Marine Pollution Bulletin 136 (2018) 22–32

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Baseline

Bioavailability, mobility, and origination of metals in sediments from Anzali Wetland, Caspian Sea

Kazem Darvish Bastami[a,*], Mahmoud Reza Neyestani[b,e], Neda Molamohyedin[c], Elnaz Shafeian[c], Sara Haghparast[d], Imam Ali Shirzadi[e], Mehrnaz Baniamam[f]

[a] Iranian National Institute for Oceanography and Atmospheric Science (INIOAS), No. 3, Etemadzadeh St., Fatemi Ave., 1411813389 Tehran, Islamic Republic of Iran
[b] Department of Chemistry, Faculty of Science, University of Zanjan, Postal Code 45371-38791 Zanjan, Iran
[c] Department of Marine Science and Technology, Science and Research Branch, Islamic Azad University, Tehran, Iran
[d] Department of Fisheries, Faculty of Animal Science and Fisheries, Sari Agricultural Sciences and Natural Resources University, Km 9 Darya Boulevard, P.O. Box, 578, Sari, Iran
[e] Novin Shimyar Chemical Laboratory, P.O. Box 14589-3699, Tehran, Iran
[f] Agricultural Planning, Economic and Rural Development Research Institute, Tehran, Iran

ARTICLE INFO

Keywords:
Bioavailability
Mobility
Metal
Anzali wetland

ABSTRACT

We investigated the bioavailability, mobility, and origin of heavy metals present in sediments from the Anzali Wetland. Chemical speciation of the metals was performed according to the Tessier method. Results indicated that Cd and As showed the highest level of bioavailability, whereas Cr showed the lowest level. Cr, Co, and V were shown to have a terrestrial origin. The metal As was mostly found in the reducible fraction (F3), whereas other metals were highest in the residual phase. The levels of Co present in the oxidizable fraction (F4); Pb and Cd present in the carbonate fraction (F2); and the other metals present in the exchangeable fraction (F1) were found to be the lowest. On the basis of the Risk Assessment Code of metals, Cd at most stations, As and Ni at some stations, and Zn at one station revealed to have a moderate risk. Co and Pb were found to have a low risk at all stations. Considering Pollution Load Index, stations 2 and 3 were classified as moderately polluted and the remaining stations were unpolluted. As suggested by enrichment factor analysis, As was moderately enriched and other metals had a deficiency to minimal enrichment at all the stations.

During the recent years, implementation of economic, industrial, agricultural, and service development programs worldwide has disturbed the balance in nature in many ways and brought several complications at local, regional, and even global scales. Environmental sediment pollution in marine ecosystems is regarded as a significant outcome of this imbalance (Rahman et al., 2010; Solaraj et al., 2010).

The most important contaminants in sediments include heavy metals, petroleum, and organochlorine and organophosphate toxins, among which heavy metals are remarkably considered owing to their specific features such as nonbiodegradability, high toxicity, bioaccumulation, and carcinogenicity. Heavy metals are recognized as metals with a relatively high density and toxicity at a very low concentration (Buccolieri et al., 2006; ElNemr et al., 2007; Bastami et al., 2012).

Generally, sedimentary heavy metals originate from natural events (weathering), human activities (e.g., municipal and industrial wastewaters, farming operations, smoke from vehicles, etc.), and atmospheric sources, and these metals are discharged into water bodies by a variety of ways. In the aquatic environment, some heavy metals become soluble, whereas the others attach to the suspended particles and, with progression of time, settle in sedimentary substrate. The accumulation of metals is dependent on the chemical composition of the sediment, water compounds type, sedimentation rate of elements, the physiochemical condition of elements (ionic or complex), and physicochemical properties of water (e.g., pH, alkalinity, and dissolved oxygen concentration) (Christophoridis et al., 2009; Qiao et al., 2013).

Sediments are commonly thought to be a suitable indicator for monitoring water pollution, as it is the ultimate reservoir to store most contaminants, in particular heavy metals. Hence, in many current studies focusing on pollution, sediments are applied for investigating health status and detecting pollution. As measurement of total metals cannot solely indicate the actual level of pollution and its source in an environment, chemical speciation is therefore essential to determine the origination of metals and their contents in various forms (Dhanakumar et al., 2015; Bastami et al., 2017).

* Corresponding author.
E-mail addresses: darvish_60@yahoo.com, darvish.bastami@inio.ac.ir (K.D. Bastami).

https://doi.org/10.1016/j.marpolbul.2018.08.059
Received 17 June 2018; Received in revised form 25 August 2018; Accepted 27 August 2018

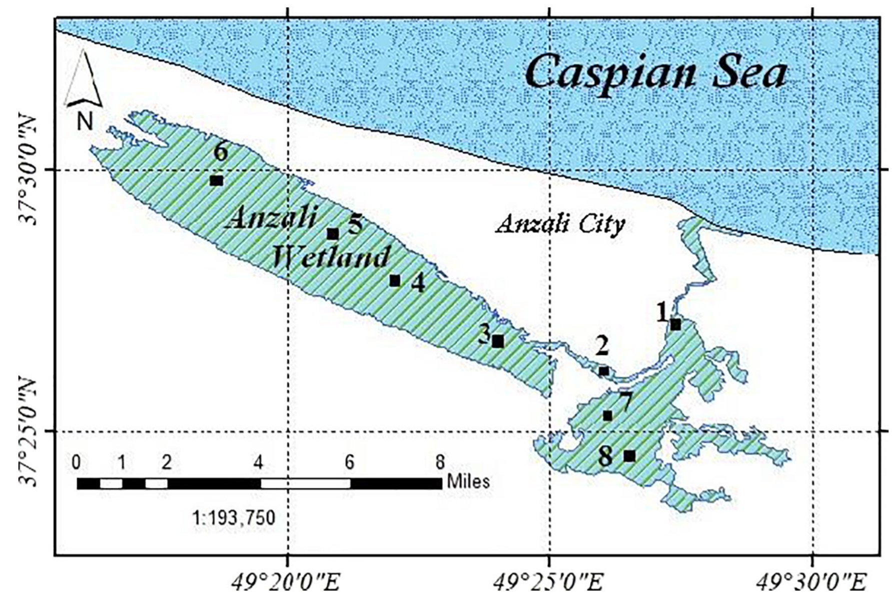

Fig. 1. Locations of the sampling sites at the Anzali Wetland.

Table 1
(a) Sequential extraction scheme of Tessier et al. (1979). (b) Recovery rates of metals obtained by sequential extraction.

Step	Fraction	Extraction reagents/conditions
(a)		
1	Exchangeable – (F1)	8 ml $MgCl_2$ (1 M), pH 7, 1 h, room temperature, continuous agitation
2	Acid-soluble (Carbonates) – (F2)	8 ml NaOAc (1 M), pH 5, 5 h, room temperature, continuous agitation
3	Reducible (Fe—Mn oxide bound) – (F3)	20 ml of 0.04 M NH_2OH.HCl in 25% (V/V) HOAc, 6 h, 96 ± 3 _C, occasional agitation
4	Oxidizable (Organically bound + sulfide bound) – (F4)	3 ml of 0.02 $MHNO_3$ + 5 ml of 30% H_2O_2, pH 2, 2 h, 85 ± 2 _C, occasional agitation. Add 3 ml of 30% H_2O_2, repeat 3 h, cool and then add 5 ml of 3.2 M NH_4OAc in 20% (v/v) HNO_3, 0.5 h, room temperature, continuous agitation
5	Residual – (F5)	$HF:HNO_3:HClO_4$ = 7:3:1, dryness, again $HF:HNO_3:HClO_4$, 1 h, 2 ml conc. HCl, dryness, 10 ml 50% HNO_3, make up to 50 ml with distilled water

	Elements								
	As	Cd	Co	Cr	Cu	Ni	Pb	V	Zn
(b) Recovery(%)	83.45–107.13	88.31–110.40	76.59–90.86	89.22–96.60	82.71–93.88	91.45–100.33	78.24–92.68	90.09–97.21	89.90–100.59

Table 2
General characteristics of sediments (average ± SD) sampled from the Anzali Wetland.

Sampling sites	Mud (%)	Sand (%)	TOM (%)
1	43.28	56.72	4.64
2	85.12	14.88	7.82
3	80.32	19.68	6.75
4	88.46	11.54	12.53
5	84.62	15.38	12.95
6	79.42	20.58	14.77
7	75.63	24.37	4.43
8	54.32	45.68	2.55
Average ± SD	73.90 ± 16.25	26.10 ± 16.25	8.31 ± 4.56

Chemical speciation provides useful information about the amounts of metals available to organisms, mobility of these metals, and risk assessment; it provides more detailed and valuable information for researchers than the measurement of total metals (Ahlf et al., 2009; Arnason and Fletcher, 2003; Bastami et al., 2017).

There are different techniques for the chemical speciation of heavy metals in sediments, one of which is proposed by Tessier et al. (1979), a perfect method for sequential extraction of sedimentary heavy metals. As a five-stage method, different forms of metals are extracted and measured at each stage.

Anzali Wetland, located between saltwater and freshwater bodies, was registered by Ramsar convection as an important international wetland in 1975. In the southwestern part of the Caspian Sea, Anzali Wetland is situated beside Sefidrud river delta, and geologically, it was formed in late Pliocene and probably Holocene. Owing to high annual humidity rate (81%), the wetland does not experience high diurnal temperature changes. Anzali Wetland is well known for its unique ecological, socio-economical features, and high diversity of fauna and flora. In other words, the wetland is enumerated as an appropriate place for wildlife continuity and animal feeding sources. Additionally, specific values of the wetland are given for increased plant materials and propagation of marine fish. To date, a huge amount of various contaminants such as heavy metals enter the Anzali Wetland and then the Caspian Sea, and this is due to the development of industries, agricultural activities around the wetland, and pollution discharge by Pir Bazar River receiving wastes from different plants surrounding it. Therefore, metals are attributed as a serious threat to the wetland food webs and the marine life of the Caspian Sea (Esmaeilzadeh et al., 2016).

Although several studies have been conducted on the determination of total heavy metals in the sediments of the Anzali Wetland, little is recorded on different forms of metals and their sources. Therefore, in