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Determination of heavy metals in surface water, sediments and planktons at the junction of multiple rivers (Punjad Headworks) and their impact on human health

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Abstract:

This study was conducted to calculate the burden of heavy metals i.e., aluminium (Al), arsenic (As), barium (Ba) and lead (Pb) in the river water of Punjnad Headworks, Bahawalpur, Pakistan. For this purpose, samples were collected from surface water, bed sediments and planktons during autumn, winter and spring seasons (September 2018 to May 2019). The results showed that in surface water Pb concentration was highest (453.87 mg L^{-1}), while in sediments and plankton, Al concentration was highest ($370.24 \text{ } \mu\text{g g}^{-1}$ and $315.05 \text{ } \mu\text{g g}^{-1}$, respectively). A significant difference ($p < 0.000$) in metal concentrations was found among surface water, bed sediments and plankton at different sampling stations during various seasons. However, findings of this study showed no adverse effects of heavy metal concentrations on human health. This study provided better understanding of various pollutants and their concentrations in water sources at the studied location.

Keywords: Aquatic toxicity, heavy metals, sediment, plankton, health risk

41 **Highlights**

- 42 • In this study, presence of heavy metals including Al, As, Ba and Pb in surface water,
43 sediments and plankton at rivers junction was determined.
- 44 • Samples were obtained from three different stations of the rivers' junction during
45 autumn, winter, and spring seasons.
- 46 • Pb concentration was highest in surface water, while in sediments and plankton, Al
47 concentration was highest.
- 48 • Although different concentrations of heavy metals were found in collected samples,
49 however no statistically adverse effect were found in human health.

Introduction

Heavy metals generally enter into the aquatic environment through natural or anthropogenic phenomenon. Among these the most important are atmospheric depositions, soil erosion, weathering of the geological matrix and the anthropogenic sources like runoffs, leachates, urban sewer, agricultural production, industrial and urban activities (Ferreira et al. 2020; Zeng et al. 2020). Pollution of the aquatic ecosystem i.e., lake, rivers stream, estuaries and bays by heavy metals has become a global concern and has raised health related issues for human and other living organisms because of their acute and chronic toxicity, bioaccumulation throughout the food chain, non-biodegradability and persistence for longer period of time (Li et al. 2020; Ustaoglu and Islam 2020; Naz et al. 2020). The Agency for Toxic Substances and Disease Registry (ATSDR) has listed As and Pb as the most hazardous heavy metals based on their toxicity, frequency as well as chances for human exposure, while Ba and Al are ranked at 136 and 183 position, respectively (ATSDR 2019). Lead (Pb) is a non-essential metal that has no known biological function and exhibits extreme toxicity. Exposure to Pb for longer period has adverse effects on reproductive efficiency, circulatory and central nervous systems as well as chronic renal insufficiency (Wani et al. 2015). Arsenic (As) is also one of the most toxic elements having adverse effects on human health including liver damage, skin lesions, diabetes, cardiopulmonary outcomes, hypertension, breast and bladder cancer (Khan et al. 2020; Mitra et al. 2020). Arsenic and Pb are among the most dominant pollutants found in different fresh water sources of Pakistan (Bhatti et al. 2019; Mahfooz et al. 2019). Along with As and Pb, toxic levels of Al and Ba were also found in industrial and river water samples in Punjab, Pakistan (Mahfooz et al. 2019). Presence of Ba in polluted water, seafood and freshwater fishes has been reported to affect different physiological systems in human beings including cardiovascular system, renal system, and nervous system (Kravchenko et al. 2014). Aluminium toxicity has also been associated with brain disorders. Higher Al concentration was reported in

patients suffering from Alzheimer's disease and neuroinflammation (Huat et al. 2019). Looking into the importance of heavy metals in different water resources, it is essential to estimate the level of heavy metals in aquatic environment to monitor the quality of the ecosystem for exposure to contaminants and their potential impact on human health and other aquatic organisms.

Heavy metal levels in the aquatic environment are usually determined by assayed of their levels in sediment, water and aquatic organism samples. The main pathway of metal input in aquatic ecosystems is the transport of sediments from upstream to downstream along the river basin, especially during high flow (Dutton et al. 2018). Investigation on sediments for monitoring long-term metal deposition in the ecosystem is more suitable than that of water (MacDonald et al. 2000). Different metals from industrial and agricultural water run-off drain into rivers and canals, ultimately accumulating in sediments (Omwene et al. 2018; Naz et al. 2020). Although, sediments diminish the bioavailability of pollutants by letting them settle down at the bottom of the water source, however, metalloids and heavy metals are trapped in the sediment in various chemical forms. Hence, heavy metals becomes the potential hazard for downstream water sources as these build-up upstream (Heise and Förstner 2007; Islam et al. 2015; Schleiss et al. 2016).

The zooplankton and phytoplankton both serve as a biomarker of metal pollution in water body owing to their capability of accumulating heavy metals in high concentrations (Javed 2006; Yuan et al. 2020). The water quality of a riverine system is largely affected by the direct discharge of nearby industrial effluents (Islam and Mostafa 2018) and concurrently, by the sustainable management of the water sources through implementing legislative policies and effective political control (Howes et al. 2017). Heavy metals were detected in higher concentration in plankton near the riverine water body's coastal area due to the discharge of

untreated waste products of sewerage treatment plants into the rivers (Rezai and Yusoff 2011; Robin et al. 2012).

The higher discharge of numerous metallic compounds into the rivers of Pakistan has adversely affected the freshwater ecosystem (Qadri and Faiq 2020). Being junction of multiple rivers, Punjnad Headworks receives a variety of pollutants from different rivers. Major pollutants include agricultural, domestic and industrial wastes from different cities e.g., Gujarat, Faisalabad, Jhang, Multan etc., which drain out their waste from textile, dying, petrochemical, hosiery, oil refineries, sugar and flour mills, distilleries, tannery industries, rubbers and plastics into the river ecosystem of the Punjnad headworks (Ali et al. 2013; Eqani et al. 2011; Hanif et al. 2016). As the Punjnad headworks was an unexploited region to evaluate heavy metals contamination in a junction of different water sources, therefore, the current study was designed to assess heavy metal concentration and to conduct multivariate relationships among water, sediments and plankton for the flow of heavy metals at three different stations of Punjnad headworks. Based on the results an assessment of the health risk to humans was carried out using some risk assessment parameters.

Materials and Methods

Study area

The Punjnad Headworks is located about 99 m above the sea level. The average annual rainfall, average annual temperature and annual average relative humidity (%RH) were recorded as 3.56 mm, 29.49 °C and 27.64%, respectively. Surface water, bed sediments and plankton samples were collected from three different locations of Punjnad Headworks during three seasons (autumn, winter, and spring). The sampling stations were visited monthly for the study period. In this study, samples was collected from September 2018 to May 2019 from three stations (Station 1: 29°20'31.8"N 71°00'40.8"E; station 2: 29°20'40.0"N 71°01'12.5"E; station 3: 29°20'59.6"N 71°01'21.2"E) (Fig. 1). The sites were selected to observe different levels of

pollutant accumulation. Three replications were conducted during each season at each site for the current study. Nine replications were considered for each experimental factor.

Sample collection and processing

Water samples for heavy metals determination were collected from each study site in acid-washed polyethylene bottles. In the field, the bottles were rinsed several times with the river water and 100 ml of water sample was then collected from 150 cm below the water surface. After that, the water samples were acidified with concentrated hydrochloric acid (HCl, 37%, Merck, Germany) for preservation. The solution was then transferred into a conical flask and heated at 105 °C on a hot plate to evaporate the solution to 25 ml. It was then transferred into a 100 ml volumetric flask and distilled water was added to fill up to the mark where it was filtered with Whatman filter paper# 44 and then transferred to a pre-cleaned sample bottle for Atomic Adsorption Spectrophotometer (AAS) analysis.

Sediment samples of the river were collected with the help of a PVC pipe (5 cm diameter) pressed with pressure through the water column to obtain the sediment layer of about 0.25 m. Polyethylene scoops and cans were used to collect samples from the PVC pipe. Each sample was consisted of 500 ± 20 g of the surface layer from river bed sediments. The samples were kept below 10 °C by placing in ice bags during transportation to the laboratory and then stored in a deep freezer at -20 °C for further analysis. After air-drying for 3 days, the sediment samples were ground into smaller particles. Samples were sieved and run through the digestion process. For the digestion process, 2 g of air-dried sediment sample was weighed and poured into a 100 ml beaker. Five-millilitre hydrogen trioxonitrate acid (HNO₃, 65%, Merck, Germany), 2 ml perchloric acid (HClO₄, 70–72%, Merck, Germany) and 5 ml hydrogen fluoride (HF, 48%, Merck, Germany) was added to the sample according to the Hseu et al. (2002) and then heated for 1 hour at 160 °C. After proper digestion, the sample was allowed to cool down and then filtered properly. The filtrate was transferred into a 100

ml volumetric flask and made up to mark with distilled water. The prepared sample solution was transferred into the pre-cleaned labelled sample bottles in readiness for AAS analysis.

The plankton samples were collected by filtering nearly 100 ± 10 L of water using the plankton net of 10 μm pore capacity and 30 cm in diameter. Sampled plankton was acidified by using HCl and then transferred to the laboratory for analysis. Plankton samples were digested using HNO_3 (65%, Merck, Germany) and HClO_4 (70% - 72%, Merck, Germany) (1:3 v/v) and analysed for metals by using methods of APHA (2005). The planktonic abundance on the dry weight basis was determined by the evaporation method (Javed 1988) through the following formula:

i: Total solids (TS) = weight of the beaker with an oven-dried sample of water – weight of the empty beaker

ii: Total dissolved solids (TDS) = weight of the beaker with an oven-dried sample of filtered water – weight of the empty beaker

iii: Dry weight of Plankton Biomass (Abundance) = TS – TDS

Both TS and TDS were calculated by the evaporation method. To calculate TS, a one-litre sample of river water was taken in a pre-weighed beaker and then placed in a laboratory oven (Model #DHG-9053A, Shanghai Sunrise Instrument Co., Ltd.) at 103 °C for evaporation. The beaker with oven-dried samples was weighed again and the weight of the empty beaker was subtracted from it to determine TS. TDS were determined by filtering the river water through Whatman filter paper# 44 and then dried weight (TDS) of the filtered water was calculated. Finally, the dry weight of plankton biomass was calculated simply by subtracting the TDS from TS.

Determination of metals and arsenic

Firstly, the standard solutions of studied metals were prepared to calibrate the instrument on the day of actual metal detection analysis to avoid possible deterioration of prepared

standards. All samples were prepared with analytical grade chemicals and double-distilled water. Water was double distilled in automatic water still (Aquatron A4000D, Cole-Parmer Ltd, UK). Atomic Absorption Spectrophotometer was set-up with the flame condition and observance was optimized for the metal analysis. Water was double distilled and deionized in a water deionizer (Aquatron, AdhSingle, Cole-Parmer Ltd, UK) which was used as blank. Blanks, standards CRMs, sample blank and samples were aspirated into the flame in a Flame Atomic Absorption Spectrometer (Analyst 400, PerkinElmer, Inc. USA). The least-square design was implemented to statistically analyse the data using the fitting of a straight line. A blank reading was also taken to adjust the calibrations for the calculation of individual metal. Concentrations of As and other heavy metals including Pb, Al, and Ba were assayed using AAS with the standard analytical protocol (Table 1) according to method# 3500-Al B, 3500-As B, 3500-Ba B, 3500-Pb B of APHA (2005), respectively. Three replications of each metal were run through the AAS for each experiment (Water, sediments and plankton).

Health risk assessment

Three major pathways are generally considered in human health risk assessment: ingestion, dermal contact and respiration. This study focused on the ingestion and dermal contact pathways. The following equations (Equation 1 and 2) are applied in calculating the exposure through these two pathways (Ezemonye et al. 2019; Filipsson et al. 2009; Iqbal et al. 2013):

$$\text{Equation 1: For sediment: } \text{Exp}_{\text{ing}} = \frac{C \times \text{IR} \times \text{CF} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}}; \text{ For water: } \text{Exp}_{\text{ing}} = \frac{C \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}}$$

$$\text{Equation 2: For sediment: } \text{Exp}_{\text{derm}} = \frac{C \times \text{CF} \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}}; \text{ For water: } \text{Exp}_{\text{derm}} = \frac{C \times \text{SA} \times \text{KP} \times \text{ET} \times \text{EF} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}}$$

Where Exp_{ing} is the ingestion exposure from the sediment or water; C represents the measured concentration in the sediment or water; IR is the ingestion rate (114 mg/day); CF represents the unit conversion factor (10^{-6} kg/mg); EF is the exposure frequency (350 days/year); ED represents the exposure duration (30 years); BW is the body weight (70 kg);

AT represents the average day (10,950 days); Exp_{derm} is the dermal uptake; SA is the exposed skin surface area (5700 cm²); AF represents the adherence factor from sediment to the skin (0.07 mg/cm²); ABS is the dermal absorption from sediment (0.001 cm/h); ET is the exposure time (assumed to be 2 h/day); KP is the dermal permeability coefficient (0.001 cm/h).

Hazardous quotients (HQs) are used to assess the noncarcinogenic health risks following exposure to heavy metals and arsenic in sediment according to the USEPA (2004) health risk assessment guidelines. The following equations are adopted to evaluate the HQs for the two exposure pathways (Equation 3 and 4):

Equation 3: For sediment: $HQ_{ing/derm} = \frac{Exp_{ing/derm}}{RfD}$, For water: $HQ = \frac{Exp_{ing}}{RfD}$

Equation 4: $HI = \sum_{i=1}^n HQ_{ing/derm}$

Where HQ is health HQs via ingestion or dermal contact under the respective exposure amount; RfD represents the reference dose for the resulting hazardous health effect caused by contaminants. The reference dose via dermal contact is typically hypothesized to be identical to the reference dose via ingestion for heavy metals in sediment (Iqbal et al. 2013). HI represents hazardous index.

Carcinogenic risk (CR)

The parameter was calculated based on equation 5 (Jiang et al. 2017):

Equation 5: $CR = ADD \cdot CSF$

ADD – an average daily dose of a pollutant,

CSF – carcinogenic slope factor (mg kg⁻¹ per day, 0.35 and 0.5 for Cd and Cr, respectively);

(ATSDR 2010; USEPA 2005).

Heavy metal transfer factor

The parameter is calculated based on equation 6 (Cui et al., 2004).

Equation 6:
$$TF = \frac{C_{plankton}}{C_{water}}$$

$C_{plankton}$ – metal concentration in plankton (mg kg⁻¹), C_{water} – metal concentration in water (mg L⁻¹).

Statistical analysis

Statistical analysis of data was carried out using the PASW Statistics Package (version 18). Two-way Analysis of Variance (Two-way ANOVA) and Student Newman-Keul (SNK) tests were performed to find-out statistical differences of different heavy metals concerning sample seasons and sample stations. The significance level was set to $\alpha = 0.05$ and values are given as mean $\pm$ standard deviation.

Results

Contamination level of heavy metals (Al, As, Ba, and Pb) in the water of Punjnad Headworks were analysed and their mean ($\pm$ SD) were compared (Table 1). The mean concentration of As and heavy metals in the water samples showed the descending order as Pb > Al > Ba > As. The highest and lowest concentration of Al during three seasons was observed in stations 1 and 3, respectively. The highest and lowest levels of Ba were reported in station 3 and 1, respectively. For arsenic and lead metals, the highest and lowest concentrations were observed at stations 3 and 2, respectively. Moreover, the highest and lowest mean level of all metals (except for lowest Pb levels) among the three stations was found in the spring and the autumn seasons, respectively. An overall significant difference ($p < 0.05$) of Al was recorded among three sampling stations. Similarly, the Al concentrations were found to be significantly different ($p < 0.05$) among the three sampling seasons. Also, using two-way ANOVA statistical analysis the effect of stations and seasons in the accumulation of heavy metals in surface water was studied. Results indicated that all heavy metals concentrations differed significantly ($p < 0.05$)

among stations and seasons. Moreover, the mean concentrations of Al and Pb in the water of Punjnad Headworks were much higher than the WHO and USEPA standards for the same metals (Table 1).

Heavy metals levels in the bed sediments were in the orders of $Al > Pb > As > Ba$ (Table 2). A comparison of the average concentrations of As and heavy metals in the different sites and samples revealed that the average Al concentration was higher ($519.19 \pm 1.808 \mu\text{g g}^{-1}$) than that of other metals. Among three seasons, the highest concentrations of Pb, As, Ba and Al metals were observed at stations 2, 1, 1 and 3, respectively, while the lowest concentrations of these metals were reported at stations 1, 2, 3, and 1, respectively. The highest and lowest concentrations of heavy metals were observed in the autumn and were related to Al ($501.96 \pm 15.24 \mu\text{g g}^{-1}$) and Ba ($3.63 \pm 1.76 \mu\text{g g}^{-1}$), respectively. The mean concentration of As and Pb determined in this study ranged from 30.95 ± 7.81 to $85.45 \pm 5.39 \mu\text{g g}^{-1}$. Findings of this study showed that two experimental factors, seasons and stations had an interactive effect on the accumulation of As and heavy metals in sediments i.e., a significant difference (two-way ANOVA; $p < 0.00$) in all metals was found among sampling stations, seasons and their interaction. The mean concentrations of As and Pb in the sediment of Punjnad Headworks were higher than the recommended limit documented by (MacDonald et al. 2000).

The concentration level ($\mu\text{g g}^{-1}$) of different As and heavy metals in plankton were studied in different seasons and at different sampling stations (Table 3). The trend of accumulation of As and heavy metals in plankton were similar to the trend in sediments, so it was found that the metals levels were $Al > Pb > As > Ba$, respectively. Also, the highest and lowest concentrations of metals in the fall were attributed to Al ($349.06 \pm 5.92 \mu\text{g g}^{-1}$) and Ba ($1.64 \pm 0.35 \mu\text{g g}^{-1}$), respectively. The highest concentrations of As and Pb were at station 1, while the lowest concentrations of these pollutants were at stations 2 and 3, respectively. An overall significant difference ($p < 0.05$) in mean of all metals were found among three sampling

stations. Similarly, the mean of all metals were significantly different ($p < 0.05$) among the three sampling seasons. Moreover, the statistical interaction between the sampling stations and sampling seasons for the mean concentration of all metals were also statistically different ($p < 0.05$). The correlation of different metals in water, sediments and plankton was also analysed (Table 4). The result obtained showed a positive correlation among all the studied metals in water, while in sediments Al was negatively correlated to all other metals. Arsenic was negatively correlated to Al and Ba. However, As did not show a significant relation with Pb. Barium was negatively correlated to Al and As, while positively correlated to Pb. The Pb was found to be positively correlated to Ba, negatively correlated to Al and non-significantly related to As. In samples collected from the plankton, a positive correlation was observed for all the metals except for the Ba and Al.

Health risk assessment

Different health risk assessment parameters were applied to evaluate the hazardous effects of As and heavy metals on human health (Table 5). The obtained Exp_{ing} and Exp_{derm} values showed that no significant adverse effects of studied heavy metals (Pb, Al, As and Ba) were observed with the quantity present in the water and sediment samples at the studied sites. However, the non-carcinogenic ($HQ_{ing/derm}$) and HI values showed adverse effects of Pb and As in the water, while a non-significant impact of Al was observed in water. Furthermore, the $HQ_{ing/derm}$ for the sediments showed a non-significant impact of As and heavy metals on human health. Carcinogenic (CR) effects of Pb and As were found to be non-significant, while these values for Al and Ba could not be calculated due to lack of required data. Lastly, the Transfer Factor (TF) values for the plankton ($TF_{plankton}$) were found highest in As (33430.38) followed by Al (1436.94) and Ba (184.39), while the lowest value was observed in Pb (86.3).

Discussion

We found a significant amount of heavy metals and As at different sampling sites (station I, station II and station III) of the Punjnad headworks. A significant variations in the number of metals were present at different sampling sites. This study concluded that the river water at this location exhibited a significantly higher level of Pb followed by Al, Ba and As. The quality of drinking water has been regarded as a major factor to influence human health. The concentrations of Pb, Al, As and Ba showed significant variations seasonally in a water bodies naturally or due to anthropogenic factors i.e., discharge of untreated contaminated water from various industries, agricultural practices, accelerated variations in physicochemical parameters of water, temperature, redox condition and river flow. Higher Pb toxicity level observed in this study could be due to agricultural runoff and heavy discharge of untreated industrial effluents in the riverine system, resulting in pH decline to elevate lead level in river water as previously determined by Yilmaz and Sadikoglu (2011). Youssef et al. (2018) recorded higher Pb levels in the river water of Sohag governorate, Egypt. Similarly, our results are coherent with Khan et al. (2018) who found higher values of As compared to other metals in the water of Kabul river, Pakistan. The mean concentration of Pb in water was 9.85 mgL^{-1} and 16.83 mgL^{-1} during summer and winter, respectively, which were higher than the drinking water quality standard (Ali et al. 2016). The chemistry of toxicity and bioavailability of Al in the aquatic environment is complex and affected by a wide range of water quality parameters including pH, water hardness and dissolved organic carbon (Camargo et al. 2009; Cardwell et al. 2018; Gensemer et al. 2018). The slow and steady dissolution and precipitation of Al was frequently observed in acidic waters (low pH) (Cardwell et al. 2018). Thus, acidic soil would be a major cause for the mobilization of Al to the aquatic ecosystems (Adams et al. 2018). In the current study, significantly higher concentrations of Al was detected in the riverine water which could be the

result of lower pH of water. Aqueous Al is measured as the main toxic agent leading to fish mortality in the water with a lower pH (Cardwell et al. 2018).

In the freshwater, the toxicity of several heavy metals has been detected by analysing their effects in water, sediments and fish (Islam et al. 2017; Pal and Maiti 2018; Naz et al., 2020). Overall, the toxicity level of all analysed metals (Al, Ba, As and Pb) recorded at Punjnad headworks were significantly lower in the water samples as compared to bed sediments and plankton. The heavy metals complex that is mobilized into the water bodies from different sources are actively absorbed by the planktons (Al-Imarah et al. 2018; Yi et al. 2017) and some quantities could be deposited on the suspended particles that sink down and ultimately become the part of sediments of a water body. Due to the physicochemical properties of water, an immobilized form of heavy metals present in sediments become mobilized again in aquatic habitat (Ekengele et al. 2017; Jindal and Sharma 2011; Pandey and Singh 2017). The toxicity level of all the metals (Al, As and Pb) except Ba were significantly higher in all the study sites of Punjnad headworks. The metals deposited in sediments of the water body become a source of substantial hazards to detritus-feeding benthic organisms and ultimately led to a permanent source of potential toxicity to the higher trophic levels of a food chain/web (Ali and Khan 2018; Hanif et al. 2016). Islam et al. (2017) reported the mobilization of heavy metals in sediment deposits of Paira River, Bangladesh. The toxicity level of both Ba and As in the water and sediments, collected from Punjnad headworks at three sampling sites, were measured significantly lower than Al and Pb. It has been reported that the toxic nature of As is due to its binding ability to the thiol groups of proteins ultimately inhibiting the enzymatic activities in a living body (Rezaei et al. 2017; Tian et al. 2018). The present study showed that accumulation of studied metals by the aquatic organism and sediments were highly dependent upon the metallic contamination of the water body. The ultimate sink of chemical effluents poured directly into the water bodies is the sediments and hence becomes a source of pollution (Das et

al. 2017; Hanif et al. 2016). However, in this study, the pollution levels observed both in plankton and sediments represent their role as bio-indicator of the metallic toxicity in the Punjnad headworks of Chenab river. The physical and biological processes have insistent potential to deduct metals from the aquatic body, accumulate and store them for a long duration even at low concentrations. Therefore, the sediment, suspended particulate matter and physicochemical characteristics of water have a significant effect on metal toxicity in an aquatic ecosystem (Boran and Altınok 2010; Das et al. 2017).

Statistical analysis using Pearson rank order correlations indicated that among heavy metals, As-Al, Ba-Al, Pb-Al, Pb-As, Pb-Ba, and Ba-As in water; and Pb-As in plankton have a strong positive correlation, and Ba-Al in sediment has a highly negative correlation. We hypothesize that heavy metals with a high positive correlation are possibly from the similar primary pollutant sources, i.e., industrial discharge, while the metal with a highly negative correlation are possibly from the different pollutant sources. These heavy metals are widely used as raw materials or process catalysts to produce alloys, steels and various other industrial purposes. Many previous studies have reported significant quantities of industrial wastes/wastewater being discharged into the Punjnad headworks (Hanif et al. 2016; Fatima et al. 2020). In addition, deposition of heavy metals through industrial emissions can also be considered as a source of metal contamination in the study area. It is found that the industrial wastes from different cities in Punjab are being dumped into the major rivers of Punjab province which ultimately sink into the Punjnad Headworks (Hanif et al. 2016). A positive correlation among trace metals and dissolved organic carbon concentration ratios was observed in freshwater ecosystem (Kikuchi et al. 2017). Similarly, Ni et al. (2016), found a significant correlation between heavy metals concentration and freshwater microbial ecology. A significant positive correlation among some metals, while negative pattern among other metals were observed in the food web in the upper Yangtze River, China (Yi et al. 2017).

370 The human health risk of Al, As, Ba and Pb were determined in the current study. The
371 human health risk assessment and $HQ_{(ing/derm)}$ values for As and Pb in water were higher than
372 1, indicating obvious health risk from these pollutants in water over a lifetime of exposure.
373 While, the hazard index (HI) values for water was less than 1, indicating no adverse health risk
374 for non-carcinogenic effect. The HQ values of the sediment and dermal contact with the
375 sediment of noncarcinogenic As and heavy metals in the river sediment are less than 1,
376 indicating that the selected metals and As would not pose any adverse non-carcinogenic health
377 risks to the inhabitants during the seasons. The noncarcinogenic health risk through ingestion
378 was higher than that of dermal contact, indicating that the ingestion pathway significantly
379 contributed to the health risk of the contaminated sediments. Moreover, the noncarcinogenic
380 HI of heavy-metal-contaminated sediment was less than 1. The TF values from water to
381 plankton were found highest and lowest in As and Pb, respectively. These values were greater
382 than 1, suggesting that the plankton will have a greater chance of the metal uptake by
383 anthropogenic activities, which can be used for phytoremediation (Mirecki et al. 2015). The
384 cancer risk (CR) was determined based on the intake level of inorganic As and Pb, which may
385 increase carcinogenic effects depending on the exposure dose (Aligol et al. 2017; EPA 2016).
386 Briefly, based on our findings, the chance of developing CR contact for both elements in water
387 was 1.85×10^{-3} and 6.02×10^{-3} , respectively. Thus, the CR values were above the safety level
388 (1×10^{-4}) recommended by the US EPA (Alidadi et al. 2019), suggesting the probability of
389 carcinogenic risk for the human consumption of drinking water. While, the mean CR values
390 for As and Pb in sediment was 7.30×10^{-5} and 6.02×10^{-7} , respectively, suggesting
391 carcinogenic risk can be acceptable for human via ingestion and dermal contact. Similarly,
392 (Sayadi et al. 2020) and (Hu et al. 2017) reported CR values between 10^{-4} and 10^{-6} .

Conclusion:

This study concluded important information on the heavy metals content at Punjnad headworks. According to this study Al, As, Ba and Pb contents were present in different concentrations at all three sites from where the samples were collected. Heavy metals and As contents were highest in spring, while lowest in winter. Presence of heavy metals and As in significant concentration in these waters is a serious health issue. Proper preventive measures including regulation of the industrial, agricultural and domestic discharge of waste materials must be carried out to reduce contamination and pollution in the rivers. Further in-depth studies are required to explore the burden of potentially hazardous heavy metals in river waters which poses serious health risk for human, animals and aquatic organism.

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411 **Authors contribution**

412 SN and BM designed the study; AMMC collected the sample, QU, ZUA and MZK wrote and
413 submitted the manuscript, AK, SS and RAB edited and reviewed the manuscript.

414 **Declarations**

415 **Ethics approval and consent to participate**

416 Not applicable.

417 **Consent for publication**

418 Not applicable

419 **Availability of data and material**

420 Do not wish to share.

421 **Competing interests**

422 The authors declare that they have no competing interests.

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638 **Table 1:** Heavy metal concentrations (Mean $\pm$ SD; $\mu\text{g L}^{-1}$) at three sampling stations (I, II & III) in the water of Punjnad Headworks

Heavy Metals	Season	Sampling Stations				Guideline value (WHO, 2017; Zhou et al. 2020)*		ANOVA			
		I	II	III	Overall Means	WHO	USEPA	Source of variance	df	F-value	P-value
Aluminum	Autumn	155.60 $\pm$ 1.07 ^{a†z‡}	116.32 $\pm$ 1.16 ^{cz}	128.91 $\pm$ 1.22 ^{bz}	133.61 $\pm$ 16.71			Stations	2	105846.43	< 0.00
	Winter	204.09 $\pm$ 0.84 ^{ay}	200.34 $\pm$ 1.02 ^{by}	195.77 $\pm$ 0.66 ^{cy}	200.07 $\pm$ 3.57			Seasons	2	1085.88	< 0.00
	Spring	331.99 $\pm$ 3.77 ^{ax}	323.32 $\pm$ 0.78 ^{bx}	316.99 $\pm$ 0.97 ^{cx}	324.09 $\pm$ 6.65			Stations x Seasons	4	356.09	< 0.00
	Overall Means	230.56 $\pm$ 75.85	213.33 $\pm$ 86.62	213.88 $\pm$ 79.33	219.25 $\pm$ 80.11	200	200				
Arsenic	Autumn	0.25 $\pm$ 0.02 ^{bz}	0.18 $\pm$ 0.016 ^{cz}	0.31 $\pm$ 0.02 ^{az}	0.25 $\pm$ 0.06			Stations	2	4369.99	< 0.00
	Winter	0.47 $\pm$ 0.013 ^{by}	0.31 $\pm$ 0.018 ^{cy}	0.64 $\pm$ 0.016 ^{ay}	0.48 $\pm$ 0.14			Seasons	2	49402.05	< 0.00
	Spring	1.56 $\pm$ 0.021 ^{bx}	1.26 $\pm$ 0.014 ^{cx}	2.13 $\pm$ 0.019 ^{ax}	1.66 $\pm$ 0.38			Stations x Seasons	4	1127.39	< 0.00
	Overall Means	0.77 $\pm$ 0.59	0.58 $\pm$ 0.49	1.03 $\pm$ 0.81	0.79 $\pm$ 0.66	10	10				
Barium	Autumn	12.25 $\pm$ 0.024 ^{cz}	13.38 $\pm$ 0.023 ^{bz}	14.89 $\pm$ 0.017 ^{az}	13.51 $\pm$ 1.09			Stations	2	84283.05	< 0.00
	Winter	13.23 $\pm$ 0.03 ^{cy}	17.39 $\pm$ 0.019 ^{ay}	16.07 $\pm$ 0.035 ^{by}	15.57 $\pm$ 1.76			Seasons	2	314568.82	< 0.00
	Spring	17.73 $\pm$ 0.022 ^{cx}	18.09 $\pm$ 0.019 ^{bx}	19.91 $\pm$ 0.019 ^{ax}	18.58 $\pm$ 0.97			Stations x Seasons	4	19204.38	< 0.00
	Overall Means	14.41 $\pm$ 2.43	16.29 $\pm$ 2.12	16.95 $\pm$ 2.18	15.89 $\pm$ 2.47	700	2000				
Lead	Autumn	347.52 $\pm$ 0.273 ^{cy}	385.61 $\pm$ 0.234 ^{bz}	525.57 $\pm$ 0.31 ^{ay}	428.56 $\pm$ 70.05			Stations	2	382048.01	< 0.00
	Winter	340.51 $\pm$ 0.273 ^{bz}	424.45 $\pm$ 0.233 ^{ay}	338.68 $\pm$ 0.26 ^{cz}	367.87 $\pm$ 40.76			Seasons	2	3481481.79	< 0.00
	Spring	559.72 $\pm$ 0.24 ^{bx}	528.49 $\pm$ 0.32 ^{cx}	607.35 $\pm$ 0.35 ^{ax}	565.18 $\pm$ 33.04			Stations x Seasons	4	437670.93	< 0.00
	Overall Means	424.92 $\pm$ 98.16	446.17 $\pm$ 61.46	490.53 $\pm$ 114.58	453.87 $\pm$ 96.86	10	15				

639 *WHO: Guidelines for drinking water quality (WHO, 2017); Zhou et al. 2020

640 †The different letters (a, b, and c) in the same row, show significant difference among stations (I, II, and III) for the same heavy metal and season ($p < 0.05$)

641 ‡The different letters (x, y, and z) in the same column, show significant difference among seasons (autumn, winter, and spring) for the same heavy metal and station ($p < 0.05$)

Table 2: Heavy metal concentrations (Mean $\pm$ SD; $\mu\text{g g}^{-1}$) at three sampling stations (I, II & III) in the sediments of Punjnad Headworks

Heavy Metals	Season	Sampling Stations				Background levels*			ANOVA			
		I	II	III	Overall Means	TEL	LEL	MET	Source of variance	df	F-value	P-value
Aluminum	Autumn	428.91 $\pm$ 1.62 ^{c†x‡}	503.78 $\pm$ 1.74 ^{bx}	519.19 $\pm$ 1.81 ^{ax}	501.96 $\pm$ 15.24				Stations	2	1838.27	< 0.00
	Winter	352.15 $\pm$ 1.23 ^{cy}	362.73 $\pm$ 2.14 ^{by}	378.75 $\pm$ 1.83 ^{ay}	364.55 $\pm$ 11.27				Seasons	2	147621.56	< 0.00
	Spring	233.39 $\pm$ 1.62 ^{cz}	242.47 $\pm$ 1.69 ^{bz}	256.79 $\pm$ 1.86 ^{az}	244.22 $\pm$ 9.96				Stations x Seasons	4	42.88	< 0.00
	Overall Means	356.15 $\pm$ 103.85	369.65 $\pm$ 108.84	384.92 $\pm$ 109.27	370.24 $\pm$ 106.60	-	-	-				
Arsenic	Autumn	40.15 $\pm$ 0.02 ^{ay}	21.39 $\pm$ 0.03 ^{cy}	31.31 $\pm$ 0.02 ^{by}	30.95 $\pm$ 7.81				Stations	2	4494756.19	< 0.00
	Winter	39.27 $\pm$ 0.02 ^{az}	19.26 $\pm$ 0.02 ^{cz}	29.56 $\pm$ 0.01 ^{bz}	29.37 $\pm$ 8.33				Seasons	2	179664.65	< 0.00
	Spring	42.36 $\pm$ 0.03 ^{ax}	23.47 $\pm$ 0.02 ^{cx}	33.74 $\pm$ 0.02 ^{bx}	33.19 $\pm$ 1.75				Stations x Seasons	4	2275.96	< 0.00
	Overall Means	40.60 $\pm$ 1.33	21.37 $\pm$ 1.75	31.53 $\pm$ 1.74	31.17 $\pm$ 8.06	5.9	6	7				
Barium	Autumn	3.93 $\pm$ 0.03 ^{bz}	5.56 $\pm$ 0.03 ^{az}	1.37 $\pm$ 0.02 ^{cz}	3.63 $\pm$ 1.76				Stations	2	89875.99	< 0.00
	Winter	4.33 $\pm$ 0.05 ^{by}	7.28 $\pm$ 0.04 ^{ay}	3.46 $\pm$ 0.03 ^{cy}	5.03 $\pm$ 1.66				Seasons	2	50863.69	< 0.00
	Spring	5.86 $\pm$ 0.03 ^{bx}	8.45 $\pm$ 0.03 ^{ax}	5.15 $\pm$ 0.03 ^{cx}	6.49 $\pm$ 1.44				Stations x Seasons	4	2374.95	< 0.00
	Overall Means	4.71 $\pm$ 0.84	7.09 $\pm$ 1.20	3.32 $\pm$ 1.57	5.05 $\pm$ 1.99	-	-	-				
Lead	Autumn	65.48 $\pm$ 0.19 ^{ay}	65.56 $\pm$ 0.29 ^{ay}	65.46 $\pm$ 0.24 ^{ay}	65.50 $\pm$ 0.23				Stations	2	2061.63	< 0.00
	Winter	40.40 $\pm$ 0.36 ^{bz}	41.51 $\pm$ 0.22 ^{az}	40.59 $\pm$ 0.32 ^{bz}	40.84 $\pm$ 0.57				Seasons	2	186240.07	< 0.00
	Spring	78.53 $\pm$ 0.28 ^{cx}	91.52 $\pm$ 0.20 ^{ax}	86.42 $\pm$ 0.29 ^{bx}	85.45 $\pm$ 5.39				Stations x Seasons	4	1601.21	< 0.00
	Overall Means	61.47 $\pm$ 16.12	66.15 $\pm$ 20.75	64.15 $\pm$ 19.09	63.93 $\pm$ 18.62	35	31	42				

* TEL: Threshold effect level; LEL: Lowest effect level; MET: Minimal effect threshold (MacDonald et al. 2000)

†The different letters (a, b, and c) in the same row, show significant difference among stations (I, II, and III) for the same heavy metal and season ($p < 0.05$)

‡The different letters (x, y, and z) in the same column, show significant difference among seasons (autumn, winter, and spring) for the same heavy metal and station ($p < 0.05$)

Table 3: Heavy metal concentrations (Mean $\pm$ SD; $\mu\text{g g}^{-1}$) at three sampling stations (I, II & III) in the plankton of Punjnad Headworks

Heavy Metals	Seasons	Sampling Stations				ANOVA			
		I	II	III	Overall Means	Source of variance	df	F-value	P-value
Aluminum	Autumn	350.25 $\pm$ 0.77 ^{b†x‡}	341.51 $\pm$ 1.12 ^{cx}	355.42 $\pm$ 1.04 ^{ax}	349.06 $\pm$ 5.92	Stations	2	753.67	< 0.00
	Winter	286.68 $\pm$ 0.67 ^{bz}	283.86 $\pm$ 1.62 ^{cz}	293.87 $\pm$ 0.77 ^{az}	287.96 $\pm$ 4.18	Seasons	2	25553.67	< 0.00
	Spring	308.71 $\pm$ 0.95 ^{by}	303.48 $\pm$ 1.06 ^{cy}	312.17 $\pm$ 0.77 ^{ay}	308.12 $\pm$ 3.75	Stations x Seasons	4	28.32	< 0.00
	Overall Means	315.21 $\pm$ 26.87	309.62 $\pm$ 24.42	320.31 $\pm$ 26.49	315.05 $\pm$ 25.99				
Arsenic	Autumn	31.46 $\pm$ 0.02 ^{ay}	25.04 $\pm$ 0.02 ^{cy}	27.40 $\pm$ 0.02 ^{by}	27.97 $\pm$ 2.70	Stations	2	735346.95	< 0.00
	Winter	23.60 $\pm$ 0.02 ^{az}	17.89 $\pm$ 0.02 ^{cz}	21.40 $\pm$ 0.02 ^{bz}	21.05 $\pm$ 2.41	Seasons	2	1650408.99	< 0.00
	Spring	33.94 $\pm$ 0.02 ^{ax}	26.95 $\pm$ 0.02 ^{cx}	29.75 $\pm$ 0.02 ^{bx}	30.22 $\pm$ 2.92	Station x Seasons	4	10008.67	< 0.00
	Overall Means	29.67 $\pm$ 4.49	23.29 $\pm$ 3.97	26.27 $\pm$ 3.47	26.41 $\pm$ 4.74				
Barium	Autumn	1.98 $\pm$ 0.01 ^{az}	1.17 $\pm$ 0.02 ^{cz}	1.78 $\pm$ 0.02 ^{bz}	1.64 $\pm$ 0.35	Stations	2	20984.12	< 0.00
	Winter	2.87 $\pm$ 0.02 ^{by}	2.09 $\pm$ 0.02 ^{cy}	3.16 $\pm$ 0.02 ^{ay}	2.70 $\pm$ 0.45	Seasons	2	125206.95	< 0.00
	Spring	4.04 $\pm$ 0.03 ^{bx}	3.76 $\pm$ 0.02 ^{cx}	5.52 $\pm$ 0.03 ^{ax}	4.44 $\pm$ 0.81	Stations x Seasons	4	4406.69	< 0.00
	Overall Means	2.95 $\pm$ 0.84	2.34 $\pm$ 1.09	3.50 $\pm$ 1.58	2.93 $\pm$ 1.29				
Lead	Autumn	50.06 $\pm$ 0.77 ^{ay}	39.84 $\pm$ 0.63 ^{by}	34.22 $\pm$ 0.62 ^{cy}	41.38 $\pm$ 6.72	Stations	2	3915.87	< 0.00
	Winter	35.02 $\pm$ 0.58 ^{az}	27.85 $\pm$ 0.55 ^{bz}	23.95 $\pm$ 0.66 ^{cz}	28.95 $\pm$ 4.70	Seasons	2	6345.09	< 0.00
	Spring	56.17 $\pm$ 0.55 ^{ax}	45.60 $\pm$ 0.57 ^{bx}	39.78 $\pm$ 0.50 ^{cx}	47.19 $\pm$ 6.93	Stations x Seasons	4	53.65	< 0.00
	Overall Means	47.09 $\pm$ 9.07	37.77 $\pm$ 7.55	32.65 $\pm$ 6.70	39.17 $\pm$ 9.80				

[†]The different letters (a, b, and c) in the same row, show significant difference among stations (I, II, and III) for the same heavy metal and season ($p < 0.05$)

[‡]The different letters (x, y, and z) in the same column, show significant difference among seasons (autumn, winter, and spring) for the same heavy metal and station ($p < 0.05$)

649 **Table 4:** Correlation matrix between heavy metals concentration in water, sediments and
650 plankton at Punjnad Headworks ($n= 81$)

Source	Heavy Metal	Al	As	Ba	Pb
Water	Al	1			
	As	0.90*	1		
	Ba	0.80*	0.82*	1	
	Pb	0.65*	0.78*	0.75*	1
Sediments	Al	1			
	As	-0.15	1		
	Ba	-0.62*	-0.43*	1	
	Pb	-0.40*	0.09	0.32*	1
Plankton	Al	1			
	As	0.52*	1		
	Ba	-0.43*	0.37*	1	
	Pb	0.36*	0.88*	0.23*	1

651 * Significant correlation coefficients at the 0.05 statistical level.

652 **Table 5:** Human health risk assessment of heavy metals in water and sediment

Source	Metal	Exp _{ing}	Exp _{derm}	HQ _{ing}	HQ _{derm}	HI	CR	TF (plankton)
Water	Pb	0.71	7.09E-08	202.50	2.02E-05	202.5	6.02E-03	86.30
	As	1.23E-03	1.23E-10	4.11	4.11E-07	4.11	1.85E-03	33430.38
	Al	0.34	3.42E-08	0.34	3.42E-08	0.34	-	1436.94
	Ba	0.02	2.48E-09	0.12	1.24E-08	0.12	-	184.39
Sediment	Pb	9.98E-05	3.49E-07	0.03	0.02	0.05	8.48E-07	
	As	4.87E-05	1.70E-07	0.16	4.11E-04	0.16	7.30E-05	
	Al	5.78E-04	2.02E-06	5.78E-04	3.42E-05	6.12E-04	-	
	Ba	7.88E-06	2.76E-08	3.94E-05	1.24E-05	5.18E-05	-	

653 Exp_{ing} = exposure through ingestion; Exp_{derm} = exposure through skin; HQ_{ing} = hazardous quotient via ingestion; HQ_{derm} =
654 hazardous quotient via skin; HI = hazardous index; CR = carcinogenic risk; TF_(plankton) = heavy metal transfer factor for plankton

655 **Figure Legends**

656 **Fig. 1** Geological map of Punjnad Headworks (28°56'59.99" N, 70°29'59.99" E) near Uch Sharif.

657 The doubled dotted lines show the Punjnad Headworks bridge. Doubled Solid lines represent
658 canals from Headworks. Square shape markers indicate the sampling stations selected at different
659 locations for taking samples from water, bed sediments and planktons.

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