Sedimentation rate determination and heavy metal pollution assessment in Zariwar Lake, Iran

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Abstract

Metal contents and enrichment factors of ten major trace metals, along with total organic matter, were studied using a 50-cm-long sediment core from Zariwar Lake in Iran. The source of elements (Fe, V, Co, Cd, Al, Cu, Zn, Ni, Cr and Mn) was investigated by chemical partitioning technique as well as cluster analysis. Results of partitioning revealed the anthropogenic portion of metals (%) to be: Zn > Cu > V > Ni > Mn > Cd > Co > Cr. Cluster analysis classified all elements into clusters A and B. The presence of Fe and Al as earth indices in both clusters indicated that all investigated elements likely originate from the lithogenic sources to some extent. Results obtained from the geochemical accumulation index, pollution index, enrichment factor and Hakanson index showed that the sediments were not contaminated and did not exhibit ecological risk. Negligible levels of pollution were seen in terms of Ni and Mn contents. Average sedimentation rate was about 5.6 mm/year according to ²¹⁰Pb activity through the depth of the core, which is about 5.5 times greater than the ones reported in other freshwater lakes. Considering the lake being small, this increasing trend in sedimentation rate may create short phases of lake sedimentation and degrade the aesthetic quality of this aquatic environment.

Keywords Anthropogenic · Aquatic · Chemical partitioning · Intensity · Lake pollution

1 Introduction

Metallic elements have always been a major cause of man-made pollution in lakes and other inland water systems threatening ecosystems and human health [1–5]. Also, sediments could reduce lake volume by time, leading to complete dry up in some cases [6, 7]. They carry a great deal of nutrients and metal loads into lakes, as well [8–10]. Therefore, sedimentation rate determination and heavy metal pollution assessment in lake's sediments would provide beneficial information to make managerial decisions and improve the lake conditions.

Zariwar Lake is one of the scant international wetlands and an Important Bird Area located in Iran [11]. Although the lake's location is in a relative geographical isolation from the surrounding populated areas and industries, it

has not been devoid of anthropological polluting agents. In recent years, ignoring the environmental aspects of this valuable lake has caused various problems such as water pollution, large sediment discharge into the lake and loss of birds, fauna and flora [12, 13]. In addition, the shrinkage of the lake's surface area due to the recent droughts has exacerbated the lake pollution and limited the beneficial lake functions. Recently, the local authorities of Kurdistan Province have shown concerns about possible problems threatening Zariwar Lake's ecosystem caused by heavy metals and sediment loads discharged into it as a result of anthropogenic activities in the lake's watershed [14–17].

Considering the above, this study aims to investigate metal pollution and sedimentation rate in Zariwar Lake to help making managerial decisions and improving the lake conditions. In this regard, chemical partitioning of copper

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(Cu), zinc (Zn), nickel (Ni), chromium (Cr), manganese (Mn), aluminum (Al), iron (Fe), vanadium (V), cadmium (Cd) and cobalt (Co) has been studied in a sediment core from Zariwar Lake, aiming to find out about past and present conditions of metals, along with the extent of pollution. Chemical partitioning and sequential extraction methods have been widely applied to determine sediments bonds with trace metals, to detect pollution [18–20]. The metallic bonds in carbonate, sulfide and organic phases are probably indicators of pollution [21]. In addition, metallic pollution in sediments was assessed using a number of pollution indices, i.e., geochemical accumulation index (I_{geo}) [22], pollution index (I_{poll}) developed by Karbassi et al. [19], enrichment factor (EF) [23] and Hakanson index [24]. Finally, sedimentation rate is determined to see how the lake has changed during the past centuries. A number of traditional and modern methods, such as hydrographic maps [25] and isotope tracing, are used to assess sedimentation dating [26]. Detecting isotopes using ^{210}Pb was chosen as the main procedure to achieve the research goals.

2 Case study

Zariwar Lake is a freshwater lake located in Kurdistan province, northwestern part of Iran (Fig. 1). The lake with a mean depth and area of about 5 m and 8 km², respectively, is located in a midlatitude and at 1285 m above sea level. Average precipitation, mean annual temperature and perspiration in the lake basin are about 905 mm/year, 13.6 °C and 1900 mm/year, respectively [27, 28]. Lake water is supplied by bottom springs, Ghezelchesoo seasonal river and other smaller streams [28]. It contains about 54 million cubic meters (MCM) of water, of which about 13 and 41 MCM are supplied by the bottom springs and surface runoff, respectively [27]. Zariwar Lake is frozen during winters [29], so it can be classified as a dimictic lake [30].

Zariwar Lake has been formed by extensive erosion of the region's geological formations [27]. Geological conditions of Mariwan plain and tectonic factors of the area generally affect the bed rock of the plain, the middle part of which is the deepest section. The alluvial depth in the western part of the lake reaches 60 m, due to the existence of a fault. The bed rock of Mariwan plain is mainly made of metamorphosed limestone. However, it partly contains acidic igneous rocks in the northern areas of the lake and shale in the south close to Ney and Rikhalan villages. A thick layer of brownish gray soil covers the lake surroundings.

There are 97 bird, 31 mammal, 13 reptile, 11 fish and 100 flora species in the Zariwar wildlife shelter. Reed covers a 1200-ha area around the lake. The lake is a weighty

part of the economic, touristic and agricultural life in the area [31, 32].

For years, the lake has been dealing with environmental problems such as water pollution, fauna and flora death and increased sedimentation rate. The sustainability of the lake was subjected to serious threats by the discharge of Mariwan city wastewater, rural wastewater and chemical fertilizers to the lake. Also, the construction of a soil dike in southern part of the lake, the construction of Ghezelchesoo diversion weir and the discharge of a great amount of sand and mud into the lake through Ghezelchesoo seasonal river have caused damages to the lake environment. In spite of the above-mentioned problems, so far few studies have targeted Zariwar Lake pollution and its causes.

3 Materials and methods

3.1 Sampling

Zariwar Lake is a small water body in terms of area (about 8 km²). In addition, the nature of sedimentation rate and metal pollution in sediments is such that one core would be enough to represent the whole area even in the case of coasts, estuaries and small lakes [33–36]. Therefore, a 50-cm-long gravity core with the diameter of 4 cm was collected, using a Phleger-type corer, from the station located at 35° 55' latitude and 46° 12' longitude, in December 2016. The core was maintained vertically at the temperature of 4 °C. In the laboratory, samples were taken from every centimeter of the core. Samples were dried at 40 °C and sieved through a 63-μm mesh [37]. Depending on the organic carbon content, the color of the sediment samples varied from black (more organic carbon) to brown (less organic carbon). The deeper the level of the sample, the blacker the color.

3.2 Bulk digestion and chemical partitioning

For bulk digestion, strong acids must be used. To avoid effervescence due to the addition of such acids, 0.1 mL of 1 N HCl was added to 0.5 g of each sediment sample in a beaker. At the first step, 7 mL of HCl mixed with HNO₃ (1:3) was added. Thereafter, a sand bath was used to heat the mixture at 125 °C, to near dryness. Subsequently, 7 mL of H₂O₂ was added to the flask before it was heated to near dryness. Then, an additional 4 mL of H₂O₂ was added to the solution before the sample was allowed to dry. The samples were left in room temperature to cool down. The final solutions were then filtered through Whatman membranes and were brought to 50 mL volume by distilled water [37].

Fig. 1 Location of Zariwar Lake in Iran along with the sampling location

One step chemical partitioning was then carried out. About 15 mL of 0.53 N HCl was added to 2 g of sediment samples. This causes loose and sulfide bonds to break. The flask was then shaken for 30 min and filtered through a Whatman membrane before being brought to the volume of 50 mL [37]. Acids used in the experiments were all Merck analytical reagent. A flame atomic absorption spectrophotometer (model 119 UNICAM) was used to measure the concentration of metals (i.e., Cu, Zn, Ni, Cr, Mn, Al, Fe, V, Cd and Co) in the sediment samples.

Loss on ignition (LOI) of samples, which shows the organic matter content, was obtained by weighing the remaining material after heating the samples at 450 °C in a furnace, for 4 h. Also, weighted pair group cluster analysis method [38] was used to determine the relationship between the heavy metal concentrations and LOI. In the digestion process, a part of trace elements may be lost.

The precision of the analyses was investigated by comparison to reference marine sediments (MESS-1,

NRC, Canada), blanks, as well as duplicate samples. Acceptable recovery rate (92–104%) was observed as a result of duplicate analysis of all metals as shown in Table 1.

3.3 Determination of sedimentation rate

Sedimentation rate was estimated by measuring ^{210}Pb activity in the core sediment. Lead-210 (^{210}Pb) can be measured using an alpha spectrometry system of high resolution. In this regard, a sample was taken from each centimeter of the 50-cm core. A microwave digestion, containing the same isotopic traces, was applied to digest the dried samples. The heating process of a HF-HNO₃ acid mixture totally dissolved the samples. HF and excess HNO₃ were eliminated by the vaporization of the digestion mixture using 2 mL of H₂SO₄. Thereafter, dilute HNO₃ was added to the solid to dissolve it, again. Fe and

Mn precipitated and the radionuclides were swept. Polonium isotopes were randomly deposited and segregated. In the end, ^{210}Pb in each sample was measured by an alpha spectrometry system of high resolution. Having ^{210}Pb concentrations and Eq. (1) would determine the sedimentation rate in the lake [39]. It is noteworthy that determination of sedimentation rate was performed at the Stable Isotope Laboratory (SIL), Swedish University of Agricultural Sciences, Umeå.

$$S = \frac{\lambda h}{\ln(A_{210\text{Pb}_0}/A_{210\text{Pb}_h})} \quad (1)$$

where λ is the decay constant of ^{210}Pb , h is the sediment depth (cm), $A_{210\text{Pb}_0}$ is the radiation of excess ^{210}Pb in sediments of sea bottom and $A_{210\text{Pb}_h}$ is the radiation of excess ^{210}Pb in sediments at depth of h . Detailed method can be found in [40].

3.4 Heavy metals pollution assessment

Heavy metals pollution level in the lake was estimated using three pollution indices, i.e., the I_{geo} [22], I_{POLL} [19] and EF [23, 41] as shown in Eqs. (2)–(4), respectively.

$$I_{\text{geo}} = \log_2 \left[\frac{C_n}{B_n \times 1.5} \right] \quad (2)$$

$$I_{\text{POLL}} = \log_2 \left[\frac{C_n}{B_n \times 1.5} \right] \quad (3)$$

$$\text{EF} = \left\{ \left[\frac{C_{\text{metal}}}{C_{\text{Fe}}} \right]_{\text{sediment}} \right\} / \left\{ \left[\frac{C_{\text{metal}}}{C_{\text{Fe}}} \right]_{\text{control}} \right\} \quad (4)$$

Table 1 Acceptable recovery rate observed as a result of duplicate analysis for each metal

Element	Acceptable recovery rate (%)	Element	Acceptable recovery rate (%)
Cu	96	Mn	98
Zn	97	Al	97
Ni	103	Fe	98
Cr	95	V	92
Co	96	Cd	93

Table 2 Pollution categorization for I_{geo} , I_{POLL} and EF [24]

Index	No pollution	Minor pollution	Medium pollution	Major pollution	Intense pollution
I_{POLL} and I_{geo}	< 0.42	0.42–1.42	1.42–3.42	3.42–4.42	> 4.42
EF	< 2	2–4	4–16	16–32	> 32

where C_n is the metal concentration in sediment, B_n is the metal concentration in shale and C_{metal} and C_{Fe} are, respectively, the concentrations of the metal and Fe in the studied sediments (the numerator) and in the earth crust (the denominator). Here, B_n denotes lithogenic portion of metals that are obtained through chemical partitioning studies.

Most of the above-mentioned indices are good in formulae but weak in scale [36]. Thus, a new scale named as Hakanson ecological risk index (Cf) was developed for such indices [22] (Table 2). Cf was determined using the following formula:

$$\text{Cf} = C_s / C_n \quad (5)$$

where C_n is the metal concentration in sample and C_s is the mean concentration of metal in shale.

Since determining Cf is not feasible for all metals, Abraham and Parker [41] have modified the formula to obtain total pollution degree as Eq. (6).

$$mC_d = \frac{1}{N} \sum_{i=1}^N CF_i \quad (6)$$

where mC_d is the total pollution index for the area, N is the number of elements and CF_i is the sum of pollution indices obtained from Eq. (5). Pollution degree is categorized as shown in Table 3.

4 Results and discussion

4.1 Sedimentation rate

The sedimentation rate of Zariwar Lake is shown in Fig. 2. According to the activity of ^{210}Pb , the average sedimentation rate was found out to be 5.6 mm/year. This means that the sediment core represents 450 years of history. Therefore, it is possible to investigate the historical geochemistry of the sediments from around 1600 to 2018. Local development, resulting in altered land use, has caused a drastic increase in the sedimentation rate of the lake during the past decades compared to the last centuries (Fig. 2).

Considering the lake being small, this increasing trend in sedimentation rate may create short phases of lake sedimentation and degrade the aesthetic quality of the aquatic environment. These side effects of development

Table 3 Pollution range for Hakanson index [22]

Range of mC_d	Pollution extent
1.5 <	Minimal to no pollution
1.5–2	Minimal pollution
2–4	Moderate pollution
4–8	High pollution
8–16	Very high pollution
16–32	Extremely high pollution
32 >	Extreme pollution

Fig. 2 Activity of ^{210}Pb in sediment core from Zariwar Lake

influence the local economy, by rising costs of lake restoration and retarding tourism development. However, mean sedimentation rate of Zariwar Lake is greater than those of Lake Superior in the USA (0.1–2 mm/year) [39], Lake Taihu in China (0.1–1.54 mm/year) [42] and Anzali wetland in north of Iran (1.4–2.45 mm/year) [43]. In general, average sedimentation rate in Zariwar Lake is more than that reported in freshwater lakes, which is 1 mm/year [44].

4.2 Metal contents and sources

Elemental concentrations (Cu, Zn, Ni, Cr, Mn, Al, Fe, V, Cd and Co), along with the LOI for each centimeter of the core

sample, are shown in Fig. 3. Also, for comparison purposes, the average values in the earth crust [45] and in shale [46] are presented in this figure. As shown in Fig. 3, most of the metals' concentrations (except Mn) are below the values of mean world sediments and earth crust for almost all years. Figure 3 reveals a clear decreasing trend for Mn concentration from the past to the present. As it was found out, when aquatic environment is close to reduction state, Mn may be released from the sediments [47]. In general, speciation of Mn is the determining factor in the geochemistry of this element. This explains why higher oxidation states occur as insoluble in well-oxygenated environments and lower oxidation states are much more soluble in oxygen-deficient conditions. Its geochemical behavior therefore varies in oxic and anoxic environments. Thus, where oxic condition is in the vicinity of anoxic one, Mn is recycled between the two environments. Modern marine sediments contain Mn in concentrations above its crustal content. Recycling of Mn causes surficial sediments to be enriched in Mn. No Mn enrichment and controlled concentrations of this element are seen in bottom sediments of permanently anoxic basins [48]. Considering these explanations and reduction condition of the lake's bottom, Mn concentrations in surface sediments (the present) in the Zariwar lake are less than those in deep sediments (the past).

The more the depth of sediment, the more the LOI percentage (Fig. 3). This happens because of the prevalence of anoxic conditions in the older layers of sediment [49]. In addition, high organic matter decay rate tends to be witnessed near the sediment–water interface rather than the deeper sediments. Thus, maximum organic content can be seen at deeper sediments [50]. The color of the core sediments seen during sampling also approved these findings where the shallower sludge was of lighter color than the deeper one. This LOI trend in depth can be seen in many similar lakes as well [51–55]. Regarding Al and Fe concentrations, they were lower than the mean world sediments and mean earth crust (Fig. 3). As expected, this can indicate the deviation from other geological units in the world [56].

One-step chemical partitioning results, distinguishing lithogenic source of metals from the non-lithogenic source [57], are illustrated in Fig. 4. The pie diagrams shown in Fig. 5 are concluded from the results of bulk analysis (Fig. 3) and chemical partitioning (Fig. 4). According to Fig. 5, in sediments of Zariwar Lake, for all the studied metals, natural phase dominates the anthropogenic one. This exhibits that the lake is not polluted generally, in terms of metallic elements. However, according to bulk analysis results, the concentration of Mn in the lake sediments slightly exceeds its amount in mean earth crust and world sediments.

Fig. 3 Mean sediment core concentrations, mean crust and world sediment concentrations, and percentage of LOI in sediment core from Zariwar Lake

Using cluster analysis, a dendrogram was made, visualizing the correlation coefficients among metal concentrations and LOI (Fig. 6). The dendrogram consists of two

clusters (A and B). The presence of Fe and Al as earth indices in clusters A and B, respectively, indicates that elements located in both clusters likely originate from

Fig. 4 Chemical partitioning analysis of sediment core (anthropogenic portion of elements) from Zariwar Lake

the lithogenic sources to some extent [19]. Organic matter has a minor role in controlling the concentration of elements.

4.3 Elemental pollution

The four aforementioned pollution factors, i.e., I_{geo} , I_{POLL} , EF and Cf (Table 4), show the level of pollution in the

study area, using mean elemental concentrations in the lake aquatic sediments. According to EF, the upper level of sediments in Zariwar Lake is almost clean in terms of all the studied metals except for Mn. An average pollution level was traced regarding these two metals. Since Mn is a mobile metal [57], its presence in the chemical partitioning section is not an indicator of pollution. As I_{geo} and I_{POLL} shown in Table 4, regarding all the studied

Fig. 5 Natural and anthropogenic portions of metals in sediment core from Zariwar Lake

Fig. 6 Dendrogram of metal concentrations and LOI in sediment core from Zariwar Lake

metals, sediment pollution is minimal. Enrichment factor also approves of this result. According to Cf, the sediments are clear from excess amounts of the studied metals. The results dragged from the studied pollution

indices are approved by the previous studies in lakes with similar conditions [37, 58].

5 Conclusions

According to the studied pollution factors, the concentration of almost all the metals was in a range which showed minimal to no pollution in the lake sediments. However, there is average pollution in terms of Mn according to EF as a pollution index, which can be concluded to be negligible according to chemical partitioning analysis and interpretation. Regarding the sedimentation rate, an increasing trend was observed which could result in short phases of lake sedimentation and degrade the aesthetic quality of the aquatic environment. In general, results of the present study provide a thorough perspective of the past and present conditions of the lake. This allows decision makers to come up with proper solutions to alleviate risks in the Zariwar Lake in future.

Table 4 I_{geo} , I_{poll} , EF and Cf pollution factors for the core sediments of Zariwar Lake

Element	Mean concentration (mg/kg)	Concentration in shale (mg/kg)	I_{geo}	EF	I_{poll}	Cf (Hakanson)
Cd	0.25	0.30	− 0.87	1.67	− 0.05	0.82
Co	9.28	19.00	− 1.62	0.94	− 5.23	0.49
Cr	74.41	90.00	− 0.86	–	− 3.00	0.83
Cu	16.97	45.00	− 1.99	0.69	0.48	0.38
Fe	2.26	4.70	− 1.64	1.00	0.74	0.48
Mn	999.77	850.00	− 0.35	2.39	− 8.77	1.18
Ni	47.64	68.00	− 0.56	2.24	0.94	0.70
Zn	34.23	95.00	− 2.06	0.93	− 0.37	0.36
V	50.51	130.00	− 1.95	–	− 0.55	0.39
Al	2.56	8.00	− 2.23	–	–	0.32

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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