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Survey of heavy metal (Copper, Iron, Lead, Cadmium, Zinc and Nickel) concentrations and their effects on the water quality of Anzali wetland

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ABSTRACT
Anzali International wetland is one of the most valuable water resources as registered in Ramsar convention with an extent of about 150 km2 in the south Caspian Sea. This wetland, not only has ecological and biological importance for migratory birds and rare fish species, but also is used for farms to discharge into the Caspian Sea through this wetland. Therefore its pollution control is very important for human life. In this study 6 elements (copper, iron, lead, zinc, cadmium and nickel) in Anzali wetland were analyzed by Atomic Absorption spectroscopy method. . Water samples were collected from ten sampling sites seasonally and the results were compared with each other. The detection limits obtained were 0.016 ng/ml for cadmium, 0.02 ng/ml for copper (Cu), lead (Pb) and zinc (Zn), 0.025 ng/ml for iron (Fe) and 0.026 ng/ml for nickel (Ni). Relative Standard Deviation (RSD) was 1.7%. The results showed that these heavy metals were present in the water. Concentrations of Cu (0.6 mg/l) were higher than international standards reported in some stations. This can be due to industries around the wetland. The average level of heavy metals was higher in spring than in the other seasons which can be due to increase in seasonal rainfall and intensity of flow from rivers to wetland.

Keywords: *Anzali wetland, Caspian Sea, heavy metals, pollution, Atomic absorption spectroscopy.*

INTRODUCTION
Mercury, one of the important trace element in aquatic habitats, is a water pollutant which directly endangers the life of aquatic animals and indirectly threatens their health and other land creatures around them (Madrakian *et al.*, 2010, Soylak and Aydin, 2011, Batzias and Siontorou, 2008). Pollution is an undesirable change in chemical and biological quality of water that endangers the stability of human health and activities of living creatures. Heavy metals are the most important toxic pollutants which threaten the environment especially watery perimeters. These pollutants are created naturally or through the mines near natural water resources, entrance of industrial sewage, different petrochemical industries and the leakage of oil, gas etc. They can directly or indirectly threaten human through the food chain (Soylak *et al.*, 2002).

In the north of Iran, especially in Guilan province, urban, industrial and agricultural sewages are discharged into the water that are limited to Anzali wetland and the Caspian Sea. This is because there are not enough suitable bases and development of urbanization around these areas. Therefore, controlling the pollution of this wetland is very important because it is a valuable ecosystem and is registered in Ramsar convention in June 1975. In the Ramsar convention, wetlands are defined as lagoon areas, leftover water, running water, fresh water, salty water or sea water not exceeding depths of six meters during ebb. According to the last definition a wetland is: the area in which its soil becomes saturated by surface, underground water during wetland

formation and is created in a natural situation during an adequate period and has biological succession. This ecosystem has special plants and animals that are in harmony with these ecological situations. Most wetlands have many benefits and international importance in terms of ecology, botany, zoology and hydrobiology, and especially they can play an important role in ecology and energy cycling in environments (Karr, 2010).

The Anzali wetland is deep that has roots in the Caspian Sea water withdrawal and the water of over 11 rivers which are collected in this wetland, before reaching the Caspian Sea. This wetland is located in the western part of the Sea. This area is about 150 km2 and its depth is between 2 and 3 meters. The water entering the Anzali wetland exits the wetland by five big waterways, which merge together and enter into the Caspian Sea (Sabet Rafter, 1995) (Fig. 1).

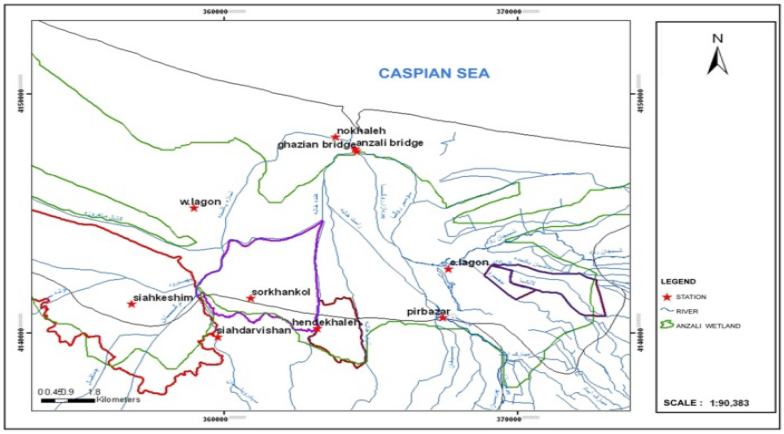

Fig.1. Anzali wetland and sampling points

Anzali wetland is a shallow coastal wetland that has many kinds of fish, other commercially important aquatic organisms as well as migratory birds. This area is the most important part in the south Caspian Sea for birds. This wetland has fresh water in terms of physico-chemical characteristics. Connected to the Caspian Sea, the water volume and depth of this wetland change according to the height of sea level.

According to definition, heavy metals are some kinds of metals with over 6 g/cm3 concentration. Melting and boiling points of these metals are different.

Low levels of these metals can be found in organisms but they can have extreme effects on these organisms. These heavy metals have a selectivity property, and can change these actions by substituting these complexes and can also disturb them. For example, heavy metals such as silver, cadmium, tin, mercury and lead and also metals with high electronegativity such as copper, nickel and cobalt have severe combination attitudes to Amin and Sulfhydryl (SH) groups, meanwhile their power decreases and their activity is disturbed in the way of contact with enzymes. Furthermore, metals enter into the body activity and disturb metabolism. So, in this study attempts were made to measure some heavy metals in Anzali wetland and to compare the obtained data with their respective standards.

MATERIALS AND METHODS

First, ten stations were chosen on the basis of distribution of various industrial units with different activities using GPS for sampling. "Table1".

Sampling from stations in the wetland were taken according to standard methods (APHA standard 3010) (Miller and Miller 2000). Sampling was carried out in the middle of each month, in all seasons. The measurement of these metals was done by atomic absorption spectroscopy set (Perkins Elmer company model M2100) with Acetylene–Air fuels, and after pre concentration according to standard methods (APHA standard 3010).

Quantity measurement was done using standard addition method. It was also carried out for each metal separately. In

order to calibrate the atomic absorption spectroscopy for analyzing heavy metals, standard solutions special for atomic absorption were used in 1000mg/L concentration. For statistical analysis, SPSS V.17 software was used. Limit of detection was calculated by multiplying standard deviation by 3, plus background signal (APHA 1998).

Calibration procedure was carried out by stock solution of each element prepared from Merck (Titrisol) with the concentration of 1000 mg/L. For each element, solutions with 1, 2, 5 and 10 mg/L were prepared from stock solution. These tests were done by diluting with distilled water and calibration curves were obtained for each element separately.

Table 1. Sampling stations UTM coordinate systems

Station Number	Station Name	Lat. & Long.
1	Pirbazar	36° 74′ 62″ N 41° 40′ 64″ E
2	Nokhaleh river	36° 38′ 04″ N 41° 48′ 19″ E
3	East lagoon	36° 76′ 52″ N 41° 42′ 68″ E
4	Hendekhaleh	36° 31′ 70″ N 41° 40′ 19″ E
5	Sorkhankol	36° 09′ 03″ N 41° 41′ 45″ E
6	Siyah darvishan	35° 97′ 86″ N 41° 39′ 84″ E
7	Siyah kishim	35° 68′ 49″ N 41° 41′ 21″ E
8	West lagoon	35° 89′ 77″ N 41° 45′ 24″ E
9	Ghazian bridge	36° 45′ 16″ N 41° 47′ 61″ E
10	Anzali bridge	36° 44′ 65″ N 41° 47′ 70″ E

RESULTS AND DISCUSSION

Sampling and investigating heavy metals in sampling areas was done on a monthly basis. The results are presented as mean values, for each month of the year and for each metal (Tables 2-5; Figs. 2-5).

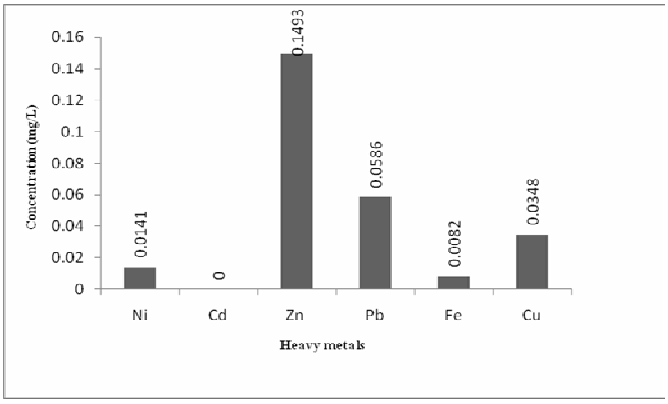

Fig. 2. Concentration of heavy metals in Anzali wetland in summer

Table 2. Concentration of heavy metals in Anzali wetland in summer

Station Number	Heavy Metals (mg/L)					
	Cu	Fe	Pb	Zn	Cd	Ni
1	0.048	0.011	0.040	0.094	-†	0.018
2	0.048	0.003	-	-	-	0.014
3	0.044	0.011	-	0.057	-	0.02
4	0.033	0.009	0.019	0.089	-	0.016
5	0.03	0.012	-	0.051	-	0.014
6	0.029	0.004	0.089	0.164	-	0.017
7	0.106	0.018	0.074	0.334	-	0.017
8	0.010	0.003	0.190	0.259	-	-
9	-	0.004	0.062	0.343	-	0.013
10	-	0.007	0.112	0.102	-	0.012

†- Under detection limit

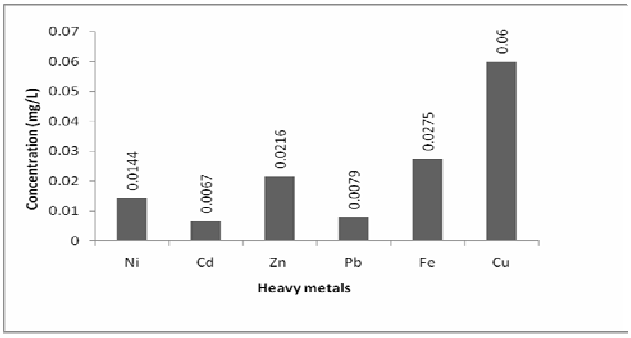

Fig. 3. Concentration of heavy metals in Anzali wetland in autumn

Table 3. Concentration of heavy metals in Anzali wetland in autumn

Station Number	Heavy Metals (mg/L)					
	Cu	Fe	Pb	Zn	Cd	Ni
1	- †	0.044	-	0.080	0.007	0.012
2	-	0.035	-	0.015	0.005	0.010
3	-	0.037	0.020	0.016	0.006	0.010
4	-	0.052	0.020	0.030	0.007	0.020
5	-	0.012	-	0.014	0.006	0.013
6	-	0.009	-	0.009	0.006	0.015
7	-	0.007	-	0.015	0.007	0.009
8	0.600	0.039	0.009	0.015	0.007	0.012
9	-	0.006	0.020	0.012	0.010	0.022
10	-	0.034	0.010	0.010	0.006	0.021

†- Under detection limit

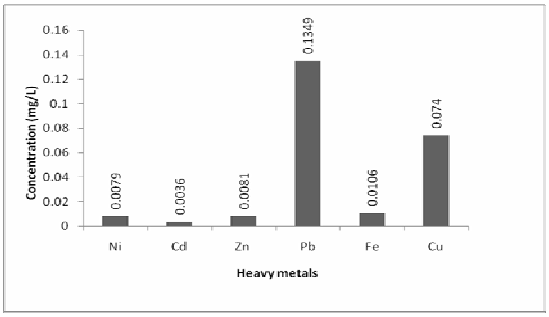

Fig. 4. Concentration of heavy metals in Anzali wetland in winter

Table 4. Concentration of heavy metals in Anzali wetland in winter

Station Number	Heavy Metals (mg/L)					
	Cu	Fe	Pb	Zn	Cd	Ni
1	0.010	0.004	- †	0.031	0.001	0.002
2	0.009	0.006	0.005	0.018	0.004	0.001
3	0.010	0.003	0.066	0.024	0.002	-
4	0.005	0.005	-	0.036	0.001	-
5	0.006	0.003	0.091	0.019	0.001	0.001
6	0.012	0.015	0.004	0.022	0.005	0.001
7	0.010	0.004	0.014	0.026	0.001	-
8	0.007	0.003	0.135	0.023	0.001	-
9	0.006	0.006	0.049	0.036	0.002	-
10	0.008	0.005	0.011	0.038	0.003	-

†-Under detection limit

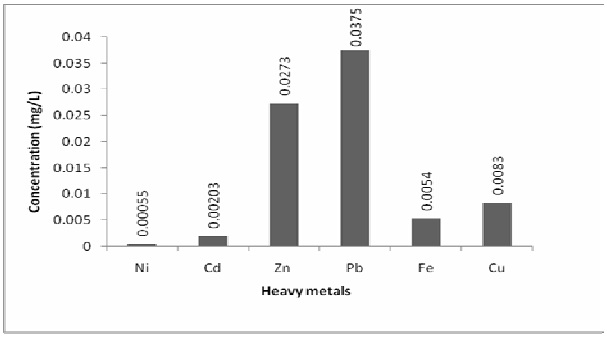

Fig. 5. Concentration of heavy metals in Anzali wetland in spring

Table 5. Concentration of heavy metals in Anzali wetland in spring

Station Number	Heavy Metals (mg/L)					
	Cu	Fe	Pb	Zn	Cd	Ni
1	- †	0.034	0.010	0.010	0.006	0.021
2	-	0.006	0.020	0.012	0.010	0.022
3	0.600	0.039	0.009	0.015	0.007	0.012
4	-	0.007	-	0.015	0.007	0.009
5	-	0.009	-	0.009	0.006	0.015
6	0.040	0.002	0.310	0.010	-	-
7	0.030	0.005	0.340	0.010	-	-
8	0.030	0.002	0.260	-	-	-
9	0.020	0.001	0.170	-	-	-
10	0.020	0.001	0.230	-	-	-

Table 6 shows the average annual concentration of heavy metals in Anzali wetland, which is obtained from the average monthly results. For statistical analysis descriptive statistics, correlation coefficient of data and analysis of significant relation of heavy metals in four seasons and ten stations were used (Mendenhall, 1990). First, descriptive statistics is considered for metal concentrations in each station and season, the results are shown in Table 7.

Homogeneity test was conducted on heavy metals collected from each station and season. Since the test showed data variances were unequal, nonparametric Kruskal–Wallis test was used for studying significant relations. This test showed significant relation between heavy metals action in different seasons. This relation is true for all mentioned metals except lead, but in different stations no significant relations between mentioned metals were detected. Tables 8 and 9 show the results of test based on seasons and sampling sites. Correlation between measured densities was also calculated for each metal in stations and different periods by spearman method.

Table 6. Average concentration of heavy metals in Anzali wetland in four seasons

Metal	Concentration (mg/L)
Cu	0.045
Fe	0.032
Pb	0.059
Zn	0.197
Cd	0.013
Ni	0.036

Table 7. Descriptive Statistics for sites and seasons

Metal	N	Mean	Std. Deviation	Variance
Cu	40	0.0443	0.1307	0.01701
Fe	40	0.0129	0.0140	0.00020
Pb	40	0.0598	0.0908	0.00825
Zn	40	0.0516	0.0827	0.00681
Cd	40	0.0031	0.0032	0.00001
Ni	40	0.0092	0.0080	0.00006

As shown in Table 10, the highest correlation was found between Fe, Pb and Cd. The correlation of Fe and Cd was direct while other showed indirect correlations. Also there was no correlation between Zn and other metals.

Table 8. Kruskal Wallis Test for variation of seasons

	Cu	Fe	Pb	Zn	Cd	Ni
df	3	3	3	3	3	3
Sig.	P<0.05	P<0.05	P>0.05	P<0.05	P<0.05	P<0.05

Table 9. Kruskal Wallis Test for variation of sites

	Cu	Fe	Pb	Zn	Cd	Ni
df	9	9	9	9	9	9
Sig.	P>0.05	P>0.05	P>0.05	P>0.05	P>0.05	P>0.05

Because of the extent of Anzali wetland and diversity of entrance resources and sampling from water, a specific correlation among metals could not be clarified. Studying and comparing mean data of metal measurements at different stations showed that stations 3 and 8 had increasing trends in copper and lead concentrations among other stations. In contrast, station 5 showed lower concentration of metals, but zinc concentration in this station was higher than the other elements. Comparison of the heavy metal concentrations obtained in the present study with permitted levels of pollution as stated in international standards and average annual metal concentrations according to EPA standards showed that, metal concentrations were lower than EPA permitted levels. However higher level were seen in the case of certain stations. For example, Cu concentration in station 8 in autumn and station 3 in spring wa0.6 mg/L, which is categorized as slightly polluted according to EPA standards (EPA standard).

In all other stations, the average concentrations in each season and year were lower than declared levels in EPA standards.

CONCLUSION

In similar investigations, heavy metals in Anzali wetland were measured mainly in sediments and tissues of living organisms. According to these studies, wetland sediments contained considerable levels of heavy metals which enter it from the rivers (Vesali Naseh, et al., 2012).

Study of heavy metals in Anzali wetland show that the concentrations of mentioned heavy metals determined in this study were lower than permitted levels of pollution. It can be said that water in this wetland along with other elements can be used for aquaculture and discharging into surface water.

Studying the concentration of each metal in each sampling station shows that concentrations of certain metals in some stations were abnormally high. This can be explained according to kind of sewage, their entrance place and also the industrial centers around the station. In some stations such as 3, 7 and 8, heavy metal concentrations were higher than in others.

Table 10. Spearman test for nonparametric correlation between heavy metals

	Cu	Fe	Pb	Zn	Cd	Ni
Cu	1.000	-0.225	0.258	0.094	-0.571**	-0.189
Fe	-0.225	1.000	-0.529**	0.103	0.548**	0.587**
Pb	0.258	-0.529**	1.000	0.030	-0.486**	-0.341*
Zn	0.094	0.103	0.030	1.000	-0.284	0.071
Cd	-0.571**	0.548**	-0.486**	-0.284	1.000	0.290
Ni	-0.189	0.587**	-0.341*	0.071	0.290	1.000

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

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بررسی پراکندگی غلظت فلزات سنگین (مس، آهن، سرب، کادمیوم، نیکل و روی) وتاثیر آنها بر کیفیت آب تالاب بندر انزلی

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چکیده

تالاب بین المللی انزلی به عنوان یکی از تالابهای با اهمیت ثبت شده در کنوانسیون بین المللی رامسر با مساحت ۱۵۰ کیلومتر مربع در جنوب دریای خزر واقع شده است. این تالاب از لحاظ اقتصادی و زیستی دارای اهمیت بوده و محل مهاجرت پرندگان و زندگی گونه های نادری از ماهیان می باشد همچنین آب آن جهت مصارف کشاورزی مورد استفاده قرار گرفته و در نهایت وارد دریای خزر می گردد. بنابراین کنترل آلودگی آن برای زندگی انسانها دارای اهمیت می باشد. دراین مقاله پراکندگی غلظت ۶ عنصر از فلزات سنگین در آب نقاط مختلف این تالاب با روش جذب اتمی مطالعه و اندازه گیری شده است. این فلزات عبارتند از مس، آهن، سرب، کادمیوم، نیکل و روی. نمونه ها در طول ۴ فصل از ۱۰ ایستگاه با روشهای مخصوص جمع آوری شده نتایج بدست آمده با یکدیگر مقایسه گردید. حد تشخیص بدست آمده ۰/۰۱۶ نانوگرم بر میلی لیتر برای کادمیوم، ۰/۰۲ نانوگرم بر میلی لیتر برای مس، سرب و روی، ۰/۰۲۵نانوگرم بر میلی لیتر برای آهن و ۰/۰۲۶ نانوگرم بر میلی لیتر برای نیکل بود. انحراف استاندارد نسبی نیز برابر با ٪۱/۷ محاسبه گردید. نتایج بدست آمده نشاندهنده وجود فلزات سنگین در نمونه های مورد مطالعه بود به نحوی که غلظت مس با ۰/۶ میلی گرم بر لیتر در یک ایستگاه بالاتر از استانداردهای پذیرفته شده بین المللی بود که این مسئله با صنایع موجود در حاشیه ایستگاه نمونه برداری قابل ارتباط می باشد همچنین میانگین غلظت اندازه گیری شده فلزات سنگین در فصل بهار بیشتر از سایر فصول بود که می تواند به دلیل افزایش بارندگی فصلی و افزایش ورودی آب رودخانه ها به این تالاب باشد.

*مولف مسئول