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Investigation and Measurement of Heavy Metals Amount (As, Pb, Cd, Hg) within Rivers Estuaries Located in the West Side of Urmia Lake

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ABSTRACT: The ecosystem of Urmia Lake is almost close ended and the water of rains and rivers play an important role in Biological activities of this lake. It is worth stating that the national park of Urmia Lake is almost one of the rare one in world class, since the watery environment of this park is so salty and the only living being which could survive in this lake is named Artemia. Since this park has special natural condition and various ilks of ecosystems, it can be considered one of best domicile for numerous kinds of birds and prominent national park of Iran. Although for now, the West Azerbaijan province is not among the geographical regions of Iran that lead to production of pollution and the extension of industrial activities in this region still do not pollute the watery regions, but the amount of pollution in this area is moving toward pick points and if no measurement is taken in order to control the industrial activities and other polluters, the water source of this province will face with a serious ecological crisis. The rivers that flow into the Urmia Lake have a mineral load, since the urban, agriculture and rural sewage pour into these rivers. This survey aims at identifying the amount of pollution, polluters, self-purification capacity of rivers and offering a solution for resolving the pollution issue, especially when the water level of Urmia Lake is decreased, which lead us to consider polluters and their effects.

Keywords: Urmia Lake, Ecosystem, Sewage, Heavy Metals, Artemia, Environment.

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INTRODUCTION

Pollution of the environment by heavy metals is very prominent in areas of mining sites and reduces increasing distance away. In 1998 a number of Parties to the Convention on Long-Range Transboundary Air Pollution (hereinafter the Convention) signed the Protocol on Heavy Metals (Barbour et al., 1987).

Heavy metal pollution has become a serious health concern in recent years, because of industrial and agricultural development. In general, heavy metals of industrial biowaste broadly contaminate the drinking water, food and air (Goyer, 1996). It is recognized that heavy metals may exercise a definite influence on the control of biological functions, affecting hormone system and growth of different body tissues (Teresa, 1997).

Due to high level of toxicity, persistence and tendency to accumulate in surface waters, heavy metals and metalloids are very dangerous for living organisms if their concentration is higher than allowed. On the other hand, decomposition of heavy metals in water is a very slow process and they cannot be detoxicated by metabolic processes (Wiener and Giesy, 1979).

Heavy metals constitute a very heterogeneous group of elements widely varied in their chemical properties and biological functions. The term "heavy metals" defined as commonly held for those metals, which have specific weights more than 5g cm^3 (Holleman, and Wiberg, 1985). Heavy metals are kept under environmental pollutant category due to their toxic effects in plants, human and food. Some of the heavy metals i.e. Arsenic (As), Cadmium (Cd), Lead (Pb), Mercury (Hg) are cumulative poison. Heavy metals are persistence, accumulate and not metabolized in other intermediate compounds and do not easily breakdown in environment. These metals are accumulating in food chain through uptake at primary producer level and then through consumption at consumer level. Metals are entering the human body either through inhalation or injection. The human body either through inhalation or injection. Heavy metals such as Cd, Ni, As, Pb pose a number of hazards to humans (Mildvan 1970).

High concentrations of heavy metals in water, sediments, and organisms may result in serious ecological consequences. Most heavy metals released into the environment enter the aquatic phase as a result of direct input, atmospheric deposition and erosion due to rain (Veena et al., 1997). Kim et al. (2004) reported the geochemical composition and the processes governing the distribution of elements in surface sediments from the Saemangeum tidal flat.

These guidelines evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality (Wenning and Ingersoll, 2002). They have been largely developed for marine waters but a few have been specifically developed for estuarine waters (Chapman and Wang, 2001).

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A common approach to estimate how much the sediment is impacted (naturally and anthropogenically) with heavy metal is to calculate the Enrichment Factor (EF) for metal concentrations above un-contaminated background levels (Ho et al., 2010). Pollution will be measured as the amount or ratio of the sample metal enrichment above the concentration present in the reference station or material (Abrahim, and Parker, 2008; Mediolla et al., 2008). Ololade et al. (2008) examined the distribution of heavy metals in stream bed sediment from an oil-producing region in Nigeria in the two seasons (dry and wet) of the year. Comparison of sediment with guidelines values indicated anthropogenic enrichment and it was considered that only Cu, and possibly Pb posed potential threats to the ecology of the area. Karimi et al. (2009) published an article named "Measurement of heavy metals in drinking water by atomic fluorescence spectrometry with an examination of drinking waters of Taleghan. In this study, the frequency of heavy metals in drinking water of Taleghan area was measured by using atomic fluorescence. Behroosh et al. (2011) attempted to study the accumulation of heavy metals (Cd_2Cu) within the sediments of Anzali Lagoon. Throughout this study, we have used 4 stage fraction measurements in order to determine the density of heavy metals. Abedini et al. (2006), tried to investigate the process of heavy metals in Pirbazar River. The comparison of resulted data in this investigation with the reference values indicated that the density of metals is higher than the standard limit.

MATERIAL AND METHODS

a) The method of sampling: because of climate conditions and rainfalls, the samples from water and sediments of rivers and from the estuaries of rivers are collected according to a specific schedule. The containers that are used during the sampling process are made of polyethylene which is specifically designed for gathering sediments and water. The water samples along with aquafortis are fixed and transferred to laboratories; the soil samples did need any fixing measure.

b) Experimental part: Surveying Method: With regard to conditions and former studies that are done during past years, factors such as turbidity, EC, PH, Do and temperature are considered as physical parameters and Pb, Hg, Cd, As in water and sediment of river entering into the lake, are analyzed.

Methods of Measuring and Experiment: In order to measure the various parameters, we have used two source of information, first one is the book called "standard methods for measuring water and wastewater (1992)" and the second one was given instructions in catalog of devices that are mostly used for doing experiments. The parameters such as PH, Electricity Conduction, Dissolved oxygen, temperature and salinity are measured at sampling site and sometimes TDS is also measured during sampling or post sampling phase. The heavy metal dose in water and sediment samples is analyzed at laboratories. The most important used devices throughout this survey are followings:

1-Atomic Absorption

2-Measurement of conductivity, turbidity, PH, dissolved oxygen and water temperature by using a -portable device called "U10".

3-TDS measured by the device electrodes. WTW.

4. Sources of pollutants in rivers entering into Urmia Lake: The most important pollutants of the rivers that entering the Urmia Lake are named as followings: a) Effluents and sewage of villages and areas located near rivers; b) On urban water flowing; c) Agricultural Waste Effluents.

The most prominent pollutants among these factors can be the sewage of villages situated near the border of rivers. Most rural wastewaters are formed from washing of clothes, dishes, kitchenware and sewage of stables and livestock waste, which are directed toward the out of rural regions, so after passing kennels they enter into the rivers. The pollutants that result from urban runoff are mostly subordinated by accumulation-leaching process. This process is depended on percent of impenetrable surfaces like street, roof and generally speaking all surfaces that are insulated. It should be stated that the density of pollutions in urban runoff is variable since it is depended in factors like seasons, conditions, quality of drinking water and raw sewage. The main sources of urban and rural runoff which located near the river border and enter into the rivers are described in following table:

Details of the Urmia Lake basin

The basin of this lake with scope of 52700 Km, which is located in northwestern of Iran, occupies 3.21 percent total area of the country. North of this lake is limited to the Aras River basin, northeast of it, is limited to the Sahand Mountains and Sabalan, the southeast of this lake, is limited to Gezel-Ozan area, south of it is limited to the mountains of Kurdistan and West side of this lake is limited to Boundary Mountains. A sluice section of the Urmia lake basin is the biggest permanent internal sluice of Iran, which is located in the West of the Iranian plateau between 37 ° C and 5 minutes to 38 degrees 16 minutes north and 45 degrees 10 minutes east longitude and 45 degrees 45 minutes. This section extends from north to south and has divided Azerbaijan into two sections of east and west. The altitude of surface water of this lake is about 1275 meters from the surface of open water. The greatest latitude of this basin located near to the peak of Sabalan is equal to 2850 meters, which is the altitude variation linked to the basin is equal to 2576 meters, approximately. Dieng is a volcanic region with some active crater. The average height of this area is about 2,000 meters above sea. The main sluice of the basin has length and width of 130 and 16 Km, respectively. The average depth of this lake is about 6 meters, which can reach to 15 meters in the south and southwest areas. The basin of this lake sluice is formed from almost even surface which is enclosed with extended east, south and west heights, in the north. The northeast and southeast parts of the lake, the surrounding plains slope is small, so that during the high watery years the lake elevation is greater than normal, large portions of land are drawn into the water.

In other areas around the lake slope of the plains are relatively high and the scope of foothills and coastal land area is limited. The bed of the rivers within this area possess high slope and the major particles within the water of these rivers are coarse particles, which are directed toward the downstream with floods.

Urmia Lake watershed hydrology

The Basin of sluice of this lake is divided into three parts called east, west and south, from zoning point of view. In north section we can observe no trace of the river (with a huge amount of current), so this section cannot have significant importance during this survey. The river flows to the lake on convergence way, reasons such as limited scope of the basin, short length of rivers and sprawl salty domes has leaded to the emergence of the saltiest lakes of Iran. The whole basin can be divided into 5 regions called triplet regions, lake and plural lands (s) milieu of Urmia Lake. The amount of water that releases into the lake within these triplet regions is equal to 58% in the south section, 24% in west basin and 18% in the east basin per year. Do we consider the low depth and scope of Urmia Lake; we will conclude that this lake is considerably impressible.

The total inflow of water into the Urmia Lake per average 10-years, according to statistics, is about 99/3621 million cubic meters, 74 percent of this value is originating from the southern half region.

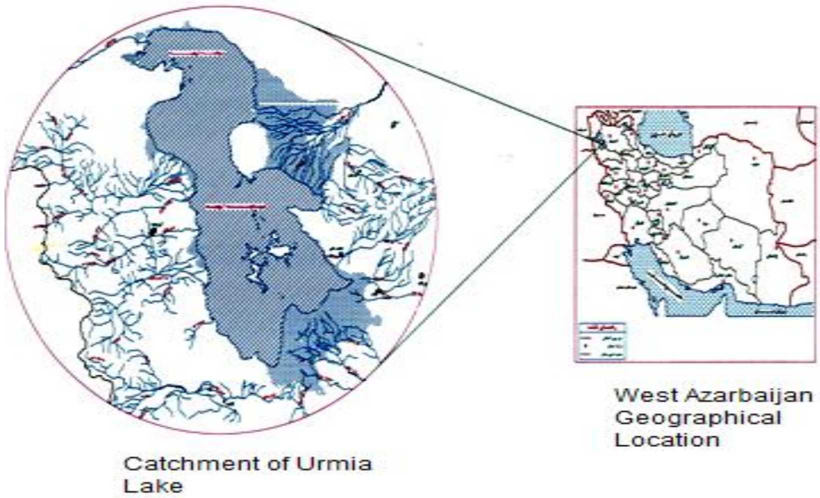

Figure 1. Location of the catchment area of Urmia Lake

RESULTS

1) The physical and chemical characteristics of rivers entering into the National park of Urmia Lake: The result of sampling from stations those are located at estuaries. Of rivers, are presented in table 2, all parameters were recorded as mean.

2) The average values of heavy metals within sediments and water of rivers and the values of heavy metals existing in water and sediments of rivers entering into the lake are given in table 3 and 4. As for table 3, the amount of variation of As is between the minimum and maximum values of 789 μg/g to 2589.6 μg/g, respectively. The average rate of As within the whole river is equal to 1270.844 μg/g. The other factor of which is responsible for polluting rivers can be pesticides which are widely used against vegetable Pests. These chemical substances are carried by runoff into the rivers. By entrance of these substances into the river it is hard to expect that the ecosystem of rivers remain in balance, meanwhile they also endanger the rivers ecosystems which indirectly lead to the death of thousands of fish. Generally, the amount of all chemical pesticides and fertilizers that are used during agricultural activity have an important role in polluting rivers, but the amount of pollution also depends on dose of chemical and agricultural activity that take place in villages that are located around the rivers.

Table 1. Segmentations and characteristics of Catchment Basin of Urmia Lake

Region	Specifications and rivers.	Extent km^2	Compared with the total area of	Annual Estimates of the proportion of streams
Eastern region	Includes Talkherud, BiokChay, Galechay, SufiChay, MardughChay and LeilanChay Rivers	17075	32.4 %	%18
Southern Region	Zarinerud, Siminerud, Mahabadchay and GhedarChay Rivers	19815	%37.6	%58
Western Region	BaranduzChay, ShaharChay, RouzehChay, ZulaChay, NazluChay Rivers	8116	%15.4	%24
Lake Surface	Due to changes in lake level from 1274 to 1277, includes an area of approximately 4,700 square kilometers to 5700 which during subsidence, of 500 square kilometers, appears to be completely swamp lands.	4900 to 5700	%9.5 to %10.5	
Adjacent lands and swamps around Lake	The northern strip is considered within the eastern and western parts of the country and the internal islands are also counted as part lake area. Islamic island that sometimes is considered as peninsula is also counted in the lake area.	2116	%4.1	

Table 2. Mean values of measured physical parameters of river water inflow to Urmia Lake

Row	River Name	Station location		The mean concentrations of measured parameters						
		Longitude	Latitude	PH	Temp °C	Cond ms/cm	T.DS mg/l	Turb JTU	DO mg/l	Sal %
1	ZulaChay	44° 58.477'	38° 14.266'	8.11	8.55	0.43	1258.7	>999	10.31	0.01
2	NazluChay	° 14.050' 45	37° 42.233'	8.29	21.9	1.34	1411.33	175.66	10.43	0.01
3	RouzehChay	45° 12.607'	37° 39.920'	8.83	6.56	0.709	851.33	292.66	9.97	0.026
4	ShaharChay	45° 12.607'	37° 33.275'	8.52	19.07	0.378	474.6	216.3	12.04	0.006
5	BaranduzChay	45° 15.661'	37° 24.423'	8.06	11.67	0.669	562.71	146.6	9.83	0.02
6	GhedarChay	45° 38.511'	36° 58.570'	7.74	12.62	0.768	665.28	232.85	9.80	0.025
7	MahabadChay	45° 43.835'	37° 01.197'	7.80	13.6	1.27	1274	291.7	10.18	0.04
8	Siminehrud	45° 48.876'	37° 01.614'	8.24	13.81	1.21	1574.42	185.80	10.98	0.04
9	Zarinehrud	45° 53.390'	37° 5.167'	7.99	13.37	1.01	1081.57	186.85	9.64	0.04

Table 3. Mean values of heavy metals in sediments of rivers entering into Urmia Lake

Row	River Name	Station location		The mean concentrations of measured parameters			
		Longitude	Latitude	Pb (µg/g)	Cd (µg/g)	As (µg/g)	Hg (µg/g)
1	ZulaChay	44° 58.477'	38° 14.266'	16.4	0.83	1096.2	0.63
2	NazluChay	° 14.050' 45	37° 42.233'	19.58	0.89	1126.4	1.03
3	RouzehChay	45° 12.607'	37° 39.920'	17.54	0.9	2589.6	1.03
4	ShaharChay	45° 12.607'	37° 33.275'	19.542	0.752	797.2	0.704
5	BaranduzChay	45° 15.661'	37° 24.423'	14.46	0.7475	1457.6	0.788
6	GhedarChay	45° 38.511'	36° 58.570'	14.18	0.85	1206.8	0.82
7	MahabadChay	45° 43.835'	37° 01.197'	16.704	0.692	1227.2	0.886
8	Siminehrud	45° 48.876'	37° 01.614'	18.666	0.852	789	0.772
9	Zarinehrud	45° 53.390'	37° 5.167'	20.506	0.858	1157	1.116

Table 4. Mean values of heavy metals in water of rivers entering into Urmia Lake

Row	River Name	Station location		The mean concentrations of measured parameters			
		Longitude	Latitude	Pb (µg/g)	Cd (µg/g)	As (µg/g)	Hg (µg/g)
1	ZulaChay	44° 58.477'	38° 14.266'	18	>1	>3	2.15
2	NazluChay	45° 14.050'	37° 42.233'	11	>1	3.75	>1
3	RouzehChay	45° 12.607'	37° 39.920'	27	>1	4.21	>1
4	ShaharChay	45° 12.607'	37° 33.275'	20	>1	4.25	>1
5	BaranduzChay	45° 15.661'	37° 24.423'	12	>1	>3	>1
6	GhedarChay	45° 38.511'	36° 58.570'	>10	>1	4.5	1.2
7	MahabadChay	45° 43.835'	37° 01.197'	>10	>1	3.5	1.4
8	Siminehrud	45° 48.876'	37° 01.614'	11	>1	>3	2.65
9	Zarinehrud	45° 53.390'	37° 5.167'	>10	>1	3.32	>1

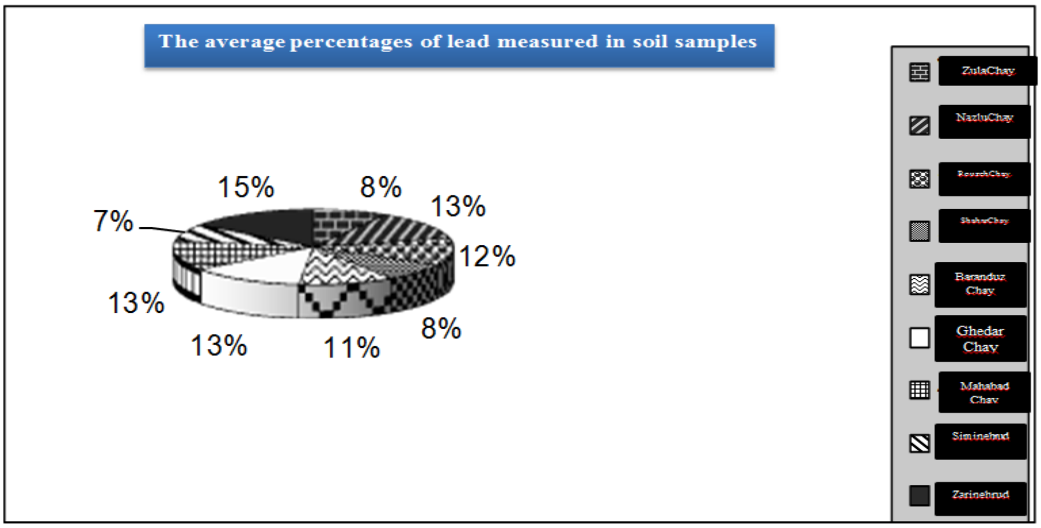

Figure 2. Mean lead concentrations in soil samples

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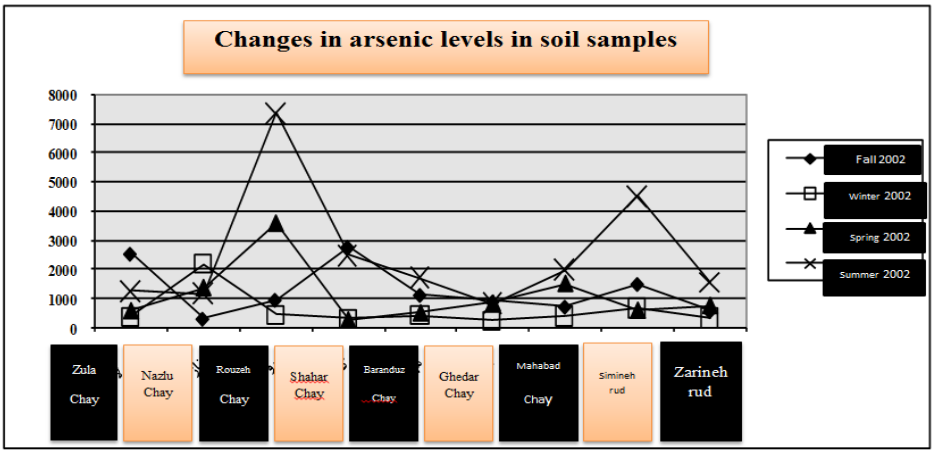

Figure 3. Changes in the concentration of arsenic in different seasons for soil samples

Table 5. Sources of Pollution in the Rivers

Source of Pollution	Minerals	Suspended solids	Nutritive Materials	Heavy Metals	Bacteria
Dung	*		*		*
Rainfalls	*		*	*	
Soil Erosion	*	*		*	
Runoff of Insulated surface	*	*		*	

DISCUSSION

In order to evaluate the resulted data, we have taken into consideration physical factors of rivers water like its temperature, electricity conductivity, turbidity and the amount of heavy metals, and we have also compared these values with international and national standards which leaded to following results:

1) The temperature of Water (Temp) Investigation of the heat factor in estuaries and in different months indicates that filtration mechanism of rivers passes through stable variation of temperature in sampling stations and at different times. With regard to the distance dimension of rivers from source to estuaries and permissible scale, we can conclude that rivers within this area possess self-filtration potential and the amount of pollution is low.

2) The PH of Water PH of any solution is considered a factor for measuring the density of Hydrogen ions in solution. By measuring the PH of any solution we can make judgment about the acidity and alkalinity of water. Almost all natural waters are alkalinity (PH= 6.5-8.5) and the PH of surface waters which are accommodation of fish, is variable between 6.7 to 8.6. The food spoilage of water of river can be due to high value of PH, Moreover the high PH can lead to sediment of heavy metals in form of Hydroxide.

By taking into consideration the laboratorial results it can be concluded that PH is not subordinated by stable pattern and represent few alterations.

3)Turbidity of Water Polluted water allows less light to be passed through it and that kind of water so-called dark or muddy water. This darkness within water is due to various materials which deserve outmost importance to be surveyed and studied. First of all, this issue should be studied from such point of view: because of contaminated surface it is obvious that different living organisms can conceal themselves behind hanging particles (these particles are the main reason of turbidity). The darkness of water is done according to JTU unit, so for agriculture uses the turbidity level of water is acceptable up to 50 levels. The analysis of laboratorial results implies that the turbidity of rivers water differ at various seasons. The differences indicate the increase of pollution amount over the river, especially at branches in highland torrential flow of rivers water.

4)Electricity Conductivity

One of the key elements which implies good quality and state of water is the procedure of electricity conductivity. By comparison of laboratorial results with permissible standards we could draw conclusion that general state and quality of water is desirable especially for agricultural and drinking purposes.

5)The Amount of Dissolved Oxygen in Water

In most cases, the amount of dissolved oxygen is deterministic, since the survival of aquatics in water of rivers is highly depended on the existence of dissolved oxygen. So that, any reduction in amount of dissolved oxygen lead to death of aquatics which results in undesirable smell and stench. This kind of issues is result of disintegration of anaerobic materials in water. One of the factors which is responsible for reduction of dissolved oxygen in water is existence of excessive minerals in sewage and agricultural fertilizers that flow into river via runoff. In most of the rivers, sources and heights since there are no pollutants, we encounter with large amount of dissolved oxygen. Thus, Do is considered as index for measuring the rate of hygiene of water. The maximum amount of oxygen which can be dissolved at normal thermal temperature in water is equal to 9 mg/lit; with increase of this temperature it is so logical to expect reduction in amount of dissolvable oxygen. In some cases such as occasions when there are natural impediments like high steep and photosynthetic algae it is important to investigate and calculate the percent of saturated oxygen.

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CONCLUSION

1) it is important to note that since this region of country is agricultural area and the use of chemical substances like fertilizer and pesticide is requirement of agriculture, some metals like arsenic are released to runoff, moreover, the fact that some regions of West Azerbaijan province include mines (gold mine of Tekab) and sewage of industrial activities are released to flowing waters, as result it is not abnormal to envisage with arsenic in runoffs.

2) The existence of Plumb in surface water is also one of the incontrovertible facts, because of several reasons; first, almost all of the rivers passes through urban regions and these regions are repleted with automotives, the foam of vehicles dispense Plumb over the city, second, pellet bullets helps to sediment of Plumb which is result of PH variations.

With regard to all mentioned points and result, it can be deduced that one of the main pollutants of all rivers around Urmia Lake is urban and rural sewage that merges with runoff and enters into the lake, so serious measures which focus at improving sewage system and its purification should be adopted. Therewith, it is not ungraceful to eschew from excessive use of chemical substances in agricultural activities especially those ones that carry heavy metals. Continuum sampling and studying of this region will lead to be more cognizant of ecological changes of Urmia Lake.

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