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Evaluation of heavy metals accumulation in the liver of great cormorants in the Southern Coast of Caspian Sea

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Abstract

In order to study heavy metals pollution in the Caspian ecosystem this project has defined. The sampling for heavy metals analyses were done from the soils, water and so the liver of great cormorant in Persian and Russian Caspian basin randomly. Caspian Sea that is the largest lake in the world, located in the playa where drained water from the catchment areas of Northern Iran, East Azerbaijan, from North to South of Russia, West Kazakhstan and West Turkmenistan. The results showed a significant increasing of lead in sea water more than maximum permitted amounts with an increasing peak in summer. The copper amounts in sea water is low with a slightly growing in winter. Copper amounts in soil in coastal location in the province of Gilan in Iran was more than other coastal areas. From determinations of heavy metals in the cormorant liver were showed that the five years old birds which sampled in the Turkmen port on the southeast coast of the Caspian Sea, the amount of copper increased more than maximum levels. However, in the birds with two-years old and three years old copper contents was negligible. Maximum amounts of zinc were observed in floodplain soils near Volga delta. From comparison of heavy metals in river, flood plain and sea, were concluded the major sources of Pb, Cu and Zn in Caspian ecosystem are from Volga river in Russia and so partly from the rivers and port activities in the province of Gilan in Iran.

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Introduction

Because of higher speed of the distributions of pollutions in aquatic environments related to dry ones, sustainable land use of coastal regions of Caspian see is more important. It is necessary for the nature and human protections in the all surrounding countries. With controlling of Caspian Sea pollutions can be protected the life and sustainable economic activities in Caspian watersheds. As a sample of researches in this area can be pointed to Darvish Bastami *et al.* (2014), that they compared heavy metals concentrations in the south east Caspian sediments, in summer and winter. They reported that only concentration of arsenic was higher than maximum permitted related to other elements of Copper, Zinc, Pb, Nickel. Also can be pointed to Taghipoor (2014), he works in environmental department of Behshahr and Sari cities as environmental protection staff, in his MSc dissertation was evaluated environmental parameters in coastal area of Miandorud in south east of Caspian Sea but did not reported any water pollution. Orian *et al.* (2008), experimented the effect of polymorphic aromatic hydrocarbons on the fish (*Cynoglossus bilineatus*) from an oil pollution area.

They concluded that this toxic cancer induced compound (PAH_s) was absorbed by fish organism significantly. Noori (2003), in his PhD dissertation in Moscow State University of Lomonosov, in department of geography reported the influence of the fluctuation of Caspian Sea surface on the environment and geography of the region. According to Noori, Caspian Sea has an area about 400,000 km^2 that it is only about 12% of the area of all the watershed with a total of 3.5-3.7 mil.km^2. This sea has a distribution of asymmetric, longitude shape with a direction from north to south. The long diameter and short diameter of this sea are 1200km and 300km respectively. The north part of Caspian Sea located in the eastern south part of Russia platform that has depressed graduately and so its southern part located in Alpine geo synclynical. The geological formations of this sea contain of Paleozoic, Mesozoic, and Cenozoic to Quaternary. Agroforestry is a method for optimizing Caspian ecosystems land uses for the all countries in Caspian watersheds. On the point view of agroforestry, Sapanov (2003), Sizemskaya and Bychkov, 2005, Sapanov *et al.*, 2005have studied and evaluated the rehabitation of arid and semiarid zones of Northern Caspian with reforesting. Akbarpoor (2015) in his PhD thesis in the state university of Saint Petersburg studied on the oil technologies affects to marinas ecosystems of Bushehr port in Persian Gulf in Iran. He according to chemical analyses results has concluded the high contents of heavy metals over than maximum allowable concentrations in the region. Bozkurt *et al.* (2014) studied on the marinas waters in the coastal areas of Mediterranean Sea in Istanbul.

They compared their analyses results to the standard ones and concludes some pollutions of heavy metals in the sea. Szymczyk and Zalewski (2003) surveyed the concentration of some heavy metals in the tissue of a species of wild duck.

They with using this method evaluated ecological parameters of sea water. Lafebervet (2012) is an official company that give us consultation about the effect of metal toxics on the birds. Zhuang *et al.* (2014), studied the concentration of some heavy metal on the tissue of chickens in the region of mining in China and compares the results with the world standards. Barbier (2009), with the survey on the concentration of heavy metals in the tissue of green turtles concluded more concentrations of Pb, Cd, Cu, and Ni in older ones relates to younger turtles. Also they found that in the liver in compare with other tissues of turtles were concentrated more quantities of heavy metals. Donia (2014), studies accumulation of heave metals in migratory quail in Egypt. She tried to trace the way of quail migration and she classified them in to the level of pollution intensities. According to Zuang *et al.* (2014), and Ecpete (2013), the permissible concentrations of heavy metals in birds at the international level and Chinese and so other standards were presented in Table 1.

a. The 2002 FAO / WHO Codex Aliment Arius, List 1 of the proposed
Draft Codex Common Standards for Pollutants and Toxins
In food. The Joint FAO/WHO Food Standards Program,
Codex Committee, Rotterdam. Reference CX/FAC 02/16.

b. EC (Commission of the European Communities) 2006
Commission Decision No. 1881/2006 of 19 December 2006
By setting maximum levels for certain contaminants in food.
Official Journal of the European Communities, L 364/18-19.

c. MHPRC (Ministry of Health of the People's Republic of
China) limits of contaminants in food (GB 2762-2005 for Pb
And Cd, GB 15199-1994 for Cu, GB 13106-1991 for Zn).
Beijing, China: MHPRC [in Chinese]

d. Standards of the World Health Organization
e. Institute of Standards and Industrial Research of Iran.

Veschev (2003), in his doctor dissertation with the topic of ecological and biological principles of conservation and restoration of stocks of stellate sturgeon in modern conditions, the Volga-Caspian looked at the value of heavy metals in floodplain soils in the Volgograd and Astrakhans regions of the Volga River. He came to the conclusion that the greatest amount of zinc and copper in the Astrakhan region is found in Seroglazka, zinc reaches to 102 mg/kg and copper to 84 mg/kg, which is 3-4 times higher than the background values.

Main characteristics of the Caspian climate

According to information from the meteorological center of the province of Gilan (2017), the strongest wind in the Caspian Sea is northeast in the winter, especially in the north of the Caspian Sea. Such the wind will change as weaker in the summer. In the north, four months a year, from January to April, there will be frosts with an ice thickness from 40 to 50 cm. In the northeast, the ice cover depth reaches up to 70 cm. One of the reasons for the change in the water level in the Caspian is climate change and other reasons are man-made factors. The usage water management from the river in uplands flowing into the Caspian Sea, especially the Volga, is a major man made reason for sea surface level fluctuations. The flow of water in the Caspian Sea begins with the delta of the Volga on the western shore to the south and continues to the province of Gilan. Then from the coast of the province of Gilan, the water is heated and begins a reverse movement to the north, to the delta of the Volga.

Material and methods

Sampling positions

After collaborative agreements with the coastal countries like as Russia, Uzbekistan, Azerbaijan and Kazakhstan, the initial soil and water sampling were done in the summer of 2016.

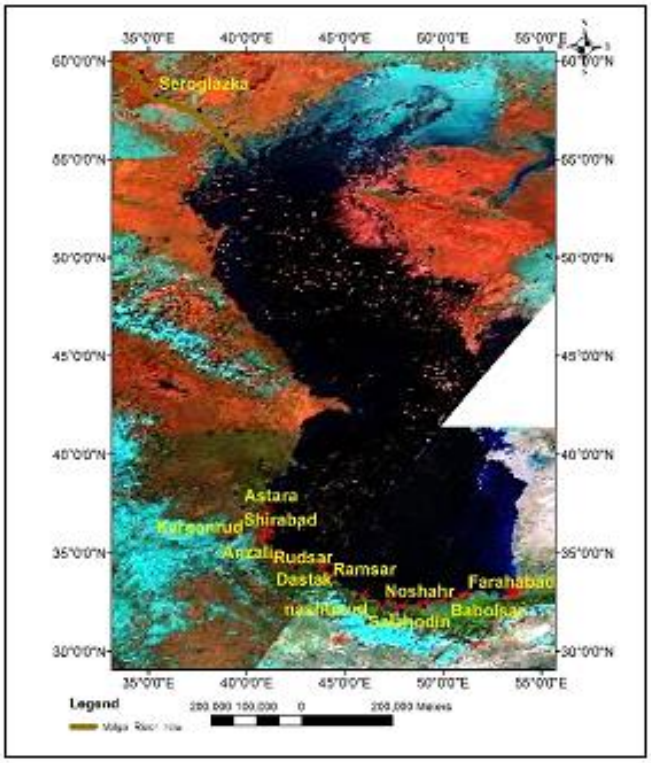

Fig. 1. Sampling point in Iranian coastal line in Southern Caspian Sea on MODIS imagery.

The sampling in Southern parts of Caspian sea were done with the help of Iranian environmental conservation departments in coastal provinces Gilan, Mazandaran and Golestan and with license of Iran Environmental Organization and so supporting by the Center for International Scientific Studies & Collaboration (CISSC).This step continued in two sub step that everyone was done in the time of about a week. The sampling across southern coastal line divided to 18 parts which every part was about 60km which sampling in about equal distance was randomized statistically. As shown in figure 1, the path of sampling in southern part of Caspian Sea in Iranian coastal line and so the name of districts, town or cities on MODIS imagery.

After primary surveying in the summer of 2016, for more detail surveying, second sampling was done in December 2016 in the province of Gilan. In this step were taken the soil and water from the territories nearby Anzali port. Also from the rivers of Karganrood and Shafarood the soil and water samples were taken.

Also in this step with the licenses from environmental conservation organization and the departments in Golestan province, were hunted some great cormorant for the heavy metals analyses from their liver tissues (Fig. 2).

The Experiments

From the sea water samples were done usual analyses with routine methods. The water reaction, salinity, Electric Conductivity (EC), Anion and Cation contains in sea water and some compounds as Nitrate, Phosphate were measured in soil and water laboratory of Natural Resources Department of Yazd University. For doing complementary analyses on the sample we brought a part of samples to Moscow in Russian Agrarian Government University & Timiriazev Agricultural Academy. The bird's tissues dried and grinded for the analyses.

The first analyses on the bird tissues and the soils were taken with the X ray fluorescents' spectrometer (XRF) using S4 Explorer and its software of Spectra Plus made of Bruker company of USA, in Arid lands and Desert Institute of Yazd University.

For more accurate analyses on the soil and water were uses Atomic Absorption instrument in Yazd university analytical chemistry laboratory and so in laboratory of soil science, ecology and agro chemistry faculty in Russian Government Agrarian University and Agriculture Timiryazev Academy.

Results and discussion

According to Wikipedia (2017), Although the vast majority of seawater has a salinity of between 31 g/kg and 38 g/kg, that is 3.1-3.8%, seawater is not uniformly saline throughout the world but the mean of total salinity of Caspian sea is 1.13% with a sodium-magnesium salinity type.

Table 1. The maximum permissible level of metals (mg/kg) in the liver of birds, waters and soils established by the Chinese, Iranian (Institute of Standards and Industrial Research of Iran) and international standards.

	Pb	Cd	Zn	Cu
	mg / kg			
Liver of a bird				
FAO / WHO[a]	0.1	0.05 for meat, 0.5 for the liver	20	1
EC[b]	0.1	0.05 for meat, 0.5 for the liver	20	1
CN[c]	0.2	0,1 for meat, 0.05 for the liver	100	10
water				
WHO[d]	0.01	0.003	3	1
Iran[e]	0.01	0.003	3	1
Soil				
WHO	0.0	0.01	15	1.5

The amounts of nitrates and phosphates in Caspian Sea are 19.09% and 0.37% respectively. The results of heavy metals in Caspian ecosystem are presented below:

Lead

As shown in figure 3, the means of Pb concentrations from all positions in Caspian Sea were exceeded from maximum permitted amount.

Table 2. The content of metals (mg / kg) in the liver of cormorant and floodplain soils of the Caspian Sea from the Iranian coast.

	Pb	Cd	Zn	Cu
Samples of the liver and floodplain soils	mg / kg			
Cormorant liver at different ages				
2 years (Iran)	-	-	14	-
3 years (Iran)	-	-	40	-
5 years (Iran)	-	-	35	18
floodplain soils				
Astra (Iran)	-	-	-	62
Shirabad (Iran)	-	-	-	78
Karganrud_river (Iran)	-	-	-	72
Kapurchal_sea (Iran)	-	-	-	66
Kapurchal_river (Iran)	-	-	24	55
Anzali (Iran)	-	-	-	48
Farahabad (Iran)	-	-	-	-
Seroglazka (Volga river in Russia)	-	-	102	48

Also according to figure 3, the mean of lead concentration was increased in summer violently.

But according to table 2 lead concentration in cormorant liver and floodplain soils at Caspian shores were not observed.

Copper

The means of copper contents of sea water in winter with comparison to summer slightly were increased (Fig. 3).

But copper contents in sea were not exceeded from standard concentrations in Table 1. The amounts of copper in the water of Gilanbeach and four samples of river water were shown in Figure 4. The rivers are statistically similar with the confidence level of 80 percent, but at the level of reliability of 60 percent the river of Bitza from Moscow and Gilan beach in Sea-Nokande were at the same category.

Fig. 2. The great cormorant (Right) in Turkmen port selected for analyses of liver and tissue as index of pollution and sampled water at the same location (left).

According to Table 2 the content of copper is greatly increased in the liver of the five years old Cormorant. In comparison with floodplain soils in different rivers, the contents of copper of Anzali in Gilan and Seroglazka area of Volga River in Russia are equal.

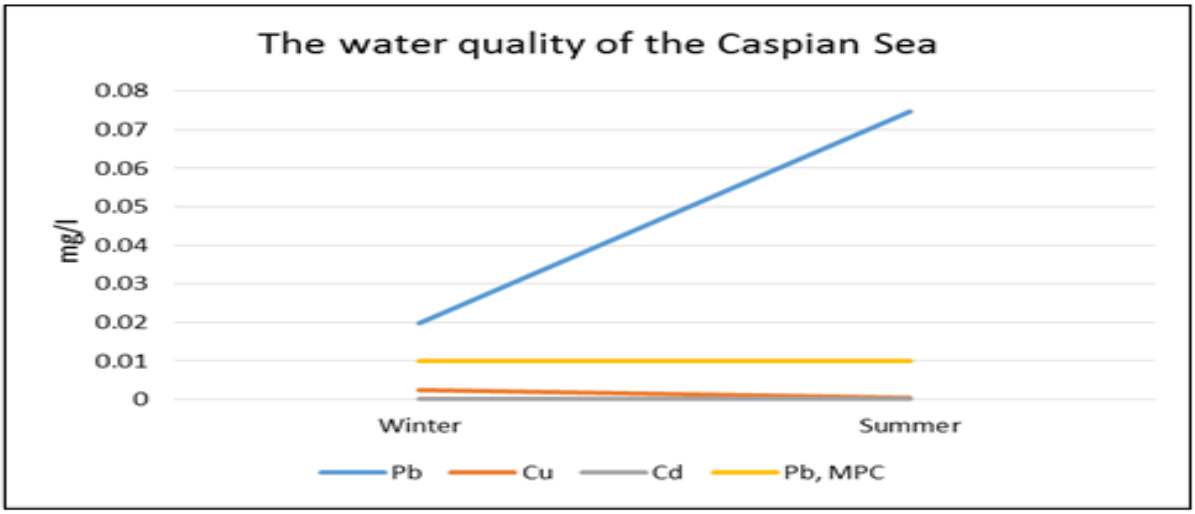

Fig. 3. Differences between winter and summer in concentrations of Cu and Pb.

Zinc

The content of zinc in three and five year's old birds were increased more than international standards except of Chinese ones (Table 1).

The amount of zinc in in floodplain soils of Volga River in Seroglazka was increased more than 4 time from Kapurchal river floodplain soils.

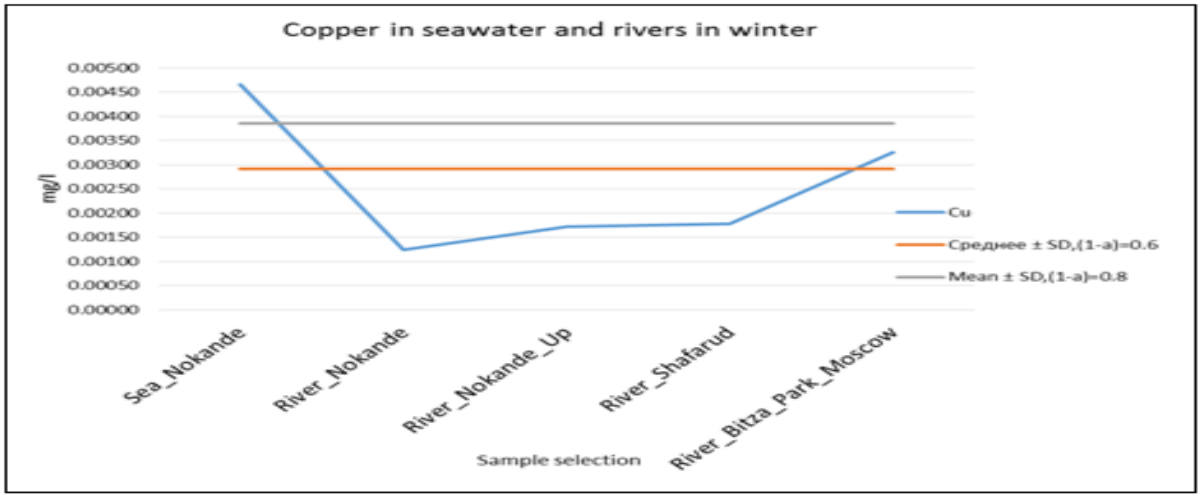

Fig. 4. Comparison of sea and river water between Iran (Gilan) and Russia (Moscow).

Cd

Cadmium accumulation was not observed in Caspian ecosystem neither in water nor in soil and the bird's tissues.

Conclusion

The Caspian Sea because of relatively high magnesium content to calcium and the decrease in salinity of the sea has favorable conditions for organizing beach rest, swimming and so fishing. For this it is necessary to protect its aquatic environment with monitoring of the ecosystem. It is also necessary to control and keep the concentration of heavy elements in the region under permissible levels. The concentration of lead in sea water was increased more than the maximum limits with maximum amounts in

summer, the swimming season. Higher concentration of lead in summer may be due to the abundance of sea voyages. From maximum lead pollution in Gilan beaches con be concluded that the source of lead can be from the northern part of the sea, Volga delta that has reached to south by sea water circulations to Gilan. Also according to figure 4, from higher similarity between Russian river and Caspian Sea water, the source of copper in sea water can be from Russian rivers too. Relatively increasing in the amounts of copper in winter may be partly from southern parts of the sea, due to usage of anti-algae, such as copper sulfate on fishing tackles in Gilan, Iran. Because of maximum amount of zinc (102 ppm) in Seroglazka (Volga River in Russia) according to table 2, can be concluded higher role of Volga River in accumulation of zinc in the bird's tissues. In order to prevent the contamination of seawater by heavy metals, it is necessary artificial or biological wastewater treatments. Then must to create a green barrier between the sea and the areas of agricultural, industrial and urban land uses to prevent rapid discharging pollutants into the sea. For this purpose, it is recommended to plant certain species of native trees and shrubs with a large volume of root system on the all coastal areas around the Caspian Sea.

Acknowledgement

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