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Original Research

Seasonal Variability of Heavy Metals in Manchar Lake of Arid Southern Pakistan and Its Consequential Human Health Risk

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Abstract

Water pollution related to trace elements has emerged as a worldwide concern owing to their increasing concentration and damages to the aquatic ecosystems. The water ecosystem of Manchar Lake situated in the arid region of Pakistan has also been degraded and posing a severe health risk to the dependent communities. This study aims to investigate the seasonal variability in the influx of trace elements (As, Cd, Cr(III), Cr(VI), Cu, Fe, Hg, Mn, Ni, Pb, and Zn) into the lake during pre-monsoon, monsoon, and post-monsoon seasons and its consequential health risks. The highest mean concentrations (μg/l) of As (43.2), Cr(III) (101.4), Zn (41), Cu (43.12), Fe (318), Cd (18.5), Mn (27.2), Ni (99.7), Pb (65.91) and Hg (6.8) have been observed in pre-monsoon and Cr(VI) (0.2) in monsoon seasons. The elements exceeding safe limits in pre-monsoon season are As, Cd, Cr(III), Hg, Ni, and Pb, while in monsoon season As, Cd, Ni, and Pb exceed the limit. Evaluation of the degree of contamination depicted high levels of pollution in pre-monsoon and monsoon seasons and the Heavy Metal Evaluation Index indicated a high level of pollution in pre-monsoon, medium in monsoon, and low in the post-monsoon season. The study revealed that oral consumption of lake water potentially causes carcinogenic and non-carcinogenic health risks. However, potential dermal related health risks associated with these metals concentrations in water are within the tolerable ranges. The findings of this study suggest prompt actions to control these pollutants influx into the lake.

Keywords: Manchar Lake, metals and metalloids, human health risk assessment, pollution assessment

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Introduction

A serious environmental concern that has appealed worldwide attention, is the degraded quality of many freshwater bodies since these are potentially harmful to human health and to the ecosystem [1]. Particularly in developing countries, wetlands are under threat due to climate change and growing human populations coupled with industrial and agricultural intensifications and little attention has been paid to protect these environments [2]. These heavy metals and metalloids are contributed from various sources, including atmospheric precipitation, geologic weathering, agricultural runoffs, and domestic and industrial discharges [3]. However, in the recent era, the contribution of trace elements into the water bodies from the anthropogenic activities have surpassed natural sources [4]. Consequently, deteriorated water quality affects the services offered by the aquatic ecosystems directly to humans, agriculture, and tourism [5].

Pollution of the aquatic environment by heavy metals is of great concern due to their toxicity, long persistence, and bioaccumulation into the food chain [6]; as such, they are harmful to humans and the aquatic life [7]. These trace elements in water can affect the human body through oral ingestion and dermal exposure. Although the presence of certain trace elements within limits is necessary to maintain human health, their excess can be injurious [8]. The exposure of the human body to these elements may cause acute and chronic diseases and long-term contact with these metals can cause severe diseases such as Alzheimer's, Parkinson's, multiple sclerosis, and cancer [4].The problem of trace elements accumulation in an aquatic ecosystem is worst particularly in the freshwater bodies of arid regions. Less rainfall, continuous influx of pollutants from various sources and less frequent spilling away of water are the major factors contributing to the rise in metals concentrations. Gradually, these pollutants accumulate into the water bodies to a limit where it becomes difficult to restore the ecosystem easily, resulting in a continued and lasting hazard to the ecosystem [9, 10].

Manchar Lake in Sindh province of the arid region of Pakistan is an important freshwater lake that is facing these challenges. Its ecosystem has been gradually deteriorated, not only because of all these predominant factors but also due to a decline in the adequate freshwater inflows into the lake due to low rainfalls and higher evaporation losses. Consequently, the water quality of the lake has been degraded and it is not fit for human consumption. The deteriorated water quality of the lake has also affected the land productivity cultivated with the water from Manchar Lake, loss of lake dependent biodiversity, including migratory birds, and this has ultimately affected the livelihood of the farmers and the fishermen [11].

Currently, Manchar Lake receives water through three sources, i.e. (i) the rainwater from the catchment area in the west of Sindh province and southeastern Baluchistan province through the Gaj River and numerous other streams originating from the Khirthar and the Lakki range of mountains, (ii) River Indus inflows during high flood seasons through the Aral wah (canal) and Danister wah (canal) and (iii) the Main Nara Valley Drain (MNVD). Aral wah brings water into the Manchar Lake during summer high flood and drains out the lake water into the river Indus during low flow and it serves as two ways flow. However, during the study period, Aral wah was flowing from Manchar to Indus river in monsoon and post-monsoon seasons due to high water level in Manchar lake. MNVD was supplemented in 1932, initially as a flood canal but later remodeled to bring agricultural and municipal wastewater from upper Sindh to provide additional water to the lake during the dry season and it is responsible for the highest pollution influx. Besides, the lake also receives untreated domestic wastewater round the year from the surrounding villages.

The Manchar lake water is used for drinking purposes by the communities living in boat villages as well as on the banks of the lake. It is the only source of water to them because the groundwater in the vicinity is saline and not fit for human consumption [12]. The Reverse Osmosis (RO) plants installed by the government to treat lake water are mainly non-operational and also not sufficient to meet the drinking water demand of the inhabitants.

Studies conducted in Manchar Lake suggest pollution of the lake with metals and metalloids [13, 14]. Due to the increasing water demand of other sectors and declined flows of Indus River, Manchar Lake has not been receiving much water from River Indus during the last few years. MNVD, carrying a certain level of pollutants, is continuously flowing into the lake. Besides, not much volume of water is spilling away from the lake which could have drained a certain quantity of contaminants and might help to improve the water quality. Therefore, it has been hypothesized that due to these factors, the water quality of Manchar Lake has been degraded significantly and posing a severe health risk to the dependent communities. Thus, the current study aims to (1) evaluate the concentration of trace elements (As, Cd, Cr(III), Cr(VI), Cu, Fe, Hg, Mn, Ni, Pb, and Zn) of the lake water during different seasons in a year; (2) assess the pollution status of surface water; (3) determine the non-carcinogenic and carcinogenic risks for populations exposed to heavy metals and the metalloid.

Materials and Methods

Description of the Study Area

Manchar Lake is located in Sindh Province of Pakistan at a distance of around 18 km from the city of Sehwan Sharif, in district Jamshoro [15]. It lies at 67º34′-67º43 E and 26º23′-26º28′N, at an altitude of

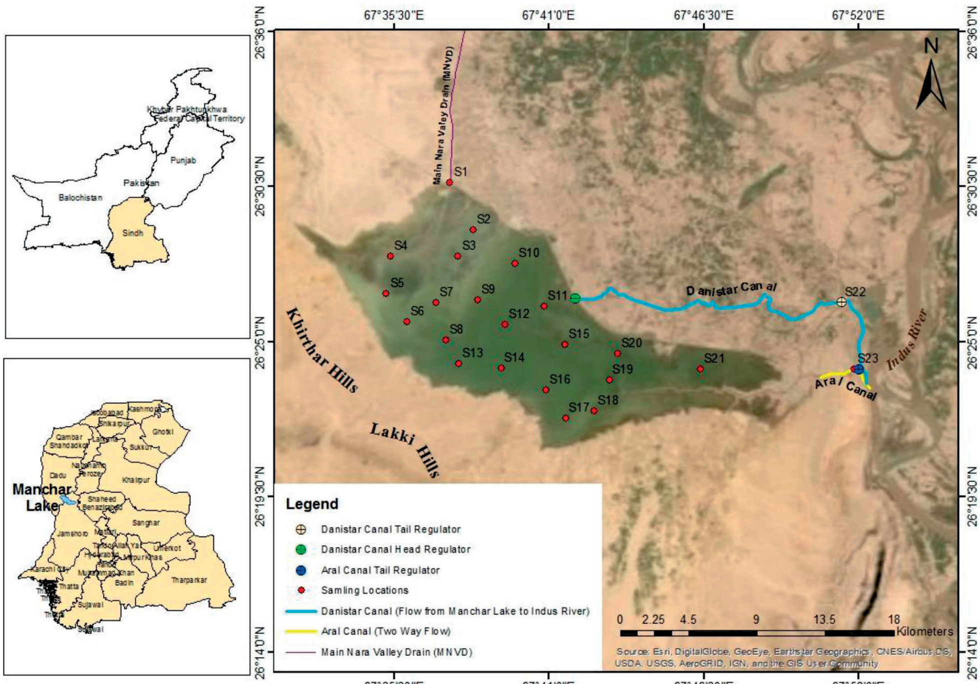

Fig. 1. Map showing the study area with sampling locations (Manchar Lake, Pakistan).

34.14 meters above mean sea level. The mean depth of the lake varies between 0.5 to 3.75m [12] and its area fluctuates seasonally with average being 233 km^2 [11]. It is a vast natural depression bordered in the west by the Khirthar hills, in the south by the Lakki hills and in the east by the Indus River as shown in Fig. 1 [15]. The original command of the lake has varied significantly due to various human interventions. These interventions include the erection and widening of the canals (Aral and Danister), connecting river Indus with the lake, the building of the flood barriers in 1932 in its northern and northeastern borders, and the construction of the MNVD, bringing polluted water from upper Sind into the lake [11].

Sample Collection and Processing

To determine the temporal variations of heavy metals (Cd, Cr(III), Cr(VI), Cu, Fe, Hg, Mn, Ni, Pb, and Zn) and a metalloid (As) in lake water, 23 sampling locations were marked with the help of Global Positioning System (GPS) (Fig. 1), and the sampling was carried out in three seasons, i.e., pre-monsoon (April), monsoon (August) and post-monsoon (November) in 2019. The rationale for selecting many sampling sites was to precisely evaluate the spatial variations in metal concentrations across the entire lake.

Water samples were collected, handled, and transported by following standard methods [16]. Three replicate water samples were collected at each site from the surface (0.153 m below top), mid and near the bottom (0.153 m above bottom) of the lake using a submersible pump (BC-MF double channel, Pedrollo, Italy) and each level replicates were combined into one sample in 300 ml acid-washed polyethylene bottles. A total of 207 (including three samples at each location per round from 23 locations) water samples were collected to assess the concentration of trace elements. The water samples were immediately stored in ice boxes with ice pads and transported to the laboratory.

In the laboratory, water samples (300 ml) were first divided into two subsamples (200 ml and 100 ml). Subsamples (100 ml) for trace elements detection using Inductively Coupled Plasma Mass Spectrometry (ICPMS) were filtered through Maxipore syringe filters (pore size: 0.45 µm) to remove solid microparticles and were acidified with 1% analytical grade HNO_3 (70 % purity, DaeJung) to adjust pH<2 [17, 18], to preserve trace elements in solution and avoid adsorption and precipitation. Remaining water samples (200 ml) for Cr(VI) detection were added with the 1,5-diphenylcarbazide solution (Sigma-Aldrich, Germany) and sulfuric acid (H_2SO_4, 95-98%, Sigma-Aldrich, Germany) to maintain pH 2±0.5.

Sample Analyses

The concentrations of trace elements (As, Cd, total Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) in water samples were determined using Inductively Coupled Plasma Mass Spectrometry (ICPMS) (NexIon 350, Perkin Elmer, New York, USA) by following procedures recommended by manufacturers. Mixed standards solutions (PerkinElmer Pure Plus) were used for the calibration of the equipment. The concentrations of Cr(VI) in water samples were measured by using a UV spectrophotometer (Schimadzu UV 1800, Germany) at the wavelength of 540 nm as per the standard method of EPA (Method no. 7196A) [19] within 24 hours of sampling. The minimum detection limit (MDL) of the trace elements on an ICPMS and UV spectrophotometer were determined to be 0.001, 0.0005, 0.0005, 0.0005, 0.1, 0.0005, 0.002, 0.0005, 0.002 and 0.001 $\mu g \cdot L^{-1}$ for As, Pb, total Cr, Cd, Cr(VI), Cu, Fe, Mn, Ni, and Hg respectively. The concentration of Cr(III) was obtained by subtracting Cr(VI) from total Cr.

Quality Control (QC) and Quality Assurance (QA)

Quality control and assurance measures were adopted as defined in Standard Methods for the Examination of Water and Wastewater [16] during sample collection and processing. The laboratory glassware were immersed in nitric acid (5%) for 24 hours and rinsed three times with de-ionized water to avoid contamination. All equipment were calibrated each time before use. For analytical precision, each sample was analyzed in triplicate, and to control contamination during analyses, procedural blanks and duplicates run in each batch of ten samples were incorporated, and only certified standard reference materials were used for the calibration of the equipment. The recoveries of samples spiked with standards were observed to range from 95.2 to 102.1%.

Pollution Assessment

In this study, two pollution indices i.e. degree of contamination (C_{deg}) and the heavy metal evaluation index (HEI) were used to determine the quality of the water used for drinking and to meet the domestic and the agricultural needs. The C_{deg} sums up the collective effects of elements studied that may degrade the water quality [3, 18, 20]; and was calculated by using Eq. 1.

$$C_{deg}=\sum_{i=1}^{n}\left(\frac{M_i}{MAC_i}-1\right) \quad (1)$$

...where, M_i and MAC_i (10, 3, 50, 50, 1000, 200, 6, 50, 20, 1.5, and 10 in µg/l for As, Cd, Cr(III), Cr(VI), Cu, Fe, Hg, Mn, Ni, Pb, and Zn respectively [18] represents the monitored and the maximum admissible concentrations respectively for the i^{th} element. Based on C_{deg}, a water body polluted with heavy metals is classified into various categories as: (low pollution when C_{deg} is less than 1, moderate pollution when C_{deg} is between 1 and 3 and highly polluted when C_{deg} is higher than 3). However, heavy metal evaluation index (HEI) describes the overall quality of water in terms of heavy metals and metalloids in an aquatic ecosystem [3, 18, 21]; and was calculated using Eq. 2.

$$HEI=\sum_{i=1}^{n}\frac{M_i}{MAC_i} \quad (2)$$

The grouping of water quality based upon HEI is: (low pollution when HEI is lower than 10, moderate pollution when HEI is between 10-20 and highly polluted when HEI is higher than 20).

Human Health Risk Assessment

Due to saline groundwater in the vicinities [12] and poor performance of RO plants, the communities are left with no choice but to use the lake water without treatment. Consumption of water polluted with trace elements potentially harm the health of the communities and therefore, human health risk assessments were carried out to estimate the threats to an individual's health exposure to trace elements through water. The humans can be exposed to trace elements present in the water through various exposure routes, including oral intake as drinking water, dermal absorption through the skin, and inhalation through mouth and nose [22]. However, in this study only most common exposure pathways, i.e., oral ingestion of lake water as drinking water and dermal absorption during bathing, washing, or recreation in the lake were considered [23].

The chronic daily intake (CDI), which is the amount of pollutant ingested or adsorbed per kilogram of body weight per day ($mg \cdot (kg \cdot d)^{-1}$), was calculated as shown in Eq. 3 and Eq. 4 for oral ingestion (CDI_{oral}) and for dermal absorption (CDI_{dermal}) respectively [24].

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

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

...where C represents the mean concentrations ($mg \cdot L^{-1}$) of metals and metalloid in the surface water. The values of all other parameters used in Eqs. 3 and 4 are given in Table 1.

To estimate the non-carcinogenic risk from exposure to water polluted with trace elements, the Hazard Quotient (HQ) was calculated for each trace element as shown in Eq. 5 [18, 25].

$$HQ=\frac{CDI}{RfD} \quad (5)$$

...where R_fD is the reference dose for oral and dermal exposure routes [26]. The values of RfD_{oral} and RfD_{dermal} are presented in Table 1. At places where RfD_{dermal} values were not available, they were calculated by using Eq. 6 [27].

$$RfDdermal = RfDoral\times GIABS \quad (6)$$

In this study, the values of gastrointestinal absorption factor (GIABS) used in calculations were

Table 1. Values used in the calculation of CDI through different exposure routes.

Parameters	Units	Values	References
Body weight (BW)			
Male	Kg	78	[29]
Female	Kg	66	[29]
Child	Kg	32.7	[30]
Skin surface area (SA)			
Male	cm^2	18450	[31]
Female	cm^2	16450	[31]
Child	cm^2	10724	[31]
Water intake rate (IR)			
Adult	$L\cdot d^{-1}$	2	[31]
Child	$L\cdot d^{-1}$	1	[31]
Exposure frequency (EF)	$d\cdot y^{-1}$	365	[31]
Exposure duration (ED)			
Male	Y	66	[32]
Female	Y	67	[32]
Child	Y	15	[32]
Averaging time (AT)	EF × ED		
Exposure time (ET), dermal			
Adult	$hr\cdot d^{-1}$	0.58	[25, 33]
Child	$hr\cdot d^{-1}$	1	[34]
Conversion factor (CF)	cm^{-3}	1×10^{-3}	[31]
Permeability Coefficient (P)			
As, Cd, Cr(III), Hg, Mn and Zn	$cm\cdot h^{-1}$	1×10^{-3}	[25, 27, 35, 36]
Ni	$cm\cdot h^{-1}$	2×10^{-4}	[25]
Cr(VI)	$cm\cdot h^{-1}$	2×10^{-3}	[25, 36]
Reference dose (R_fD) oral/dermal			
As	$mg\cdot(kg\cdot d)^{-1}$	$3\times10^{-4}/12.3\times10^{-5}$	[24]
Cd	$mg\cdot(kg\cdot d)^{-1}$	$5\times10^{-4}/2.5\times10^{-5}$	[24]
Cr(III)	$mg\cdot(kg\cdot d)^{-1}$	$1.5/19.5\times10^{-3}$	[24]
Cr(VI)	$mg\cdot(kg\cdot d)^{-1}$	$3\times10^{-3}/7.5\times10^{-5}$	[24]
Fe	$mg\cdot(kg\cdot d)^{-1}$	$0.3 / 0.14\times10^{-3}$	[24]
Hg	$mg\cdot(kg\cdot d)^{-1}$	$3\times10^{-4}/2.1\times10^{-5}$	[24, 25, 27]
Mn	$mg\cdot(kg\cdot d)^{-1}$	$0.14/9.6\times10^{-4}$	[24]
Ni	$mg\cdot(kg\cdot d)^{-1}$	$0.02/5.4\times10^{-3}$	[24]
Pb	$mg\cdot(kg\cdot d)^{-1}$	$3.6\times10^{-3}/4.2\times10^{-4}$	[37]
Zn	$mg\cdot(kg\cdot d)^{-1}$	$0.3/6\times10^{-2}$	[38]
Slope factor (SF) oral/dermal			
As	$kg\cdot d\cdot(mg)^{-1}$	1.5/3.66	[39]
Cr(VI)	$kg\cdot d\cdot(mg)^{-1}$	0.5/20	[26]

5×10^{-2}, 1.3×10^{-2}, 2.5×10^{-2} and 7×10^{-2} for Cd, Cr(III), Cr(VI), and Hg respectively [27-29]. To determine the overall potential for non-carcinogenic health effects from exposure to lake water, the calculated HQ for every individual element i was added to determine the Hazard Index (HI) for each exposure route was calculated using Eq. 7.

$$HIi = HQ_1 + HQ_2 + HQ_3 + \cdots + HQ_n \quad (7)$$

...when HQ≥1, heavy metals and metalloids may be related to a likely non-carcinogenic risk. The overall cancer risk (CR) from exposure to all individual elements in lake water was calculated by Eq. 8 [24].

$$CR = CDIi \times SFi \quad (8)$$

The values of slope factors are shown in Table 1. The SF_{dermal} for Cr(VI) was calculated by using Eq. 9 [27].

$$SFdermal = \frac{SForal}{GIABS} \quad (9)$$

At places where the concentrations of the measured metals and metalloid were lower than the MDL of ICPMS and UV Spectrophotometer, one-half the values of MDL were used for risk assessment calculations [30]. Since Cr(VI) was observed below analytical detection limits in all samples collected in the pre-monsoon season, as such carcinogenic and non-carcinogenic risks due to Cr(VI) in pre-monsoon season have not been considered.

Principal Components and Cluster Analyses

Principal component analysis (PCA) was used to develop fewer sets of components or factors that helped to investigate the relationships of the concentration of the metals. The number of components were identified using Eigenvalues coupled with parallel analysis. Kaiser-Meyer-Olkin (KMO) measure was used to confirm the sampling adequacy. Bartlett's Test was used to check if the correlation matric was significantly different from the identity matrix. Varimax rotation method was employed to identify the variables with high loading factors in each component. Hierarchical Cluster analysis (CA) was also performed to develop clusters of closely associated heavy metals using Ward's method. PCA and CA were performed using the Statistical Package for Social Sciences (SPSS).

Results and Discussion

Temporal Variations of Trace Metals and a Metalloid

Higher seasonal variability in water quality was observed due to more rainfall during the study period. The mean concentrations and standard deviations of metals and a metalloid observed in Manchar Lake water by season are shown in Table 2. The highest concentrations of metals and the metalloid were noted at site 1, which is the inlet point of the lake represents the pollution status of MNVD which is the primary source of lake pollution.

It was observed that the overall concentrations of metals and the metalloid in water samples were in the order of Fe>Cr(III)>Ni>Pb>Zn>As >Cu>Mn>Cd>Hg>Cr(VI), Fe>Ni>Cr(III)> Pb>Zn>Cu >As>Mn>Cd>Hg>Cr(VI), and Fe>Zn>Pb>Mn >Cu>Ni >As>Cr(III)>Cd>Hg>Cr(VI) during pre-monsoon, monsoon and post-monsoon seasons, respectively. The observed highest mean concentrations (µg/l) of As (43.2), Cr III (101.4), Cu (43.12), Cd (18.5), Fe (318), Hg (6.8), Mn (27.2), Ni (99.7), Pb (65.91) and Zn (41) at various sampling locations in pre-monsoon and Cr(VI) (0.2) in monsoon seasons were more likely attributed to the anthropogenic activities including domestic wastewater discharges and irrigation return flows through MNVD.

Overall, the measured concentrations were observed to follow a trend of pre-monsoon>monsoon>post-monsoon, regardless of the sampling locations. It might be due to low water levels during the pre-monsoon season, with no freshwater inflows and continuous entry of pollution from MNVD, which thereby increases the overall concentrations of the trace elements. Similar findings were observed by Saleem et al. [18] that higher freshwater inflows due to rainfall during monsoon and post-monsoon season mix a considerable volume of non-contaminated water with the contaminated water to reduce total metal concentrations. Around 80% of annual rainfall in this region falls during monsoon season, which may dilute pollutants [18]. It is also interesting to note that due to an uneven rainfall pattern, the lake does not necessarily receive sufficient volume of freshwater each year. The average concentrations of heavy metals and the metalloid in lake water were compared with their respective permissible limits and it was observed that the concentration of As, Cd, Cr(III), Hg, Ni and Pb were higher than permissible limits in pre-monsoon season; whereas As, Cd, Ni and Pb exceeded permissible limits in monsoon season. However, in post-monsoon season trace elements were observed within permissible limits, since rainfall continued in post-monsoon the year this study was conducted and the findings are in agreement with Mastoi et al. [13].

Average trace elements concentrations in Manchar Lake water were compared with previously reported literature on Manchar lake, and other Pakistani lakes reported levels in agricultural and municipal wastewater impacted lakes. In Manchar Lake, the concentrations of Cd, Cu, Mn, Ni, Pb and Zn were observed lower than the concentrations reported in other Pakistani lakes in all seasons, with one exception of lower concentrations of Cd, Cu, Mn, Ni and Zn in

Table 2. Observed concentrations (μg·L^{-1}) of trace metals and metalloid (average ± standard deviation) in Manchar Lake water compared with other Pakistan lakes, and acceptable water quality guidelines.

Locations	As	Cd	Cr III	Cr VI	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Manchar Lake [a]											
Pre-Monsoon	17.5±8.1	6.2±2.6	78.3±12.2	0.0±0.0	16.3±7.9	197.1±67.8	3.00±1.47	11.6±5.7	57.4±13.9	25.4±13.3	24.3±8.3
Monsoon	9.9±4.4	2.22±0.86	13.4±14.86	6.05±2.55	9.41±5.12	108.55±39.2	0.60± 0.52	6.1±2.97	24.5±7.6	15.4±7.9	14.85±5.81
Post-Monsoon	2.7±0.5	0.52±0.44	1.72±1.61	0.64±0.34	2.17±1.73	84.93±30.01	0.03± 0.07	2.67±2.50	1.91±1.6	4.31±4.08	8.38±5.01
Mangla Lake [b]											
Pre-monsoon	-[f]	40.2	-	-	30.5	151	-	17.4	134	394	28.9
Monsoon	-	34.3	-	-	26.6	120	-	16.1	117	330	23.6
Post-monsoon	-	23.7	-	-	22.1	135	-	10.6	93.2	287	21.4
Rawal Lake [b]											
Pre-monsoon	-	6.1	-	-	9.9	79.5	-	3.8	41	139	14.9
Monsoon	-	8.8	-	-	10.6	103	-	9.3	54	202	16.5
Post-monsoon	-	26.7	-	-	18.7	73.2	-	11.2	62	232	23.9
Simly Lake [b]											
Pre-monsoon	-	23.3	-	-	63.1	201	-	43.2	77	312	50.1
Monsoon	-	19.9	-	-	45.5	146	-	33.1	49	267	34.8
Post-monsoon	-	16.9	-	-	22.2	60.7	-	14.2	35	202	25.5
Khanpur Lake [c]											
	-	20	-	-	9	51	-	11	-	221	15

a. This study; b. Saleem et al., 2019; c. Iqbal and Shah, 2014; d. Grey shaded cells exceeded [32, 42] limits in μg·L^{-1} of: As = 10, Cd = 3, Cr(III) and Cr(VI) = 50, Cu = 2000, Fe = 300, Mn = 400, Ni = 200, Pb = 10, Hg = 1, and Zn = 10000; e. Dark Grey shaded cells exceeded Pakistan [43] limits in μg·L^{-1} of: As = 50, Cd = 10, Cr(III) and Cr(VI) = 50, Cu = 2000, Fe = no limit promulgated, Mn = 500, Ni = 20, and Pb = 50, Hg = 1, and Zn = 5000; f. "-" indicates no data available

Table 3. Pollution assessment indices for trace elements in the Manchar Lake water.

	HEI			C_{deg}		
	Pre-Monsoon	Monsoon	Post-Monsoon	Pre-Monsoon	Monsoon	Post-Monsoon
	$\frac{M_i}{M_{\mathrm{ACi}}}$			$\frac{M_i}{M_{\mathrm{ACi}}} - 1$		
As	1.750	0.990	0.270	0.750	-0.010	-0.730
Cd	2.067	0.740	0.173	1.067	-0.260	-0.827
Cr(III)	1.566	0.268	0.034	0.566	-0.732	-0.966
Cr(VI)	0.000	0.121	0.013	-1.000	-0.879	-0.987
Cu	0.016	0.009	0.002	-0.984	-0.991	-0.998
Fe	0.986	0.543	0.425	-0.015	-0.457	-0.575
Hg	3.000	0.60	0.030	2.000	-0.400	-0.970
Mn	0.232	0.122	0.053	-0.768	-0.878	-0.947
Ni	2.870	1.225	0.096	1.870	0.225	-0.905
Pb	16.933	10.267	2.873	15.9	9.27	1.87
Zn	2.430	1.485	0.838	1.430	0.485	-0.162
Total	31.850	16.370	4.808	20.850	5.370	-6.192

Rawal Lake during pre-monsoon season [18, 42]. In contrast, the Fe concentrations were higher in Manchar Lake than the levels reported in other Pakistan Lakes, except higher in Mangla lake during post-monsoon and the Simly lake during monsoon [18, 42]. However, the concentrations of Fe observed during the study period have been significantly lower than reported by Arain et al. [15], but is in agreement with Jahangir et al. [12]. The concentrations of trace elements including As, Fe, Pb and Zn as reported by Arain et al. [15] were observed as reduced, while Cr, Mn and Ni were increased. However, no significant differences were observed in the concentrations of Cd and Cu as shown in Table 2.

Pollution Assessment

The pollution evaluation indices for trace metals and the metalloid in Manchar Lake water are shown in Table 3. The C_{deg} results revealed high levels of pollution (i.e., >3) in Manchar Lake water in the pre-monsoon and monsoon seasons but low-level contamination (i.e., less than 1) in the post-monsoon season. This is likely due to the lower concentrations of Pb in the post-monsoon season. However, using HEI, a high level of pollution (i.e., HEI>20) was observed in the pre-monsoon season, medium-level pollution in monsoon (i.e., 10-20) and a low level of pollution in post-monsoon (i.e., less than 10).

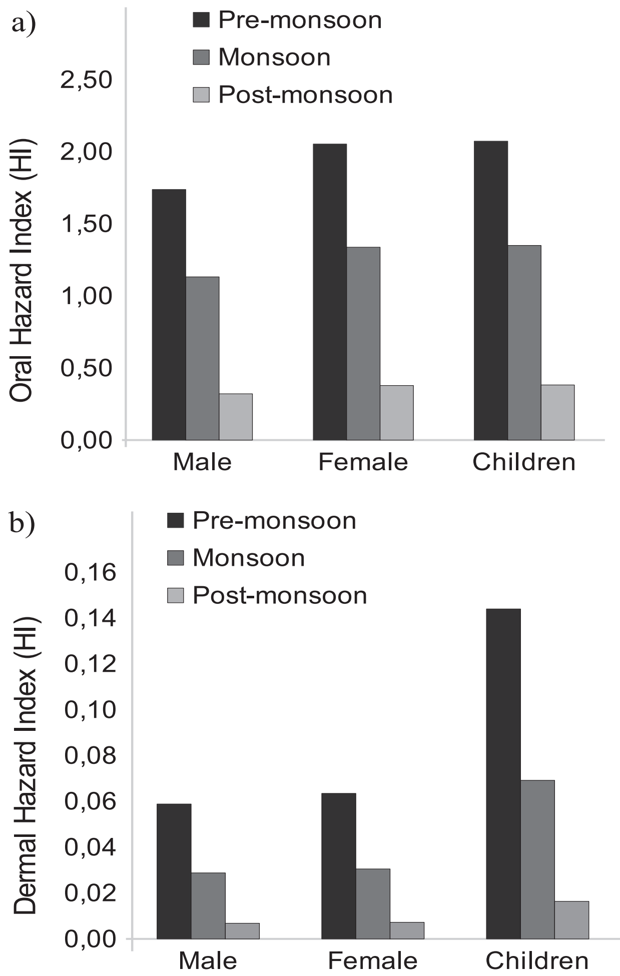

Fig. 2. Hazard index (HI) values for male, female and children in three seasons. a) Oral Hazard Index, b) Dermal Hazard Index.

Health Risk Assessment

Non-Carcinogenic Health Risk Assessment

Ingestion and dermal absorption are regarded as the most critical impact paths of heavy metals and metalloid for human health. The oral hazard quotient (HQ_{oral}) and dermal hazard quotient (HQ_{dermal}) from exposure to water polluted with heavy metals and the metalloid were computed for male, female, and children separately for each season as shown in Fig. 2. The HI for each location was calculated as it is expected that the populations are usually using water near their residence. Generally, the absolute non-carcinogenic risk from exposure to Manchar Lake water arises from the consumption of water for drinking, as HI was >1. However, if the populations were to use an alternate source of drinking water and were only exposed to the water for recreation, bathing or washing, the non-carcinogenic risk from dermal contact was observed as acceptable for all males, females, and children.

Carcinogenic Health Risk Assessment

Cancer risk is defined as an increase in the probability that individuals will develop cancer over a lifetime due to exposure to a potentially carcinogenic substance [38]. The carcinogenic risk from exposure to water contaminated with Cr(VI) and As for male, female and children from oral and dermal paths of exposure were calculated as shown in Fig. 3. The major carcinogenic risk arises from oral exposure to As in water that is used for drinking with the probability of cancer risk exceeding 10^{-4} to 10^{-6} individuals for all males, females and children in all seasons. However, the cancer risk from Cr(VI) exists only in monsoon season. Nonetheless, if the lake water was used only for recreation, washing or bathing purposes, the likelihood of cancer exceeds 1 in 1,000,000 individuals except at location 1 in the pre-monsoon season. Therefore, the water cannot be considered fit to use in drinking.

Relationships and Associations between Heavy Metals

All three data sets including pre-monsoon, monsoon, and post-monsoon, were separately analyzed using PCA. The results of Kaiser-Meyer-Olkin (KMO) Measure of sampling adequacy and Bartlett's Test of Sphericity are shown in Table 4, confirm that the data is suitable to run PCA and investigate the principle components of each data set and their associated

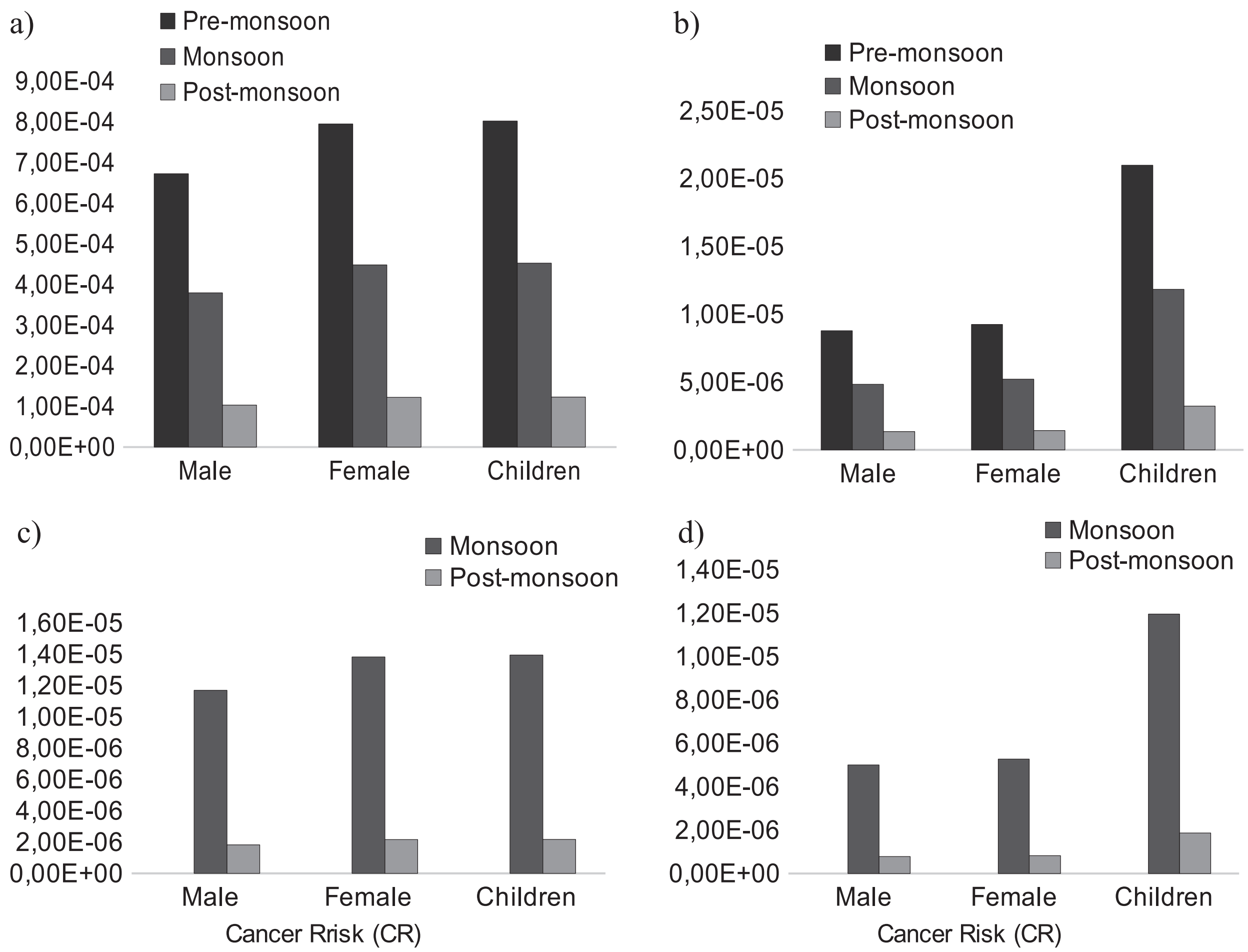

Fig. 3. Oral and dermal carcinogenic risk (plots a, b, c, and d,) from exposure to As and Cr(VI) in Manchar Lake water.

Table 4. Component loading matrix of pre-monsoon, monsoon and post-monsoon metal concentration.

	Pre-monsoon				Monsoon				Post-monsoon		
	Components				Components				Components		
Metals	PC-1	PC-2	PC-3	Metals	PC-1	PC-2	PC-3	Metals	PC-1	PC-2	PC-3
Mn	0.848			Ni	0.828			Pb	0.748		
Cd	0.761			Cu	0.603			Mn	0.73		
As	0.685			As	-0.585			Hg	0.696		
Ni		0.815		Fe	0.564			Ni	0.589		
Fe		0.618		Cd		-0.700		Fe		-0.769	
Cu		0.573		Mn		0.664		Zn		0.629	
Cr(III)		0.531		Pb		0.584		Cd		0.557	
Hg			0.703	Zn		-0.476	0.408	As		-0.411	
Zn			0.688	Hg			0.775	Cu			0.836
Pb			0.523	Cr(III)			0.718	Cr(III)			0.825
KMO Measure for sampling			0.628	KMO Measure for sampling			0.570	KMO Measure for sampling			0.567
Bartlett's Test of Sphericity (Chi-Square value)			154.443	Bartlett's Test of Sphericity (Chi-Square value)			83.056	Bartlett's Test of Sphericity (Chi-Square value)			120.125
		P-value	0.000			P-value	0.000			P-value	0.000

characteristics. Three principal components of data of each season were determined using Eigenvalues >1 of the principal components followed by parallel analysis to keep a certain number of principal components. The principal components of pre-monsoon data explain more than 58% of the total variance, while the principal component of monsoon data explains about 51% and in post-monsoon explains about 55% of the total variance.

Considering the PCs of pre-monsoon data, PC1 explained about 28% of the total variance with a high loading of Mn, Cu, and As. However, PC2 explained around 17% of the variance with a high loading of Ni, Fe, Cu and Cr(III), while PC3 explained around 14% of the total variance with a high loading of Hg, Zn and Pb as shown in Table 4. There is a negligible volume of freshwater flows into the lake during the pre-monsoon season; however, MNVD is the major source of pollutant influx from upstream. Besides, there is a certain level of pollutant influx into the lake from the surrounding farmlands and communities through drains which could be the possible reasons for correlations of these elements and variance in the water body.

Whereas, in case of monsoon, PC-1 explained 22% with a high loading of Ni, Cu, As and Fe, PC-2 explained 16% with a high loading of Cd, Mn, Pb and Zn, and PC3 explained 12% with a high loading of Hg and Cr(III) as shown in Table 4. These results indicate that As and Cd gets diluted due to freshwater inflow due to monsoon floodwater; however, it is essential to know that monsoon flood water cause high variability of Ni, Cu, and Fe in the water body of the lake.

PCA results of post-monsoon data analysis indicate that PC-1 explained 22% of the variance with a high loading of Pb, Mn, Hg, and Ni, PC-2 explains 21% of the variance with a high loading of Cu and Cr(III), and PC3 explained 13% of the variance with a high loading of Fe, Zn and Cd as shown in Table 4. Post-monsoon variances of the metal concentration are the upshots of pollutants influx from upstream through monsoon floodwater.

Cluster analysis helps to determine the associations and similarities among trace elements and identifies homogenous groups of trace elements which are mutually correlated in the given data set. The dendrogram shown in Fig. 4 represents different clusters of the correlated heavy metals within each season separately (i.e., pre-monsoon, monsoon and post-monsoon). During pre-monsoon, cluster-1 represents Cd, Mn, As, Cd and Zn with Hg. All four heavy metals in this cluster except As, are potentially being added either from locally untreated wastes into the lake, while As is possibly coming from geogenic sources. However, Ni, Pb make cluster with Cu and Fe. In terms of monsoon concentration, Cu, Ni, Fe, Mn and Pb were observed as closely correlated and these are mostly from anthropogenic sources. Cr(III), Hg and Zn from another closely associated cluster getting accumulated from anthropogenic sources. The cluster representing Cd and As shows that during monsoon, these metals get diluted. In post-monsoon Cr (III) and Cu show a strong relationship and develop cluster 1 together with Zn and Cd. In cluster 2, Mn, Pb, Hg and Ni represents strong correlations. The third cluster represent Fe and As. The distributon and

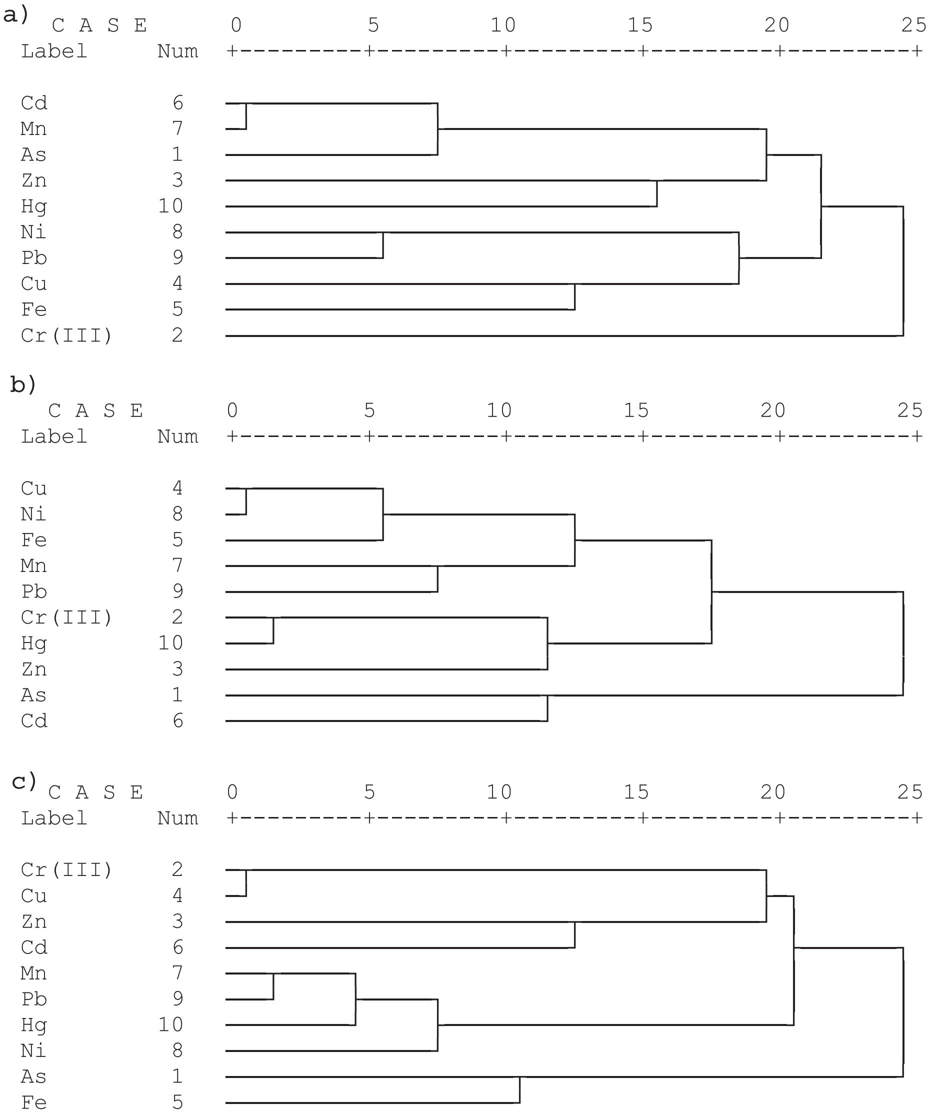

Fig. 4. Dendrogram displaying clusters of heavy metals as per seasons. a) Pre-Monsoon, b) Monsoon, c) Post-Monsoon.

relationship of the metals during post-monsoon depends on the volume and pollution level of drained water inflow into the lake.

Limitations of the Study

Human health risk assessments involve certain uncertainties and variability [43], resulting in under or overestimation of the risks, which necessitates to include a discussion of the limitations associated with such studies. The inconsistency in exposure estimation, like assuming exposure to an entire lifetime, may overestimate the duration of use of the Manchar Lake water and thus overestimated the risk. This study also involves an assumption that receptors do not travel and only use Manchar lake water without any treatment. Due to absence of Pakistan specific population data, exposure factors used in this study for calculations were from USEPA and WHO, which might not fit the real conditions and might led to either over (more skin surface area in USEPA guidelines) or under (excessive body weight in USEPA guidelines) estimation. The use of one half of the detection limit in samples where trace elements were not detected might result in an overestimation of risk. The study did not consider any treatment of the water before its use as drinking water. However, the use of RO plants, 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.

Conclusions

In this study, the seasonal variability in heavy metals and metalloid concentration in Manchar Lake water has been observed. The anthropogenic wastewater inflow from the settlements and farmlands comprise a constant polluting source, whereas only monsoon rainfall-runoff occurs within the catchment might contribute a certain amount of metals from natural sources through water inflow into the lake. Results revealed that As, Cd, Cr(III), Hg, Ni, and Pb concentration are exceeding the recommended drinking water standards. Pollution assessment indices suggested a high level of pollution in the pre-monsoon season, medium-level pollution in monsoon and low level of pollution in post-monsoon due to dilution caused by freshwater inflows. Depending upon the amount of precipitation in a year, this medium and low-level pollution occurs only for a few months and then the concentrations start increasing. Being in the arid region, this high level of pollution remains for many months during the year. The health risk assessments based on average concentrations suggest the potential for adverse carcinogenic and non-carcinogenic effects on individuals using the water for drinking purposes. Nevertheless, water used for recreation, bathing or washing poses risk within the tolerable range. Overall, the results suggest that there is a need to manage and regulate the toxic pollutants entering the Manchar Lake, mainly from agricultural runoffs and urban domestic waste discharges, entering the lake through MNVD. The findings of this study will also inform residents and visitors to the lake regarding possible health threats from exposure to metal-contaminated water.

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Conflict of Interest

The authors declare no conflict of interest.

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