Pollution Loads and Ecological Risk Assessment of Metals and a Metalloid in the Surface Sediment of Keenjhar Lake, Pakistan

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Abstract

This study aims to analyze the concentrations of heavy metals and a metalloid in the surface sediments of Keenjhar Lake, Sindh, Pakistan that pose a risk to the lake ecosystem. The concentrations and ecological risks associated with eight metals and a metalloid (As, Pb, Cd, Cu, Mn, Fe, Ni, Hg, and Cr) from surface sediments of the lake, was evaluated at 10 sampling locations. The overall 95th percentile concentrations of trace elements were observed as As (29.1), Pb (7.6), Cd (0.68), Cu (9.3), Mn (56.43), Fe (352.3), Ni (10.36), and Cr (29.61) mg/kg. Metal wise as well as aggregated levels of contamination were studied. It was observed that all metals except Hg were detected in the lake sediment. Based on the geo-accumulation index and enrichment factor, Cr, Cu, Mn, Ni, and Pb showed low pollution levels, while As, Cd, and Fe showed a high degree of contamination. Based on the 95th percentile, the average values of EF for As, Cd and Fe were observed as 274%, 300% and 907% respectively. Pollution Load Index reflected metals and metalloid contamination near the warning threshold, with an average value of 0.825. The Nemerow integrated pollution index (range 6.79-7.59, i.e., >3) and degree of contamination (range 12-24) suggested strong pollution levels. According to the findings of the ecological risk index, Cd showed high ecological risk (between 160-320) at all sampling sites, and potential ecological risk index was at moderate risk level (between 150-300) at all locations. Multivariate analysis of the metals and a metalloid classified as As, Cd, and Fe in one group with the remaining metals in another group show that metals of each group originate from the same source.

Keywords: sediment pollution, heavy metals and metalloid, ecological risk assessment, multivariate analysis

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Introduction

Heavy metals and metalloids contamination in aquatic environments have received ample attention due to their toxicity, persistence, and bioaccumulation [1-5]. Heavy metals and metalloids in sediments come from both natural and anthropogenic sources. Natural sources include flow variations, rocks wearing away, and benthonic activities, etc. [6, 7], while anthropogenic sources include domestic and industrial wastewater disposal, atmospheric fallout, agricultural runoff, and fertilizer overflows, etc. [8]. Recently, rapid industrial growth along with expansion and intensification of agriculture and their associated inputs (i.e. fuel, fertilizers, and pesticides) have contributed significantly to the pollution of freshwater ecosystems through the disposal of wastewater comprising heavy metals and metalloids [9, 10].

In water environs, heavy metals and metalloids exhibit higher deposition in sediments [10]. Once engrossed and settled down on sediments, these heavy metals and metalloids can desorb from sediments and get dissolved into the water column due to some physio-chemical and biological processes [11, 12]. As such, these sediments serve as a repository [1, 13, 14] and a prospective secondary source of pollutants in water environs, thus warning of threats for both aquatic biota and human health [15].

The presence of heavy metals and metalloids in the aquatic food chain contributes to various kinds of issues ranging from molecular alterations to deaths in native fish populations [16]. Furthermore, the presence of trace elements in benthic organisms leads to a sharp decline in the variety, growth, and reproduction rates of these organisms [13], and thus a threat to aquatic biodiversity. Therefore, it is necessary to assess the quality of the freshwater sediments, as this approach offers a substantial understanding of the trace elements’ contaminations and associated threats in order to protect water environments [17]. Assessment of the metals and metalloids contamination in lake sediments, which acts as a repository of pollution, depicts the status of the lake pollution and alerts us to the necessary measures to control pollution sources for better management.

Keenjhar Lake in Pakistan is a major freshwater reservoir, supplying water mainly for drinking to Karachi, the largest city in Pakistan, and several other towns. It supplies water to industry and partly to agriculture. Besides being a freshwater reservoir, it is a Ramsar site, a wildlife habitat, a popular tourist attraction and a place where fishing is the primary source of livelihood for the people living in its surrounding areas. The quality of the lake ecosystem greatly influences the functioning and dynamics of all these aspects. It is situated close to the Indus delta and, therefore, is vulnerable to all the upstream industrial, agricultural and urban pollutants if disposed-of in streams without any treatment. Wastewater treatment in Pakistan is not a common practice, and if treatment facilities exist, they are often inefficient.

Due to untreated industrial and domestic as well as agricultural discharges into freshwater streams and ultimately into Keenjhar Lake, it was hypothesized that heavy metals and metalloids exist in the lake and the contamination of lake surface sediment provides a closer representation of the lake pollution level [10]. Therefore, this study has been conducted to determine the concentrations of selected metals and a metalloid in surface sediments of Keenjhar Lake, Pakistan, and to assess the ecological risks associated with them.

Materials and Methods

Study Area and Sampling Locations

Keenjhar Lake is one of the largest semi-natural lakes in Asia [18]. It is located at 24°47´N and 68°2´E, at a distance of about 120 km from Karachi. It is situated in Thatta district, Sindh, Pakistan, on the right bank of the Indus River [19]. The lake is spread over an area of about 139 km². Keenjhar Lake was recognized as a Ramsar site for migratory birds in 1976 and a wildlife sanctuary in 1977 [20, 21]. The major source of water to Keenjhar Lake is Kalari Baghar (KB) feeder canal, bringing water from the Indus the whole year and is supplemented by occasional floods from the surrounding areas [18]. It is the primary source of water for Karachi, the largest and most populous city in the country [22]. Nearly 50,000 people living in the surroundings directly rely on the lake for their living, mainly through fishing and tourism [21, 23].

In order to determine the spatial distribution of metals and a metalloid in the lake surface sediments, 10 sampling locations were selected (Fig. 1). The sampling points were selected, keeping in mind the closeness to the possibly significant contamination sources and receiving the most credible information of the entire lake. Sampling location ‘S1’ is the point where KB feeder canal water enters into the lake. Locations ‘S2’ and ‘S3’ are near large settlements from where untreated domestic wastewater is directly discharged into the lake [18]. Location ‘S4’ is near a mega windmill project and settlements where the inhabitants are also involved in agricultural activities. Location ‘S5’ is the point where Noorabad industrial waste finds its way to the lake when it rains. Location ‘S6’ is near a famous tourist spot in the middle of the lake. Locations ‘S7’ and ‘S8’ are close to two other recreation points. Location ‘S9’ is near a village. Location ‘S10’ is near the lake outlet, which gives the status of the metals and metalloid deposition just before leaving the lake.
Sampling, Handling, Transporting, and Preserving Sediment Samples

Sampling, handling, transporting, and preserving sediment samples was carried out according to standard methods prescribed by the Environmental Protection Agency [24]. A total of ninety (90) composite lake bed sediment samples (top layer of 0-15 cm) were collected by using a submersible pump (BC-MF double channel, Pedrollo, Italy) from September 2017 to August 2018. Each composite sample comprised 3 to 5 subsamples from an area of nearly 25 m². Polyethylene bottles (1000 ml) soaked for 24 hours in 0.1% hydrochloric acid (HCl) and rinsed three times with distilled water were used to collect sediment samples. To avoid any contamination, the bottles were double zip-locked separately in polythene plastic bags and properly labeled. After sampling, the samples were immediately kept in an icebox and shifted to the laboratory.

Preparation of Samples

Sediment samples were prepared by using guidelines provided by the Environmental Protection Agency [24]. Immediately after transporting samples to the laboratory, excess water present at the top of the sediment slurry was removed. The sediment slurry was poured in a china dish and dried in an oven at a temperature of about 105°C for 24 hours. Dried samples were crushed, homogenized and sieved through a 2 mm sieve and packed in pre-cleaned polyethylene bags and refrigerated until further processing [25]. For digestion, 1 g of sieved sediment samples were precisely weighed and placed into 250 ml volumetric flasks and treated with 10 ml of 1:1 HNO₃. The samples were heated on a hot plate without boiling at a temperature of 95°C for 10 to 15 minutes. The samples were then allowed to cool for 5 minutes, and this process was repeated with the addition of 5 ml concentrated HNO₃ until brown color of the fumes stopped coming from the samples. Then the samples were placed on a hot plate without boiling for 2 hours until the samples were reduced to 5 ml, and the flasks were covered with watch glasses. After that, de-ionized water of 2-3 ml and 3 ml of 30% H₂O₂ was added and placed on a hot plate for complete oxidation. Again the samples were cooled and 1 ml of 30% H₂O₂ was added. The samples were heated without boiling and reduced to 5ml. Samples were diluted with de-ionized water up to 100ml and filtered through Whatman No. 41 and stored in pre-cleaned polyethylene bottles until analyzed.

Instrumental Analyses

The heavy metals and metalloids, including As, Fe, Mn, Cu, Ni, Cd, Pb, Hg, and Cr, were analyzed by the ‘APHA 311A’ method [26] on a flame atomic absorption spectrophotometer (AAS) (A1200, Aurora Biomed, Canada). The calibration line method was adopted for the quantification of the selected trace elements [25].
The detection limits of the trace elements on the AAS were observed to be 0.0002, 0.0013, 0.0019, 0.0002, 0.00001, 0.0112, 0.0006, 0.0001 and 0.01 milligram per liter (mg L\(^{-1}\)) for As, Pb, Cr, Cd, Cu, Fe, Mn, Ni, and Hg respectively.

Quality Control and Quality Assurance

All the samples were analyzed under the best analytical environments as per the recommendations of equipment manufacturers. Standard operating procedures were used to provide quality control and quality assurance, including the use of high-purity chemicals and reagents to regulate contamination during preparation of sediment samples, and properly washing laboratory glassware first with tap water, then with liquid detergent, and immersed in deionized (DI) water with 5% nitric acid for 24 hours, and finally rinsed with DI water. It was finally rinsed with acetone to avoid any risk of contamination with residual organic matter. In the end, the glasswares were kept for about 8 hours in an oven to dry at 85°C. A stock solution was used to make new metals standards by consecutive dilutions on the day of analysis, and the dilutions were achieved only with DI water [27]. Recovery and reproducibility studies were undertaken to validate the accuracy of the methods implemented in the analysis. The certified standard reference solutions for As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, and Pb were used. The percentage recoveries of the metals and metalloid in the standard reference material samples ranged from 92 to 100%. All the measurements were made in triplicate. The accuracy of the results was verified by analyzing a few sediment samples from another independent laboratory, and the difference between the two results was observed to be maximum ±2.3%.

Surface Sediment Contamination Level of the Lake

The contamination level of heavy metals and metalloids in the lake surface sediments was evaluated by using various developed indices that exist in literature. These selected indices include the geo-accumulation index (I\(_{\text{geo}}\)), enrichment factor (EF), pollution load index (PLI), Nemerow integrated pollution index (Pn), degree of contamination (Cd) and potential ecological risk index (PERI). The I\(_{\text{geo}}\), EF, and Cd are commonly used to find out the contamination levels caused by each element. However, PLI, Pn, and PERI assess the cumulative ecological risk caused by various elements under study [25, 28-30].

The calculations of most of these indices require background values of the elements. In this study, background concentrations were used to compute these indices were taken from literature as 7.8, 19, 0.1, 35, 514, 35, 33 and 37.5 mg/kg for As, Pb, Cd, Cu, Mn, Fe, Ni and Cr respectively [1, 6, 11, 31-34], and were kept lower than the threshold limits [35].

**Geo-Accumulation Index (I\(_{\text{geo}}\))**

The I\(_{\text{geo}}\) developed by Müller in 1969 [10, 36], was used to assess the pollution level in sediments through a comparison of the existing concentrations of each metal and metalloid to that of the uncontaminated or pre-industrial time. Due to the absence of pre-industrial data, global average shale [37] was adopted as the standard for reference [38, 39]. I\(_{\text{geo}}\) was calculated by using Equation (1):

\[
I_{\text{geo}} = \log_{2}\frac{C_n}{1.5 \times B_n}
\]

...where \(C_n\) and \(B_n\) are the measured and background concentrations of the elements \(n\) respectively, and the factor 1.5 compensates the likely variations of the background data due to geogenic variations. The I\(_{\text{geo}}\) divides the contamination degree into seven categories, and the ranges of values and their interpretation are given in Table 1.

**Enrichment Factor (EF)**

The EF was used to assess the extent of anthropogenic metals and metalloid contamination levels in the surface sediment using Equation (2) [40]:

\[
EF = \left( \frac{C_n}{B_n} - 1 \right) \times 100
\]

The classes into which EF is divided are given in Table 1.

**Pollution Load Index (PLI)**

The PLI denotes the number of times by which the metal concentrations in the sediment exceeds the background concentrations [41] and was calculated by employing Equation (3):

\[
PLI = (CF1 \times CF2 \times CF3 \times CF4 \ldots \ldots \ldots CFn)^{1/n}
\]

...where CF is the contamination factor, and it is the ratio of the concentration of individual metals or metalloids present in the studied sediment ‘Cn’ by its background ‘Bn’ value as given in Equation (4):

\[
CF = \frac{C_n}{B_n}
\]

If the value of PLI exceeds 1, it reflects significant contamination [42]. However, if less than 1, then it shows no contamination.

**Nemerow Integrated Pollution Index (Pn)**

Pn was used to determine the pollution level in sediments using Equation (5) [40]:

\[
Pn = \sum_{i=1}^{n} \left( C_{ni}/(B_{ni}) \right)^{1/n}
\]

...where \(C_{ni}\) and \(B_{ni}\) are the measured and background concentrations of the elements \(i\) respectively, and the factor 1.5 compensates the likely variations of the background data due to geogenic variations. The Pn divides the contamination degree into seven categories, and the ranges of values and their interpretation are given in Table 1.
...where 'CF_{iav}' is the average value of the CFs while 'CF_{imax}' maximum values of CFs in location 'i' respectively. The contamination factors of all metals and metalloids computed in Equation (4) were used to compute 'CF_{iav}' and 'CF_{imax}'. The five classes of Pn are shown in Table 2.

### Degree of Contamination (C_d)

The C_d was determined using equation (6) [33], and it shows the aggregated value of CF of all metals and the metalloid under discussion:

\[
P_d = \left( \frac{(CF_{iav})^2 + (CF_{imax})^2}{2} \right)^{1/2}
\]

(5)

...where 'CF_{iav}' is the average value of the CFs while 'CF_{imax}' maximum values of CFs in location 'i' respectively. The contamination factors of all metals and metalloids computed in Equation (4) were used to compute 'CF_{iav}' and 'CF_{imax}'. The five classes of Pn are shown in Table 2.

### Potential Ecological Risk Index (PERI)

PERI has been used to determine the potential risk due to heavy metals and metalloid contamination by representing the lethalness of the specific metals and metalloids; and the sensitivity of the environment to the contaminants. PERI was calculated by using formulas (7) and (8):

\[
PERI = \sum_{i=1}^{n} E_{ri}
\]

(7)

\[
ERI = Tr \times CF
\]

(8)

...where ‘Eri’, ‘CF’, and ‘Tr’ are the monomial ecological risk value, contamination factor, and toxic/lethal response value or factor. The ‘Tr’ values of Pb, Cu, Fe, Ni, Cr, Mn, Cd and As were 5, 5, 5, 2, 1, 30, and 10 [33]. The ERI [43] and PERI [33, 40, 44-48] are classified into five (5) classes as shown in Table 2.

### Statistical Analyses

In order to extract a small number of independent factors, principal component analysis (PCA) has been employed to identify the relationship of the metal accumulations in the sediments. Standardized principal component analysis using the Varimax rotation method has been employed to identify the variables with a high loading factor on each component. Principle components (PCs) have been selected based on Eigenvalues >1. Besides PCA, cluster analysis (CA) has also been employed to organize and group the metals

---

### Table 1. Contamination levels as per Geo-Accumulation Index (Igeo), Contamination Factor (CF), and Enrichment Factor (EF).

<table>
<thead>
<tr>
<th>Classes</th>
<th>Igeo Value</th>
<th>Contamination level</th>
<th>Classes</th>
<th>CF Value</th>
<th>Contamination level</th>
<th>Classes</th>
<th>EF Value</th>
<th>Contamination level</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Igeo ≤ 0</td>
<td>Unpolluted</td>
<td>1</td>
<td>CF &lt; 1</td>
<td>Low</td>
<td>1</td>
<td>EF &lt; 1</td>
<td>Not contaminated</td>
</tr>
<tr>
<td>1</td>
<td>0 &lt; Igeo &lt; 1</td>
<td>Unpolluted to moderately polluted</td>
<td>2</td>
<td>1 &lt; CF &lt; 3</td>
<td>Moderate</td>
<td>2</td>
<td>EF &gt; 1</td>
<td>Contaminated</td>
</tr>
<tr>
<td>2</td>
<td>1 &lt; Igeo &lt; 2</td>
<td>Moderately polluted</td>
<td>3</td>
<td>3 &lt; CF &lt; 6</td>
<td>Considerable</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2 &lt; Igeo &lt; 3</td>
<td>Moderately to heavily polluted</td>
<td>4</td>
<td>6 &lt; CF</td>
<td>Very High</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>3 &lt; Igeo &lt; 4</td>
<td>Heavily polluted</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>4 &lt; Igeo &lt; 5</td>
<td>Heavily to extremely polluted</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>5 &gt; Igeo</td>
<td>Extremely polluted</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 2. Contamination levels as per Potential Ecological Risk Index (Eri and PERI) and Nemerow Integrated Pollution Index (Pn).

<table>
<thead>
<tr>
<th>Classes</th>
<th>Eri Value</th>
<th>Ecological Risk</th>
<th>Classes</th>
<th>PERI Value</th>
<th>Ecological Risk</th>
<th>Classes</th>
<th>Pn Value</th>
<th>Contamination level</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Eri ≤ 40</td>
<td>Low</td>
<td>1</td>
<td>PERI &lt; 150</td>
<td>Low</td>
<td>1</td>
<td>0 ≤ Pn ≤ 0.7</td>
<td>Unpolluted</td>
</tr>
<tr>
<td>2</td>
<td>40 &lt; Eri ≤ 80</td>
<td>Moderate</td>
<td>2</td>
<td>150 &lt; PERI &lt; 300</td>
<td>Moderate</td>
<td>2</td>
<td>0.7 ≤ Pn ≤ 1</td>
<td>Warning Limit</td>
</tr>
<tr>
<td>3</td>
<td>80 &lt; Eri ≤ 160</td>
<td>Appreciable</td>
<td>3</td>
<td>300 &lt; PERI &lt; 600</td>
<td>Considerable</td>
<td>3</td>
<td>1 ≤ Pn ≤ 2</td>
<td>Low Polluted</td>
</tr>
<tr>
<td>4</td>
<td>160 &lt; Eri ≤ 320</td>
<td>High</td>
<td>4</td>
<td>600 &lt; PERI</td>
<td>Very High</td>
<td>4</td>
<td>2 ≤ Pn ≤ 3</td>
<td>Moderately Polluted</td>
</tr>
<tr>
<td>5</td>
<td>320 &gt; Eri</td>
<td>Serious</td>
<td>5</td>
<td></td>
<td></td>
<td>5</td>
<td>3 &gt; Pn</td>
<td>Strongly Polluted</td>
</tr>
</tbody>
</table>
into two or more than two clusters using the hierarchical cluster analysis approach. The distances among the metals define the clusters of the metals. Pearson's pairwise correlations have been computed to determine the inter-parameter relationship, which eventually helps to illustrate the source of metals and metalloid. All these analyses have been performed using the Statistical Package for Social Science (SPSS).

Results and Discussion
Metals and Metalloid Concentrations in Lake Surface Sediments
Table 3 shows the descriptive statistics of heavy metals and metalloid in Keenjhar Lake sediments. The overall 95th percentile concentrations and ranges of all metals and the metalloid in lake surface sediments were observed as: As 29.1 (0.41-42.30), Pb 7.6 (0.09-9.48), Cd 0.68 (0.00-0.69), Cu 9.30 (0.1-1.15), Fe 352.30 (155.52-362.53), Mn 56.43 (12.28-64.98), Ni 10.36 (0.00-13.36), and Cr 29.61 (0.12-44.63) in mg/kg. Besides these metals, Hg was also analyzed but not detected from any sampling location and, therefore, not reported in the tables.

The mean measured concentrations of heavy metals in surface sediments of Keenjhar Lake were compared with the reported values from some important lakes in Pakistan and a few from other countries as shown in Table 4. Most of these lakes supply water to downstream cities and got contaminated due to upstream anthropogenic activities. It was observed that the concentrations of Pb, Cd, Cu, Fe, and Mn were found to be higher than the two most important lakes in Pakistan: Khanpur Lake (winter) [36] and Rawal Lake [49]. The concentration of Cr was found to be higher than in Rawal Lake. Both Khanpur and Rawal Lakes supply water to Islamabad (the capital city of Pakistan) and Rawalpindi [49]. The values of Cd were higher than in Sapanca Lake, Turkey [50]. However, the concentrations observed in Keenjhar Lake for As, Pb, Cd, Cu, Fe, Mn, Ni, and Cr were lower than in Simly Lake [25], Khanpur Lake (summer) [36], Mangla Lake...

<table>
<thead>
<tr>
<th>Locations</th>
<th>As (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Fe (mg/kg)</th>
<th>Mn (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>Cr (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall</td>
<td>TEL 5.90</td>
<td>35.00</td>
<td>0.60</td>
<td>35.70</td>
<td>-</td>
<td>-</td>
<td>18.10</td>
<td>37.30</td>
</tr>
<tr>
<td></td>
<td>Mean 9.52</td>
<td>4.54</td>
<td>0.31</td>
<td>3.57</td>
<td>256.32</td>
<td>34.52</td>
<td>5.25</td>
<td>10.17</td>
</tr>
<tr>
<td></td>
<td>95th Percentile 29.14</td>
<td>7.56</td>
<td>0.68</td>
<td>9.03</td>
<td>352.30</td>
<td>56.43</td>
<td>10.36</td>
<td>29.61</td>
</tr>
<tr>
<td>S1</td>
<td>Mean 9.20</td>
<td>3.90</td>
<td>0.25</td>
<td>2.50</td>
<td>247.90</td>
<td>32.90</td>
<td>4.20</td>
<td>10.11</td>
</tr>
<tr>
<td></td>
<td>95th Percentile 25.17</td>
<td>6.49</td>
<td>0.68</td>
<td>6.21</td>
<td>362.24</td>
<td>63.90</td>
<td>6.33</td>
<td>25.26</td>
</tr>
<tr>
<td>S2</td>
<td>Mean 11.20</td>
<td>4.20</td>
<td>0.23</td>
<td>3.40</td>
<td>246.90</td>
<td>33.80</td>
<td>6.70</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>95th Percentile 25.67</td>
<td>7.63</td>
<td>0.65</td>
<td>7.87</td>
<td>329.30</td>
<td>42.96</td>
<td>9.86</td>
<td>37.17</td>
</tr>
<tr>
<td>S3</td>
<td>Mean 12.30</td>
<td>5.60</td>
<td>0.25</td>
<td>4.90</td>
<td>255.40</td>
<td>50.20</td>
<td>8.20</td>
<td>14.00</td>
</tr>
<tr>
<td></td>
<td>95th Percentile 26.19</td>
<td>8.22</td>
<td>0.67</td>
<td>8.82</td>
<td>352.31</td>
<td>59.26</td>
<td>10.99</td>
<td>25.61</td>
</tr>
<tr>
<td>S4</td>
<td>Mean 12.00</td>
<td>4.30</td>
<td>0.28</td>
<td>4.00</td>
<td>257.20</td>
<td>43.60</td>
<td>7.40</td>
<td>10.10</td>
</tr>
<tr>
<td></td>
<td>95th Percentile 18.40</td>
<td>6.72</td>
<td>0.64</td>
<td>7.65</td>
<td>352.35</td>
<td>54.49</td>
<td>11.71</td>
<td>23.78</td>
</tr>
<tr>
<td>S5</td>
<td>Mean 12.67</td>
<td>4.70</td>
<td>0.32</td>
<td>4.87</td>
<td>245.80</td>
<td>32.40</td>
<td>5.20</td>
<td>11.70</td>
</tr>
<tr>
<td></td>
<td>95th Percentile 16.17</td>
<td>7.50</td>
<td>0.66</td>
<td>5.60</td>
<td>346.90</td>
<td>45.02</td>
<td>10.24</td>
<td>31.59</td>
</tr>
<tr>
<td>S6</td>
<td>Mean 6.90</td>
<td>4.60</td>
<td>0.32</td>
<td>3.70</td>
<td>245.80</td>
<td>32.40</td>
<td>5.20</td>
<td>11.70</td>
</tr>
<tr>
<td></td>
<td>95th Percentile 18.79</td>
<td>6.59</td>
<td>0.69</td>
<td>8.36</td>
<td>327.77</td>
<td>42.16</td>
<td>9.03</td>
<td>29.14</td>
</tr>
<tr>
<td>S7</td>
<td>Mean 9.30</td>
<td>4.30</td>
<td>0.30</td>
<td>3.40</td>
<td>237.40</td>
<td>27.00</td>
<td>3.70</td>
<td>9.60</td>
</tr>
<tr>
<td></td>
<td>95th Percentile 18.79</td>
<td>5.67</td>
<td>0.66</td>
<td>7.16</td>
<td>337.54</td>
<td>35.95</td>
<td>6.14</td>
<td>21.79</td>
</tr>
<tr>
<td>S8</td>
<td>Mean 10.20</td>
<td>4.00</td>
<td>0.24</td>
<td>4.50</td>
<td>251.90</td>
<td>35.30</td>
<td>6.20</td>
<td>10.10</td>
</tr>
<tr>
<td></td>
<td>95th Percentile 29.38</td>
<td>5.37</td>
<td>0.63</td>
<td>8.58</td>
<td>349.54</td>
<td>44.40</td>
<td>11.07</td>
<td>19.58</td>
</tr>
<tr>
<td>S9</td>
<td>Mean 6.60</td>
<td>4.00</td>
<td>0.23</td>
<td>3.00</td>
<td>238.10</td>
<td>24.90</td>
<td>4.80</td>
<td>6.50</td>
</tr>
<tr>
<td></td>
<td>95th Percentile 19.42</td>
<td>5.30</td>
<td>0.67</td>
<td>5.71</td>
<td>324.99</td>
<td>32.41</td>
<td>7.23</td>
<td>14.21</td>
</tr>
</tbody>
</table>

TEL = Threshold Effect Level for Fresh Water Sediments by Environment Canada 1994. Numbers in bold indicate mean or 95th percentile concentration in surface sediments exceeding TEL Limits.
Table 4. Comparison of the mean concentrations of metals and a metalloid from Keenjhar Lake with national and international reported levels.

<table>
<thead>
<tr>
<th>Studied Lakes</th>
<th>As</th>
<th>Pb</th>
<th>Cd</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keenjhar Lake</td>
<td>9.52</td>
<td>4.54</td>
<td>0.31</td>
<td>3.57</td>
<td>256.32</td>
<td>34.52</td>
<td>5.25</td>
<td>10.17</td>
<td>Present study</td>
</tr>
<tr>
<td>Simly Lake, Pakistan</td>
<td></td>
<td></td>
<td>4.10</td>
<td>1.55</td>
<td>23.40</td>
<td>6122</td>
<td>647</td>
<td>41.00</td>
<td>[25]</td>
</tr>
<tr>
<td>Khanpur Lake, Pakistan (Summer)</td>
<td></td>
<td></td>
<td>33.71</td>
<td>1.883</td>
<td>36.84</td>
<td>4630</td>
<td>447.5</td>
<td>34.66</td>
<td>[36]</td>
</tr>
<tr>
<td>Khanpur Lake, Pakistan (Winter)</td>
<td></td>
<td></td>
<td>0.085</td>
<td>0.058</td>
<td>0.098</td>
<td>2.069</td>
<td>0.078</td>
<td>37.65</td>
<td>[36]</td>
</tr>
<tr>
<td>Rawal Lake, Pakistan</td>
<td></td>
<td></td>
<td>0.869</td>
<td>0.043</td>
<td>0.161</td>
<td>21.50</td>
<td>0.386</td>
<td>0.309</td>
<td>[49]</td>
</tr>
<tr>
<td>Mangla Lake, Pakistan (Summer)</td>
<td></td>
<td></td>
<td>17.20</td>
<td>1.33</td>
<td>13.40</td>
<td>3870</td>
<td>324</td>
<td>21.30</td>
<td>[51]</td>
</tr>
<tr>
<td>Mangla Lake, Pakistan (Winter)</td>
<td></td>
<td></td>
<td>306.00</td>
<td>1.52</td>
<td>23.30</td>
<td>3800</td>
<td>612</td>
<td>42.00</td>
<td>[51]</td>
</tr>
<tr>
<td>Plateau Lake Wetland, China</td>
<td>15.46</td>
<td>53.19</td>
<td>0.76</td>
<td>31.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>35.99</td>
<td>[52]</td>
</tr>
<tr>
<td>Lake Karla, Thessaly, Greece (Summer)</td>
<td></td>
<td></td>
<td>35.00</td>
<td>-</td>
<td>35.20</td>
<td>-</td>
<td>-</td>
<td>158</td>
<td>285.00 [53]</td>
</tr>
<tr>
<td>Lake Karla, Thessaly, Greece (Winter)</td>
<td></td>
<td></td>
<td>38.90</td>
<td>-</td>
<td>37.70</td>
<td>-</td>
<td>-</td>
<td>192</td>
<td>290.00 [53]</td>
</tr>
<tr>
<td>Lake Sapanca, Turkey</td>
<td>15.20</td>
<td>0.29</td>
<td>36.68</td>
<td>337.8</td>
<td>37.8</td>
<td>-</td>
<td>-</td>
<td>19.09</td>
<td>[50]</td>
</tr>
</tbody>
</table>

Numbers in bold indicate the average concentration of metals and metalloids in surface sediments of national and international reported levels lower than Keenjhar Lake, while dashed cells indicate information not available.

(summer and winter) [51], Plateau Lake wetland, China [52], Karla Lake Thessaly, Greece (summer and winter) [53] and Sapanca Lake, Turkey; with the exception of Cd higher than Sapanca Lake [50].

Fig. 2. Metal-wise Geo-Accumulation Index ($I_{geo}$) scores: mean value a) and 95 percentile b).

Fig. 3. The metal wise score of enrichment factor (EF) mean value a) and 95 percentile b).
To scrutinize if there is any influence of human activity on the variation of concentrations of metals specific to sampling locations, the orders of the concentrations of metals were compared across locations. It was observed that the orders of the concentrations vary except for Fe, Mn and Cd. Spatial distribution of selected metals and a metalloid based on the 95th percentile concentration were following the orders at each site as: S1 (Fe>Mn>Cr>As>Pb>Ni >Cu>Cd); at sites S2, S4 and S7 (Fe>Mn>Cr> As>Ni>Pb>Cu>Cd); sites S3, S9 and S10 (Fe>Mn>Cr> As>Ni>Cu>Pb>Cd); sites S5 and S6 (Fe>Mn>Cr>As>Ni>Pb>Cu>Cd); and site S8 (Fe>Mn>Cr>As>Cu>Ni>Pb>Cd).

Ecological Risk Assessment

Geo-Accumulation Index (Igeo)

In order to investigate the average and maximum potential pollution levels, the Igeo of metals and metalloids were estimated based on the average as well as 95th percentile values. Both approaches were used considering the spread of the data, since reporting based on average values alone may underestimate the potential environmental hazards and similarly, the 95th percentile may overestimate. Among the seven categories of Igeo, with category 0 representing unpolluted to category 6 indicating extreme pollution, results of this study show that Igeo of Pb, Mn, Cu, Ni, and Cr were found less than zero as shown in Fig. 2, indicating unpolluted concerning these metals. Concerning As, the lake is unpolluted (based on average values; Fig. 2a) and moderately polluted (based on 95th percentile; Fig. 2b). The values of Igeo of Cd indicate moderate pollution, while Fe indicates moderate to heavy pollution. Overall, Keenjhar Lake was observed to be polluted by Fe, As, and Cd, and these metals might be contributed through both geogenic and anthropogenic sources into lake sediments.

Enrichment Factor (EF)

EF is used to evaluate the influence of anthropogenic input of single metal and metalloid in the lake surface sediment. The EF values of As, Fe, and Cd were

---

Table 5. Degree of Contamination and Pollution Load Index as per sampling locations.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Contamination Factor (CF)</th>
<th>C_1</th>
<th>PLI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
<td>Pb</td>
<td>Mn</td>
</tr>
<tr>
<td>S1</td>
<td>3.23</td>
<td>0.34</td>
<td>0.12</td>
</tr>
<tr>
<td>S2</td>
<td>3.29</td>
<td>0.40</td>
<td>0.08</td>
</tr>
<tr>
<td>S3</td>
<td>3.36</td>
<td>0.43</td>
<td>0.12</td>
</tr>
<tr>
<td>S4</td>
<td>2.36</td>
<td>0.35</td>
<td>0.11</td>
</tr>
<tr>
<td>S5</td>
<td>3.43</td>
<td>0.45</td>
<td>0.08</td>
</tr>
<tr>
<td>S6</td>
<td>2.07</td>
<td>0.39</td>
<td>0.09</td>
</tr>
<tr>
<td>S7</td>
<td>2.26</td>
<td>0.35</td>
<td>0.08</td>
</tr>
<tr>
<td>S8</td>
<td>2.41</td>
<td>0.30</td>
<td>0.07</td>
</tr>
<tr>
<td>S9</td>
<td>3.77</td>
<td>0.28</td>
<td>0.09</td>
</tr>
<tr>
<td>S10</td>
<td>2.49</td>
<td>0.28</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Fig. 4. Sampling location-wise scores of Nemerow Integrated Pollution Index (Pn).
higher than one, indicating that these metals in surface sediments belong to both geogenic and anthropogenic sources. Nevertheless, the values of EF of Pb, Mn, Cu, Ni, and Cr were observed to be less than zero, which indicates that the lake is not polluted because of these metals. Analysis based on 95th percentiles, the values of EF for As (range 107.31-276.67%) with an average value of 274%, the value of EF for Cd (range 530-590%) with an average value of 300%; the value of EF for Fe (range 828.54-934.97%) with an average value of 907% as shown in Fig. 3b). EF calculated based on the mean values also indicate severe enrichment of As, Cd, and Fe as shown in Fig. 3a).

The findings from Igeo and EF are in agreement that As, Fe and Cd confirm that human activities in the upstream or around the lake are primarily responsible for higher concentrations of these metals in the surface sediment of Keenjhar Lake.

**Pollution Load Index (PLI) and Degree of Contamination (Cf)**

As shown in Table 5, the values of CF for As in the (range 2.07-3.77) showed moderate contamination at some sites and considerable contamination at other sites. Fe and Cd indicated high concentration on all sites, while Pb, Mn, Ni, Cu, and Cr at all the sampling sites were observed to be less than one, revealing low contamination. The results of CF match that of Igeo and EF.

Though in the above analysis we observed that some metals are not significantly contributing to the pollution load to the lake surface sediment, the concentrations of other metals are significantly high. Nonetheless, we observed that at all of the locations, the values of Cф range between 12-24, which reflects that Keenjhar lake surface sediment has a considerable degree of pollution.

**Nemerow Integrated Pollution Index (Pn)**

As shown in Fig. 4, we observed that the Pn values of the studied samples ranged 6.79-7.57. The values at all locations were above 3 (the minimum threshold level of Pn), which means that the integrated pollution level exceeded the threshold level and reached a strongly polluted level. The highest value of Pn occurred at Site S1, and the lowest at S10. The highest value of Pn at

<table>
<thead>
<tr>
<th>Sites</th>
<th>As</th>
<th>Pb</th>
<th>Mn</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>PERI</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>32.27</td>
<td>1.71</td>
<td>0.12</td>
<td>204.00</td>
<td>0.89</td>
<td>0.96</td>
<td>1.35</td>
<td>241.30</td>
</tr>
<tr>
<td>S2</td>
<td>32.91</td>
<td>2.01</td>
<td>0.08</td>
<td>195.00</td>
<td>1.12</td>
<td>1.49</td>
<td>1.98</td>
<td>234.59</td>
</tr>
<tr>
<td>S3</td>
<td>33.58</td>
<td>2.16</td>
<td>0.12</td>
<td>201.00</td>
<td>1.26</td>
<td>1.67</td>
<td>1.37</td>
<td>241.16</td>
</tr>
<tr>
<td>S4</td>
<td>23.59</td>
<td>1.77</td>
<td>0.11</td>
<td>192.00</td>
<td>1.09</td>
<td>1.77</td>
<td>1.27</td>
<td>221.60</td>
</tr>
<tr>
<td>S5</td>
<td>34.35</td>
<td>2.26</td>
<td>0.08</td>
<td>201.00</td>
<td>0.96</td>
<td>1.19</td>
<td>1.54</td>
<td>241.38</td>
</tr>
<tr>
<td>S6</td>
<td>20.73</td>
<td>1.97</td>
<td>0.09</td>
<td>198.00</td>
<td>0.80</td>
<td>1.55</td>
<td>1.69</td>
<td>224.83</td>
</tr>
<tr>
<td>S7</td>
<td>22.59</td>
<td>1.73</td>
<td>0.08</td>
<td>207.00</td>
<td>1.19</td>
<td>1.37</td>
<td>1.55</td>
<td>235.51</td>
</tr>
<tr>
<td>S8</td>
<td>24.09</td>
<td>1.49</td>
<td>0.07</td>
<td>198.00</td>
<td>1.02</td>
<td>0.93</td>
<td>1.16</td>
<td>226.76</td>
</tr>
<tr>
<td>S9</td>
<td>37.67</td>
<td>1.41</td>
<td>0.09</td>
<td>189.00</td>
<td>1.23</td>
<td>1.68</td>
<td>1.04</td>
<td>232.12</td>
</tr>
<tr>
<td>S10</td>
<td>24.90</td>
<td>1.39</td>
<td>0.06</td>
<td>201.00</td>
<td>0.82</td>
<td>1.10</td>
<td>0.76</td>
<td>230.03</td>
</tr>
</tbody>
</table>

Threshold limit for ERI = 40

As shown in Table 6, the values of ERI for metals and a metalloid at different sites.
location 1 indicates the highest pollution influx from upstream coming through KB feeder and entering the lake at its inlet. Nevertheless, the Pn values of other locations also indicate that the KB feeder is not the only source of pollution influx, but other sources of pollution are also contributing to the pollution of the lake.

**Potential Ecological Risk Index (PERI)**

Except for Cd, the values of ERI as calculated for all metals and metalloid at all the sampling locations were below 40 (Table 6), which indicates low ecological risk. The values of Cd at all sites were in the range of 160-320, which indicates a high ecological risk. Similarly, the values of PERI as calculated for all metals and metalloid for all the sampling locations were above 150 and lower than 300, manifesting moderate ecological risk. The values of PERI were lowest at location S4 and highest at S5. Cd was the main contributor to potential ecological risk.

**Multivariate Analysis**

In order to analyze the association among the variables in the dataset, PCA was employed to explore the sources of heavy metals. As shown in Table 7, two principle components with eigenvalues >1 have been considered, and explain more than 61% of the total variance. PC1 explained about 35% of the variance with a high loading of Cd, Fe, and As. However, PC2 explained around 26% of the variance with high loading of the remaining studied metals, including Cu, Mn, Pb, Cr, and Ni. In some studies, the association of

![Fig. 5. Dendrogram of sampling location a) and metal concentration b) using Ward Method.](image-url)
elements with PCs has been used to distinguish natural or anthropogenic sources [30]. Therefore, the elements belonging to the first group, such as As, Cd, and Fe, could be identified as the result of an “anthropogenic factor” due to their high EF values. On the other hand, the elements in the second group (Cu, Mn, Pb, Cr, and Ni) are likely derived from natural sources, given their low EF value. The correlation coefficients of metals are provided in Table 8. Fig. 5 represents the sampling location relationships a) and metal-wise relationships b).

Conclusions

To investigate the level of degree of ecological risk of heavy metals and the metalloid in surface sediments of Keenjhar Lake, the concentrations of eight metals (Pb, Cd, Cu, Fe, Mn, Ni, and Cr) and a metalloid (As) were evaluated from 10 sites on the lake. Results showed that the 95th percentile values of As, Pb, Cd, Cu, Mn, Fe, Ni, and Cr were 29.14, 7.56, 0.68, 9.03, 352.3, 56.43, 10.46, and 29.16 mg/Kg respectively. Based on the 95th percentile, the results of EF – As (274%), Cd (300%) and Fe (907%) and Igeo (moderately polluted to highly polluted by Fe) – of Fe, As and Cd were mainly contributing to lake contamination, while Pb, Mn, Cu, Ni, and Cr have less contribution to lake contamination. The Cd shows considerable contamination (between 160-320) at all the sites, and PLI indicates no significant contamination at a few sites, but its value at some sites was near the threshold limit of 1. The results of Pn Index (ranging between 6.79-7.59, i.e., >3) showed strongly polluted level at all sites. Cd results (between 160-320) of ERI showed that ecological risk from individual metals and the metalloid at all the sites were low, and only because of Cd, and ERI showed high ecological risk. The values of PERI (between 150-300) at all the sampling sites indicate moderate ecological risk. The result of PCA shows that the elements belonging to the PC1 are As, C₃, and Fe could be identified as a result of anthropogenic factors due to their high EF values. On the other hand, Cu, Mn, Pb, Cr, and Ni are grouped in PC2, indicating that these elements have high correlations and therefore the sources of these elements might be the same. Since the lake is receiving contamination from several on-site and upstream economic activities, ranging agriculture, urban and industrial activities, it is difficult to establish the sources of these pollutants. Nevertheless, this study may be taken as a reference point to investigate the sources of these pollutants.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

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