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Risk associated with spatio-temporal variations in trace metals and a metalloid in a major freshwater reservoir of Pakistan

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ABSTRACT

Keenjhar Lake in Pakistan provides several ecosystems services including drinking water to millions of people. The seasonal variation (pre-, during, and post-monsoon) in Keenjhar Lake water quality was investigated during nine sampling rounds at ten locations. Water samples ($n = 270$) were analyzed for As, Cd, Cr(III), Cu, Fe, Hg, Mn, Ni, and Pb using atomic absorption spectrophotometry, Cr(VI) with a UV spectrophotometer, and water quality parameters (solids, oxygen, conductivity, and pH). Several elements exceeded WHO or Pakistan safe limits for unrestricted use including As ($0.038 \text{ mg} \cdot \text{L}^{-1}$, 95th upper confidence limit), Cr(III) ($0.15 \text{ mg} \cdot \text{L}^{-1}$), Cd ($0.11 \text{ mg} \cdot \text{L}^{-1}$), Fe ($0.42 \text{ mg} \cdot \text{L}^{-1}$), Ni ($0.037 \text{ mg} \cdot \text{L}^{-1}$), and Pb ($0.04 \text{ mg} \cdot \text{L}^{-1}$). Monsoon levels of chromium, Cu, Fe, Mn, and Pb were higher than other seasons, while As was highest during post-monsoon, and Ni was highest during pre and post-monsoon. There were significant spatial differences in metals concentrations in the lake. As, Cu, and Fe significantly declined in concentration with distance from the lake inlet. Using the lake as a source of drinking water presented unacceptable carcinogenic risk and non-carcinogenic hazards. This study suggests measures should be taken to limit discharge of pollution to the lake and future monitoring should consider seasonal monsoon effects on lake quality.

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Introduction

The contamination of freshwater reservoirs with metals, metalloids, organic chemicals, and waterborne pathogens is of global concern. While some trace elements can enter surface water from various lithogenic sources like geological materials, anthropogenic sources typically release metals in much higher concentrations (Hanif et al. 2005; Khan et al. 2017). Common anthropogenic sources of metals and metalloids contributing to water pollution include untreated wastewater originating from manufacturing activities,

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mining, and municipal wastewater (Genthe et al. 2018; Saha et al. 2017; Wang et al. 2018; White and Liber 2018). These contaminants make reservoir water unacceptable for human consumption and crop cultivation, (Nawab et al. 2018) and pose a threat to aquatic organism health and tourism (Wang et al. 2019; Yi et al. 2011). Thus, there is a need to explore heavy metal and metalloid concentrations in freshwater reservoirs, determine their potential effect on human health (Kumar et al. 2017; Liu et al. 2018; Valencia-Avellan et al. 2018), and identify the source(s) of the pollution so as to target remediation efforts. Confounding these investigative efforts however, is the influence of stormwater runoff from urban and agricultural areas, monsoon rain seasonal effects and discharge of untreated wastewater with varying strength.

While multiple researchers have investigated trace elements in lakes worldwide (Azizullah et al. 2011; Matouke and Abdullahi 2020; Utete and Fregene 2020) and fewer studies have investigated the monsoon rainfall effect on water quality in freshwater reservoirs. Understanding the monsoon effects on water quality will become increasingly important as climate change compounds the intensity of rainfall events and flushes additional pollutants to receiving waters (Panthi et al. 2017). To understand the effects of seasonal rainfall on freshwater reservoir water quality in a system impacted by urban and agricultural wastewater discharges, a case study of Keenjhar Lake of Pakistan was undertaken. In this study seasonal and spatio-temporal investigations of metals and a metalloid were investigated and linked to human health risk and overall water quality indices.

Keenjhar Lake of Pakistan is one of the biggest semi-natural reported by World Wildlife Fund (WWF 2008) lakes in Asia and is located in the Thatta district of Sindh (Korai et al. 2008). Keenjhar Lake is the primary source of water to Karachi (Abro et al. 2018; F. Saleem et al. 2019), the most populous city of Pakistan and the tenth most populous city of the world (Baig et al. 2018). About 50,000 people live near Keenjhar Lake and are directly dependent on the lake for their livelihood, especially ecotourism and fishing (Mangan et al. 2013). The lake was acknowledged as a Ramsar site of migratory birds in 1976 by UNESCO and a wildlife sanctuary in 1977 (Nergis et al. 2013). Annually, around 385,000 tourists visit the lake (Khan et al. 2012; Mangan et al. 2013; Mangan and Lohano 2015).

The lake is mainly supplied by the Kalri Baghar (KB) Feeder canal, which carries (1) Indus River water year-round, (2) floodwater from the catchment seasonally (WWF 2008), (3) effluent from the Nooriabad industrial area (31 km from the lake) (SUPARCO (Space and Upper Atmosphere Research Commission of Pakistan), 2012), and (4) effluent from the Kotri industrial area (nearly 79 km from the lake). Keenjhar Lake also receives untreated domestic wastes and agricultural wastes from surrounding villages (WWF 2008). Municipal and industrial discharges to Keenjhar Lake have been linked to elevated levels of metals in fish species such as *Catla catla* (Ham.) and *C. mrigala*. Others have reported on levels of Pb exceeding World Health Organization (WHO) limits in the lake and in KB feeder canal (Farooq et al. 2013; Korai et al. 2008, 2010; Shafiq et al. 2011). Sporadic studies conducted in Keenjhar Lake suggest impairment (Farooq et al. 2013; Korai et al. 2010), but to date, there has been no reported systematic study evaluating seasonal and spatial variations in water quality. While not directly attributable to lake water quality at this time, residents surrounding the lake

have been observed to have severe dermal ailments, cancer and tuberculosis (Pakistan Relief Foundation 2013). Keenjhar lake represents an ideal lake for the investigation of spatio-temporal variations in lake water quality linked to human health effects as (1) communities around Keenjhar lake are dependent on it for drinking water, (2) there is one main feeder canal and several non-point sources of pollution, (3) it experiences a well defined monsoon season and (4) it provides vital ecosystem services.

The current study was designed to (1) examine the spatio-temporal concentration of the trace elements arsenic (As), cadmium (Cd), chromium in the +3 and +6 oxidations states (Cr(III) and Cr(VI), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni) and lead (Pb); (2) determine the spatio-temporal variation in physicochemical water parameters (pH, temperature (T), electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), Cl^- , and turbidity); and (3) evaluate the human health risks from oral and dermal exposures to the lake water. The results of this study can aide in regulating priority pollutants in lake inputs and to communicate to residents and visitors to the lake the likely risk from exposure to the water.

Materials and methods

Study location and selection of sampling points

A total of ten sampling locations dispersed along the length of the lake were included in the study and were selected as follows: S1 is the inlet point and represents water entering the lake from the KB Feeder canal; S2 is near to Sonehri village with nearly 200 houses which discharge untreated domestic waste into the lake (WWF 2008); S3 is near to village Ameer Peer, where a large number of people visit a shrine; S4 is near to Jhampir, containing a mega windmill project and the Jhampir settlements close to the lake; S5 is the point near to Nooriabad drain, where seasonal floods carry industrial waste; S6 is near to Noori tomb, a tourist destination; S7 and S8 are near to recreation points where a large number of tourists visiting the lake may contribute pollution; S9 is near to village Khambo; and S10 is near to Chilya village, which is the exit point of the lake (Figure 1).

Sampling, handling, transportation, and preservation of samples

Water samples were collected from the ten sampling points in nine sampling rounds from September 2017 to August 2018 in the three seasons, i.e., pre-monsoon (from January to June), monsoon (from July to September) and post-monsoon (from October to December) (Muthukrishnavellaisamy et al. 2009). Five pre-monsoon, three monsoon and one post-monsoon sample set were collected. Sampling, handling, and transportation of water samples were carried out according to standard methods (Rice et al. 2012). From each sampling location, water samples were collected from surface (15 cm below top), mid and near the bottom (15 cm above bottom) of the lake with a submersible pump (BC-MF double channel, Pedrollo, Italy). Therefore, a total of 270 samples were collected for determining trace element concentrations and physicochemical water quality parameters. Physico-chemical parameters including temperature (T), total dissolved solids (TDS), electrical conductivity (EC), pH, and dissolved oxygen (DO) were

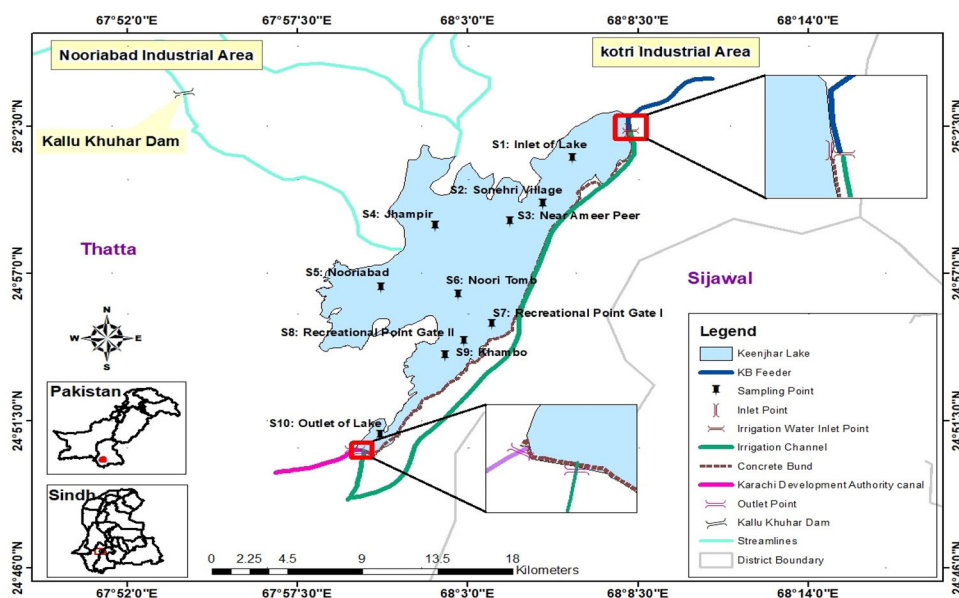


Figure 1. Map of the study area and sampling locations.

measured on-site immediately after sample collection by using a portable multi logger (Multi 3630 IDS, GmbH & Co. KG, Germany) while turbidity was determined using Turbichack-Tintometer (Lovibond, Germany). Water samples collected for elemental analysis and Cl^- were collected in 1 L acid-washed polyethylene bottles. After sampling, the samples were placed on ice for transport to the laboratory. Subsamples collected for Cl^- analysis were stored at 4°C until analysis. Samples collected for metals and metalloid determination were filtered using glass fiber filters (Membrane Filter Products System, CA, USA). Except subsamples collected for Cr(VI), all other samples were preserved with 1% analytical grade HNO_3 (70% purity, DaeJung) to adjust $\text{pH} < 2$ (M. Saleem et al. 2019; Varol 2013), to prevent metals precipitation, adsorption on the walls of bottle and degradation caused by microbial activity. Adding nitric acid in samples converts metal ions into their nitrate salts, which are highly soluble. Analytical grade HNO_3 was run as sample, but no background value of the investigated metals and metalloid were detected by Flame Atomic Absorption Spectrophotometer. Each acidified sample was heated at 100°C on a hot plate to reduce by 10 times (i.e., from 1000 to 100 mL) then stored in pre-cleaned bottles until analysis. However, filtered subsamples collected for Cr(VI) were mixed with 1,5-diphenylcarbazide solution (Sigma-Aldrich, Germany) and sulfuric acid (H_2SO_4 , 95–98%, Sigma-Aldrich, Germany) to maintain $\text{pH} 2 \pm 0.5$.

Analytical methods

The Cl^- concentrations were determined in the laboratory by the standard titrimetric methodology (Rice et al. 2012). Heavy metals (Cd, Cu, Fe, Hg, Mn, Ni, Pb, and total Cr) and the metalloid (As) were determined by the APHA 311 A method (Rice et al. 2012) on a Flame Atomic Absorption Spectrophotometer (AAS) (A1200, Aurora Biomed, Canada). The detection limits of the trace elements on the AAS were

determined to be 2×10^{-4} , 1.3×10^{-4} , 1.9×10^{-4} , 2×10^{-5} , 1×10^{-5} , 11.2×10^{-4} , 6×10^{-5} , 1×10^{-5} , and $1 \times 10^{-3} \text{ mg} \cdot \text{L}^{-1}$ for As, Pb, total Cr, Cd, Cu, Fe, Mn, Ni, and Hg, respectively. The concentration of Cr(VI) was detected by using a UV spectrophotometer (Schimadzu UV 1800, Germany) at an absorbance of 540 nm as per the standard method of EPA (Method no. 7196 A) within 24 h of sampling. The concentration of Cr(III) was achieved by subtracting Cr(VI) from total Cr measured by AAS.

Quality control (QC) and quality assurance (QA)

The quality control and quality assurance measures were undertaken by following procedures defined in Standard Methods for the Examination of Water and Wastewater (APHA 2012) throughout sampling, handling, and analysis in order to exclude or reduce errors. To avoid contamination of samples, the laboratory glassware was dipped in de-ionized (DI) water with 5% HNO_3 for 24 h and then rinsed with DI water. All field and laboratory equipment used for water quality analyses were calibrated each time before use. To ensure reproducibility of results and to control pollution during processing of water samples, procedural blanks and duplicates run in each batch of ten samples were included, and only certified standard reference materials (SRM-1643d) for As, Fe, Mn, Cu, Ni, Cd, Pb, Hg, and Cr were employed. Fresh metals and metalloid standards were prepared from stock solution by consecutive dilutions with only DI water on the day of analysis. Recovery studies were conducted by spiking of water samples with known concentrations and then tested for metals detection. Recovery studies indicated that the percentage recovered for As, Fe, Mn, Cu, Ni, Cd, Pb, Hg, and total Cr from spiked samples were 97%, 98%, 98%, 100%, 96%, 93%, 100%, 98%, and 100%, respectively.

Pollution assessment

In this study two pollution indices commonly used to assess contamination in freshwater were utilized, namely degree of contamination (C_{deg}) and the heavy metal evaluation index (HEI). The C_{deg} (Eq. (1)) quantifies the collective effects of various quality parameters that may damage the water (Bhuiyan et al. 2015; Kumar et al. 2019; M. Saleem et al. 2019),

$$C_{\text{deg}} = \sum_{i=1}^n \left(\frac{Ca_i}{Cn_i} - 1 \right) \quad (1)$$

where Ca_i and Cn_i denote the analytical concentration and upper permissible concentrations, respectively. Here, Ca_i was taken as the 95 percent upper confidence limit on the arithmetic average concentration (aka 95th percentile). The HEI (Eq. (2)) defines an overall quality of the water concerning heavy metals and metalloids in a system. It is the ratio of the 95th percentile of the measured metal concentrations ' H_c ' and the maximum permissible metal concentrations (H_{mac}) (Bhuiyan et al. 2015; Kumar et al. 2019; M. Saleem et al. 2019),

$$HEI = \sum_{i=1}^n \frac{H_c}{H_{\text{mac}}} \quad (2)$$

Human health risk assessment

The human exposure to heavy metals and metalloids in lake water could occur through various exposure routes, including: oral ingestion as drinking water, dermal absorption through skin, and inhalation via nose and mouth (Chen et al. 2019). In this study only the most common exposure pathways are considered, specifically oral ingestion of lake water as drinking water and dermal absorption during bathing, washing, or recreation in the lake (Qu et al. 2018). The chronic daily intake (CDI), which is the pollutant mass ingested or adsorbed per kilogram of body weight per day ($\text{mg} \cdot (\text{kg} \cdot \text{d})^{-1}$) was calculated as shown in Eq. (3) for oral ingestion (CDI_{oral}) and Eq. (4) for dermal absorption ($\text{CDI}_{\text{dermal}}$) (US EPA 1989).

$$\text{CDI}_{\text{oral}} = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (3)$$

$$\text{CDI}_{\text{dermal}} = \frac{C \times SA \times ET \times P \times CF \times EF \times ED}{BW \times AT} \quad (4)$$

where C represents the 95th percentile of the metals and metalloid concentrations ($\text{mg} \cdot \text{L}^{-1}$) in the surface water. Use of the 95th percentile is recommended when modeling the reasonably maximally exposed (RME) individual exposed to contaminants in water. The RME approach is preferred in most situations, as long-term contact with the maximum observed concentration is not reasonable (US EPA 1989). All other parameters in Eqs. 3 and 4 and the values used are defined in Table 1.

To evaluate the non-carcinogenic risk from exposure to water contaminated with heavy metals and the metalloid, the Hazard Quotient (HQ) was calculated as $\text{HQ}_i = \text{CDI}/\text{RfD}$ for each metal and metalloid (M. Saleem et al. 2019; Shah et al. 2012), where RfD is the reference dose for oral and dermal exposure routes (US EPA 2018). The values of RfD_{oral} and $\text{RfD}_{\text{dermal}}$ are shown in Table 1. Pb was not included in the hazard assessment as there is no acceptable threshold level of Pb exposure at which there are no adverse effects observed and the inability to account for preexisting body burdens of Pb from other sources such as food (US EPA 2004). When $\text{RfD}_{\text{dermal}}$ values were not available they were calculated by $\text{RfD}_{\text{dermal}} = \text{RfD}_{\text{oral}} \times \text{GIABS}$ (Imran et al. 2019; F. Saleem et al. 2019; USEPA 2004). The values of the gastrointestinal absorption factor (GIABS) used in this study were 5×10^{-2} , 1.3×10^{-2} and 2.5×10^{-2} for Cd, Cr(III), and Cr(VI), respectively (Naz et al. 2016; USEPA 2004). To evaluate the overall potential for non-carcinogenic health effects from exposure to lake water, the calculated HQ for every element, i, was added to determine the Hazard Index (HI) for each exposure route as $\text{HI} = \sum \text{HQ}_i$. Acceptable non-carcinogenic effects are assumed when $\text{HI} < 1$.

The total cancer risk (CR) from exposure to elements in lake water was calculated by $\text{CR} = \text{CDI}_i \times \text{SF}_i$ (USEPA 1989). The slope factors are shown in Table 1. The $\text{SF}_{\text{dermal}}$ for Cr(VI) was calculated as follows: $\text{SF}_{\text{dermal}} = \text{SF}_{\text{oral}}/\text{GIABS}$ (USEPA 2004).

Statistical analyses

Non-metric multidimensional scaling (NMDS) of the elemental concentrations and distance from the mouth of the lake was used to visually discriminate between the sampling sites using Paleontological Statistics Software Package (PAST) (Hammer et al. 2001). The

Table 1. Parameters used in the calculation of CDI via oral and dermal routes of exposure.

Parameters	Values	Units	References
Body weight (BW)			
Male	78	kg	(US EPA 2011)
Female	66	kg	(US EPA 2011)
Child	32.7	kg	(Khan et al. 2013; Wang et al. 2005)
Skin surface area (SA)			
Male	18,450	cm ²	(ATSDR 2005)
Female	16,450	cm ²	(ATSDR 2005)
Child	10,724	cm ²	(ATSDR 2005)
Water intake rate (IR)			
Adult	2	L·d ⁻¹	(ATSDR 2005)
Child	1	L·d ⁻¹	(ATSDR 2005)
Exposure frequency (EF)	365	d·y ⁻¹	(ATSDR 2005)
Exposure duration (ED)			
Male	66	Y	(WHO 2017)
Female	67	Y	(WHO 2017)
Child	15	Y	(WHO 2017)
Averaging time (AT)	EF × ED		
Exposure time (ET), dermal			
Adult	0.58	hr·d ⁻¹	(Naz et al. 2016; US EPA 2004)
Child	1	hr·d ⁻¹	(Kansal et al. 2013)
Conversion factor (CF)	1 × 10 ⁻³	cm ⁻³	(ATSDR 2005)
Permeability coefficient (P)			
As, Cd, Cr(III), and Mn	1 × 10 ⁻³	cm·h ⁻¹	(Karim 2011; Obiri et al. 2016; US EPA 2004)
Ni	2 × 10 ⁻⁴	cm·h ⁻¹	(US EPA 2004)
Cr(VI)	2 × 10 ⁻³	cm·h ⁻¹	(Obiri et al. 2016; US EPA 2004)
Reference dose (R _f D) oral/dermal			
As	3 × 10 ⁻⁴ /12.3 × 10 ⁻⁵	mg·(kg·d) ⁻¹	(US EPA 2018)
Cd	5 × 10 ⁻⁴ /2.5 × 10 ⁻⁵	mg·(kg·d) ⁻¹	(US EPA 2018)
Cr(III)	1.5/19.5 × 10 ⁻³	mg·(kg·d) ⁻¹	(US EPA 2018)
Cr(VI)	3 × 10 ⁻³ /7.5 × 10 ⁻⁵	mg·(kg·d) ⁻¹	(US EPA 2018)
Mn	0.14/9.6 × 10 ⁻⁴	mg·(kg·d) ⁻¹	(US EPA 2018)
Ni	0.02/5.4 × 10 ⁻³	mg·(kg·d) ⁻¹	(US EPA 2018)
Slope factor (SF) oral/derm			
As	1.5/3.66	kg·d·(mg) ⁻¹	(Naz et al. 2016; RAIS 2018)
Cr(VI)	0.5/20	kg·d·(mg) ⁻¹	(Naz et al. 2016; RAIS 2018)

two-dimensional NMDS plot was generated based on a Bray-Curtis distance matrix. A total of 11 replicate plots were generated, and the plot with the least stress was selected. Correlations between elements and the location sampled were determined using Pearson product-moment correlation analysis in PAST. When the concentrations of the metals and metalloid measured were lower than the MDL of AAS, one-half the values of MDL were used for correlations and risk calculations (Wu and Chen 2014). Analysis of variance in the means of metals and metalloid concentrations by season were determined in Sigma Stat v13 (Systat Software, Inc; San Jose, CA) and groups were determined by the Tukey test with a decision rule of $P < 0.05$. As the physicochemical water parameters were not normally distributed, ANOVA on Ranks (Sigma Stat) and with a post hoc Dunn's test ($P < 0.05$) were used to assess differences among seasons.

Results and discussion

Physicochemical water characteristics

There were significant variations in physicochemical water parameters by season and location as shown in Figures S1 and S2 (supplemental information). In general, TDS,

EC, and Cl^- concentrations were significantly higher in the pre-monsoon season (ANOVA on Ranks, Dunn's pairwise comparison, $P < 0.05$), while turbidity, pH, and temperature were significantly higher in the monsoon season. The average concentration of EC, TDS, and Cl^- in Keenjhar Lake water was lower than the WHO (2008, 2017), Pakistan Ministry of Environment (2010), and USEPA (2018) guidelines. These levels suggest that the lake can be classified as freshwater with low salts and minerals. The few exceedances of the standards for secondary water quality are discussed below.

In total, approximately 80% of the 270 samples analyzed for turbidity exceeded the maximum permissible limit of 5 NTU (WHO 2017) for unrestricted drinking water purposes. The average \pm standard deviation concentrations of turbidity were 25 ± 36 , 61 ± 91 , and 15 ± 31 NTU during the pre-monsoon, monsoon and post-monsoon seasons, respectively. This significantly higher (Tukey test, $P < 0.001$) turbidity in the lake water during the monsoon season as compared to the post-monsoon season is likely due to sediment transport associated with rain (Parra et al. 2018). Higher turbidity allows higher absorption of sunlight (Keogh et al. 2017), raising water temperature, reducing the DO and ultimately affecting aquatic life (Gupta et al. 2017). It also hinders photosynthesis in water plants by blocking light from penetrating into the water, thus affecting aquatic organisms dependent on these plants for their food and oxygen (Hammerschlag et al. 2019; Suplee et al. 2019).

The pH of the lake was alkaline in all seasons with concentrations of 8.46 ± 0.17 , 8.55 ± 0.17 , and 8.46 ± 0.09 during the pre-monsoon, monsoon and post-monsoon seasons, respectively. While, on average, the pH of the lake water was generally within the acceptable pH range for drinking water or 6.5–8.5 (WHO 2008, 2017), there were occasional exceedances of this limit. The slightly alkaline surface water in the Keenjhar Lake suggests a predominance of bicarbonates (Adams et al. 2001), which may be due to alternating layers of limestone and sandstone in the lake bed and surrounding geology (Dehlavi and Adil 2011). Alternatively, increased pH may be due to anthropogenic causes such as untreated industrial or domestic wastewater discharged to the lake. Spatially, the lowest pH (7.95) and the highest pH (8.9) were observed at the inlet of the lake at the Chul site during pre-monsoon, suggesting an influence from inlet water quality. These pH values were similar to those reported for Manchar Lake and the Main Nara Valley Drain that feeds Manchar Lake in Pakistan. Where the lake pH was 8.4 and the Main Nara Valley Drain was 8.9 (Mastoi et al. 2008).

The EC and TDS are usually affected by anthropogenic interferences in lake catchments. During pre-monsoon, monsoon and post-monsoon periods, the average concentration of EC and TDS values in the surface water were 731 ± 80 , 550 ± 87 , and 689 ± 98 $\mu\text{S}\cdot\text{cm}^{-1}$; and 475 ± 52 , 358 ± 56 , and 448 ± 64 $\text{mg}\cdot\text{L}^{-1}$, respectively. EC and TDS in all sampling rounds and locations were within permissible limits of 1500 $\mu\text{S}\cdot\text{cm}^{-1}$ and 1000 $\text{mg}\cdot\text{L}^{-1}$, respectively (WHO 2017). The significantly lower EC (Tukey test, $P < 0.001$) during the monsoon season suggests that non-stormwater associated flow to the lake from the KB feeder and its industrial inputs may be impacting the water quality. Given the elevated pH and turbidity, and correlations of pH, EC and turbidity with distance from the lake inlet, additional investigations should be conducted to determine the source of pollution or definitively link it to natural sources.

Spatio-temporal variations of trace metals and metalloid

The average and RME concentration of each metal during the three seasons varied significantly (Table 2), and in some cases there were multiple exceedances of acceptable limits in different seasons (Figure 2). Concentrations of metals and the metalloid observed in Keenjhar Lake by location and season are shown in Figures S3 and S4 (Supplemental information). Mercury was below analytical detection limits in all water samples tested and was not further considered. The RME or 95th percentile concentrations of As, Cd, Cr(III), Fe, Ni, and Pb exceeded acceptable drinking water or secondary water quality limits in at least one season (Table 2) while only As, Cd, and Pb average concentrations exceeded acceptable limits in at least one season. Only one sample of 270 had Cr(VI) concentrations that exceeded acceptable limits. While both Mn and Cu were below acceptable WHO limits (Figure 2).

Significant differences in metals concentrations by season were observed (Figure 2). While the maximum concentrations of the metals Cr(III), Cr(VI), Mn, Ni, Cu, and Fe were observed in the monsoon season, only the concentrations of Cu, Fe and Ni were significantly higher in the monsoon season (Tukey test, $n = 270$ per metal, $P < 0.05$). Cr(III), Cr(VI), Mn, and Cd had significantly lower concentrations in the post-monsoon season (Tukey test, $n = 270$ per metal, $P < 0.05$). The metalloid arsenic was in high concentration throughout all seasons sampled and greatly exceed acceptable WHO limits. The origin of arsenic in water-bodies has been attributed to both geological and anthropogenic sources (Shahid et al. 2018).

Approximately 80% of annual rainfall in this region occurs during monsoon season (Adnan et al. 2015; M. Saleem et al. 2019; Sanap et al. 2015), which may dilute pollutants or may carry higher concentrations of metals if flooding of contaminated areas occurs. In Keenjhar Lake as there are both anthropogenic and natural sources of the contamination, some metal concentrations were high in the monsoon season, as reported in other studies (Li and Zhang 2010; F. Saleem et al. 2019; Vega et al. 1998). Hence, seasonal anthropogenic activities and precipitation can both influence the concentration of metals in lake surface water (Li and Zhang 2010).

Average metal levels in Keenjhar Lake were compared with metal concentrations observed in other Pakistani lakes, as well as worldwide reported levels in industrial and municipal wastewater impacted lakes. In Keenjhar Lake, Cd, Cu, Fe, Mn, Ni, and Pb, concentrations were typically lower than the concentrations reported in other Pakistani lakes in all seasons, with one exception. In contrast, the As and Pb concentrations were an order of magnitude higher in Keenjhar Lake than the levels reported in the Turkish Kralkizi and Dicle Reservoirs (Varol 2013), Taihu Lake in China (Jiang et al. 2012), and Kainki Dam in Nigeria (Ochieng et al. 2008). Only in the Kanyaboli Lake of Kenya were comparable concentrations of Pb, Cd, Cu, Mn, and Ni reported (Oyewale and Musa 2006).

Significant spatial variation of contaminant concentrations and water quality parameters were observed in Keenjhar Lake water during the study period (Figures S1–S4, supplemental). The highest level of Fe was noted at site 1, As and Cr III at site 4, Cr VI at site 2, Mn at site 5, Cd at Site 6, Cu at site 7, and Ni at site 9. The highest total contaminant levels in the Keenjhar Lake were found at S1, the inlet of lake, while the lowest total metal content was observed at S10 the outlet of lake toward Karachi. This high concentration at the lake inlet suggests the KB Feeder canal may be the primary source of pollution. The different locations sampled in Keenjhar Lake tended to cluster

Table 2. Observed concentrations ($\text{mg}\cdot\text{L}^{-1}$) of trace metals and metalloid (average \pm standard deviation and RME concentration) in Keenjhar Lake water compared with other Pakistan lakes, international lakes and acceptable water quality guidelines.

Location	As ^{e,f}	Cd	Cr(III)	Cr(VI)	Cu	Fe	Mn	Ni	Pb
Keenjhar Lake ^a									
Pre-monsoon, X \pm SD	4×10^{-3}	4×10^{-3}	4×10^{-3}	1×10^{-3}	2×10^{-3}	$5.2 \times 10^{-2} \pm 3.8 \times 10^{-3}$	3×10^{-3}	1.1×10^{-2}	2×10^{-2}
Monsoon, X \pm SD	$\pm 9 \times 10^{-3}$	$\pm 3 \times 10^{-3}$	$\pm 1.4 \times 10^{-2}$	$\pm 3 \times 10^{-3}$	$\pm 3 \times 10^{-3}$		$\pm 6 \times 10^{-3}$	$\pm 1.1 \times 10^{-2}$	$\pm 1.2 \times 10^{-2}$
	5×10^{-3}	4×10^{-3}	2.6×10^{-3}	3×10^{-3}	6×10^{-3}	$6.8 \times 10^{-2} \pm 1.3 \times 10^{-3}$	1.7×10^{-2}	5×10^{-3}	1.4×10^{-2}
	$\pm 1 \times 10^{-2}$	$\pm 2 \times 10^{-3}$	$\pm 5.3 \times 10^{-3}$	$\pm 1.2 \times 10^{-2}$	$\pm 1.1 \times 10^{-2}$		$\pm 3.9 \times 10^{-2}$	$\pm 1.3 \times 10^{-2}$	$\pm 1.2 \times 10^{-2}$
Post-monsoon, X \pm SD	1×10^{-3}	5×10^{-4}	1.1×10^{-2}	2×10^{-3}	2×10^{-3}	$1.2 \times 10^{-2} \pm 5 \times 10^{-3}$	3×10^{-3}	1.1×10^{-2}	1.2×10^{-2}
	$\pm 2 \times 10^{-2}$	$\pm 9 \times 10^{-3}$	$\pm 6 \times 10^{-3}$	$\pm 2 \times 10^{-3}$	$\pm 1 \times 10^{-3}$		$\pm 3 \times 10^{-3}$	$\pm 1.5 \times 10^{-3}$	$\pm 9 \times 10^{-3}$
Pre-monsoon, RME ^b	2.8×10^{-2}	1.1×10^{-2}	3.5×10^{-2}	4.4×10^{-3}	4×10^{-3}	8.0×10^{-2}	1.0×10^{-2}	2.5×10^{-2}	4.0×10^{-2}
Monsoon, RME	3.2×10^{-2}	5.7×10^{-3}	1.5×10^{-1}	7.2×10^{-3}	2.8×10^{-2}	4.2×10^{-2}	1.1×10^{-1}	2.4×10^{-2}	4.0×10^{-2}
Post-monsoon, RME	3.8×10^{-2}	2.3×10^{-3}	2.2×10^{-2}	4.1×10^{-3}	4.8×10^{-3}	2.0×10^{-2}	1.0×10^{-2}	3.7×10^{-2}	3.0×10^{-2}
Mangla Lake ^c									
Pre-monsoon	^g	4.0×10^{-2}	–	–	3.0×10^{-2}	1.5×10^{-1}	2.0×10^{-2}	1.3×10^{-1}	3.9×10^{-1}
Monsoon	–	3.4×10^{-2}	–	–	3.0×10^{-2}	1.2×10^{-1}	2.0×10^{-2}	1.2×10^{-1}	3.3×10^{-1}
Post-monsoon	–	2.4×10^{-2}	–	–	2.0×10^{-2}	1.4×10^{-1}	1.0×10^{-2}	9.0×10^{-2}	2.9×10^{-1}
Rawal Lake ^c									
Pre-monsoon	–	6.1×10^{-3}	–	–	1.0×10^{-2}	8.0×10^{-2}	3.8×10^{-3}	4.0×10^{-2}	1.4×10^{-1}
Monsoon	–	8.8×10^{-3}	–	–	1.0×10^{-2}	1.0×10^{-1}	9.3×10^{-3}	5.0×10^{-2}	2.0×10^{-1}
Post-monsoon	–	2.7×10^{-2}	–	–	2.0×10^{-2}	7.0×10^{-2}	1.0×10^{-2}	6.0×10^{-2}	2.3×10^{-1}
Simly Lake ^c									
Pre-monsoon	–	2.3×10^{-2}	–	–	6.0×10^{-2}	2.0×10^{-1}	4.0×10^{-2}	8.0×10^{-2}	3.1×10^{-1}
Monsoon	–	2.0×10^{-2}	–	–	5.0×10^{-2}	1.5×10^{-1}	3.0×10^{-2}	5.0×10^{-2}	2.7×10^{-1}
Post-monsoon	–	1.7×10^{-2}	–	–	5.0×10^{-2}	6.0×10^{-2}	1.0×10^{-2}	4.0×10^{-2}	2.0×10^{-1}
Khanpur Lake ^d	–	2.0×10^{-2}	–	–	9.0×10^{-2}	5.0×10^{-2}	1.0×10^{-2}		2.2×10^{-1}
Reported worldwide levels									
Kralikizi Dam	2.4×10^{-3}	3.6×10^{-5}	–	–	2.8×10^{-3}	5.9×10^{-2}	–	15.8×10^{-3}	2.6×10^{-3}
Reservoir, Turkey									
Dicle Dam	1.6×10^{-3}	3×10^{-5}	–	–	2.1×10^{-3}	6.2×10^{-2}	–	15.9×10^{-3}	1.8×10^{-3}
Reservoir, Turkey									
Taihu Lake, China	18.6×10^{-4}	6×10^{-5}	–	–	5.8×10^{-3}	–	–	5.3×10^{-3}	2.7×10^{-3}
Kainji dam, Nigeria	–	–	–	–	1.3×10^{-3}	1.3×10^{-2}	9×10^{-3}	9×10^{-4}	1.2×10^{-3}
Kanyaboli Lake, Kenya	–	4.4×10^{-3}	–	–	2.0×10^{-2}	–	2.8×10^{-1}	2.0×10^{-2}	2.0×10^{-2}

^aThis study.^bRME = reasonable maximum exposure risk level, namely the 95 percentile of the observed concentration distribution.^cF. Saleem et al. (2019).^dIqbal and Shah (2014).^eGold values exceeded (WHO 2008, 2017) limits in $\text{mg}\cdot\text{L}^{-1}$ of: As = 0.01, Cd = 3×10^{-3} , Cr(III) and Cr(VI) = 0.05, Cu = 2, Fe = 0.3, Mn = 0.4, Ni = 0.07, and Pb = 0.01;^fItalics values exceeded Pakistan (Pakistan Ministry of Environment 2010) limits in $\text{mg}\cdot\text{L}^{-1}$ of: As = 0.05, Cd = 0.01, Cr(III) and Cr(VI) = 0.05, Cu = 2, Fe = no limit promulgated, Mn = 0.5, Ni = 0.02, and Pb = 0.05;^g– “indicates no data available.

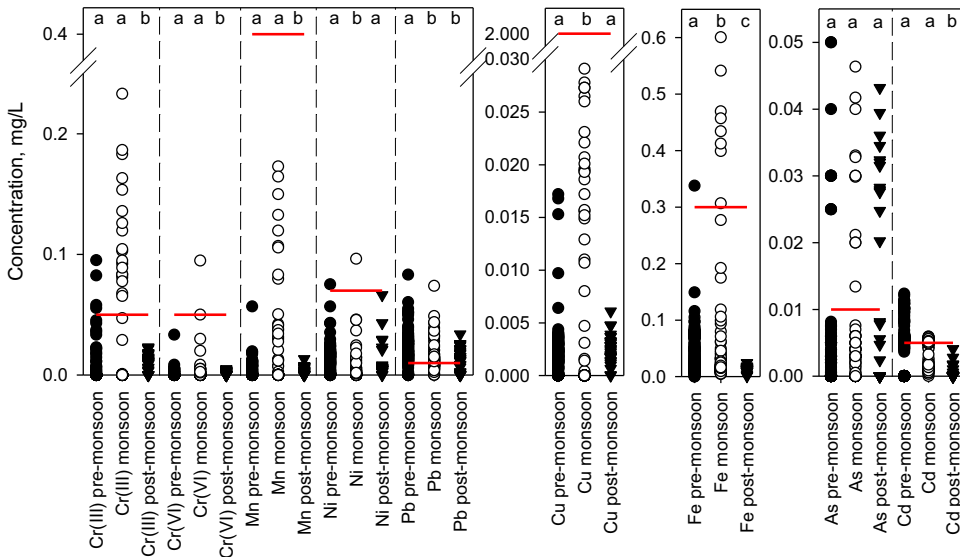


Figure 2. Concentrations of metals and the metalloid observed in the pre-monsoon, monsoon and post-monsoon sampling events. Horizontal lines indicate the acceptable drinking water limits (As, Cd, total Cr, Cu, and Pb) or secondary water guidance (Fe, Mn, and Ni) published by the World Health Organization. Means of the observations within the metalloid and metal groups (indicated by dashed lines) with different letters are significantly different (ANOVA, Tukey test, $P < 0.05$).

together based on distance from the lake inlet (Figure 3). The clustering of the sites together, regardless of the season sampled or depth sampled suggested that the water quality was greatly influenced by the quality of the water sources discharging into the lake rather than the time of year (monsoon versus pre-monsoon). These NDMS clusters suggest a similarity in metals and metalloid concentrations when a location is sampled repeatedly. The environmental factors most influencing the ordination among the sampling sites included Fe, As, and Cr.

The concentrations of several metals were significantly positively correlated with one another, including Cu with Cr, Fe, Mn, and Pb; Cr with Fe, Mn, and Pb; Fe with Mn and Pb; and Ni with Pb (Table S1, Supplemental). Conversely, the metalloid, As was significantly inversely correlated with Cd and Pb, that might be related to pH, as higher pH would not result in As precipitating as an oxide as the other metals would (Guo et al. 2018). While Cd was also inversely correlated with the metals Cu and Cr. Distance from the lake inlet was also shown to result in a significant decrease in As, Fe and turbidity and a less significant decrease in Cu concentrations. Conversely pH and EC increased with distance from the lake inlet. Given the correlation of turbidity with Cu, Fe, and Mn (Table S1) a simple method for reducing these metals in drinking water include simple sand filtration or even membrane filtration.

Pollution assessment

The pollution evaluation indices for trace metals and the metalloid in Keenjhar Lake water are shown in Table 3. The C_{deg} results revealed high levels of pollution (i.e., >3)

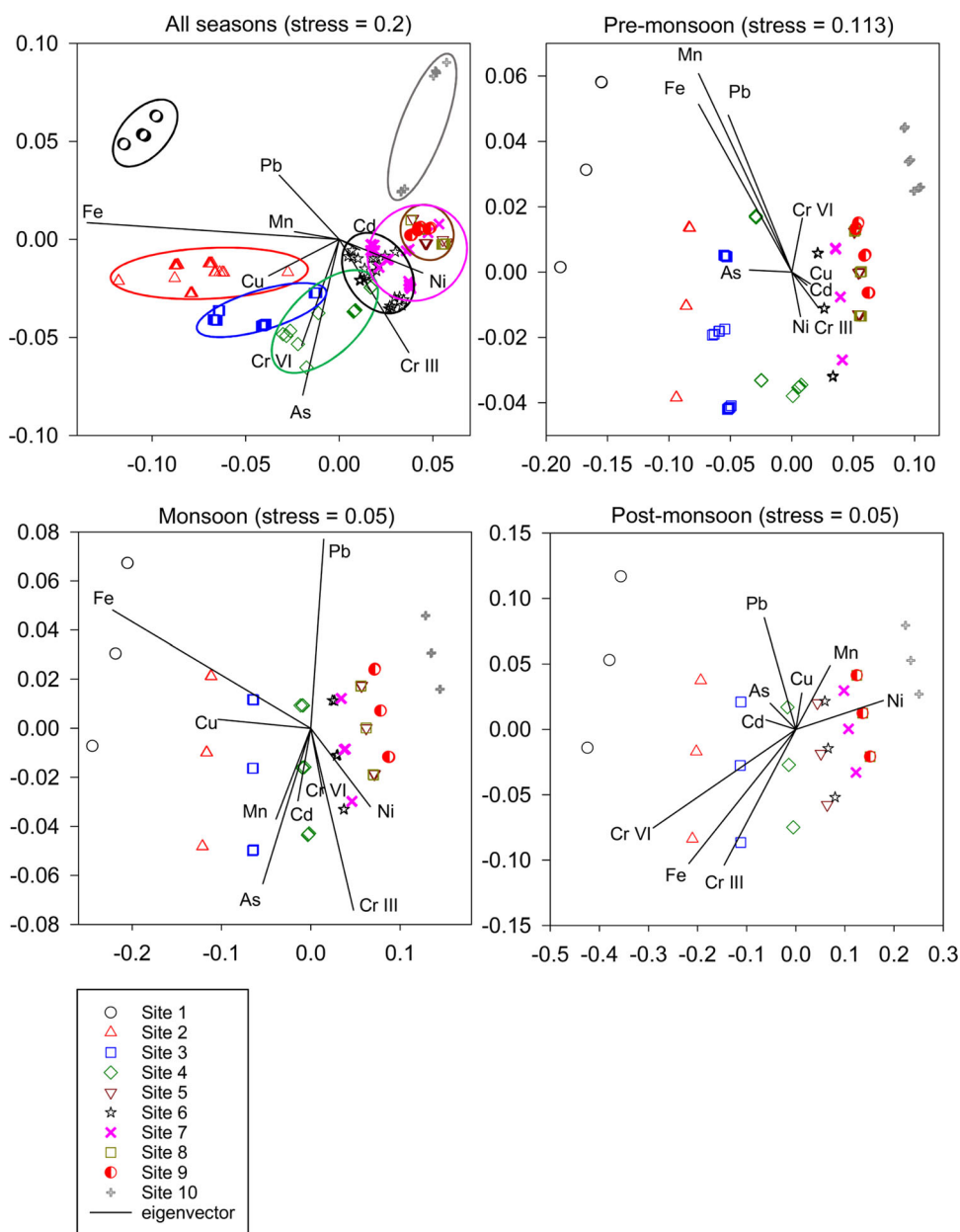


Figure 3. Overview of the separation of sampling locations by NMDS of all sampling rounds and depths. Lines indicate the eigenvectors and are arbitrarily scaled, so only their direction and relative length should be considered. Circled sites in the upper left image indicate groupings of concentration results by location.

in Keenjhar Lake water in the monsoon seasons but medium contamination (i.e., between 1 and 3) in the pre and post-monsoon seasons (Bhuiyan et al. 2010; Edet and Offiong 2002). This is likely due to the lower concentrations of Pb in the pre and post-monsoon seasons. However, using HEI, a low level of pollution (i.e., <150) was observed in all seasons. Our results are in contrast to those reported by F. Saleem et al.

Table 3. Pollution evaluation indices for trace metals and metalloid in the Keenjhar Lake water.

	HEI			C_{deg}		
	H_C/H_{MAC}^a			$\left(\frac{C_i}{C_{Ni}} - 1\right)^b$		
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
As	0.43	0.55	1.36	-0.57	-0.45	0.36
Cd	1.38	1.28	0.16	0.38	0.28	-0.84
Cr(III)	0.09	0.52	0.22	-0.91	-0.48	-0.78
Cr(VI)	0.02	0.06	0.03	-0.99	-0.94	-0.97
Cu	2×10^{-3}	6×10^{-3}	2×10^{-3}	-1.00	-0.99	-1.00
Fe	0.26	0.34	0.06	-0.74	-0.66	-0.94
Mn	0.06	0.34	0.07	-0.94	-0.66	-0.93
Ni	0.57	0.26	0.53	-0.43	-0.74	-0.47
Pb	8.08	13.54	9.40	7.08	12.54	8.40
Summation	10.88	16.90	11.833	1.88	7.90	2.83

^aMaximum admissible concentrations (MAC, mg·L⁻¹).

^b C_{Ni} were derived from WHO guidelines (see Table 2).

(2019), who reported much higher HEI and C_{deg} pollution levels in the Mangla, Rawal, and Simly lakes in Pakistan. However, this discrepancy likely arises as F. Saleem et al. (2019) used a conservative value for Pb of $1.5 \mu\text{g}\cdot\text{L}^{-1}$, rather than the $10 \mu\text{g}\cdot\text{L}^{-1}$ used herein. The $10 \mu\text{g}\cdot\text{L}^{-1}$ is recommended by the World Health Organization (WHO 2008).

Health risk assessment

Non-carcinogenic health risk assessment

Ingestion and absorption through the skin, are considered the most critical impact pathways of heavy metals and metalloid for human health. The oral hazard quotient (HQ_{oral}) and dermal hazard quotient (HQ_{dermal}) from exposure to water contaminated with heavy metals and the metalloid were calculated for male, female, and children separately for each location as shown in Figure 4. The HI for each location was calculated as it is likely the residents are typically using water near their residence rather than tens of kilometers away. Overall, the highest non-carcinogenic risk from exposure to Keenjhar Lake water arises from the use of the water for drinking purposes, as HI was >1 . However, if the residents were to find an alternative source of drinking water and were only exposed to the water for recreation, bathing or washing, the non-carcinogenic risk from exposure is acceptable for all age groups. There were also distinct differences in the risk posed by each site, with S4 and S6 posing the highest risk.

Carcinogenic health risk assessment

Carcinogenic risk is defined as an increase in probability that individuals will develop cancer once in lifetime because of exposure of chemicals under the specific scenario (Chen and Liao 2006; Obiri et al. 2016). The carcinogenic risk from oral and dermal exposure to Cr(VI) and As for male, female and children was calculated as shown in Figure 4. The primary carcinogenic risk driver is oral exposure to As in water used for drinking with the probability of cancer risk exceeding 1 in 10,000 individuals for all ages and genders. However, even if the lake water was used only for recreation, washing or bathing purposes, the probability of cancer exceeds 1 in 1,000,000 individuals. Therefore, the water is not fit to use for drinking water or dermal contact.

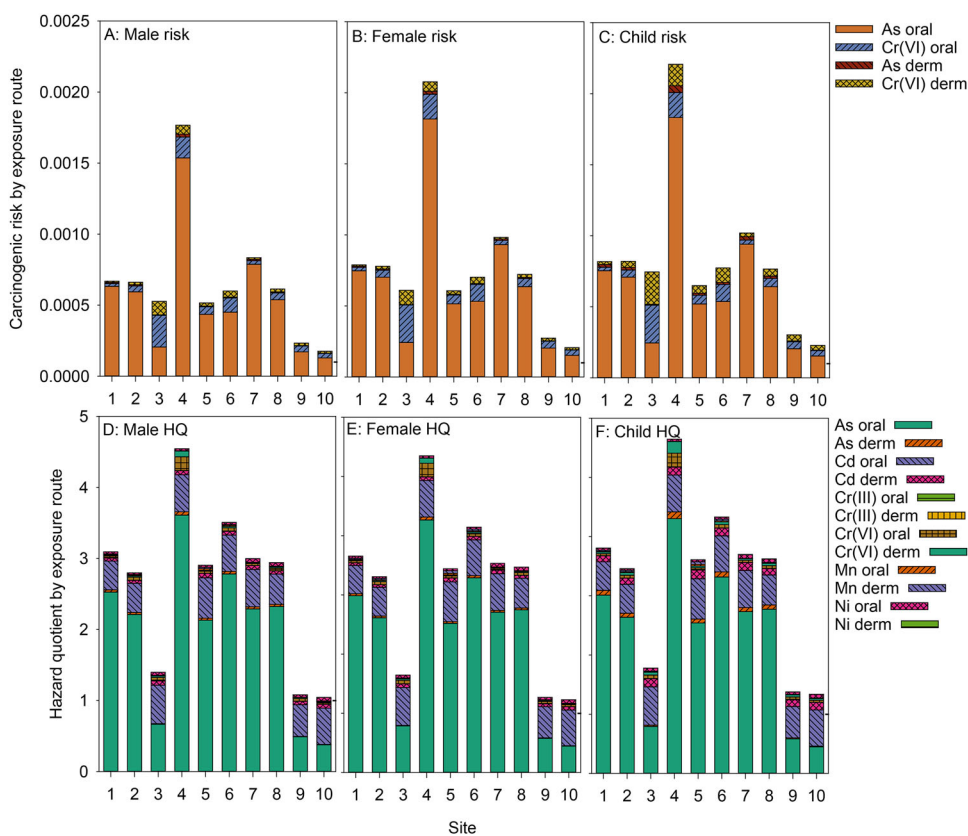


Figure 4. Carcinogenic risk (plots A, B, and C) from exposure to As and Cr(VI) and non-carcinogenic hazards (plots D, E, and F) from exposure to As, Cd, Cr, Mn, and Ni at different sites of Keenjhar Lake.

Limitations of the study

Uncertainty and variability are two factors that are unavoidable when conducting human health risk assessments (Hoffman and Hammonds 1994). As such, risk assessments should always include a discussion of the limitations associated with the study. Herein, the following sources of error could have resulted in an under or overestimation of the risk to receptors. Concerning variability in exposure estimation, exposure duration of the entire lifetime and 365 days per year may overestimate the duration of use of the Keenjhar Lake water and thus overestimated risk. However, as this assessment was developed for the RME individual, the assumption of no travel and no moving outside the lake area is valid. Exposure factors used in this study were from USEPA, WHO and elsewhere, which might not be appropriate to the local conditions and might led to either over (greater skin surface area in USEPA values) or under (excessive body weight in USEPA values) estimation due to unavailability of Pakistan specific population data. With respect to uncertainty in the environmental concentrations, the use of one half of the detection limit for any sample where contaminants were not detected may result in an overestimation of risk during the calculation of the 95th percentile concentrations. The use of one half the detection limit is a standard practice in risk assessments,

although emerging research suggests the use of Bayesian frameworks on left-censored data is gaining in importance (Shoari and Dubé 2018). Finally, the assessment herein did not assume any treatment of the water prior to its use as drinking water. However, the use of cloth filters or letting the water sediment settle before drinking may result in lower concentrations of metals, especially those associated with turbidity such as Cu, Fe, and Mn (Tables S3 and S4, Supplemental).

Conclusions

Significant spatial and temporal variability in contaminants were observed in the Keenjhar Lake of Pakistan. The different locations sampled in the lake tended to cluster together based on distance from the inlet and ordination analysis was also influenced by Fe, As, and Cr concentrations. Concentrations of most metals (excluding Cu) and the metalloid exceeded safe limits for unrestricted use in at least one season sampled. Concentrations of Cu, Cr(III), Cr(VI), Fe, Mn, and Ni, were significantly higher in the monsoon season than the pre- or post-monsoon season. Higher metals and metalloid concentrations were observed adjacent to the urbanized parts or close to the lake feeder canal. The average values of a majority of the trace elements were observed to be lower than the published values for other Pakistani Lakes. Pollution assessment indices suggested low pollution levels in the lake. However, health risk assessments based on the RME individual suggest the potential for adverse carcinogenic and non-carcinogenic effects to individuals using the water for drinking purposes and recreation, bathing or washing. Overall the results suggest that there is a need to manage and regulate toxic pollutants entering Keenjhar Lake from various industrial and municipal sources. Both industrial and municipal wastewater should be treated at the source or at combined effluent treatment facilities before discharging treated water into the lake. The populations living in the vicinity of the lake should be educated regarding potential risks from exposure to trace elements and provided suggestions on how to treat domestic wastewater (e.g., sand filtering, ion exchange and/or membrane filtering) at the community level.

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Disclosure statement

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