Available online at www.sciencedirect.com
ScienceDirect
Desalination 229 (2008) 118–124
DESALINATION
www.elsevier.com/locate/desal

Behavior of Cu, Zn, Pb, Ni and Mn during mixing of freshwater with the Caspian Sea water

A.R. Karbassi[a], J. Nouri[b]*, Gh.R. Nabi Bidhendi[a], G.O. Ayaz[c]

[a]*Graduate Faculty of the Environment, University of Tehran, P .O .Box 14155-6135, Tehran, Iran*
[b]*Department of Environmental Health Engineering, School of Public Health, Medical Sciences, University of Tehran, Tehran, Iran*
Tel./Fax +98 (21) 88989133; email: jnouri@tums.ac.ir
[c]*Department of Environmental Science, Graduate School of the Environment and Energy, Science and Research Campus, IAU, Tehran, Iran*

Received 22 October 2006; accepted revised 21 June 2007

Abstract

Behavior of metals during estuarine mixing can significantly influence the chemical mass balance between rivers and seas or lakes. Present investigation describes the results of mixing of a sample of filtered (0.45 μm) Caspian Sea water with a filtered water sample taken from the Babolrud River in 9 different salinity proportions. Flocculation of colloidal size fraction of heavy metals was investigated on a series of mixtures with water salinities ranging from 1.5 to 9.5‰ during mixing of the Babolrud River with the Caspian Sea water. The flocculation trend of Cu (77.9%) > Zn (74.6%) > Mn (64.97%) > Pb (38.2%) > Ni (12.2%) indicates that Cu, Zn, Pb and Mn have non-conservative behavior and Ni has relatively conservative behavior during estuarine mixing. The highest flocculation of heavy metals occurs between the salinities of 1.5–3.5‰. Statistical analysis indicates that the flocculation of Cu is governed by pH and PO_4. The flocculation rate of the studied metals showed that the overall colloidal metal pollution loads can be reduced by various percentages (ranging from as low as 12 to as high as 78) during estuarine mixing.

Keywords: Behavior; Heavy metals; Seawater; Estuary; The Caspian Sea

1. Introduction

During estuarine mixing, dissolved metals come into the particulate phase due to flocculation processes [3,8,21]. Flocculation is enhanced by increased pH, turbulence, concentration of suspended matter, ionic strength and high algal concentration [15]. This investigation seems to be one of the only such studies carried out in the

*Corresponding author.

0011-9164/08/$– See front matter
doi:10.1016/j.desal.2007.06.035

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 [9–11,19,22]. However not much information is available on recognition of dissolved metal flocculation processes during estuarine mixing of river water with brackish lake water [11,12,18].

The salinity of the Caspian Sea water ranges from 4‰ in the northern parts to almost 13‰ in the southern parts. The Babolrud River has a length of 161 km with a discharge of 560×10^6 m^3/y. The catchments area of the river is about 1659 km^2 with an average precipitation of 765 mm/y. Fig. 1 depicts the sampling locations.

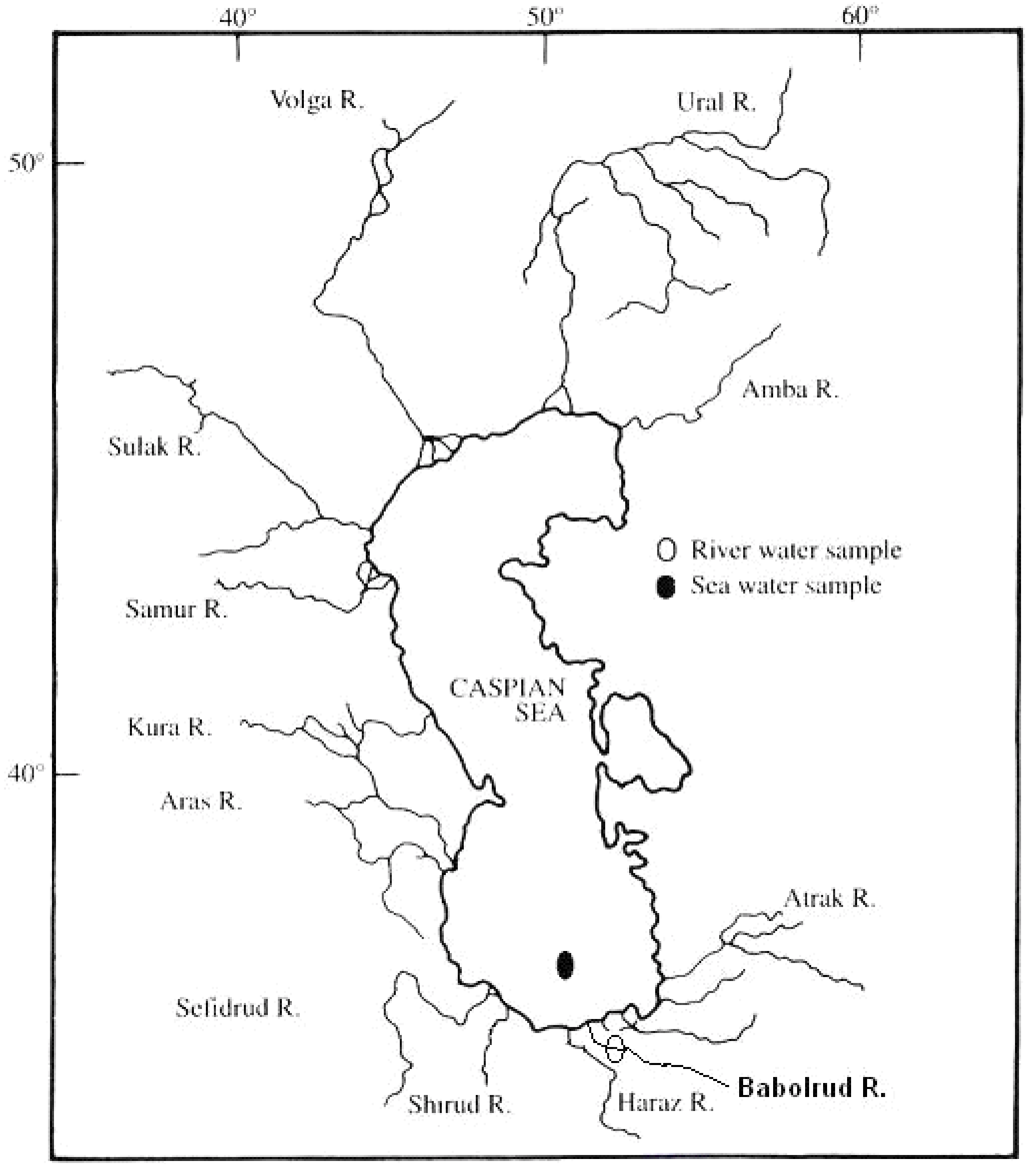

Fig. 1. Locations of water samples from the Babolrud River and the Caspian Sea.

2. Materials and methods

Freshwater samples were collected from the Babolrud River and the Caspian Sea. The locations of water samples from the Babolrud River and the Csspian Sea are shown in Fig. 1. The collected samples were taken in a 25 l clean polyethylene bucket on 12 December 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 the filtered water was also stored in the refrigerator. On the same day, the Caspian Sea water sample was collected approximately 20 km away from the coast to ensure that the sample was not diluted by river water (salinity = 13‰). Filtered river water and seawater were mixed together at room temperature (ca. 25°C) in nine proportions yielding salinities of 1.5–9.5‰. 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 using 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. Calibration of AAS was done by dilution of single concentrated standards purchased from Merck Company. The accuracy of the analysis was about ±5% for all elements in the dissolved and flocculant phases. Salinity, pH and electrical conductivity (EC) of the water samples were measured using a Siemens multi-channel portable apparatus. Nitrates, phosphates and sulfates were measured using a photometer (model 8000) in accordance with ASTM procedure (2003). Total dissolved organic carbon (DOC) of water samples was measured using a TOC meter (Shimatzu model TOC-VCSH-3000a). Total hardness (TH) was determined titrimetrically. Cluster analysis was carried out according to the Weighted Pair Group (WPG) method [4].

3. Results and discussion

Table 1 shows the concentrations of Cu, Zn, Pb, Ni and Mn found in flocculants at various salinities as well as fresh river water. The concentration of total dissolved organic carbon (DOC) in the river water was about 2.4 mg/l that increased to 51.3 mg/l at a salinity of 9.5‰ (Table 2). Such

Table 1
Heavy metal concentrations in the Babolrud River water and laboratory flocculants (mixing the Babolrud River water with the Caspian Sea water)

Sample	Cu (µg/L)	Mn (µg/L)	Ni (µg/L)	Zn (µg/L)	Pb (µg/L)	pH	S (‰)
River water	20.8	19.7	40.15	85	22	9.06	0.21
1	3.9 (18.7)	1.95 (9.9)	2.6 (6.5)	25.5 (30.0)	0.48 (2.2)	8.54	1.55
2	8.35 (40.1)	4.27 (21.7)	1.8 (4.5)	38.3 (45.0)	1.0 (4.5)	8.52	2.55
3	12.3 (59.1)	6.85 (34.6)	2.85 (6.6)	47.6 (56.0)	3.3 (15.0)	8.50	3.55
4	14.8 (71)	6.27 (31.8)	2.46 (6.1)	26.2 (30.8)	3.8 (17.3)	8.48	4.55
5	6.3 (30.3)	7.73 (44.3)	1.32 (3.3)	50.8 (59.0)	0.84 (3.8)	8.46	5.55
6	16.2 (77.9)	8.65 (13.9)	2.28 (5.7)	57.4 (67.5)	0.42 (1.9)	8.44	6.55
7	4.1 (37.0)	10.4 (52.8)	2.54 (6.3)	49.6 (58.3)	0.0 (0.0)	8.42	7.55
8	2.2 (20.0)	11.4 (57.8)	2.74 (6.8)	38.2 (44.9)	7.2 (32.7)	8.39	8.55
9	4.7 (41.7)	12.8 (65)	4.9 (12.2)	63.4 (74.6)	8.42 (38.2)	8.37	9.55

*Percentile of removal is given within parentheses.

Table 2
Physico-chemical parameters in the Babolrud River water and actual heavy metal concentrations in flocculants (mixing the Babolrud River water with the Caspian Sea water)

Sample	Cu (µg/L)	Mn (µg/L)	Ni (µg/L)	Zn (µg/L)	Pb (µg/L)	EC (µs/cm)	pH	S (‰)	DOC (mg/L)	N_T (mg/L)	PO_4 (mg/L)	SO_4 (mg/L)	TH (mg/L)
River water	20.8	19.7	40.15	85	22	916	9.06	0.21	2.4	0.235	0.06	191	210
1	3.90 (18.7)	1.95 (9.90)	2.60 (6.5)	25.5 (30.0)	0.48(2.20)	9832	8.54	1.55	5.42	1..27	0.14	495	1420
2	4.45 (21.4)	2.32 (11.77)	0.0 (0.0)	12.8(15.05)	0.52(2.36)	11273	8.52	2.55	9.45	1.18	0.25	201	1850
3	3.95 (18.99)	2.58 (13.09)	0.25 (0.62)	9.3(10.94)	2.3(10.45)	11915	8.50	3.55	26.2	0.094	0.18	206	2430
4	2.5 (12.02)	0.0 (0.0)	0.0 (0.0)	0.0(0.0)	0.50(0.58)	12764	8.48	4.55	28.7	0.698	0.21	207	2250
5	0.0 (0.0)	0.88 (4.46)	0.0 (0.0)	3.20(3.76)	0.0(00)	13539	8.46	5.55	31.4	0.817	0.09	205	2600
6	1.4 (6.73)	0.92 (4.67)	0.08 (0.19)	6.60(7.76)	0.0(0.0)	14132	8.44	6.55	36.8	0.869	0.13	367	2250
7	0.0 (0.0)	1.75 (8.88)	0.0 (0.0)	0.0(0.0)	0.0(0.0)	15034	8.42	7.55	37.2	0.701	0.06	493	2400
8	0.0 (0.0)	1.00 (5.07)	0.20 (0.49)	0.0(0.0)	3.4(15.45)	15640	8.39	8.55	44.15	0.632	0.07	465	2400
9	0.0 (0.0)	1.40 (7.10)	2.16 (5.38)	6.0(7.05)	1.22(5.54)	15894	8.37	9.55	51.3	0.531	0.07	450	2300
Total removal	16.2 (77.9)	12.8 (64..97)	4.90 (12.2)	63.4(74.6)	8.42(38.2)	—	—	—	—	—	—	—	—

*Percentile of natural removal is given within parentheses.

an increase is suggestive of a marine carbon source in the estuarine zone. Other parameters such as SO_4 and total hardness (TH) show a trend similar to that of DOC. The increasing trend of SO_4 is mainly due to the redox conditions that prevail in the Caspian Sea [18]. The concentration of total nitrogen (N_T) increases at low salinities (1.5 to 2.5‰) and sharply decreases at 3.5‰ salinity. Generally, the concentration of N_T is higher in saline water than in fresh water in the area of study.

During estuarine mixing, flocculation processes may not occur as shown in Table 1. In fact, in the very first stages of mixing of river water with lake water, some of the colloidal metals ooze out of the freshwater in the form of flocculants [18,22]. Thus, at the later stages of mixing (i.e., higher salinities) freshwater is impoverished in base metals and fewer flocculates form (Table 2). We, therefore, do not discuss the data of Table 1 as they are indicative of laboratory conditions/setup. In other words, during laboratory mixing, a constant amount of fresh water is mixed with various proportions of seawater. The values presented in Table 2 are actually derived from Table 1 by subtracting the concentrations of flocculates at a specific salinity from the previous steps. In this way, the flocculate quantity is not calibrated to the very first concentration of the metals in the river water [12]. According to the data shown in Table 2, the maximal removal of Cu, Zn and Mn occur between salinities of 1.5 and 3.5‰ where as Ni removal is confined to salinity ranges of 1.5–9.5‰. The behavior of Pb is similar to that of Ni at salinities of 3.5 and 8.5‰. The variation in the maximal removal of the metals studied may be due to destabilization of dissolved metals, corresponding to the different stages of mixing with seawater and a decrease in their negative net charge [1]. The flocculation rates of the metals in the Babolrud River are in the following order:

Cu (77.9%) > Zn (74.6%) > Mn (64.97%) > Pb (38.2%) > Ni (12.2%)

Thus, rapid flocculation in the earlier stages of mixing freshwater with lake water (salinity of 1.5–3.5‰) occurs that is in accordance with the findings of other researchers [2,7]. Interestingly, reports from other rivers flowing into the southern Caspian Sea show that Pb and Ni undergo minimum flocculation when compared with Cu, Zn and Mn [12]. However, a near conservative behavior of Ni is in conflict with what is documented for the nearby estuaries [18]. It is widely accepted that dissolved organic carbon (DOC) represents a dynamic component in the interaction between geosphere, biosphere and hydrosphere. Conservative DOC behavior is reported during estuarine mixing in the Beaulieu Estuary, England [17]. A linear decrease in DOC over the salinity range of 17–28‰ is reported for the Bristol Channel [14]. However, in the present study a consistent linear DOC increase with an increase in salinity is documented (Table 2) that is indicative of non-terrigenous DOC. Aquatic fulvic acids account for 50–80% of the total DOC in coastal water [13]. Interestingly, positive relationships are recorded amongst DOC, EC and TH with the salinity of Caspian Sea water (Fig. 2). This indicates that seawater is a controlling mechanism for these parameters in the estuarine zone. Cluster analysis (Fig. 2) shows that pH and S‰ do not govern the flocculation of Zn, Ni, Pb and Mn. Probably; there are other mechanisms for the flocculation of metals in the Babolrud estuary. More investigations are needed to justify this statement. For the removal of Fe from water, NaClO has been used [23]. Therefore, more studies should be carried out to find out about the possibility of formation of NaClO in the estuarine zone where Na and Cl are present in plentiful. It is evident that pH controls Cu flocculation in the area of study. Interestingly, PO_4 shows a meaningful similarity coefficient with pH and Cu. The processes that are responsible for removing dissolved PO_4 at high concentrations encountered in the Babolrud estuary include precipitation of apatite (calcium phosphate), vivianite (ferrous phosphate) and magnesium-ammonium phosphate

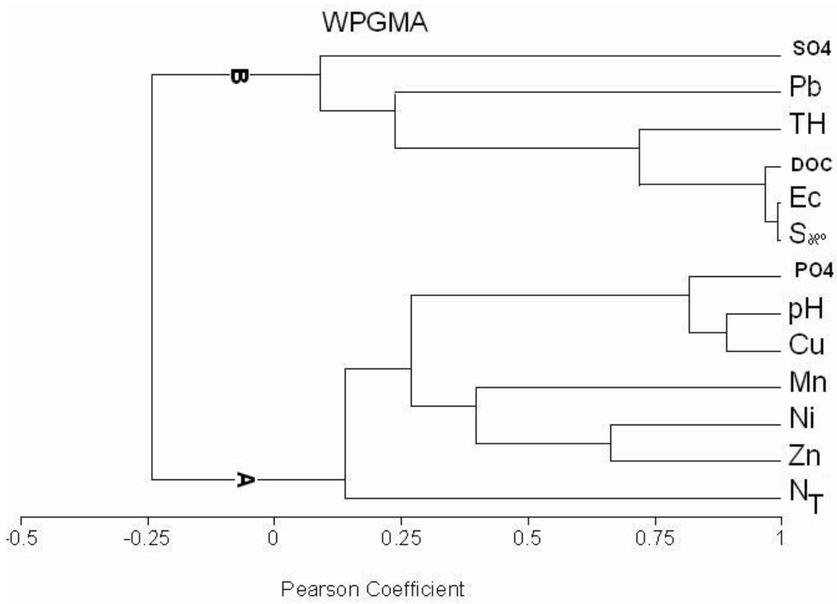

Fig. 2. Dendrogram of cluster analysis for metals and other physico-chemical characteristics of the Babolrud River and the Caspian Sea water.

but these have not been identified in situ or in laboratory experiments simulating estuarine conditions [6,18]. Finally, considering the concentrations of dissolved metals in the Babolrud River water [Cu (20.8 μg/l), Zn (85 μg/l), Pb (22 μg/l), Ni (40.15 μg/l) and Mn (19.7 μg/l)] and the mean discharge of the river (560×10^6 m^3/y), the mean annual inputs of dissolved Cu, Zn, Pb, Ni and Mn into the Caspian Sea via this river would be 11.60, 47.60, 12.32, 22.48 and 11.03 ton/y, respectively. However, the results of the present study show that 77.9, 74.6, 38.2, 12.2 and 64.97% of dissolved concentrations of Cu, Zn, Pb, Ni and Mn, respectively, flocculate during estuarine mixing. Therefore, the mean annual discharge of dissolved Cu, Zn, Pb, Ni and Mn from the Babolrud River into the Caspian Sea would reduce from 11.6 to 2.57, 47.6 to 12.10, 12.32 to 7.62, 22.48 to 19.74 and 11.03 to 3.87 ton/y, respectively.

4. Conclusion

The results obtained in this study show that Cu, Zn, Pb, Ni and Mn flocculate at salinities of 1.5–9.5‰. The maximum removal is at lower salinities (1.5–4.5‰) for Cu, Zn and Mn. While Pb flocculates at salinities of 3.5 and 8.5‰, Ni flocculation is found at 1.5 and 9.5%. Dissolved organic carbon, total hardness, electrical conductivity, SO_4, N_T and PO_4 do not play any role in the flocculation of Cu, Zn, Pb, Ni and Mn. Flocculation of Cu is controlled by pH and PO_4. Statistically, salinity does not play a significant role in the flocculation of metals. Besides, pH controls Cu only. Thus, other constituents of seawater (other than salinity) might be involved in the flocculation processes. Further investigation is suggested on NaClO formation and its possible role in the flocculation of metals. Flocculation rates of metals studied show that the overall colloidal metal pollution loads can be reduced by various percentages (ranging from as low as 12 to as high as 78) during estuarine mixing of the Babolrud water with the Caspian Sea water. This not only shows the importance of flocculation of colloidal metals in the natural self purification of estuarine zones, but also the ecological importance of the estuarine processes. Whereas a part of the geochemical cycle of a few heavy metals is quantified in this study, more detailed studies such as sediment–water interactions that have a significant influence on the behavior of metals are needed.

References

[1] S.R. Aston and R. Chester, The influence of suspended particles on the precipitation of Fe in natural water, Estuarine Coastal Marine Sci., 1 (1973) 225–231.

[2] J.M. Bewers, A.I.D. Mac and B. Sundby, Trace metals in the water of Gulf of St. Lawrence. Canadian J. Earth Sci., 11 (1974) 939–950.

[3] E.A. Boyle, J.M. Edmond and E.R. Sholkovitz, The mechanism of Fe removal in estuaries. Geochim. Cosmochim. Acta, 41 (1977) 1313–1324.

[4] J.B. Davis, Statistic and Data Analysis in Geology. New York, Wiley International, 1973, pp. 456–473.

[5] J.W. Day, C.A.S. Hall, W.M. Kemp and A.A. Ynez, Estuarine Ecology. New York, Wiley, 1989.

[6] B.L. Deck, Nutrient-element distribution in Hudson estuary. PhD, Columbia University, USA, 1981.

[7] J.C. Duinker and R.F. Nolting, Distribution model for particular trace metals in Rhine estuary, Southern Bight and Dutch Wadden Sea. Netherlands J. Sea Res., 10 (1976) 71–102.

[8] J.M. Eckert and E.R. Sholkovitz, The flocculation of Fe, Al and humates from river water by electrolytes. Geochim. Cosmochim. Acta, 40 (1976) 847–856.

[9] A.M. Featherstone and B.V. O'Grady, Removal of dissolved Cu and Fe at the freshwater-seawater interface of an acid mine stream. Marine Poll Bull., 34 (1997) 332–337.

[10] A.R. Karbassi, Some geochemical and magnetic susceptibility studies of marine, estuarine and riverine sediments near Mulki (Karnataka) India. PhD, University of Mangalore, India, 1989.

[11] A.R. Karbassi and Sh. Nadjafpour, Flocculation of dissolved Pb, Cu, Zn and Mn during estuarine mixing of river water with the Caspian Sea. Environ Poll., 93 (1996) 257–260.

[12] A.R. Karbassi, J. Nouri and G.O. Ayaz, Flocculation of trace metals during mixing of Talar River water with Caspian Sea water. Int. J. Environ. Res., 1 (2007) 66–73.

[13] R. Krachler, F. Jirsa and S. Ayromlou, Factors influencing the dissolved iron input by river water to the open ocean. Biogeosci. Discussions, 2 (2005) 537–549.

[14] R.F.C. Mantoura and S.V. Mann, Dissolved organic carbon in estuaries. In: R.T. Severn, D. Dineley and L.E. Hawker, eds., Tidal Power and Estuary Management. Bristol Scientechnical, 1979, pp. 279–286.

[15] S.V. Matagi, D. Swai and R. Mugabe, A review of heavy metal removal mechanisms in wetlands. African J. Hydrobiol. Fish., 8 (1998) 23–25.

[16] M. Meybeck, Nutrients (N, P, C) transport of world rivers. Amer. J. Sci., 282 (1982) 401–450.

[17] R.M. Moore, J.D. Burton, P.J.B. Williams and M.L. Young, The behavior of dissolved organic material, Fe and Mn in estuarine mixing. Geochim. Cosmochim. Acta, 43 (1979) 919–926.

[18] M. Saeedi, A.R. Karbassi and N. Mehrdadi, Flocculation of dissolved Mn, Zn, Ni and Cu during the estuarine mixing of Tadjan River water with Caspian Sea water. Intl. J. Env. Studies, 60 (2003) 567–576.

[19] R. Shankar and A.R. Karbassi, Flocculation of Cu, Zn, Ni and Fe during mixing of Mulki River water and Arabian Sea water, west coast of India. Paper presented at the 7th International Symposium on Water Rock Interaction, Utah, USA, 12–13 July 1992.

[20] E.R. Sholkovitz, Flocculation of dissolved and inorganic matter during the mixing of river water and sea water. Geochim. Cosmochim. Acta, 40 (1976) 831–845.

[21] E.R. Sholkovitz, E.A. Boyle and N.B. Price, Removal of dissolved material in the Amazon estuary. EOS, Trans. Amer. Geophysics., 58 (1977) 423–439.

[22] L.E. Zhiqing, Z. Jianhu and C. Jinsi, Flocculation of dissolved Fe, Al, Mn, Si, Cu, Pb and Zn during estuarine mixing. Acta Oceanologica Sunica, 6 (1987) 567–576.

[23] G.U. Zhimang, J. Fang and B. Deng, Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. Environ. Sci. Technol., 39 (2005) 3833–3843.