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Metals removal during estuarine mixing of Arvand River water with the Persian Gulf water

Research Article

Abdolreza Karbassi[1], Gholam Reza Nabi Bidhendi[1], Mohsen Saeedi[2*], Azadeh Rastegari[1]

1 Graduate Faculty of Environment, University of Tehran, P.O.Box 14155-6135, Tehran, Iran

2 Environmental Research Laboratory, Department of Hydraulics and Environmental Engineering, School of Civil Engineering, Iran University of Science and Technology, Narmak, Tehran, 16846, Iran

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Abstract: In the present study, the removal of dissolved and colloidal Cd, Co, Cu, Ni and Zn in Arvand River water during estuarine mixing with the Persian Gulf water is investigated. The flocculation process was investigated for a series of mixtures with salinities ranging from 0.48 to 30.3‰. The flocculation rates were indicative of the non-conservative behavior of studied metals during estuarine mixing. Rapid flocculation in the low salinity regimes was observed. The order of the final flocculation rate of metals in the river water was as follows: Co (91.2%)> Cd (86.9%)> Zn (83%)> Cu (75.2%)> Ni (74.3%). Salinity, pH, EC and dissolved oxygen do not govern the flocculation of metals during estuarine mixing. The results of the present investigation show that estuarine processes can be considered as an effective mechanism in self purification of colloidal metals that are anthropogenically introduced into the fresh water ecosystem.

Keywords: heavy metals • estuarine mixing • flocculation • Arvand River • Persian Gulf

1. Introduction

Rivers that drain watersheds carry nutrients and environmental pollutants into the sea through estuaries [1]. From an ecological point of view estuaries are among the most important environments which affect marine aquatic organisms. Metal enriched discharges from different sources like acid mine drainages have caused serious ecological damage to estuaries around the world [2, 3]. The effect of metals on estuarine ecology, to some extent, depends on the phase in which the metals are carried into the estuaries [4]. Since the transport mechanisms and pathways for dissolved metals may be different to that for particulate metals, understanding the processes and mechanisms controlling metals transport from rivers to the sea is important.

The flocculation of metals during estuarine mixing can significantly influence the chemical mass balance and chemical/physical forms of the metals in the sea. Mixing of freshwater and seawater in estuaries can cause rapid changes in chemical/physical characteristics of the water environment resulting in coagulation/flocculation/ pre-

*E-mail: msaeedi@iust.ac.ir, Fax: +98 21 77249398

cipitation of some substances like heavy metals. Many investigations have been carried out on flocculation of dissolved substances in order to find the the controlling mechanisms. Previous studies have mainly focused on colloidal stability, surface properties, humic acids, salinity and pH [5? –11]. Some researchers have also considered the role and presence of other factors such as total organic carbon (TOC), anions (i.e. nitrate, sulphate, phosphate), dissolved organic carbon (DOC), total hardness and the concentration of metals themselves [12–14]. Karbassi (1998) showed that a significant part of V (80.2%)> Ni(71.1%)> Fe(59.36%)> Co (41.9%)> Cu(41.2%)> Zn(36.1%)> Mn(29.1%) are removed in hot 50% HC1 fraction. This clearly shows that sources of Co, Cu, Zn and Mn in the surficial sediment of The Persian Gulf are anthropogenic [15]. However, limited information is available on the recognition of dissolved metals flocculation processes during estuarine mixing of river waters with the Persian Gulf water.

The Persian Gulf (24°-30°30′N, 48°-56°30′E), in the south of Iran, is an extension of the Indian Ocean located between Iran and the Arabian Peninsula. The Persian Gulf is 989 km in length and covers an area of about 251000 km^2 and connectsto the Gulf of Oman in the east, by the Strait of Hormuz. In the northwest it ends by the major river delta of the Arvand River which carries the waters of the Euphrates, Tigris and Karun rivers. The waters of the Persian Gulf are generally very shallow; with a maximum depth of 90 m and an average depth of 50 m, with a salinity range of 37-40 ppt. Unfortunately, the ecology of the Persian Gulf has come under pressure from industrialization of the coastal regions (i.e. watershed of the major rivers flowing into the Gulf) and in particular repeated petroleum spills during recent wars (Iran-Iraq, Gulf War 1991, 2003).

The only rivers flowing into the Persian Gulf as freshwater sources are from north side. The major rivers discharging into the Gulf are the Arvand, Hella and Mond. The Arvand river is about 170 km in length and is a part of Iran-Iraq border to the southwest of Iran. This river is a continuation of the Tigris and Euphrates rivers which join together at Qurna. The Karun river has an average flow rate of 435 m^3 s^{-1} that comes from where the Iranian side joins the river, making the Arvand which flows towards the Persian Gulf. Since these three rivers have huge watersheds in Iran, Iraq, Syria and Turkey and drain most of their waterj in these countries, the main pollution source originating from watersheds of the Persian Gulf is the Arvand River. The Arvand itself and the three rivers that produce it are used as transport agents for the disposal of industrial, agricultural and urban wastes. Therefore, it is vitally important to investigate the overall geochemical cycle of trace metals and their behavior in this region.

Taking into account the vulnerable ecology of the Persian Gulf and the considerable discharge of the Arvand River which, leads to huge fluxes of contaminants, study of the mechanisms controlling the behavior of metals in Arvand estuary seems to be important.

In the present study, for the first time in the Persian Gulf waters, removal of dissolved heavy metals (Co, Cd, Cu, Ni and Zn) during estuarine mixing of Arvand River water with the Persian Gulf waters in relation to the parameters such as pH, salinity, electrical conductivity (EC) and dissolved oxygen is investigated. In an attempt to study flocculation of dissolved metals a series of laboratory experiments on river water samples originating from Arvand River and the Persian Gulf water samples were carried out.

2. Materials and methods

Freshwater samples were collected from the surface of the Arvand River (ca. 16 km upstream) using a 25 L clean polyethylene bucket in January 2009. At each station three water samples (totally six samples) were collected. Furthermore, the three freshwater samples were mixed to achieve a composite sample. This process was repeated for the seawater samples. On the same day samples were filtered through 0.22 µm Millipore AP and HA filter. Approximately 1L of filtered water was acidified with concentrated HNO_3 to a pH of about 1.8 and stored in polyethylene bottles within a refrigerator. The rest of filtered water was also kept in a refrigerator. On the same day, The Persian Gulf water was collected approximately 16 km away from the coast to ensure that the sample was not diluted by river water (salinity =37‰). Map showing the sampling points is presented in Figure 1.

In order to prevent sample contamination 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 seawater were mixed together at room temperature in various proportions and in 3 different batches (totally 30 mixtures) yielding salinities from 1.5 to 30.3‰whichwere kept for 24 h with occasional stirring. The resulting flocculants were collected on 0.22 µm Millipore membrane filters. Millipore filters were digested with 5 ml of concentrated HNO_3 overnight. The concentrations of Cu, Zn, Ni, Co and Cd were determined by AAS (Philips model PU-9004). The results of the triplicate experiments were used to calculate the mean values used in this study. Procedural blanks and duplicates were run with the samples in a similar way. The inner standards for determination were obtained by using the single concentrated

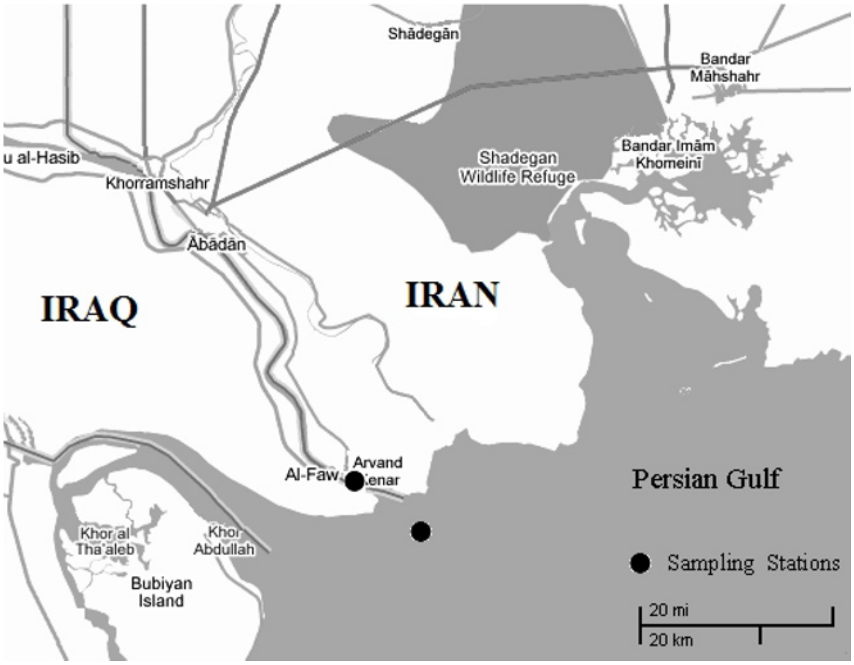

Figure 1. Water sampling sites in Arvand River and The Persian Gulf.

calibration standards produced by Merck Company. The accuracy of analysis was about ±5% for all elements in dissolved and flocculant phases. Standard sample CASS-4 was used to check the precision of the analyses. The concentrations of the elements were in accordance with the reported data (Table 1).

Table 1. Published and obtained data for CASS-4 (µg L^{-1})

Metal	Published data[a]	Obtained data
Cd	0.026 (0.003)	0.024
Co	0.026 (0.003)	0.023
Cu	0.592 (0.055)	0.581
Ni	0.314 (0.030)	0.303
Zn	0.381 (0.057)	0.361

[a]CASS-4, Nearshore Seawater Reference Material for Trace Metals [19] Standard deviations are given within parentheses.

The pH value of the samples was determined using a Cyber Scan PC510 (Eutech, Singapore) pH meter which had been calibrated with a 13000 µs cm^{-1} standard solution and pH 4, 7 and 10 buffer solutions. Salinity, pH and EC of water samples were measured using Siemens multichannel portable apparatus. Among the existing clustering techniques [16–18], the weighted-pair group method [18] was chosen as the most suitable method for the study.. This method uses the linear correlation coefficient as a similarity measure. The highest similarities are clustered/ linked first, and variables are connected only if they are highly correlated. After two variables are clustered, their correlations with all the other variables are averaged. The multivariate statistical package (MVSP) that performs a variety of ordination and cluster analyses was used for cluster analysis. The results of clustering are displayed in the form of a Dendrogram.

3. Results and discussion

The studied metal (Cd, Co, Cu, Ni and Zn) concentrations found in flocculants after flocculation at various salinities, as well as other physical/chemical characteristics [pH, electrical conductivity (EC) and dissolved oxygen] of the mixtures are presented in Table 2. However, it is important to note that during natural estuarine mixing, flocculation processes may not occur as shown in Table 2. In this way, the flocculate quantity is not calibrated to the first concentrations of the metals in the river water [12–14, 20]. In fact, at the first stage of the mixing of the river water with the lake water, some of the dissolved metals may be removed out of the fresh water in the form of flocculates. Thus, at the later stages of mixing (i.e. at higher salinities) the fresh water is impoverished in trace metals and less flocculates form. The values given in Table 3 are derived from Table 2 by subtracting the concentrations of flocculates at each salinity from the previous step. According to the results shown in Tables 2 and 3, the maximal removal of all studied metals occurs between salinities of 0.48-1.5 in the first step of mixing experiments. Nickel removal occurs only at the first step of mixing up to salinity of 1.5‰. About 73% of Cu removes at salinities between 0.48 - 6.8‰while all 83% of Zn removal occurs at this range of salinity. All 83.96% of Cd removal occurs in the first two steps of mixing in salinities between 0.48 to 3.2‰. For the 91.23% of cobalt removal, 71.94% occurs in the first two steps and the rest of it (19.29%) is removed at salinities of about 16.8‰.

Many researchers have reported rapid flocculation in the earlier stages (at a salinity of about 2‰) of the mixing process [21–23] ,which is in agreement with the results of this study. On the other hand, more distributed removal in terms of salinity has been reported for studies on the riverine mixings with the Caspian Sea as a lake [12–14, 20]. There seems to be some differences in the contents of effective agents of flocculation in the Persian Gulf and other open sea water with the Caspian Sea water as a large lake. When compared to other case studies like the Persian Gulf, the salinity and composition of the Caspian Sea water is different. More detailed studies are needed to evaluate the role of chemical species and to determine the main effective agents in sea water for the estuarine removal of dissolved metals and differences of flocculation patterns in different estuaries.

In summary, flocculation rates of studied metals in the Arvand river estuary are in the following order: Co (91.2%)> Cd(86.9%)> Zn(83%)> Cu(75.2%)> Ni(74.3%).

These removal rates show that the overall dissolved metal loads into the Persian Gulf may be reduced by 74-91.2% from the initial amount. Karbassi et al. (2010) showed that flocculation rate in the strait of Hormouz (connection between The Persian Gulf and Sea of Oman) is in the order of Cu(83.3%)> Ni(82.9%)> Zn(75.5%)> Mn(69.4%)> Pb(38%) [24].

Figure 2 shows the results of cluster analysis of the data. The dendogram consists of 3 distinctive branches namely "A", "B" and "C". Salinity, pH and EC that form cluster "C" have high similarities which seems reasonable according to sea water as their source of variation.

It can also be seen that DO, Cd, Co and Ni that form cluster "B" join each other at moderate similarity coefficients. This clearly shows that oxygen is the most important governing factor in the flocculation of Cd, Co and to a lesser extent Ni. Cluster "A" that contains Zn and Cu join cluster "B" at lower similarity coefficient. This shows that further research is needed to find out about the governing factors

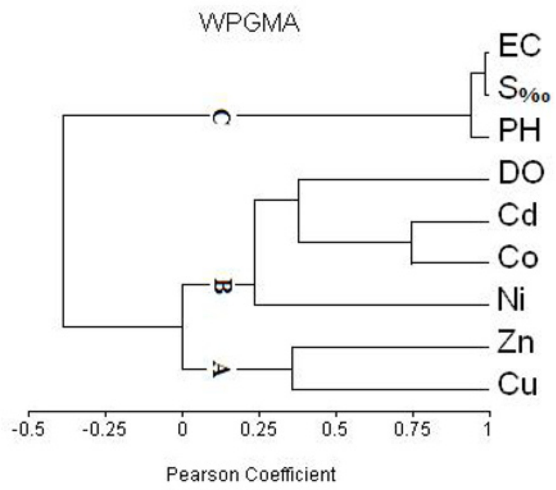

Figure 2. Dendrogram of cluster analysis for metals and other physical-chemical characteristics of Arvand River and Persian Gulf waters in experimental mixtures.

of these two elements. Finally, cluster "B" and "C" join cluster "A" at a very low similarity coefficient of -0.4.This may indicate that there are some other parameters in the seawater that have an effect on the estuarine removal of these metals.

4. Conclusion

Flocculation of metals during estuarine mixing has not been subjected to intensive investigation. Though such studies date back to 1970s, the number of studies is scarce. Most of previous studies confirm pH and salinity as the main governing factors for the flocculation of metals during estuarine mixing. The present study shows that pH and salinity do not have a major role in flocculation of metals. The flocculation rate of studied metals showed that the overall metal pollution load can be reduced by various percentiles (ranging from 74 to 91%) during estuarine mixing of Arvand river water with the Persian Gulf water. Therefore, estuarine processes can be considered as an effective mechanism in the self purification of colloidal metals that are anthropogenically introduced into the fresh water ecosystem. Future studies should focus on the utilization of seawater in the treatment of heavy metals during industrial wastewater purification. Conse-

Table 2. Metal concentrations and physical-chemical parameters in Persian Gulf water, Arvand River water and experimental mixtures containing Persian Gulf water.

Sample	Cu(μg L^{-1})	Zn(μg L^{-1})	Ni(μg L^{-1})	Co(μg L^{-1})	Cd(μg L^{-1})	pH	S(‰)	EC(mS cm^{-1})	DO(mg L^{-1})
Persian Gulf						7.98	37	61.8	1.2
River Water	141	183	39	57	23	7.97	0.48	2.44	7.5
1	51 (36.17)	80 (43.72)	29 (74.36)	39 (68.42)	14 (60.87)	6.7	1.5	16.55	5.5
2	55 (39.01)	81 (44.26)	24 (61.54)	41 (71.93)	20 (86.96)	6.9	3.2	25.5	5
3	103 (73.05)	94 (51.37)	23 (58.97)	36 (63.16)	14 (60.87)	7	6.8	30.7	5.3
4	51 (36.17)	152 (83.06)	23 (58.97)	37 (64.91)	13 (56.52)	7.1	10.0	35.9	4.9
5	47 (33.33)	41 (22.40)	24 (61.54)	52 (91.23)	18 (78.26)	7.1	16.8	45.4	4.9
6	48 (34.04)	50 (27.32)	21 (53.85)	39 (68.42)	16 (69.57)	7.2	20.5	50.7	5
7	43 (30.49)	51 (27.87)	22 (56.41)	36 (63.16)	12 (52.17)	7.2	23.5	54.3	5
8	45 (31.91)	62 (33.88)	25 (64.10)	34 (59.65)	10 (43.48)	7.3	25.2	56.5	4
9	106 (75.18)	93 (50.82)	22 (56.41)	35 (61.40)	12 (52.17)	7.5	27.8	57	4.6
10	48 (34.04)	45 (24.59)	20 (51.28)	35 (61.40)	12 (52.17)	7.4	30.3	59.4	4.6

Percentile of removal is given within parentheses.

Table 3. Actual metal concentrations in flocculants of mixed waters of Arvand River with Persian Gulf water.

Sample	Cu(μg L)	Zn(μg L)	Ni(μg L^{-1})	Co(μg L^{-1})	Cd(μg L^{-1})	pH	S(‰)	EC(mS cm^{-1})	DO(mg L^{-1})
River Water	141	183	39	57	23	7.97	0.48	2.44	7.5
1	51 (36.2)	80 (43.7)	29 (74.4)	39 (68.4)	14 (60.9)	6.7	1.5	16.55	5.5
2	4 (2.8)	1 (0.5)	0.0 (0.0)	2 (3.5)	6 (26.1)	6.9	3.2	25.5	5
3	48 (34)	13 (7.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	7	6.8	30.7	5.3
4	0.0 (0.0)	58 (31.7)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	7.1	10.0	35.9	4.9
5	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	11 (19.3)	0.0 (0.0)	7.1	16.8	45.4	4.9
6	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	7.2	20.5	50.7	5
7	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	7.2	23.5	54.3	5
8	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	7.3	25.2	56.5	4
9	3 (2.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	7.5	27.8	57	4.6
10	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	7.4	30.3	59.4	4.6
Total	106 (75.2)	152 (83)	29 (74.3)	52 (91.2)	20 (86.9)				

Percentile of removal is given within parentheses.

quently, the mean annual discharge of dissolved Co, Cd, Zn, Cu and Ni from Arvand river into Persian Gulf would be reduced from 855, 345, 2745, 2115 and 585 ton yr^{-1} to about 75, 45, 467, 525 and 150 ton yr^{-1}, respectively.

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