(µg/L) | Mn(µg/L) | pH | DO(mg/L) | S(‰) |
|---|---|---|---|---|---|---|---|---|---|
| River water | 34 | 890 | 37 | 25 | 5 | 102 | | | 0.16 |
| 1 | 16 | 140 | 7 | 12 | 1 | 49 | 8.71 | 8.36 | 1.5 |
| 2 | 18 | 185 | 9 | 17 | 2 | 57 | 8.55 | 8.12 | 3.5 |
| 3 | 22 | 215 | 5 | 16 | 1 | 63 | 8.57 | 7.1 | 5.5 |
| 4 | 20 | 220 | 4 | 16 | 1 | 78 | 8.6 | 6.41 | 7.5 |
| 5 | 20 | 230 | 4 | 14 | 1 | 70 | 8.62 | 5.9 | 9.5 |

Table 2: Actual flocculation of metals during mixing of Chalus River water with Caspian Sea water

| Sample | Cu(µg/L) | Zn(µg/L) | Pb(µg/L) | Ni(µg/L) | Cd(µg/L) | Mn(µg/L) | pH | DO(mg/L) | S(‰) |
|---|---|---|---|---|---|---|---|---|---|
| River water | 34 | 890 | 37 | 25 | 5 | 102 | | | 0.16 |
| 1 | 16(47.06) | 140(15.73) | 7(18.92) | 12(48) | 1(20.00) | 49(48.04) | 8.71 | 8.36 | 1.5 |
| 2 | 2(5.88) | 45(5.06) | 2(5.41) | 5(20) | 1(20.00) | 8(7.84) | 8.55 | 8.12 | 3.5 |
| 3 | 4(11.76) | 30(3.37) | 0(0.00) | 0(0.00) | 0 | 6(5.88) | 8.57 | 7.1 | 5.5 |
| 4 | 0 | 5(0.56) | 0(0.00) | 0(0.00) | 0 | 15(14.71) | 8.6 | 6.41 | 7.5 |
| 5 | 0 | 10(1.12) | 0(0.00) | 0(0.00) | 0 | 0 | 8.62 | 5.9 | 9.5 |
| Total | 22(64.71) | 230(25.84) | 9(24.32) | 17(68.00) | 2(40.00) | 78(76.47) | | | |

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

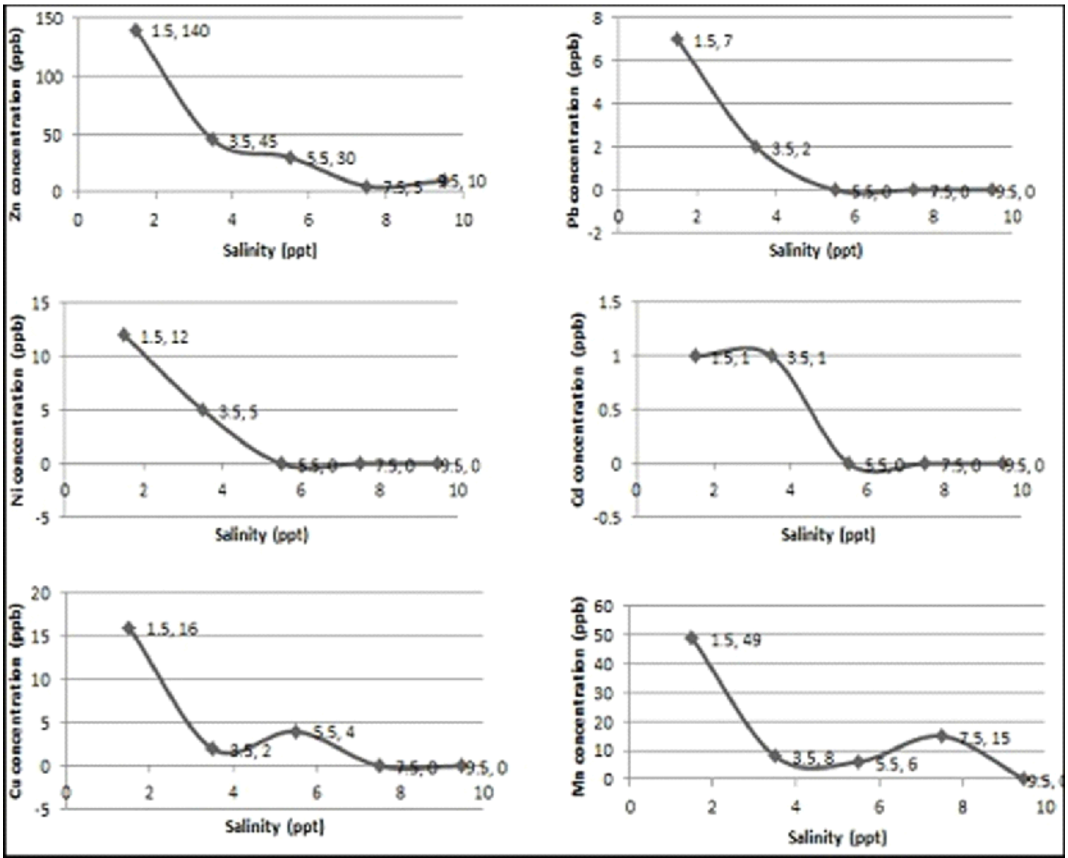


Fig. 2: Flocculation of Cu, Zn, Pb, Ni, Cd and Mn during estuarine mixing



can be clearly seen that during estuarine mixing, about 3% of Zn and 6% of Mn are flocculated at salinity of 5.5 ppt, pH = 8.57 and DO = 7.1 mg/L, while the flocculation rate of other heavy metals studied here is 0.00%. It is also appealing to note that in the salinity of 9.5 ppt, pH = 8.62 and DO = 5.9 mg/L, only lead has a tendency to flocculate. According to dendrogram of cluster analysis (Fig. 3), the flocculation mechanism of Mn, Zn and Cu are controlled by salinity. In addition, due to high similarity coefficient between DO and Pb, DO has positive effect on flocculation trend of lead. The results of such a study demonstrate about 24.32% of Pb, 24.38% of Zn, 40.00% of Cd, 64.71% of Cu, 68.00% of Ni and 76.46 % of Mn come into the particulate phase during mixing of Chalus River with Caspian Sea. Consequently, the aggregate pollution load entering to the sea reduces from 58.26 to 39.18 ton per year.

According to Table 2, Mn and Pb demonstrate the maximum and minimum removal at various salinity regimes (1.5 to 9.5 ppt), pHs (pH = 8.71, 8.55, 8.57, 8.6 & 8.62) and DO (DO = 8.36, 7.78, 7.1, 6.41 & 5.9 mg/L) respectively which is disagreement with other studies (Saeedi *et al.*, 2003; Karbassi *et al.*, 2007; Karbassi *et al.*, 2008). Moreover, Cu, Ni, Cd and Mn show non-conservative behavior. On the other hand, Zn and Pb relatively reveal a conservative behavior. Fig. 2 shows all studied elements undergo their highest flocculation rate at low salinity regimes which acknowledges the results of other researches (Biati and Karbassi, 2012; Karbassi *et al.*, 2013, 2014). Based on gained results, it can be clearly seen that during estuarine mixing, about 3% of Zn and 6% of Mn are flocculated at salinity of 5.5 ppt, pH = 8.57 and DO = 7.1 mg/L, while the flocculation rate of other heavy metals studied here is 0.00%. It is also appealing to note that in the salinity of 9.5 ppt, pH = 8.62 and DO = 5.9 mg/L, only lead has a tendency to flocculate. According to dendrogram of cluster analysis (Fig. 3), the flocculation mechanism of

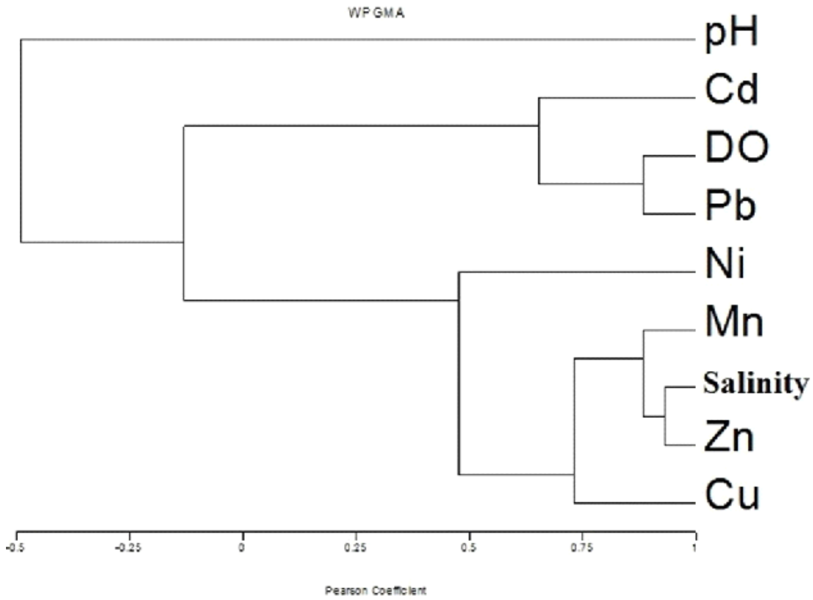


Fig. 3. Cluster analysis of heavy metals

Mn, Zn and Cu are controlled by salinity. In addition, due to high similarity coefficient between DO and Pb, DO has positive effect on flocculation trend of lead. The results of such a study demonstrate about 24.32% of Pb, 24.38% of Zn, 40.00% of Cd, 64.71% of Cu, 68.00% of Ni and 76.46 % of Mn come into the particulate phase during mixing of Chalus River with Caspian Sea. Consequently, the aggregate pollution load entering to the sea reduces from 58.26 to 39.18 ton per year.

## CONCLUSION

In the present study, the flocculation trend of cadmium, copper, manganese, nickel, zinc, and lead during the estuarial mixture of Chalus River and the Caspian Sea was perused. The results of analysis reveal the percentage of flocculation of manganese is higher in comparison with other heavy metals. Furthermore, all the studied metals (except Zn & Pb) have non-conservative behavior. The flocculation rate of lead is intensified by DO and copper, manganese and zinc is controlled by salinity noticeably. Nevertheless, pH does not play any function on flocculation trend of Cu, Zn, Pb, Ni, Cd and Mn. Because of mixing of Chalus River with Caspian Sea the total heavy metal contamination load is on the decrease from 58.26 to 39.18 ton. It is fascinating to note that much of metal flocculation occurs at the very lower (less than 2 ppt) salinity regimes.

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