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# Non-carcinogenic Health Risk Assessment and Source Apportionment of Selected Metals in Source Freshwater Khanpur Lake, Pakistan

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**Abstract** Selected metals (calcium, cadmium, cobalt, chromium, copper, iron, potassium, lithium, magnesium, manganese, sodium, lead, strontium and zinc) were measured in water samples from a source freshwater Lake. Average levels of cadmium, cobalt, chromium and lead in the waters were significantly higher than the guideline values. Health risk assessment was then carried out to determine health risk via oral route and dermal contact. Hazard quotient (via ingestion) levels of cadmium, cobalt, chromium and lead were higher than unity; suggesting potential adverse effects on local residents. Principal component analysis revealed considerable anthropogenic contributions of the metals in the water reservoir.

**Keywords** Freshwater · Risk Assessment · Metal · Multivariate Analysis

The demand for fresh water has considerably increased all around the world mainly due to the population growth, socioeconomic development, technological and climatic changes. The lack of clean drinking water is adversely affecting the general health and life expectancy of the people (Ayers and Westcot 1994). The quality and quantity of surface water bodies, such as, lakes depend upon the climate, catchments, geography of the area, the geologic and anthropogenic inputs/outputs. The water quality can be degraded due to agricultural runoff and drainage as well as industrial and municipal wastewater. Trace metals are one of the most important pollutants in the aquatic ecosystem (Goldhaber 2003; WHO 2008). Prolonged exposure to the metals can result in bioaccumulation and cause numerous health problems. Elevated levels of toxic metals in drinking water have been associated with metabolic/gastrointestinal disorders, in addition to cytotoxic, neurotoxic and carcinogenic effects (WHO 2008). The monitoring and assessment of water quality of freshwater lakes such as Khanpur near Islamabad, Pakistan is, therefore, crucial in order to assess the risks to humans, and aquatic life consuming the water.

The objective of the current study was to assess the water quality of Khanpur Lake and to compare the observed levels of physicochemical parameters and selected metals (Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Pb, Sr and Zn) with the corresponding WHO and other guideline values. Then potential non-carcinogenic health risks associated with exposure to the selected metals via oral ingestion and dermal absorption were evaluated. Multivariate methods were used for the source apportionment and identification of the selected metals in the freshwater reservoir. It is anticipated that the study would be helpful in the management and control of the pollutants in the lakes.

## Materials and Methods

Khanpur Lake (longitude:72°56′E and latitude:33°48′N) is located on the Haro river near the town of Khanpur, about 40 km north-west of Islamabad, Pakistan. It supplies drinking water to Islamabad and Rawalpindi and irrigation water to the agricultural areas surrounding the cities. It was constructed in 1983 with the storage capacity of 140 million cubic meter of water. It is 51 m high with average depth of 15 m. The gross storage of the reservoir is

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0.132 $km^3$ with a total catchment area of 798 $km^2$. The surface area of reservoir varies from maximum of 1,806 ha to minimum of 215 ha. In past, the Lake has been leased for commercial exploitation. The area around the Lake has been planted with flowering trees and laid out with gardens, picnic spots, and secluded path.

A total of 50 surface water samples from the depth of 0.5–1.5 m were collected in triplicate in pre-cleaned and dried containers from Khanpur Lake in May 2009, following the standard procedure (APHA 1995). Each water sample was divided into two parts: one part was stored as such for the measurement of physicochemical parameters while, other part was preserved by acidifying with concentrated nitric acid (AR grade) to $pH < 2$ for the metal analysis (US EPA 2003). Sampling bottles were kept in airtight large plastic ice-cold containers at 4°C and were transported to laboratory within 6 h of their collection for further processing. Temperature (T), pH, dissolved oxygen (DO), electrical conductivity (EC) and total dissolved solids (TDS) were determined immediately after the sample collection, while, chloride contents ($Cl^-$) and total alkalinity (TA) were estimated by titrimetry (APHA 1995; Radojevic and Bashkin 1999). Selected metals (Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Pb, Sr and Zn) in water samples were analyzed using flame atomic absorption spectrophotometer (Shimadzu AA-670, Japan) under optimum analytical conditions, employing the calibration line method. The metal standards were prepared from stock solutions of 1,000 mg/L by successive dilutions. A blank consisting of doubly distilled water was processed in the same manner along with each batch. Standard reference material (SRM 1643d) was also used to ensure the reliability of the metal data. All the measurements were made in triplicate (Fig. 1).

Statistical methods were applied to process the analytical data in terms of its distribution and correlation among the studied parameters. STATISTICA software was used for the computation of the data. Basic statistical parameters such as, minimum, maximum, mean, standard error (SE) and skewness were calculated, while multivariate statistics in terms of principal component analysis (PCA) was also carried out using varimax normalized rotation on the dataset (Shah et al. 2011). PCA is mainly used for data reduction and it aims at finding a few components that explain the major variation within the data.

## Results and Discussion

The descriptive statistics related to the distribution of physicochemical parameters and selected metals in the water samples from Khanpur Lake is given in the Table 1. The pH values varied from 7.860 to 8.280 with a mean value of 8.176, which were within the permissible limit for drinking water as per WHO, US-EPA and Pak-EPA guidelines. However, the measured pH values were higher than background values, indicating alkaline nature of the water samples. In present study, T of the water samples ranged from 17.2 to 17.9°C with an average value 17.7°C, whereas, the DO contents of water ranged from 5.87 to 6.66 mg/L with an average value of 6.13 mg/L. Generally, warm-water aquatic ecosystem should have more than 5 mg/L DO levels in order to support the diversified biota (Radojevic and Bashkin 1999). In the present study, TA values ranged from 138 to 207 mg $CaCO_3$/L with an average value of 168 mg $CaCO_3$/L. The EC values varied from 296 to 321 μS/cm with a mean value of 311 μS/cm

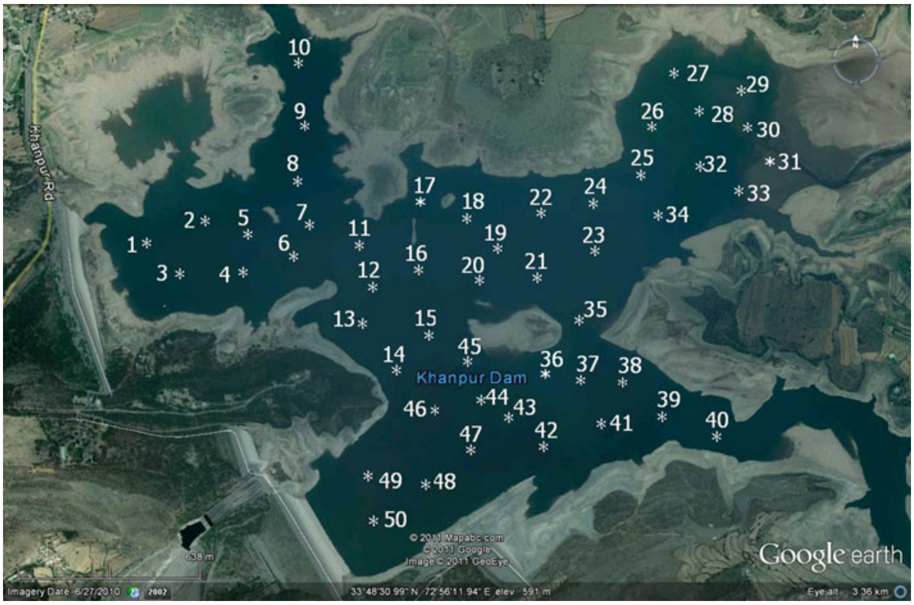

**Fig. 1** Location of the sampling sites (*asterisk*) in the Lake

**Table 1** Statistical summary for physicochemical parameters and selected metal levels in water samples and comparison with standard/guideline and background (BG) values

| | Min | Max | Mean | SE | Skew | WHO | US EPA | Pak EPA | BG |
|---|---|---|---|---|---|---|---|---|---|
| pH | 7.860 | 8.280 | 8.176 | 0.014 | −1.729 | 6.5–8.5 | 6.5–8.5 | 6.5–8.5 | 6.5–6.9 |
| T (°C) | 17.2 | 17.9 | 17.7 | 0.023 | −0.891 | – | – | – | – |
| DO (mg/L) | 5.87 | 6.66 | 6.13 | 0.026 | 1.164 | – | – | – | – |
| EC (μS/cm) | 296 | 321 | 311 | 0.680 | −0.510 | 1,500 | – | – | 205–830 |
| TDS (mg/L) | 149 | 161 | 156 | 0.357 | −0.203 | 1,000 | 500 | 1,000 | 1,600–6,300 |
| TA (mg $CaCO_3$/L) | 138 | 207 | 168 | 1.904 | 0.656 | 200 | – | – | – |
| $Cl^-$ (mg/L) | 5.890 | 16.50 | 10.33 | 0.319 | 0.466 | 250 | 250 | 250 | – |
| Ca (mg/L) | 14.33 | 18.29 | 16.50 | 0.147 | −0.439 | 100 | – | 200 | 12.6 |
| Cd (mg/L) | 0.003 | 0.069 | 0.034 | 0.002 | −0.070 | 0.003 | 0.005 | 0.001 | 0.006 |
| Co (mg/L) | 0.081 | 0.848 | 0.303 | 0.021 | 1.360 | 0.04 | – | – | 0.044 |
| Cr (mg/L) | 0.008 | 0.519 | 0.241 | 0.020 | 0.146 | 0.05 | 0.1 | 0.05 | 0.015 |
| Cu (mg/L) | 0.003 | 0.100 | 0.046 | 0.003 | 0.033 | 2.0 | 1.3 | 2.0 | 0.029 |
| Fe (mg/L) | 0.020 | 0.623 | 0.255 | 0.020 | 0.460 | 0.3 | 0.3 | – | 0.013 |
| K (mg/L) | 2.161 | 2.993 | 2.570 | 0.032 | 0.054 | 12 | – | – | 0.64 |
| Li (mg/L) | 0.001 | 0.055 | 0.016 | 0.002 | 1.367 | – | – | – | 0.003 |
| Mg (mg/L) | 13.04 | 16.96 | 15.23 | 0.133 | −0.412 | 50 | – | – | 6.41 |
| Mn (mg/L) | 0.004 | 0.217 | 0.077 | 0.008 | 0.850 | 0.1 | 0.05 | 0.5 | 0.016 |
| Na (mg/L) | 4.832 | 6.782 | 5.784 | 0.051 | −0.192 | 200 | – | – | 6.47 |
| Pb (mg/L) | 0.291 | 1.068 | 0.565 | 0.025 | 0.547 | 0.01 | 0.015 | 0.05 | 0.059 |
| Sr (mg/L) | 1.041 | 1.260 | 1.148 | 0.008 | 0.096 | – | – | – | – |
| Zn (mg/L) | 0.025 | 0.098 | 0.063 | 0.003 | 0.219 | 3.0 | 5.0 | 5.0 | 0.019 |
| Ref. | Present study | | | | | WHO (2008) | US EPA (2009) | Pak EPA (2008) | Shah et al. (2011) |

which were below the recommended limit of WHO and background levels, demonstrating the suitability of water samples for the drinking purpose. The minimum–maximum levels of TDS were 149–161 mg/L containing an average value of 156 mg/L, which were within the acceptable levels of international and national standards, indicating low content of soluble salts in the water samples which can be safely used for drinking purpose. Likewise, the $Cl^-$ levels were also within the permissible limits of international and national standards.

Among the selected metals, Ca (16.50 mg/L) and Mg (15.23 mg/L) showed the dominant contributions, followed by Na (5.784 mg/L) and K (2.570 mg/L), while Sr (1.148 mg/L), Pb (0.565 mg/L) and Co (0.303 mg/L) exhibited relatively low concentrations. The water samples were observed to have lowest levels of Cu (0.046 mg/L), Cd (0.034 mg/L) and Li (0.016 mg/L), while the average levels of Fe, Cr, Mn and Zn were slightly higher. Based on mean values in water samples, the selected metals followed the decreasing concentration order: Ca > Mg > Na > K > Sr > Pb > Co > Fe > Cr > Mn > Zn > Cu > Cd > Li. The average levels of Cd, Co, Cr and Pb were examined elevated than the acceptable limits set by national and international authorities (WHO 2008; US EPA 2009; Pak EPA 2008). It elaborated that the waters were unsuitable for drinking due to gross pollution of toxic metals like Cd, Co, Cr and Pb. However, the average levels of the remaining metals were found to be lower than the permissible levels. Nevertheless, mean values of most of the metals were detected elevated than the background levels ($p < 0.05$). Cd, Cu and Mg exhibited relatively lower values of skewness, indicating normal/Gaussian distribution in the water samples. The remaining metals exhibited relatively higher dispersion and random distribution. Maximum disperse in terms of elevated SE was exhibited by Ca, Mg, Na, K and Pb. Comparatively broad spread was observed for Cr, Li and Mn, followed by Fe, Cu, Cd, Co, Pb and Zn, which manifested inconsistent and varying levels of these metals.

The correlation data pertaining to water samples indicated significantly strong correlations between Sr and Na (r = 0.999), while significant correlation was observed between Ca–Cd (r = 0.513), Ca–K (r = 0.478), Ca–Cr (r = 0.475) and Ca–Cu (0.497). This indicated that Ca had a strong association with Cd, K, Cr and Cu statistically, and it may share a common origin with them. Other positively correlated relationships such as K–Cd, Cu–Cr and Mn–Co were also examined. The sources of these metals would further be investigated by multivariate statistics. Some of the metals revealed inverse relationships such as Fe with

Pb and Zn, and Mn with Cd, Ca and K; indicating their opposing distribution in the water samples.

The multivariate PCA was employed in order to understand the multiple relationships and apportionment among the metals in water samples. The principal component loadings for the metals in water samples are shown in Table 2. Five principal components (PCs) with eigen values greater than 1 were extracted, which explained 68.04% of the total variance. PC1 exhibited the positive loadings in the favour of Ca, Cd and K, which were assumed to be contributed by anthropogenic sources like untreated urban waste and agricultural run off. PC2 and PC3 were mainly contributed by Mn–Sr–Na and Co–Fe–Li–Mg, respectively. These metals were believed to be contributed by natural sources like rock weathering and soil erosion. PC4 and PC5 exhibited the elevated loadings of Cr–Cu and Pb–Zn, respectively. These metals were believed to be contributed by anthropogenic intrusion like agricultural run off, untreated municipal and industrial wastes and dry deposition of the suspended particulates in the hydrogeoenvironment.

The human health risk assessment methodology related to water media has been described elsewhere (US EPA 1989, 2004; Li and Zhang, 2010; Wu et al. 2009, 2010; Liang et al. 2011). Exposure of human being to the metals could occur via three main pathways including direct ingestion, inhalation through mouth and nose, and dermal absorption through exposures skin; while, ingestion and dermal absorption are common for water exposure (Wu et al. 2009, 2010; US EPA 1989, 2004). The numeric expressions for risk assessment have been obtained from US EPA Risk Assessment Guidance for Superfund methodology (US EPA 1989).

**Table 2** Principal component loadings for selected metals in water samples

| | PC1 | PC2 | PC3 | PC4 | PC5 |
|---|---|---|---|---|---|
| Eigen value | 3.123 | 1.797 | 1.774 | 1.499 | 1.333 |
| % Total variance | 22.30 | 12.84 | 12.67 | 10.71 | 9.524 |
| % Cumulative variance | 22.30 | 35.14 | 47.81 | 58.52 | 68.04 |
| Ca | 0.514 | 0.144 | 0.065 | 0.708 | −0.211 |
| Cd | 0.561 | 0.445 | −0.343 | 0.282 | 0.072 |
| Co | −0.465 | 0.392 | 0.575 | −0.148 | 0.077 |
| Cr | 0.442 | −0.167 | 0.097 | 0.586 | 0.032 |
| Cu | −0.240 | 0.043 | −0.064 | 0.895 | −0.091 |
| Fe | 0.117 | −0.043 | 0.759 | 0.215 | −0.049 |
| K | 0.770 | 0.125 | −0.012 | 0.068 | 0.063 |
| Li | −0.122 | −0.253 | 0.516 | −0.254 | 0.046 |
| Mg | 0.194 | 0.162 | 0.565 | 0.069 | 0.562 |
| Mn | −0.532 | 0.665 | 0.160 | −0.014 | −0.124 |
| Na | −0.319 | 0.564 | 0.138 | −0.111 | −0.126 |
| Pb | 0.041 | −0.070 | −0.086 | −0.164 | 0.861 |
| Sr | −0.045 | 0.730 | −0.180 | 0.207 | −0.011 |
| Zn | 0.071 | −0.132 | 0.192 | −0.304 | 0.804 |

$$\mathrm{Exp_{ing}} = \frac{\mathrm{C_{water} \times IR \times EF \times ED}}{\mathrm{BW \times AT}} \tag{1}$$

$$\mathrm{Exp_{derm}} = \frac{\mathrm{C_{water} \times SA \times K_p \times ET \times EF \times ED \times CF}}{\mathrm{BW \times AT}} \tag{2}$$

where, $\mathrm{Exp_{ing}}$—exposure dose through ingestion of water (μg/(kg day)); $\mathrm{Exp_{derm}}$—exposure dose through dermal absorption (μg/(kg day)); $\mathrm{C_{water}}$—concentration of metals estimated in surface waters (μg/L); IR—ingestion rate (2.2 L/day); EF—exposure frequency (365 day/year); ED—exposure duration (30 year); BW—average body weight (70 kg); AT—averaging time (25,550 day); SA—exposed skin area (18,000 $\mathrm{cm^2}$); ET—exposure time (0.58 h/day); CF—unit conversion factor (0.001 $\mathrm{L/cm^3}$); and Kp—dermal permeability coefficient (0.001 for Cd, Cu, Fe, Li and Mn; 0.004 for Co and Pb; 0.002 for Cr; and 0.0006 for Zn). These parameter values were taken from reference values or statistical data of local population (US EPA 2004; Wu et al. 2009).

The characterization of non-carcinogenic risks such as hazard quotients (HQ) and hazard index (HI) was carried out using US EPA guidelines (US EPA 1989, 2004):

$$\mathrm{HQ_{ing/derm}} = \frac{\mathrm{Exp_{ing/derm}}}{\mathrm{RfD_{ing/derm}}} \tag{3}$$

$$\mathrm{HI_{ing/derm}} = \sum_{i=1}^{n} \mathrm{HQ_{ing/derm}} \tag{4}$$

where, $\mathrm{HQ_{ing/derm}}$ refers to hazard quotient via ingestion or dermal contact; $\mathrm{HI_{ing/derm}}$ shows hazard index via ingestion or dermal contact; and $\mathrm{RfD_{ing/derm}}$ denotes oral/dermal reference dose (μg/kg/day).

Non-carcinogenic health risk assessment summary for the selected metals in the water samples from Khanpur Lake via ingestion and dermal routes is given in Table 3. The observed mean levels of $\mathrm{Exp_{ing}}$ and $\mathrm{Exp_{derm}}$ were found in the order of Sr > Pb > Co > Fe > Cr > Mn > Zn > Cu > Cd > Li and Cr > Sr > Fe > Pb > Co > Mn > Cu > Zn > Cd > Li, respectively, in the water samples. The results manifested that Cr, Sr, Pb and Co were major contributors to chronic exposures to the inhabitants, while Li and Cd were found to be the least participants via oral and dermal paths. Cd, Co, Cr and Pb ($\mathrm{HQ_{ing}} > 1$) posed adverse hazards and potential non-carcinogenic health risks to the consumers, while rest of the metals posed little or no adverse effects via ingestion path. However, the mean levels of $\mathrm{HQ_{derm}}$ for the selected metals were found to be lower than safety limit unity, indicating that the selected metals posed little or no adverse effect and non-carcinogenic health risk to

**Table 3** Summary of health risk assessment for selected metals in water samples

| | $^{a}RfD_{ing}$ (µg/kg/day) | $^{a}RfD_{derm}$ (µg/kg/day) | $Exp_{ing}$ | $Exp_{derm}$ | $HQ_{ing}$ | $HQ_{derm}$ |
|---|---|---|---|---|---|---|
| Cd | 0.5 | 0.025 | 1.081 | 2.1E−03 | 2.162 | 8.4E−02 |
| Co | 0.3 | 0.06 | 9.525 | 7.4E−03 | 31.75 | 1.2E−01 |
| Cr | 3 | 0.075 | 7.566 | 3.0E−02 | 2.522 | 3.9E−01 |
| Cu | 40 | 8 | 1.444 | 2.8E−03 | 0.036 | 3.5E−04 |
| Fe | 700 | 140 | 8.006 | 1.6E−02 | 0.011 | 1.1E−04 |
| Li | 2 | 1 | 0.487 | 9.5E−04 | 0.244 | 9.5E−04 |
| Mn | 24 | 0.96 | 2.416 | 4.7E−03 | 0.101 | 4.9E−03 |
| Pb | 1.4 | 0.42 | 17.76 | 1.4E−02 | 12.69 | 3.3E−02 |
| Sr | 600 | 120 | 36.10 | 2.8E−02 | 0.060 | 2.3E−04 |
| Zn | 300 | 60 | 1.967 | 2.3E−03 | 0.007 | 3.8E−05 |
| $\sum HI_{ing/derm}$ | | | | | 49.58 | 6.4E−01 |

[a] $RfD_{ing}$ and $RfD_{derm}$ of selected metals from Wu et al. (2009); Li and Zhang (2010); US EPA (2004)

the consumers via dermal contact. $HI_{ing}$ and $HI_{derm}$ were computed to assess the overall non-carcinogenic risk posed by selected metals via ingestion and dermal contact of water as a whole. Among the selected metals, Cd, Cr, Pb and Co were observed to be major contributors to the mean levels of $HI_{ing}$ (49.58), suggesting that these metals deserved serious health concern via ingestion route. However, the mean value of $HI_{derm}$ (0.641) was found to be lower than unity, demonstrating that all the selected metals posed little or no hazard to residents through dermal contacts. Since the largest contributors to chronic non-carcinogenic risk are Cd, Cr, Pb and Co in the present investigation. Therefore, special attention should be paid to manage these toxic metals in the study area.

In conclusions, the present study shows divergent disparity of selected metals in the water samples from the freshwater reservoir. The mean levels of Cd, Co, Cr and Pb were found to be elevated than national and international acceptable levels. Cd, Cu and Mg revealed normal distribution, while the resting metals were found to have asymmetrical distribution. Non-carcinogenic health risk assessment revealed that Cd, Cr, Co and Pb would pose non-carcinogenic adverse health risks to the inhabitants via ingestion route.

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