Marine Pollution Bulletin xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

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Preliminary assessment of metal distribution in the surface sediments along the coastline of the southern Caspian Sea

Siamak Jamshidi *, Kazem Darvish Bastami

Iranian National Institute for Oceanography and Atmospheric Science (INIOAS), No. 3, Etemadzadeh St., Fatemi Ave., 1411813389 Tehran, Islamic Republic of Iran

ARTICLE INFO

Article history:
Received 17 September 2016
Received in revised form 15 November 2016
Accepted 12 December 2016
Available online xxxx

Keywords:
Metals
Coastline
ERM quotient
Sediment
Caspian Sea

ABSTRACT

In the present study, the concentrations of metals in sediments along the coastline of the southern Caspian Sea were investigated. For this purpose, sediments were collected from 13 sampling sites in the southern Caspian Sea. The samples were then analyzed by inductively coupled plasma-optical emission spectrometry. Results showed that compound oxides may be responsible for the distribution of metals in the sediments of the southern Caspian Sea. According to mean effects range-median quotient, 61.5% of the studied sites from the southern Caspian Sea had a 21% probability of metal toxicity. On the basis of the enrichment factor, all metals were in the category of deficiency to minimal enrichment. Pollution load index showed that the other sampling sites had no pollution.

An increased number of industries brings countless benefits, but is unfortunately associated with critical issues such as environment pollution. The pollution of aquatic ecosystems with metals is an important issue that has been recently linked to the development of industries, and several studies (De Mora et al., 2004; Bastami et al., 2015) have been conducted in this context. Various anthropogenic activities cause entry of these pollutants into the aquatic ecosystem (ElNemr et al., 2007; Bastami et al., 2015). These elements enter through direct and indirect discharge caused by runoff such as rain runoff and through atmosphere. One of the most important properties of metals is that they are nondegradable. The sediments act as pollutant reservoir and accumulate pollutants from different sources. The amount of metals in the sediments depends on various factors such as organic matter, grading of sediment, pH, and redox potential. Changes in these factors affect the amount of metals present in the sediments (Hakanson, 1980; Wright and Mason, 1999; Tam and Wong, 2000; Buccolieri et al., 2006; ElNemr et al., 2007; Bastami et al., 2012; Bastami et al., 2015). In general, normal concentrations of some metals such as copper and zinc are necessary; however, when the concentrations of metals exceed beyond the normal levels, they cause damage to the aquatic organisms. The Caspian Sea is surrounded by five countries, namely Iran, Azerbaijan, Russia, Kazakhstan, and Turkmenistan, which are important from ecological and geopolitical point of view. More than a hundred big and small rivers discharge into the Caspian Sea, but the most important supplier of water to the Caspian Sea is the Volga river. Oil activities in Azerbaijan play an important role in the pollution of the Caspian Sea. The aim of the present study was to survey the amount of metals in the sediments along the coastline of the southern Caspian Sea and to determine the correlation between the distribution of metals and the characteristics of sedimentology.

To survey the sedimentology characteristics and determine the amount of metals in the sediments along the coastline and at the inlet of the river that discharges into the Caspian Sea, 13 stations were selected during winter (February) 2016 (Fig. 1). The samples were collected using a Van Veen grab sampler. The samples were then poured into a plastic container and were transferred to the laboratory for recording the characteristics. In the laboratory, the samples were initially dried and then crushed and powdered to remove the coarse particles (Bastami et al., 2015). The analysis of metals was performed according to ASTM standard practice D5258-92 (ASTM, 2013), i.e., 0.5 of sample was digested using HF-HCl-HNO_3-$HClO_4$. The concentrations of metals were measured by inductively coupled plasma-optical emission spectrometry (Varian VISTA-MPX). In addition, the concentrations of metal oxides were measured by X-ray fluorescence spectrometry (Bruker Model). It was used as the standard reference material to determine the accuracy of measurement. The measured recovery values were between 93% and 108%.

The organic matter concentration was measured by the loss of ignition method. Briefly, the sediment was dried in the oven at 72 °C for 24 h and then was burned in the oven at 550 °C for 4 h. The

* Corresponding author.
E-mail address: si.jamshidi@gmail.com (S. Jamshidi).

http://dx.doi.org/10.1016/j.marpolbul.2016.12.033
0025-326X/© 2016 Published by Elsevier Ltd.

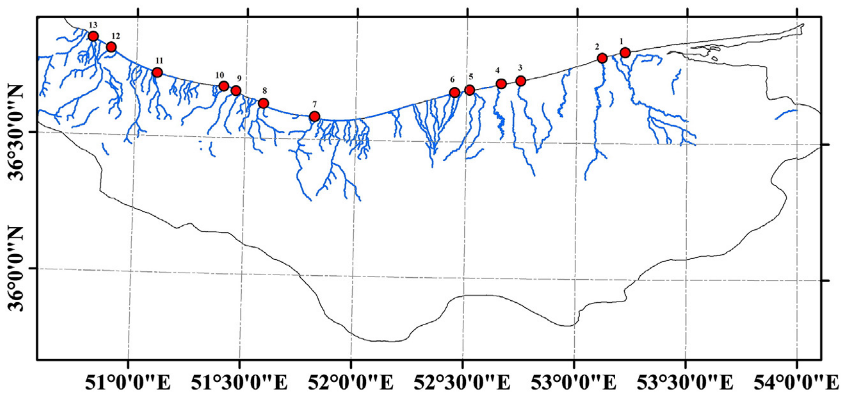

Fig. 1. Locations of the sampling sites along the coastline of the southern Caspian Sea.

amount of total organic matter (TOM) was calculated by the following equation:

$$\text{Total organic matter}\ (\%) = [(B-C)/B] \times 100 \quad (1)$$

where B and C are the weights of dried sediment before and after combusting in the oven, respectively (Abrantes et al., 1999). For grading scales, the sediment was first burned at 550 °C for 4 h and then at 950 °C for 2 h to burn the organic and biogenic matter, and finally, it was used for grading the sediment using a particle size analyzer device (HORIBA-LA950, France & Japan).

To specify the source and proportion of natural and human factors in the surface sediments, enrichment factor was used (Reddy et al., 2004; Selvaraj et al., 2004; Vald'es et al., 2005; Çevik et al., 2009; Bastami et al., 2012; Bastami et al., 2014). Aluminum is an element that is present in the Earth's crust and is rarely affected by human activities. In the present study, aluminum was used as the norm element to differentiate between human-related and natural pollution (Lee et al., 1998; Woitke et al., 2003: Bastami et al., 2015) and was measured as follows:

$$\text{Enrichment Factor} = (H_s/Al_s)/(H_c/Al_c) \quad (2)$$

where H_s and H_c are metal concentrations in sample and background reference, respectively, and Al_s and Al_c are the aluminum contents in sample and background reference, respectively. Background concentrations of metals in sediments from the Caspian Sea were previously found to be 12.5, 0.16, 51.5, 18, 34.7, 85.3, 116, 15.9, and 85.2 ppm for As, Cd, Ni, Pb, Cu, Zn, V, Co, and Cr, respectively, and 6.05% for Al (Bastami et al., 2014; De Mora et al., 2004).

For measuring the amount of pollution, the pollution load index (PLI) was used and was calculated according to the following formula (Suresh et al., 2011):

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots CF_n)^{1/n} \quad (3)$$

where CF of a metal is the ratio of the content of each metal to the background values and

$$CF_{metal} = CH_{metal}/CH_{back} \quad (4)$$

where CH_{metal} is the concentration of that metal and CH_{back} is the background value of the metal.

To calculate the amount of ecological risk in one ecosystem, we used the potential ecological risk (PER) index. The equations for measuring

Table 1
General characteristics of the sediments (mean ± SD) sampled along the coastline of the southern Caspian Sea.

Sampling sites	TOM (%)	Sand (%)	Mud (%)	Carbonate (%)	Inorganic carbon (%)
1	1.46	98.35	1.65	9.9	1.98
2	0.37	97.24	2.76	7.1	1.41
3	0.74	99.38	0.62	10.8	2.13
4	0.82	97.61	2.39	8.0	1.59
5	1.02	91.24	8.76	15.3	3.03
6	0.75	98.52	1.48	15.7	3.11
7	0.67	95.83	4.17	12.4	2.46
8	1.23	97.65	2.35	19.4	3.88
9	1.27	95.24	4.76	12.0	2.39
10	1.37	98.98	1.02	13.0	2.60
11	1.66	93.02	6.98	12.6	2.52
12	1.54	98.27	1.73	18.0	3.61
13	1.44	95.41	4.59	20.4	4.07
Mean ± SD	1.10 ± 0.40	96.67 ± 2.43	3.33 ± 2.43	13.4 ± 4.2	2.68 ± 0.83

Table 2
Oxide compounds in the sediments (mean ± SD) sampled along the coastline of the southern Caspian Sea.

Sampling sites	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	MnO_2 (%)	Na_2O (%)	P_2O_5 (%)	TiO_2 (%)
1	50.50	6.30	11.75	3.97	1.03	5.34	0.052	1.38	0.17	0.57
2	67.38	11.02	5.65	3.78	0.85	1.63	0.041	3.03	0.14	0.20
3	63.12	9.53	7.80	4.16	1.06	1.99	0.061	2.20	0.17	0.62
4	59.73	8.90	10.09	4.44	0.82	1.54	0.051	1.98	0.13	0.56
5	57.71	7.53	10.74	5.50	0.50	2.86	0.075	1.21	0.08	0.60
6	56.34	6.11	13.67	4.29	0.78	1.88	0.042	1.17	0.13	0.35
7	64.14	7.58	8.96	3.84	0.60	1.74	0.043	1.85	0.10	0.33
8	53.35	6.28	13.68	4.82	0.78	2.51	0.071	1.35	0.13	0.49
9	62.82	8.55	9.57	3.93	0.80	1.38	0.054	1.85	0.13	0.42
10	64.20	6.39	9.59	4.32	0.71	1.40	0.057	1.26	0.12	0.42
11	66.82	5.53	9.20	3.68	0.73	0.97	0.052	1.19	0.12	0.33
12	57.48	6.60	12.21	4.49	0.55	1.95	0.081	1.24	0.09	0.18
13	58.60	4.56	12.02	3.15	1.11	1.21	0.057	1.40	0.18	0.31
Mean ± SD	60.17 ± 5.12	7.30 ± 1.79	10.38 ± 2.30	4.18 ± 0.58	0.79 ± 0.19	2.03 ± 1.12	0.057 ± 0.012	1.62 ± 0.54	0.13 ± 0.03	0.41 ± 0.15

Please cite this article as: Jamshidi, S., Bastami, K.D., Preliminary assessment of metal distribution in the surface sediments along the coastline of the southern Caspian Sea, Marine Pollution Bulletin (2016), http://dx.doi.org/10.1016/j.marpolbul.2016.12.033