Original Article

Heavy Metal Contamination in the Sediments of Anzali International Wetland, Northern Iran Based on Type Regional Development

Saeed Ganjali[*1], *Amin Ghasemi* [2]

Received: 15.03.2016 *Accepted: 25.04.2016*

ABSTRACT

Background: The most important factors and problems threatening the Anzali Wetland are the contaminant load and sediments entering the wetland, as well as lack of an integrated management plan for this wetland. The main objectives of the current research were to explore whether there are significant differences in concentrations of Zn, Cd, and Pb in surface sediments among different sites (based on type region development) of the Anzali Wetland, Northern Iran.

Methods: Through a field study, samples were collected from 10 stations based on the type of regional development and contaminant source inputs of Anzali Wetland in 2015. Using a hot-block digester, the sediment samples were digested with a 4:1 combination of nitric acid (HNO3) and perchloric acid (HCLO4) for one hour at 40 °C, followed by 3 h at 140 °C. Afterwards, samples were filtered with Whatman 42, filter paper and the filtrate was kept in polyethylene containers at 4 °C, until analysis by atomic absorption spectrometry (AAS).

Results: Mean ± SD levels of metals in the sediments of different stations were 26.7 ± 3.49 (lead), 4.36 ± 0.47 (cadmium), and 88.44 ± 10.06 (zinc) µg g-1 dw. There was a significant difference between the stations of the wetland ($P < 0.05$). This difference could be due to the variations in the input of contaminant sources into the Anzali Wetland.

Conclusions: The areas, affected by urban and industrial developments, had the highest level of contamination while the agricultural and less-developed areas had the lowest level of contamination, and therefore, protective plans must be implemented in developed areas in order to lower the level of heavy metals.

Keywords: Heavy Metal, Iran, Regional Developments, Sediments.

IJT 2016 (5): 1-6

INTRODUCTION

Discharge of metals into marine environments is a worldwide problem due to their toxicity and persistence [1]. Population growth, industrial development and expansion of agricultural areas have led to the entry of high volumes of different contaminants into aquatic environments [2-3]. Pollution of aquatic ecosystems with different types of contaminants can be assessed through examination the site sediments. In general, sediments can play an important role as both carriers and sinks for contaminants, for instance sediments contaminated by metals may have harmful impacts on biota [4]. Therefore, sediments have been frequently used by many researchers for inspecting metal contamination in aquatic ecosystems [4-9].

In 1975, the Anzali Wetland was recorded under the list of international wetlands in the Ramsar Convention. Moreover, the International Bird Life Organization recognized this wetland as an important habitat for birds [4]. The most important factors and problems threatening the Anzali Wetland are the contaminant load and sediments entering the wetland, as well as lack of an integrated management plan for this wetland [10-11]. Additionally, the discharge of municipal wastewater, oil products waste, a variety of industrial-agricultural contaminants, and landfilling of wastes have been recognized as sources of contamination to this wetland [12-13].

The main objectives of the current research were to: (1) explore whether there are significant differences in concentrations of Zn, Cd, and Pb in surface sediments among different sites (based on

1. MSc in Environmental Sciences, Young Researchers and Elite Club, Hamedan Branch, Islamic Azad University, Hamedan, Iran.
2. Department of Environmental Sciences, Isfahan University of Technology, Isfahan, Iran.
*Corresponding Author: E-mail: said.ganjali@gmail.com

type region development) of the Anzali Wetland (including the eastern, western, and central parts); and (2) investigate contamination levels of Zn, Cd, and Pb in Anzali Wetland sediments and compare with the international guidelines of sediment quality.

MATERIALS AND METHODS

The Anzali Wetland (37° 26′–37° 35′ N and 49° 15′–49° 27′ E) is located in the southwest of the Caspian Sea coast, Northern Iran. This wetland, approximately 193 km^2, is situated in the northern province of Guilan, Iran [14]. Eleven main rivers as well as 30 streams resulting from irrigation of farms and rice paddies along the surface flows of the river basin flow into the wetland. The Anzali Wetland consists of three distinct sections: the eastern (Selke), western (Siahkeshim), and central (Selke and Siahkeshim) (Table 1).

In this field study, samples were collected from 10 stations based on the type of regional development and contaminant source inputs of the Anzali Wetland, northern Iran in 2015 (Figure 1). Sediment sampling (0-10 cm) was performed with three to six repetitions at each station. Geographical locations and characteristics of each station were recorded and samples were transported to the laboratory accordingly. The stations' positions in the wetland and the sites' descriptions are shown in Table 1.

At the laboratory sediment samples were placed in an oven to dry at 105 °C for 48 h [15]. Dried samples were stored in polyethylene containers until the time of chemical digestion. Using a hot-block digester, the sediment samples were digested with a 4:1 combination of nitric acid (HNO_3) and perchloric acid ($HClO_4$) for one hour at 40 °C, followed by 3 h at 140 °C [15]. Digested samples were diluted using a 25 ml of double-distilled water.

Table 1. The geographical coordinates and description of the sampling stations.

Station	Station name	Position in the wetland and site description	Replicate	Latitude	Longitude
1	Selke	Eastern, Agricultural and municipal wastewater discharge	3	41° 39′ 515″	36° 29′ 30″
2	Shijan	Eastern, Agricultural and municipal wastewater discharge	6	41° 43′ 174″	36° 61′ 32″
3	Zarjob	Eastern, Industrial and municipal wastewater discharge	6	41° 40′ 734″	36° 73′ 42″
4	Sorkhankol	Eastern, Recreational area and shipping	3	41° 44′ 581″	36° 33′ 87″
5	Tapap Roga	Central part, Agricultural	3	41° 44′ 581″	36° 33′ 90″
6	Ghalamgoodeh	Central, Recreational area and shipping	3	41° 46′ 504″	36° 41′ 890″
7	Nahang Roga	Central, Municipal wastewater discharge	3	41° 44′ 739″	36° 33′ 67″
8	Abkenar	Western, Urban and less development	6	41° 44′ 195″	35° 89′ 25″
9	Mahroozeh	Western, Agricultural and less development	3	41° 43′ 388″	36° 299′ 30″
10	Siahkeshim	Western, Agricultural and less development	3	41° 43′ 388″	35° 95′ 48″

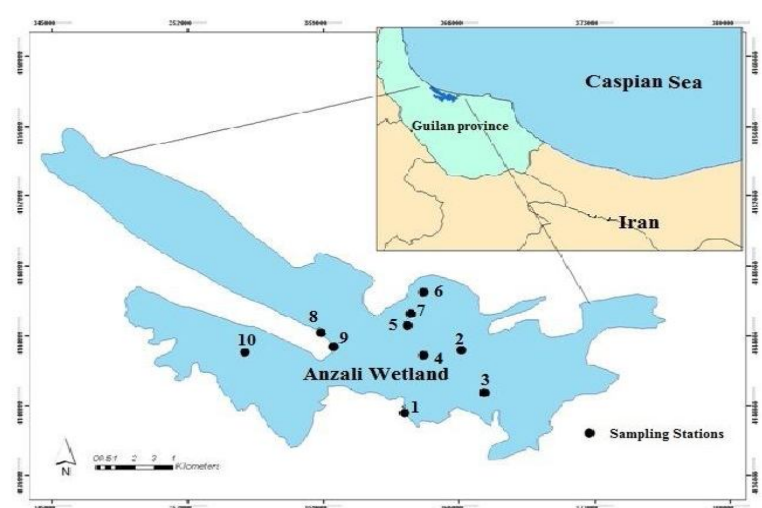

Figure 1. The geographical location of studied region and distribution of sampling stations.

Afterwards, samples were filtered with Whatman 42, filter paper and the filtrate was kept in polyethylene containers at 4 °C, until analysis by atomic absorption spectrometry (AAS). Metals' concentrations in sediment samples were measured by a Perkin-Elmer AA770 model AAS. Data are presented in µg g^{-1} of sample dw. Recoveries were 92%–97% for all trace metals measured.

Data normality was examined by using the Kolmogorov-Smirnov test. In order to compare significant differences between the concentrations of metals at various stations in the study area, an ANOVA homogeneity test and LSD test were employed (a significant difference was observed at the 95% confidence level). SPSS 16 software (Chicago, IL, USA) was applied for the statistical analysis. Metal concentrations in the sediment were compared to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life for freshwater sediment, that is, for Interim Sediment Quality Guidelines (ISQG) and Probable Effect Level (PEL).

RESULTS

Metal distribution in the sediment followed this order: Zn > Pb > Cd. Ranges of Pb concentrations were 15.8 (stations 10) to 42.1 µg g^{-1} dw (stations 3), 2.4 (stations 10) to 5.4 µg g^{-1} dw (stations 3) for Cd, and 54.24 (station 8) to 162.5 (stations 3) µg g-1 dw for Zn.

Station 3 had the highest concentration of Pb and Cd, and station 10 had the lowest levels of Pb and Cd. The highest amount of Zn existed at station 3 and the lowest amount of Zn was noticed at station 8. Moreover, the results of ANOVA showed a significant difference in Pb, Cd, and Zn concentrations among different stations of the wetland ($P < 0.05$, Figure 2-4). It showed the significant differences in the contamination level based on the level of regional developments, so that in the eastern part with the high level of development, the concentration of pollutants was high.

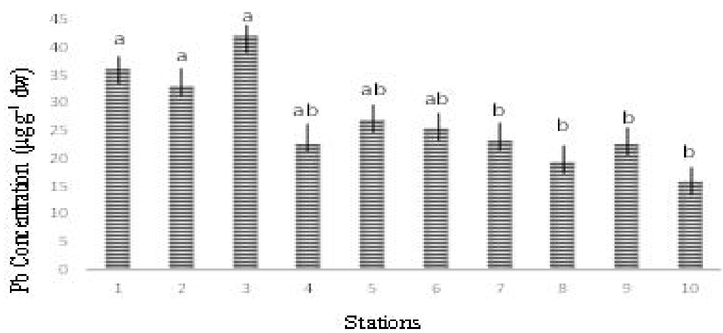

Figure 2. Concentration of Pb in the sediments of different parts of Anzali Wetland (Common letters indicate that no significant difference was observed at the 5% probability level according to one-way ANOVA).

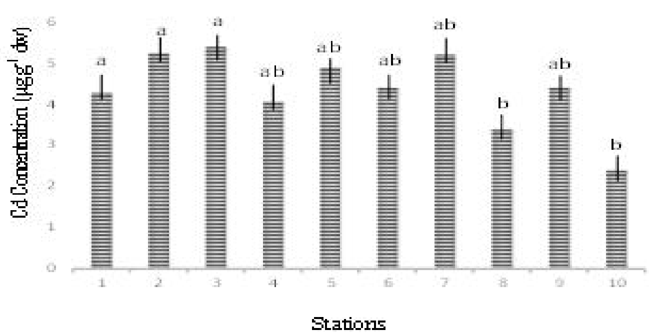

Figure 3. Concentration of Cd in the sediments of different parts of Anzali Wetland (Common letters indicate that no significant difference was observed at the 5% probability level according to one-way ANOVA).

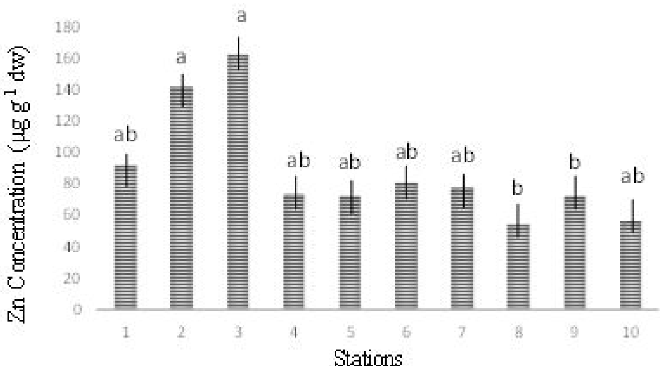

Figure 4. Concentration of Zn in the sediments in different parts of Anzali Wetland (Common letters indicate that no significant difference was observed at the 5% probability level according to one-way ANOVA).

DISCUSSION

The results demonstrated that the most contaminating sources are concentrated in the eastern part of the wetland, and have contributed more contamination in this part than the western part. The pollution of the eastern part of Anzali Wetland is higher than the western part because of the large amounts of contaminating sources in consistent with a previous study [12], who emphasized on the origin of heavy metal contamination in the sediments of Anzali Wetland. The authors measured the concentrations of heavy metals in four parts of the wetland, including Abkenar, Siahkeshim, Hendkhaleh, and Shijan (stations 8, 10, 1 and 3) [12].

The present study shows that the highest concentrations of the studied metals are observed at station 3 which receives both industrial and municipal wastewater inputs, while the lowest level has been accumulated in the western part. Considering the human activities as well as the development and establishment of various industries in the eastern part, the indirect entry of industrial wastewater through Pir-Bazar River can be considered a major source of contamination and one of the affecting factors, which has increased the metal concentrations in the wetland. With regard to a greater volume of heavy metals in the eastern part of the wetland, these results are compatible with the study of Shahsavari-Pour *et al.* [16], who carried out a research on the biomonitoring and evaluation of mercury contamination in Anzali Wetland, and also with another study [17], who measured the heavy element contents in *Astacus leptodactylus caspicus* in the same area. The findings are also consistent with another study [5], in which *Anodonta cygnea* as a potential biomonitor for Cd and Pb in the mentioned wetland was studied.

In order to determine the contamination level of heavy metals in the surface sediments of the studied area, the values were compared with the Interim Sediment Quality Guidelines (ISQG) and Probable Effect Levels (PELs), proposed by the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (Table 2). Cd and Pb are generally considered as unessential elements for organisms that may pose high toxicities to aquatic organisms. According to these results, the average Pb concentrations at stations 1, 2, and 3 exceeded the ISQG standards, proposed by the Canadian Sediment Quality Guidelines, by approximately 39.4%, 9.1%, and 19.2%, respectively.

Table 2. Comparison of Pb, Cd, and Zn in the sediments of Anzali Wetland with the international quality guidelines (μg g^{-1} dw).

Results of the present study			**CCME** [19]		**Chemical**
Average	**Maximum**	**Minimum**	**PEL**	**ISQG**	
26.7± 3.49	42.1	15.8	112	30.20	Pb
4.36 ± 0.47	5.4	2.4	4.20	0.7	Cd
88.44 ± 10.06	162.5	56.53	271	124	Zn

CCME: Canadian Council of Ministers of the Environment; ISQG: Interim Sediment Quality Guidelines; Probable Effect Level (PEL)

The sediment results showed that Cd concentrations at all sites sampled exceeded the ISQG standards. Cd in site 3 exceeded the ISQG standards by about 670% and Cd value in the sediment samples at stations 1, 2, 3, 5 and 9 exceeded the PEL standard. Zn value in the sediment samples of sites 2 and 3 exceeded the ISQG standard by about 14.6% and 31%, respectively. This result indicates that this metal is more likely to have adverse effects on the organisms that live in Anzali Wetland especially at stations 1, 2 and 3 (in the eastern part of the wetland).

CONCLUSION

The areas affected by urban and industrial developments have the highest level of contamination while the agricultural and less-developed areas have the lowest level of contamination. Accordingly, protective and managerial plans must be implemented in order to reduce the level of heavy metals. Furthermore, sampling based on the development of regions can provide more accurate results for the monitoring plans of heavy metal contamination, in the studied area. The research by Hu *et al*. [18] confirmed the same finding.

In addition, since many of freshwater fishes live and feed in the wetland areas, absorption of heavy metals in the aquatic food chain is one way of accumulating metals in their bodies, which could eventually be transferred to humans. Due to the toxic nature of metals in various concentrations, Pb and Cd can have adverse effects on the health of consumers. Because some heavy metals in the sediments can clearly be measured at concentrations that are considerably higher than the international quality guidelines, complementary studies should be conducted in the future to evaluate potential impacts to human and ecological health.

ACKNOWLEDGMENTS

We are grateful to express our deepest appreciation to Mr. Mohammadi for his valuable help during the sampling operations.

REFERENCES

1. De Zwart D. Monitoring water quality in the future. Biomonitoring. The Netherlands, Bilthoven–RIVM 1995;3:83-4.
2. Dunbabin JS, Bowmer KH. Potential use of constructed wetlands for treatment of industrial wastewaters containing metals. *Sci Total Environ*. 1992;111(2):151-68.
3. Duman F, Cicek M, Sezen G. Seasonal changes of metal accumulation and distribution in common club rush (Schoenoplectus lacustris) and common reed (Phragmites australis). Ecotoxicology 2007;16(6):457-63.
4. Kazemi A, Bakhtiari AR, Kheirabadi N, Barani H, Haidari B. Distribution patterns of metals contamination in sediments based on type regional development on the intertidal coastal zones of the Persian Gulf, Iran. Bull Environ Contam Toxicol 2012;88(1):100-3.
5. Ganjali S, Mortazavi S. The Swan Mussel (Anodonta cygnea) in Anzali Wetland of Iran, a Potential Biomonitor for Cd and Pb. Bull Environ Contam Toxicol 2014;93(2):154-8.
6. Ganjali S, Tayebi L, Atabati H, Mortazavi S. Phragmites australis as a heavy metal bioindicator in the Anzali wetland of Iran. Toxicol Environ Chem 2014;96(9):1428-34.
7. Yang Z, Wang Y, Shen Z, Niu J, Tang Z. Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. J Hazard Mater 2009;166(2):1186-94.
8. Zulkifli SZ, Mohamat-Yusuff F, Arai T, Ismail A, Miyazaki N. An assessment of selected trace elements in intertidal surface sediments collected from the Peninsular Malaysia. Environ Monit Assess 2010;169(1-4):457-72.
9. Singh KP, Mohan D, Singh VK, Malik A. Studies on distribution and fractionation of heavy metals in Gomti river sediments-a tributary of the Ganges, India. J Hydrol (Amst) 2005;312(1):14-27.
10. Ganjali S, Ildoromi A, Mortazavi S. Assessment of Anodonta cygnea as a Biomonitor Agent for Copper and Zinc in Anzali Wetland, Iran. Iranian J Toxicol 2014;8(25):1048-53.
11. JICA (Japan International Cooperation Agency). The study on integrated management of the Anzali Wetland in the Islamic Republic of Iran. 2005. p. 222.
12. Ghazban F, Zare Khosheghbal M. Studying the contamination sources of heavy metals in the sediments of Anzali wetland. J Ecol 2011; 57:45-56.
13. Pourang N, Richardson C, Mortazavi M. Heavy metal concentrations in the soft tissues of swan mussel (Anodonta cygnea) and surficial sediments from Anzali wetland, Iran. Environ Monit Assess 2010;163(1-4):195-213.
14. Ganjali S. Environmental and strategic assessment of ecotourism potential in Anzali Wetland using SWOT analysis. CJES 2014;12(1):155-65.

15. Yap CK, Ismail A, Cheng WH, Tan SG. Crystalline style and tissue redistribution in Perna viridis as indicators of Cu and Pb bioavailabilities and contamination in coastal waters. Ecotoxicol Environ Saf 2006;63(3):413-23.
16. Shahsavari-Pour N, Esmaili sari A, Vahabzadeh Roudsari H. Biomonitoring and evaluation of mercury contamination in the international Anzali wetland using aquatic plants. Int J Environ Sci Technol 2009; 3:269-80.
17. Riahi A, Fazeli MS, Paydar M. Determination of heavy metal content in Astacus leptodactylus caspicus of Anzali Wetland, Iran. Korean J. Ecol 2004;27(1):15-20.
18. Hu Y, Liu X, Bai J, Shih K, Zeng EY, Cheng H. Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. Environ Sci Pollut Res 2013;20(9):6150-9.
19. CCME (Canadian Council of Ministers of the Environment). Canadian environmental quality guidelines. Canadian Council of Ministers of the Environment. Winnipeg: Manitoba; 1999.