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Baseline

Metal contamination and its ecological risk assessment in the surface sediments of Anzali wetland, Caspian Sea

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ABSTRACT

In this study, the accumulation of metals, including Al, Fe, Zn, V, Ni, Cu, Cr, Cd, Co, As, and Pb, in sediments of Anzali wetland in the southwest region of the Caspian Sea was investigated. For this purpose, the sediments were collected from 17 sampling sites in Anzali wetland, Caspian Sea. The samples were then analyzed using inductively coupled plasma–optical emission spectrometry (ICP-OES). Pearson correlation coefficient showed significant and positive correlation between concentration of all metals (except As and Cd). Furthermore, the results implied that Al and Fe are probably responsible for the transportation of heavy metals into the sediments of Anzali wetland. According to mean effects range-median quotient (mean ERM quotient), the sediments from Anzali wetland had a 21% probability of toxicity.

Marine pollutants are part of several environmental pollution crises. With two-thirds of the Earth's surface covered by water, the effects of pollution on marine habitats are very high. Aqueous ecosystems have become more susceptible and vulnerable to pollution because of the rather higher rate of accumulation of chemical compounds, and in fact, these ecosystems act as reservoirs of various anthropogenic toxicants and contaminants that are stressful through vast inputs of pollution. The issue of marine pollution has recently attracted worldwide attention (Callender, 2005; Bastami et al., 2015).

Bottom sediment, specifically as a tool for monitoring metals in the sea, represents advantageous results of pollutant distribution. Sediments are accumulated over the years and can be regarded as fixators of contamination level. After being discharged into bodies of water, pollutants are gradually deposited at the bottom in various forms. When the pollution level of sediments exceeds a specific limit, it would disturb and eventually destroy the ecosystem equilibrium. Monitoring the deposition of metals in sediments provides a continuous surveillance of pollution in the studied area, and sediment analysis could make the specification of pollution type easier in order to adopt any management decisions for advisable controlling (ElNemr et al., 2007; Bastami et al., 2015).

Metals discharging into the aquatic system during their transport are distributed between the aqueous phase and sediments. Because of adsorption, hydrolysis, and coprecipitation of metal ions, a large quantity of them are deposited in the sediment while only a small portion of free metal ions remain dissolved in the water column. Therefore, sediments in aquatic environments can either retain metals or release them to the water column by various remobilization processes. Sediment parameters (mineralogy, texture), metal characteristics, pH, organic matter, and oxidation–reduction potential are important parameters for controlling the accumulation and availability of metals in the sediment (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). Hence, sediments are enumerated as sources of metals in marine environments, and they play a key role in transmission and deposition of metals.

Generally, normal metal concentrations found in sediments are not detrimental to inhabiting organisms. For normal metabolism, live organisms essentially require some metals like zinc, which have toxic effects above a critical threshold.

Anzali wetland is located in the southwest region of the Caspian Sea with an area of about 193 km^2. Anzali has been registered as an international wetland in the 1975 Ramsar Convention. Catchment of the wetland covers an area of about 3610 km^2 and is bounded by the Caspian Sea in the north, the Alborz mountain range in the south, the Talysh Mountains in the west, and the Sefidrud Delta in the east. Approximately 93,525 and 196,020 ha of the catchment are covered by farmlands (particularly rice farms) and forestlands, respectively. The wetland, with mean annual precipitation and evaporation rates of about 1280 and 980 mm, respectively, has no dry season. It is covered with reed bed, and it plays a key role in spawning and development of the fish. Furthermore, it provides breeding place for many water birds and serves as a staging and wintering site. Anzali wetland's environment

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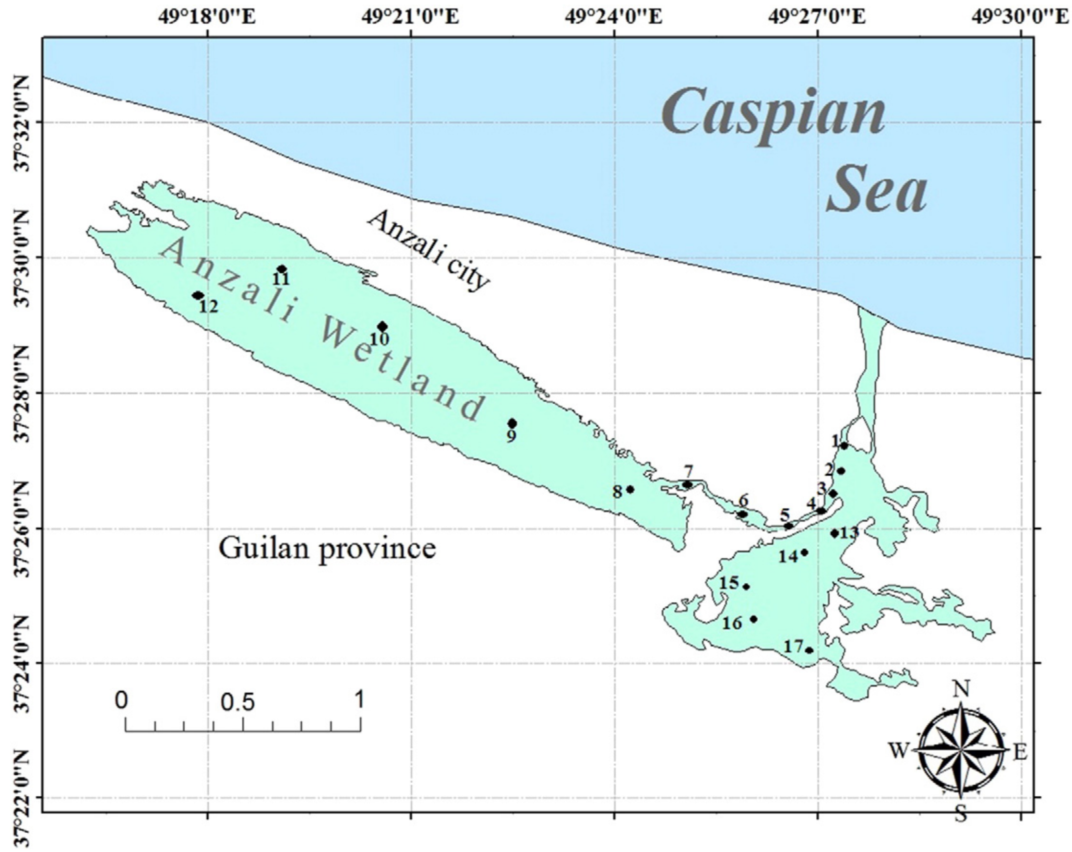

Fig. 1. Locations of the sampling sites at Anzali wetland, Caspian Sea.

has been jeopardized by the contaminants produced from urbanization; population growth; and agricultural, industrial, and tourism activities (Hargalani et al., 2014: Esmaeilzadeh et al., 2016).

The aim of this study is to investigate metal distributions in the sediments obtained from different parts of Anzali wetland and, therefore, to discover the relationship between the sediment characteristics and distribution of metals in Anzali wetland.

Sediment samples from 17 different sites were collected using Van Veen Grab sampler for analyzing metals during winter (February 2016, Fig. 1). The samples were then packed and carried to the laboratory in ice boxes and stored at 4 °C until analysis. After drying in an oven, sediment samples were ground by using a hand mortar followed by screening with a 0.5-mm sieve to remove large particles. Thereafter, the samples (0.5 g) were digested using a mixed solution of HF—HCl—HNO_3—$HClO_4$ according to the ASTM standard D5258-92 (ASTM, 2013). The samples were analyzed for Al, Fe, As, Cd, Cu, Ni, Pb, Co, Cr, V, and Zn by inductively coupled plasma–optical emission spectrometry (ICP-OES; Varian VISTA-MPX). In addition, major element contents (SiO_2, CaO, Fe_2O_3, Al_2O_3, MgO, K_2O, Na_2O, TiO_2, P_2O_5, and MnO_2) were measured using an X-ray fluorescence spectrometer (Bruker Model). The precision and accuracy of the methods were systematically and routinely verified using standard reference materials. Accepted recoveries range from 93% to 108%.

For the determination of total organic matter, sediment samples were dried at 70 °C for 24 h and then combusted in the oven at 550 °C for 4 h. Total organic matter, as described by Abrantes et al. (1999), was measured by the following equation:

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

where B and C are the weights of dried sediment before and after combustion in the oven, respectively.Grain size was analyzed using laser particle size analyzer (HORIBA-LA950, France & Japan). Before analysis, about 4 g of samples was combusted in the oven at 550 °C for 4 h and 950 °C for 2 h to remove organic matter and biogenic carbonate, respectively.Enrichment factor (EF), which is an appropriate tool to determine sedimentary metal source produced by anthropogenic events or natural origin, normalizes metal concentrations according to the sediment texture properties (Selvaraj et al., 2004; Vald'es et al., 2005; Bastami et al., 2014). In this index, aluminum is widely used, indicating aluminum silicate in coastal areas where this element is predominant. Enrichment factor was also applied as a degree of sedimentation (Lee

Table 1
General characteristics of the sediments (average ± SD) sampled in Anzali wetland.

Sampling sites	Mud (%)	Sand (%)	TOM (%)	Carbonate (%)	Inorganic carbon (IC %)
1	41.93	58.07	4.56	3.63	0.72
2	88.44	11.56	6.57	6.00	1.20
3	66.78	33.22	7.06	2.48	0.49
4	87.03	12.97	7.77	6.21	1.24
5	2.20	97.80	1.34	1.39	0.28
6	96.77	3.23	7.97	4.03	0.81
7	82.75	17.25	6.83	3.76	0.75
8	86.84	13.16	12.40	13.30	2.65
9	82.05	17.95	13.03	8.67	1.73
10	81.85	18.15	14.80	11.39	2.25
11	88.41	11.59	13.30	11.37	2.27
12	82.39	17.61	14.38	11.62	2.32
13	71.95	28.05	4.29	2.66	0.52
14	50.82	49.18	2.39	2.50	0.50
15	34.98	65.02	3.11	1.26	0.25
16	45.17	54.83	2.71	1.97	0.39
17	19.94	80.06	2.52	2.58	0.51
Average ± SD	65.31 ± 27.97	34.69 ± 27.97	7.35 ± 4.70	5.58 ± 4.20	1.11 ± 0.84