

Chemical and Physical Properties of Maharlu Salt Lake (Iran) **Prior to an Extensive Drought**

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ABSTRACT

Aims The ecology of Maharlu Lake is of great importance, especially in relation to the continuous addition of a reasonable volume of municipal and industrial effluents to it. To improve our knowledge about lake's ecology, mineral nutrients and heavy metal concentrations, among some other physical and chemical factors, are investigated.

Materials & Methods 3 stations were selected in the lake and critical factors were measured monthly from January 2000 to December 2001. Main physical and chemical properties included temperature, pH, dissolved oxygen, CO2, conductivity, salinity, dissolved solids, and concentration of major ions, including carbonate and bicarbonate, phosphate, nitrite and nitrate, calcium and total hardness, chloride, and alkalinity, and heavy metals as Co, Cd, Pb, and Hg.

Findings Averages of pH, dissolved oxygen, salinity, electrical conductivity, and dissolved CO2 were 7.9, 2.9mgL-1, 290gL-1, 375mscm-1, 342mgL-1, and 63mgL-1, respectively. The highest concentrations of heavy metals were 23µgL-1 for As, 303µgL-1 for Co, 970µgL-1 for Cd, 8510μgL-1 for Pb, and 25μgL-1 for Hg.

Conclusion Essential factors of the lake are in accordance with the soil of the catchment area, but they are in many cases altered under local attributes like precipitation, irradiation, evaporation, and deposits, as well as living elements of the lake's ecological network, as the consequences of activities of bacteria in biological processing of nitrogen and phosphorus, etc. After this research, Maharlu Lake was totally dried up, never filled again. So, the results of this investigation can be regarded as the last record of the lake situation prior to its current complete drought condition.

Keywords Saline Lakes; Nutrients; Heavy Metals; Pollution; Fars Province

CITATION LINKS

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Introduction

Saline lakes constitute an almost equal amount of the world water content to freshwater lakes (0.008% vs. 0.009%) but have received much less attention worldwide [1]. However, various benefits come from these lakes to the ecosystems around them and human life as well. There are several saline lakes in the Iranian plateau, from Urmia Lake, the world's 6th largest saline lake in North-West to dozens of large and small desert lakes and playas in Central Basin and its surroundings.

Maharlu is an athalassic saline lake in the south of the Zagros Mountains, which is formed by Pleistocene tectonic subsidence [2]. It is supposed to be a hydro-morpho-tectonic consequence of acting faults and wet rainy ages of the Quaternary [3]. The lake occurs between two climatic zones of temperate in Northwest and semi-arid in Southeast [4]. Therefore, like many other saline lakes, it has undergone several periods of drought during its history.

Maharlu Lake is a hypersaline wetland (based on definition by Cowardin [5]), which supports a simple aquatic food chain mainly consisting of the green alga Dunaliella salina (Dunal) Teodoresco, and to species of the endemic crustacean Artemia planktonic parthenogenetica (Bowen and Sterling, 1978) and artificially introduced Artemia franciscana (Kellogg 1906) as reported by Manaffar et al. [6]. Integration of local and migratory birds including greater flamingo (phoenicopterus roseus Pallas, 1811) and the common crane (Grus grus [Linnaeus, 1758]), as well as a small community of amphibians (*Pelophylax* ridibundus [Pallas, 1771] and Bufo viridis Laurenti, 1768), reptiles (Testudo graeca Linnaeus, 1758 and Mauremys caspica [Gmelin, 1774]), and a few halophilous macrophytes (eg. Aeluropus littoralis [Gouan] Parl., Alisma lanceolatum with *Atriplex* verrucifera M.B., **Butomus** umbellatus L., Halocnemum strobilaceum [Pall.] M.B., Phragmites australis [Cav.] Trin. Ex Steud., Potamogeton pectinatus L. and Suaeda maritima [L.] Dumort.) in the river delta makes a more extended food web through the whole lake and the surrounding terrestrial ecosystems [2]. The extensive area of the lake provides a source of humidity for the surrounding lands and, hence, is crucial for the survival of various plant and animal communities.

Apart from its climatic and ecological values, industrial utilizations (salt mining) and biological importance, this highly saline lake is an endpoint to a high amount of urban and industrial discharges from the capital city of Shiraz. Most significant polluting agents, which are released to the Rudkhoshk wadi and transported to the lake, are micronutrients from chemical and organic agricultural fertilizers, organic materials from pesticides, municipal and industrial wastes, and oil pollution, and heavy metals from industries, agriculture, and municipal wastes [7].

Severe extensive droughts in recent years have reduced the area and depth of the lake [8] and resulted in drastic alteration of its natural features. At the same time, changes in land use the lake catchments area overexploitation of surface and underground waters have reduced water input and caused more pressure on its ecosystem. Extensive climatic investigation analyzing precipitation data from 33 synoptic stations in the province from 1971 to 1998, using SPI precipitation index, revealed that the most persistent droughts in the period were of moderate type, and then the severe type [9].

Fotuhi *et al.* [10] reported that 3 major natural lakes of Fars Province are under severe drought due to recent climatic changes and increased water uptakes from rivers by man. Assessment of recurrent drought period using SPI in the Fars Province revealed that the magnitude of changes increases from the Northwest to the Southeast, and as the drought period prolongs, severity and spatial extent of drought increases [11]. More recently, recurrent drought periods were detected to be 2, 4, 5, and 6 years long in Maharlu station [12].

Despite a valuable set of researches on geology [13-16], no much information is available on various ecological aspects of the lake, including its chemical and physical properties.

The aim of this study was to produce data on some chemical and physical aspects of the Maharlu Salt Lake at 1-year monitoring, to record its condition under natural environment and affecting influents. As Maharlu Lake was never drained permanently since then, so that any filling after winter floods lasted only a few months all these years, these data can be regarded a base record of what the situation of the lake has been in the past, and provide a benchmark for comparisons in future.

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Materials and Methods

Site description: Maharlu basin is in the arid belt of the northern hemisphere [3]. In a detailed look, the lake itself is placed between 2 semiarid and temperate climatic zones, having a long summer of 5 to 6 dry months [4]. Wind directions are north-west and west. Air currents, which affect the climate of the region, are part of Middle-East cyclones formed on the Mediterranean Sea and conducted toward Iran by the long Mediterranean trough. Trade wind air masses of the Indian Ocean are also partly involved in the precipitation patterns. Mean precipitation in the area of the lake was 346.94 mm in a 47 years period between 1968 to 2013, ranging from the highest 647.01 mm in 1993 to the lowest 145.90 in 2008 [4]. Regularly, the highest precipitation occurs in February and March. Minimum and maximum temperatures are recorded in January (-14.4°C) and July (+43.2°C), respectively.

Maharlu Lake lies in 10 km Southeast of Shiraz, the capital of Fars Province, south of Iran, between 2 geographical points of 29°32'29"N, 52°44'17"E and 29°19'21"N 52°54'32"E. It is surrounded lengthwise by relatively high mountains (ca. 2,000 m asl), except for corners in northwest and southeast. The lakeshore has an altitude of 1460 m, with a depth of 0.5 m, which increases up to 1.0m in high precipitation years [2]. The length and width of the lake have been measured up to 31 and 11 km, although it may have fluctuations according to discharges to give areas between 175 to 250 square kilometers [17].

The highest total lake area in the last 20 years

was recorded 258 square kilometers [8]. The deepest recorded point in the lake was 3.0m [18]. The lake is fed mainly with currents and floods of a few perennial and ephemeral streams (Polfasa and Rudkhoshk, which dries up in summer). Two drainage waterways, Nazarabad and Mianjangal, and a number of modest artesian springs in lake surroundings including Barmeshur, Barme Babunak, and Cheshme Nilgunak continuously discharge limited amount of water into the lake.

Sampling stations: The length of the lake was primarily divided into 5 lengthwise sections. However, as the project advanced, the lake started to shrink due to the progressive drought. As the lower (south-eastern) part of the lake has the least depth, this part no more existed at the time of sampling. Therefore, the research focused on only 3 stations at the upper part (northern half). Geographic coordinated of these stations are given in Table 1. As proceeded, the shrinkage continued, and these stations were further reduced to 2 or even 1 in some months (Figure 1). Additionally, sampling points moved toward the lake center due to the retreat of the lake shore.

Table 1) Geographical details of selected stations

Station No.	Geographic coordinated	Locality name
1	N: 29°26′ 49″; E: 52°44′ 13″	The dock
2	N: 29°27′ 09″; E: 52°43′ 34″	Department of the Environment
3	N: 29°28′ 14″; E: 52°42′ 06″	Barmeshur inlet

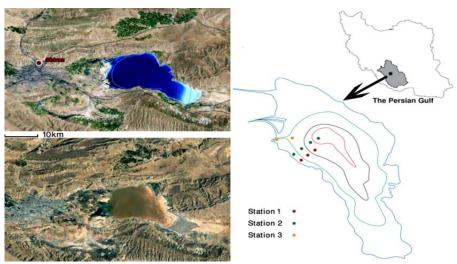


Figure 1) Lake Maharlu in 2000 (top left) and 2017 (bottom left). The lakeshore retreated with progressive drought, so sampling points had to be moved toward the lake center to reach the water (left). Outlines are speculatively drawn representing the retreating lakeshore.

Sampling methods and analyses: Water samples were taken 12 times monthly from each station during January 2000 to December 2001. Water temperature, pH, and dissolved oxygen were measured in situ, using a mercury thermometer, a portable oxygen probe, and a portable pH-meter. Carbon dioxide was measured by Titrimetric method [19], using prepared solutions as a simple kit in the location. Calculated volumes of water were collected and titrated with a pipette. Electrical conductivity was measured by an EC-meter probe. For the measurement of salinity, known volumes of water sample were diluted in order to be used by a refractometer (based on calcium chloride), immediately after the sampling trip in the laboratory.

Measured factors were total dissolved solids (by drying up water samples in 105°C in preweighed dishes), carbonate and bicarbonate (titration with chloridric acid), phosphate (ascorbic acid method), ammonium (Phenate method), nitrite (colorimetric method), nitrate (Brucin sulfate indicator), calcium and total hardness (EDTA Titrimetric method), chloride (Argentometric method and titration with silver nitrate in presence of potassium chromate), and alkalinity (sum of phosphate, carbonate, and bicarbonate). Procedures for physical and chemical properties were taken from Greenberg et al. [19]. Water samples were tested for the detection of 5 heavy metals (As, Co, Cd, Pb, and Hg), using flame atomic absorption spectrometry [19].

The data were analyzed, using ANOVA by SPSS 14.0 to compare means of 3 stations repeated for 12 months.

Findings

The deepest point in 3 stations was station 2 with 30 cm depth in April and 7 cm in September. Water temperature showed a progressive increase from April to October and returned to its winter level afterward (Diagram 1). The mean water temperature of the year in 3 stations was 20.8°C (SD=7.4).

The 3 stations showed a significant difference in their yearly average of electrical conductivity (p<0.004). Station 3 had the least values, while stations 1 and 2 reached their maxima in June. Total average of electrical conductivity in 3 stations was 375.5 mScm⁻¹ (SD=168.1). During the year, salinity had the highest value in July of 650 ppt (in station 2), and the lowest value of 5

ppt in March (in station 3; Diagram 2).

Dissolved oxygen did not show any significant variation among stations, but its winter concentrations were significantly higher than summer values (p<0.0001). The highest DO concentration was recorded at 6.82 ppm in January at station 1, while its lowest value was 0.30 ppm in May at station 2 (Diagram 3). Average dissolved CO2 concentration was as low as 1.7 ppm with a high variation between stations (SD=1.6) in mid-spring, and increased drastically in summer to reach values of 230 ppm in mid-autumn (Diagram 4), while there was no significant variation among stations. Values of pH proved to be dependent on seasons as well as it showed the highest amounts of 9.10 in March in stations 1 and 2, and the lowest amounts of 6.80 in September in station 2 (Diagram 5).

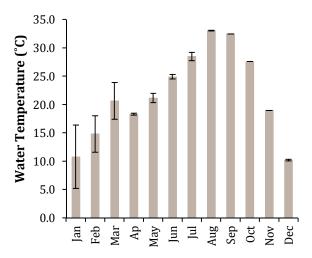


Diagram 1) Monthly changes of water temperature in Maharlu Lake

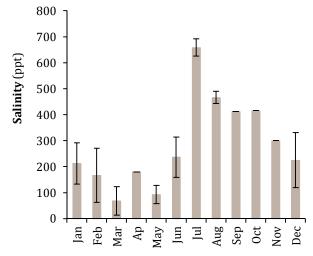


Diagram 2) Monthly changes of salinity in Maharlu Lake

Diagram 3) Monthly changes of dissolved oxygen in Maharlu Lake

May Jun

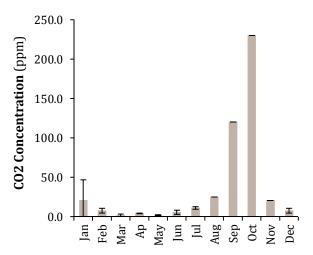


Diagram 4) Monthly changes of dissolved carbon dioxide in Maharlu Lake

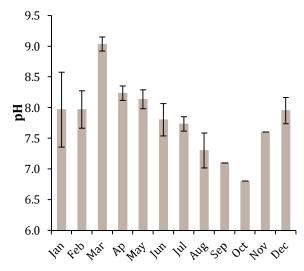


Diagram 5) Monthly changes of pH in Maharlu Lake. Values were set from 6.0 for a clear demonstration of pH fluctuation between minimum and maximum

Nitrite ion concentration showed much lower

amounts from January to May (ranging 0.003–0.03 mgL⁻¹); however, it was higher during spring and summer and showed drastic increases in June (0.20 ppm at station 3) and October (0.20 ppm at station 2). The concentration of nitrate ions had a reverse order; higher levels were recorded from June to May (up to 0.34 ppm at station 3), while lower levels were recorded from July to December (0.004 ppm at station 3). The concentration of free ammonium ions presented irregular fluctuations ranging from

0.03 to 11.18 mgL⁻¹.

Parallel to the pattern of spring conditions of dissolved CO2, bicarbonate ions had lower amounts during this time, followed by increases in summer and early autumn. Stations 1 and 2 had a similar pattern, but station 3 showed exceptional high amounts in winter-early spring period. Carbonate ions increased in August to October. Phosphate concentrations were fluctuating below 0.04 ppm in all 3 stations with exceptional increase to 0.10 ppm in May at stations 1 and 2. Calculated alkalinity was in accordance with the fluctuations in concentration of carbonate ions. Levels of total dissolved solids increased gradually from winter to reach their maxima on summer-early autumn and then turned to lower levels. A description of the major components of the lake water is given in Table 2.

Measurement of some heavy metals showed very low amounts in water (Table 3). The highest values of these were lead (8.5 ppm in March), cobalt (3.0 ppm in March), cadmium (1.0 in April), arsenic (23 ppb in April), and mercury (5.5 ppb in April). Arsenic was only detectable in January, and cadmium only in the first 4 months.

Table 2) Major ions and components (ppm) of the Maharlu Lake water in 2001

Component	Mean	SE	Min	Max
[NO ₂ -]	0.051	0.011	0.002	0.2
[NO ₃ ·]	0.111	0.017	0.004	0.340
[NH ₄ ⁺]	3.34	0.54	0.03	11.17
[CO3 ² ·]	67.75	13.64	6	24
[HCO3·]	270.88	36.08	61	780.8
[CO2]	63.57	8.71	0	154
Alcalinity	328.97	40.85	73.03	780.82
[PO4·]	0.018	0.005	0.002	0.106
[Cl·]	128046.8	14486.6	7434	277182
[Mg ⁻]	22719.2	9041	1809.3	234742
TDS	203.2	25	7.6	372.7
TPM	8.65	1.53	1.1	18

Table 3) Concentrations of some heavy metals in Maharlu Lake water in 2001

Month	Stations	As (ppb)	Co (ppm)	Cd (ppm)	Pb (ppm)	Hg (ppb)
	1	18.00	1.52	0.22	3.75	nd
January	2	20.00	nd	nd	nd	nd
-	3	23.00	2.37	0.26	4.56	nd
February	1	nd	1.72	0.70	6.11	2.20
	2	nd	2.89	0.49	6.12	1.00
	3	nd	nd	nd	nd	5.50
	1	nd	2.95	0.60	8.51	0.84
March	2	nd	2.03	0.74	8.12	2.90
	3	nd	nd	nd	nd	2.90
April	1	nd	1.94	0.77	nd	nd
	2	nd	3.03	0.97	nd	1.16
	3	nd	2.72	0.53	nd	1.64
	1	nd	2.90	nd	nd	nd
May	2	nd	2.60	nd	0.47	0.87
	3	nd	2.30	nd	nd	nd
June	1	nd	1.64	nd	1.25	0.12
	2	nd	2.00	nd	1.25	0.07
	3	nd	2.00	nd	nd	0.08
July	1	nd	1.97	nd	1.40	0.06
	2	nd	2.00	nd	0.60	0.03
	3	nd	1.62	nd	nd	0.12
August	1	nd	1.87	nd	nd	0.09
	2	nd	1.79	nd	nd	0.09
September	2	nd	1.59	nd	0.94	0.09
October	2	nd	1.90	nd	0.78	0.06
November	2	nd	2.40	nd	0.78	0.06
December	1	nd	2.10	nd	nd	0.04
December	2	nd	2.40	nd	nd	0.06

nd: not detectable

Discussion

As many other athalassic lakes, changes in physical and chemical properties of Maharlu Lake is a reflection of periodic environmental conditions. Seasonal precipitation subsequent discharges of an effective amount of water by floods, fluctuating discharges of a few freshwater springs from around the lake, seasonal drastic variations in light intensity and consequently in temperature, and wind patterns all act on different aspects of the lake, producing a cyclic entity. Monthly record of precipitation shows a better image of the hydrological situation of the lake. As recorded by Dobanae Synoptic station in the lake margin, monthly precipitation from January 2000 to December 2001 were 40.0, 19.5, 12.0, 16.0, 1.0, 5.0, 0.0, 0.0, 0.0, 0.0, 4.5, 145.0 mm, respectively. These data clearly demonstrate the drought condition and the declined amount of input water to the lake, which led to its exhaustive drought [20].

During this survey, the concentration of DO decreased as temperature rose, and increased with temperature loss in fall, due to the

decrease in gas solubility of water. On the other hand, the pressure of bicarbonate–carbonate–dissolved CO_2 in their equilibrium system could compete with oxygen for dissolution in water, and stop its further entrance. The concentration of these ions increased in August and September so that they could prevent dissolved oxygen levels to reach its previous amounts of the starting months.

Fluctuations of salinity and electrical conductivity were almost entirely interpretable with temperature, which led to the loss of water volume, as it increased with the increase of air (and water) temperature, resulting in untensive evaporation. Electrical conductivity in the catchment soil was rather diverse, ranging from 0.8 to 32.2 mS/cm (Table 4), while higher values up to 375 mS/cm in the lake water are predictable only by the highly evaporation pressure on the lake. At the end of summer, what remained from the lake was a concentrated hypersaturated viscous solution on a thick bed of salt crystals. When the autumn rainfalls added more water to this condensed solution, salinity levels returned to their natural Zamanpoore M. et al.

amounts. The salinity of the lake was previously reported as 110 g/L in February and 290g/L in October, which is in consistency with our results in winter (100 ppt) and autumn (300

ppt). As it can be expected, salinity was much lower in station 3, close to the Barmeshur spring as a result of persistent freshwater input.

Table 4) Soil physiochemical ranges in some selected localities in Maharlu Lake upstream catchment area (published data [27])

(published data)						
Locality	Soil subgroup (USDA)	pH (aqueous)	Electrical Conductivity (mS/cm)	CaCO3 (%)	Organic Carbon (%)	Clay (%)
1	typic Xerortents	7.1-7.7	8.8-23.8	46.0-87.5	0.2-11.9	10.0-20.6
2	vertic Haploxerepts	7.2-7.8	5.4-9.1	32.0-72.5	0.13-1.1	15.4-38.8
3	typic Haploxerepts	7.8-8.0	4.4-18.7	45.0-51.5	0.2-0.9	15.4-24.4
4	typic Haplosalids	7.7-8.3	3.6-32.2	35.0-45.0	0.13 - 0.80	24.4-40.6
5	hydric Haplofibrists	7.4–7.5	3.6-29.1	45.0-63.0	14.4-21.4	15.4-19.8
6	typic Xerortents	7.8-8.1	0.8 - 2.1	53.5-66.0	1.6-0.3	19.0-22.6
7	typic Haploxerolls	7.8-7.9	0.8-1.9	58.5-61.5	0.4-2.6	17.6-42.8
8	typic Haploxeralfs	7.4-8.3	3.5-8.7	43.5-49.5	0.3-1.1	35.2-55.0
9	typic Calcixerepts	7.6-7.7	2.8-4.2	44.5-49.5	0.2-0.8	26.2-35.2
10	typic Xerofluvents	7.7-7.9	3.3-7.8	47.0-50.7	0.15-0.7	22.8-32.5
11	typic Calcixerepts	7.8-7.9	0.8-1.9	50.5-61.5	0.18-0.9	34.5-40.0

Values of water pH were mostly in the range of soil pH in the catchment (Table 4) with an exceptional high value in March. Variations of the pH during summer can be explained by the fluctuations of CO2, carbonate, and bicarbonate ions as well. Dissolved CO2 values were in low amounts (below 25 ppm) from early winter to late summer. Low CO2 decreases carbonic acid, which raises pH value, as was seen in the early months of the research. After this, a rapid increase of CO2 followed by dissociation and ionization increases carbonic acid level in the water, hence reduces the pH value. Annual mean for the pH was 7.95 (SD=0.56), close to the older records with single measurement was 7.4 for the lake.

Fluctuations of dissolved CO_2 were in accordance that of phytoplankton population. Unicellular algae Dunaliella salina can increase its population size during the early months before salinity rises to the high summer levels [21, 22]. This could lead to a high photosynthetic rate, which results in intake of the most possible amounts of dissolved CO₂ [23] to be consumed by the algae and reducing its water content to 0.0 ppm. Rapid hatching and growth of Artemia sp. in spring [24] inserts a grazing effect on the algae and reduces their photosynthetic CO₂ consumption. However, this increase is followed by a rapid decrease in

summer. This reduction can be explained by the force against CO_2 dissolution exerted by increased ionic concentration, shown in higher salinity, conductivity, and TDS. As temperature drops in the autumn, the growth and activity of phytoplankton decline once again, and the pressure for CO_2 consumption is removed. Increased dissolved CO_2 has forced its equilibrium equation toward the production of carbonates and bicarbonates.

Among nitrogenous compounds, nitrite and nitrate were recorded in very low values, but a relatively higher amount of ammonia can be explained by inputs from the urban wastewater and an extensive metabolic production by the *Artemia* in the spring, the same as what can be suggested for phosphate ions. Owji [25] reported the lake ammonia and phosphate ions as 1.4 and 1.6 ppm, respectively.

Our measurements recorded relatively low amounts of the selected heavy metals. Industrial wastewater is considered as the main source of heavy metal discharges from Rudkhoshk and Polfasa wadis to Maharlu Lake [6, 26]. A thick and old layer of sediment covers the lake bed, and it was suggested that most of them can be settled and hide among the sediments after entering the lake, especially when evaporation decreases water volume in summer.

Conclusion

Rudimentary natural situation of the chemical and physical aspects in the Lake Maharlu is primarily defined by the runoff, bringing various elements and compounds from upstream, which is in turn affected by the catchment's soil characteristics, from where the water current passes through. However, climate and ecosystem metabolism are the decisive elements, which determine the ultimate property of the lake water.

Measured amounts of essential factors and constituents like pH, carbonate ions, and concentration of main salts in the Maharlu Lake are shown to be in accordance with those in the soil of the catchment area, but they are in many cases altered under local physical, chemical, and biological attributes like the scant precipitation, intensive irradiation, high evaporation, rich deposits in the lake bed, as well as living elements of the lake's ecological network.

In an ecosystem approach, the decrease of dissolved oxygen concentration in warm seasons might be regarded as most influential factor on the stability of populations of living organisms and equilibrium in ecosystem functioning in the lake [18]. Oxygen loss in Maharlu Lake due to the increase temperature and carbon dioxide intake, which is, in turn, a result of the rise in phytoplankton Dunaliella salina population, and metabolism in warmer conditions, affect the simple and fragile food web of the lake. Most probably, it can impress the normal life cycle of the crustacean Artemia, as well as all aerobic microorganisms, which are responsible for decomposition of organic matter and release of various elements from the sediment. This approach enables us to have a better understanding of the concentrations inorganic material, as the consequences of activities of Nitrobacter, Nitrosomonas, ecological processing of various nitrogen species, and *Pseudomonas stutzeri* (phosphate oxidizing bacterium), phosphate solubilizing bacteria, etc.

To get a more realistic and concise understanding of the nature and long-time behavior of Maharlu Lake, a special attention to fluctuations of material input from both industrial and urban wastewater, and winter runoffs, the lake's main source of water, which includes continuous measurements of both lake

and input waters is needed. Complicated relations of water-sediment exchange are another field, which is essential to be studied, in order to make a clear image of the pollution situation of the lake.

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