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Assessment of Health Risks Associated with Chromium and Cadmium Metals in Groundwater Samples Collected from Vicinity of Kanjli Wetland (Ramsar Site)

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ABSTRACT

Heavy metals are considered to be toxic because upon entering the living systems, these can bind to parts of cells and prevent various organs to perform their specific functions. Apart from this, metals are documented to cause irreversible damages. Considering this, the present study was planned to estimate the contents of chromium and cadmium in groundwater samples of 15 villages collected from vicinity of Kanjali wetland (Ramsar site) in Kapurthala district, Punjab (India) and to study their potential health risk using health quotients like estimated daily intake (EDI), target hazard quotient (THQ) and cancer risk (CR). The content of chromium was observed to be as 0.2628 µg/l (NP) - 0.9541 µg/l (KW), while cadmium was below detection limit (BDL) in all water samples collected using submersible pumps. For water samples collected using hand pumps, the content of chromium was observed to be below detection limit (BDL) except for two samples i.e. Surkhpur (SK) and Chakoki (CK) in which chromium content was observed to be 3.730 and 1.058 µg/l, respectively. The cadmium content was found in only one water sample collected using hand pump from Surkhpur (2.56 µg/l). For handpump samples, this sample (SK) showed the maximum values for cancer risk (CR) as 5.3008 and target hazard quotient (THQ) as 1.774 for Cr metal, while CR as 4.435 and THQ as 4.436 for Cd metal in water sample. Estimated daily intake (EDI) for Cr metal was 0.03667 µg/kg/day (CK) to 0.1292 µg/kg/day (SK) in hand pump samples and 0.0091 µg/kg/day (NP) to 0.0331 µg/kg/day (KW) for submersible pumps, while for Cd metal, EDI was observed as 0.0887 µg/kg/day for SK sample.

Key words: Health risk assessment, cancer risk, target hazard quotient, estimated daily intake, heavy metals

INTRODUCTION

Groundwater is the vital component of ecological environment which is widely used for drinking purposes by human beings, especially in the areas, where surface water is not available either due to the scarcity or the pollution load of natural water resources (Lou *et al.*, 2017). It is well evidenced over the past years that the water quality of surface water bodies has been deteriorated all over the globe due to multiple natural and anthropogenic factors (Mbugua *et al.*, 2022). The occurrence of metals in water bodies like lakes, reservoirs, streams and rivers affects the health of local people that totally depend upon these water sources for their day to day requirements. Consumption of contaminated food crops, irrigated using polluted water on the other hand poses serious health hazards. Contamination of groundwater sources via leachates from open dumping sites, landfills, oil spills and leakages through damaged sewers has been well recognized. Apart from these, agricultural runoffs, untreated or partially treated industrial waste, combustion of coal and direct discharge of domestic sewages onto land have also contributed in pollution of drinking water. Among various types of contaminants, heavy metals are of special concern because they are non-biodegradable and can get accumulated in any environment upon their entry to any ecosystem. Some of the heavy metals like chromium (Cr), nickel (Ni), copper (Cu), cadmium (Cd), lead (Pb) and zinc (Zn) are considered as more persistent

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than organic contaminants and can leach into aquifers from the soil ecosystem.

Chromium is one of the most commonly used heavy metal in industries like leather, textile, electroplating as well as melting due to its properties like enhancement of metal resistance to corrosion as well as oxidation and occurrence in various oxidation states like Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI) ranging from +6 to -2. The distribution of compounds containing chromium depends on pH, redox potential, the presence of oxidising or reducing compounds in the vicinity and total concentration of chromium. In water, chromium mostly exists in two oxidation states i.e. Trivalent Cr(III) and hexavalent Cr(VI). Chromium contamination in aquatic habitats has received great attention due to its toxicity, abundance, persistence and bioaccumulation like any other heavy metals. Because of its toxic nature, chromium creates numerous environmental problems along with various adverse health effects on human beings such as ulcers, respiratory problems, allergic dermatitis and many other diseases of serious concern.

Cadmium (Cd) is a noxious non-essential heavy metal which can cause the toxicity in living beings even at lower concentrations. Although it is a naturally occurring element, it can also enter into different ecosystem through anthropogenic activities like industrial, agricultural and transportation. Once cadmium enters to an ecosystem, being non-biodegradable in nature like other metals, it gets accumulated and ultimately enters the food chain (Ahmed and Mokhtar, 2020). Exposure of human beings to Cd primarily is caused through intake of contaminated water and food. Upon exposure, Cd has been reported to induce adverse effects on liver, kidneys, lungs, pancreas and reproductive system in human beings. Few studies have also shown that Cd can induce hypertension. Epidemiological studies revealed that Cd could pose the risk of osteoporosis and caused mitochondrial damage (Genchi *et al*., 2020). Considering this, the present study was planned to estimate the content of chromium and cadmium in groundwater samples of 15 villages of Kapurthala, Punjab. Groundwaters were also collected from two different sources viz., hand pumps and submersible pumps.

It is necessary to examine the pollution load of aquatic aquifers (surface and groundwater systems) by direct estimation of its physico-chemical characteristics (Popoola *et al*., 2019; Qureshi *et al*., 2021) but at the same time, it is equally important to estimate its ecological risks. Many indices have been established and are used to monitor the quality of both ground and surface water bodies (Ahmed *et al*., 2021; Huang *et al*., 2021). For example, estimated daily intake (EDI) for any chemical contaminant represents the total exposure of it from all known or suspected exposure pathways for an average person (Luo and Jia, 2021). In the study, EDI was used for the chromium and cadmium metal transfer from groundwater to human. Cancer risk quotient indicated the tendency of the contaminant to induce cancer, while target health quotient evaluated the overall health risks. In the present study, the health risk assessment of chromium and cadmium was carried out using estimated daily intake (EDI), target hazard quotient (THQ) and cancer risk (CR) quotients.

MATERIALS AND METHODS

Kapurthala district, once a princely state ruled by Ahluwalia Dynasty during the British India era, is located between 31°21'56.16'' N latitude and 75°17'40.56'' E longitude and has a population estimation of about 8.16 lakhs as shown in Fig. 1. Beas river flows through the district of Kapurthala. It is an area of environmental importance, due to the presence of Kanjali wetland, designated as a Ramsar site of international importance as it

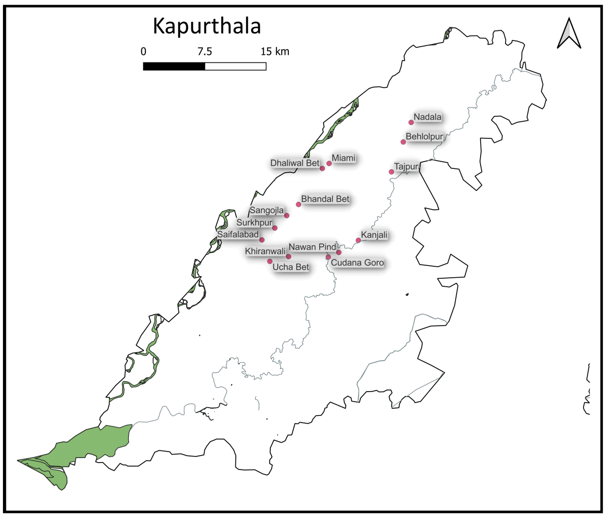

Fig. 1. Map of sampling sites of Kapurthala region prepared using QGIS software.

attracts a lot of migratory species of birds. However, due to various anthropogenic activities and high pollution of the Ramsar site, the number of species has been greatly influenced. The major occupation of the people of this area is agriculture.

Water samples were collected from 15 villages potentially exposed to anthropogenic and agricultural activities, of Kapurthala district, Punjab (India). Groundwater samples were collected using two different sources (hand pumps and submersible pumps). The geographical latitudes and longitudes were noted using global positioning system (GPS) at the time of sampling as shown in Table 1.

The water samples were collected in pre-acid washed dried bottles. After proper sealing and labelling, the samples were brought to the laboratory where the samples were filtered using Whatman no 1 filter paper. The samples were further analyzed for the contents of chromium and cadmium using Inductively Coupled Plasma - Mass Spectroscopy (ICP - MS) at CSIR - National Environmental Engineering Research Institute, Nagpur.

Human health risk assessment was conducted following the estimated daily intake (EDI), cancer risk (CR) and target hazard quotient (THQ).

Intake of heavy metals from drinking water was used as one of the criteria to assess health risks. Estimated daily intake (EDI) of metals through consumption water samples collected using hand pump source and submersible sources was calculated adopting United States Environmental Protection Agency (USEPA, 2000) as

$$EDI = \frac{C \times IR \times ED \times EF}{BW \times AT} \quad \text{...(Eq. 1)}$$

Where, 'EDI' was the estimated daily intake (µg/kg/ day--); 'C' was the concentration of chromium in water; 'IR' was the water intake rate (2 l/day); 'ED' was the exposure duration in years (assumed to be 68.8 years in India); 'EF' denoted exposure frequency (365 days/ year), 'BW' was the body weight (57.7 kg in Asia); 'AT' denoted the average life span (25112 days) according to USEPA (2011).

Target hazard quotient (THQ) can be defined as the ratio of EDI to the reference dose (RfD). It was calculated as:

$$THQ_S = \frac{EDI}{RFD} \quad \text{...(Eq. 2)}$$

Where, 'EDI' was the estimated daily intake; 'RfD' was the reference dose (Here, taken as oral reference dose) and RfD (µg/kg/ day--) represented the dose of reference of chromium and cadmium. The value of THQ < 1 implied no significant non-cancer risk, whereas THQ > 1 implied significant cancer risk (Bamuwamye *et al.*, 2017).

Cancer risk (CR) is an entity used to measure the risk of cancer due to exposure with a carcinogenic entity which can be heavy metals

Table 1. Geographical locations of sampling sites for collection of water samples from different villages of Kapurthala, Punjab (India) in vicinity of Kanjali wetland

S. No.	Name of village	Sample code	Geographic location	
			Latitude	Longitude
1.	Miami	MM	31°29' 41.4594" N	75°19' 44.868" E
2.	Dhaliwal Bet	DB	31°29' 20.328" N	75°19' 14.844" E
3.	Bhandal Bet	BB	31°26' 52.728" N	75°17' 33.180" E
4.	Sangojla	SG	31°26' 6.216" N	75°16'41.375" E
5.	Surkhpur	SK	31°25' 14.376" N	75°15' 49.320" E
6.	Saifalabad	SF	31°24' 24.696" N	75°14' 52.476" E
7.	Ucha Bet	UB	31°23' 1.356" N	75°15' 34.415" E
8.	Khiranwali	KW	31°23' 24.1074" N	75°16' 59.879" E
9.	Cudana Goro	CG	31°24' 30.852" N	75°20' 3.7674" E
10.	Nawan Pind	NP	31°23' 50.928" N	75°20' 51.108" E
11.	Kanjali	KJ	31°24' 42.768" N	75°22' 18.4794"E
12.	Tajpur	TP	31°29' 20.903" N	75°24' 35.424" E
13.	Behlolpur	BP	31°31' 21.756" N	75°25' 22.944" E
14.	Nadala	NL	31°32' 40.74" N	75°25' 54.876" E
15.	Chakoki	CK	31°49' 42.887" N	74°30' 25.632" E

or pesticides. During the present study, it was used in reference to two metals viz., chromium and cadmium. CR was calculated using following equation:

$$CR – EDI \times CSF \quad \text{...(Eq. 3)}$$

Where 'CR' represented cancer risk; 'EDI' was the estimated daily intake (µg/kg/ day--); 'CSF' was the cancer slope factor and represented (µg/kg/day). The CSF value for chromium was taken as (41 µg/kg/day), while for cadmium, it was (50 µg/kg/day) (USEPA).

In order to study the characteristics of water samples, the concentrations of heavy metals content were subjected to multivariate statistics viz., Hierarchical Cluster analysis (CA) by using Paleontological software (PAST) to determine association as well as the differences in the concentration between different sampling sites.

RESULTS AND DISCUSSION

Urbanization coupled with industrial development in many regions of the world has generated huge quantities of waste and harmful contaminants that in turn have polluted various precious natural resources. Among various resources, water aquifers are considered to be the most important to sustain life on earth. However, leachates from urban waste dumping yards, percolation of surface runoffs, leakages from sewerage systems and direct release of untreated or semi-treated industrial effluents containing contaminants like heavy metals, pesticides and other organics as well as inorganics have deteriorated the groundwater quality. Wetlands, being in the low-lying area, often receive the surface runoffs from the adjacent areas including agricultural fields and dumping sites and get contaminated. As wetlands are also one of the sources for groundwater recharge, variable pollutants from contaminated water can easily lead to the groundwater contamination. The consumption of contaminated water ultimately poses great risk to human health (Bamuwamye *et al.*, 2017; Emmanuel *et al.*, 2022). Heavy metals like chromium and cadmium are considered as hazardous elements due to their toxicity to the environment as well as long half-life and non-biodegradable nature. As most of the areas adjacent to Kanjali wetland belong to the category of agricultural fields, the risk of contamination of groundwater can lead to contamination of food crops ultimately posing threat to the living beings. Considering the same, present study was planned to estimate the contents of chromium and cadmium in groundwater samples of 15 villages collected from vicinity of Kanjali wetland (Ramsar site) in Kapurthala district, in Punjab (India) and to study their potential health risk using health quotients like estimated daily intake (EDI), target hazard quotient (THQ) and cancer risk (CR).

Results of chromium content in hand pump water sample and submersible pump water samples of Kapurthala district are summarised in Table 2 and Fig. 2. It was seen that among the water samples collected using hand pumps, only two samples viz., Surkhpur (SK) and Chakoki (CK) showed the chromium content, whereas in all the other samples chromium content was below detection limit (BDL). Mean chromium content varied from 1.058 to 3.730 µg/l (at SK) in water samples of the hand pumps. For water samples collected using submersible pumps, all 15 samples showed chromium content which varied as 0.0396 µg/l (UB) to 0.9541 µg/l (Khiranwali, KW). The cadmium content was found in only one water sample collected using hand pump from Surkhpur as 2.56 µg/l and cadmium was found to be below detection limit for water samples collected using submersible pumps. All the samples showed that chromium content was below the safe drinking limits (100 µg/l) as prescribed by World Health Organization (WHO). The level of harm caused by heavy metals to human health is directly influenced by their daily consumption. This study considered the intake of heavy metals through drinking water and absorption through the skin. The initial step in assessing non-carcinogenic effects involved calculating the chronic daily intake (CDI) values. During present study, estimated daily intake (EDI) for Cr metal varied from 0.03667 Chakoki: CK) to 0.1292 µg/kg/day (Surkhpur: SK) for hand pump samples and 0.0091 (Nawan Pind: NP) to 0.0331 µg/kg/day (Khiranwali: KW) for submersible pumps, while for Cd metal, EDI was observed as 0.0887 µg/kg/day for SK sample. Mohammadi *et al.* (2019) examined the potential carcinogenic and non-carcinogenic hazards on the drinking water of

Table 2. Content (mg/l) of chromium and cadmium in underground water samples collected from different villages of Kapurthala, Punjab (India) and its estimated daily intake, cancer risk and target hazard quotient

S. No.	Sample code	Content of metal (µg/l)		Estimated daily intake (µg/kg/day)		Cancer risk		Target hazard quotient	
		Hand pump	Submersible	Hand pump	Submersible	Hand pump	Submersible	Hand pump	Submersible
Chromium									
1.	MM	BDL	0.5963	-	0.020669	-	0.847428	-	0.068897
2.	DB	BDL	0.3009	-	0.01043	-	0.427622	-	0.034766
3.	BB	BDL	0.6514	-	0.022579	-	0.925733	-	0.075263
4.	SG	BDL	0.3554	-	0.012319	-	0.505075	-	0.041063
5.	SK	3.730	0.5860	0.129289	0.020312	5.300849	0.83279	0.430963	0.067707
6.	SF	BDL	0.7087	-	0.024565	-	1.007165	-	0.081883
7.	UB	BDL	0.0396	-	0.001373	-	0.056306	-	0.004578
8.	KW	BDL	0.9541	-	0.033071	-	1.355913	-	0.110237
9.	CG	BDL	0.7985	-	0.027678	-	1.134783	-	0.092259
10.	NP	BDL	0.2628	-	0.009109	-	0.373477	-	0.030364
11.	KJ	BDL	0.2805	-	0.009723	-	0.398631	-	0.032409
12.	TP	BDL	0.4775	-	0.016551	-	0.678596	-	0.055170
13.	BP	BDL	0.4242	-	0.014704	-	0.602849	-	0.049012
14.	NL	BDL	0.7746	-	0.026849	-	1.100818	-	0.089497
15.	CK	1.058	0.5071	0.036672	0.017577	1.5006	0.720662	0.122	0.058590
Cadmium									
1.	SK	2.56	-	0.0887	-	4.435	-	1.774	-

All samples except SK have shown the content of cadmium as BDL (Below detection limit).

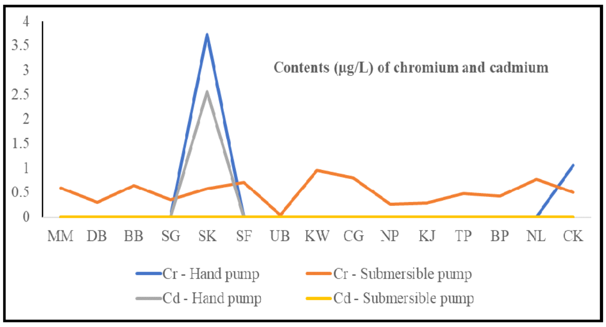

Fig. 2. Contents of chromium and cadmium in different water samples collected from Kapurthala, Punjab (India) in vicinity of Kanjali wetland.

Khorramabad, Iran. The average EDI values (in mg/kg/day) for different heavy metals were: 0.0001 for Pb (lead), 0.00116 for Cr (chromium), 0.0000134 for Cd (cadmium), 0.000016 for Mo (molybdenum), 0.00148 for Zn (zinc), 0.000213 for Cu (copper), 0.00255 for Ba (barium) and 0.000109 for Ni (nickel). Among these heavy metals, the order of EDI values for adults based on concentration levels was found to be Zn > Ba > Pb > Ni > Cr > Cu > Cd > Mo.

During the present study, for handpump samples, Surkhpur (SK) showed the maximum values for cancer risk (CR) as 5.3008 and target hazard quotient (THQ) as 1.774 for Cr metal, while for CR as 4.435 and THQ as 4.436 for Cd metal in water sample. When the target hazard quotient (THQ) was less than 1, it was generally considered safe in terms of non-carcinogenic risks. However, if the THQ exceeded 1, there was a higher probability of non-carcinogenic effects as the value increased. In a study conducted by Haque *et al.* (2018) on the human health risks, both carcinogenic and non-carcinogenic, associated with exposure to heavy metals in the surface water of Padma river, the average levels of non-carcinogenic risk (HQ) in surface water were observed in the following descending order: Cr > Cd and As > Pb > Cu > Ni > Zn through ingestion, and Cr > Cd > As > Pb > Cu > Zn > Ni through dermal contact for children. For adults, the trend was Cd and As > Pb > Cu > Ni > Zn > Cr through ingestion, and Cr > Cd > As > Pb > Cu > Zn > Ni through dermal contact.

According to International Agency for Research on Cancer, chromium (Cr), arsenic (As), nickel (Ni) and cadmium (Cd) belong to Group 1 carcinogens, indicating that the presence of these heavy metals in a specific area can contribute to cancer risk. The permissible limits for these heavy metals were 10^{-6} and < 10^{-4}, respectively. Similarly, other studies have reported potential cancer risk values for four toxic metals, namely, Cr, Ni, Cd and As, with mean values of 0.0062 for Cr, 0.00048 for As, 0.0004 for Ni and 0.000012 for Cd (Chahal *et al.*, 2022). In the research conducted by Mohammadi *et al.* (2019), the cancer risk assessment due to heavy metals was calculated, revealing that chromium had the highest likelihood of cancer risks (mean ILCR 0.00654), while nickel had the lowest chance of cancer risk (mean ILCR 0.0000916). The cumulative cancer risk associated with the studied metals was found to be 0.000349 for children and 0.000374 for adults. These results indicated a higher cancer risk for adults compared to children. The evaluation of cancer risks resulting from exposure to Cr, Cd and the cumulative cancer risk value in the present study exceeded the acceptable range for cancer health risk, which was 1.00×10^{-6} to 1.00×10^{-4} (Haque *et al.*, 2018).

The hierarchical cluster analysis using nearest neighbour method produced three major clusters, between which the variables were significantly ($P < 0.05$) different (Fig. 3). Cluster 1 was produced by aggregating the site Tajpur (TJ), Chakoki (CK) and Behlolpur (BP), cluster 2 was formed by aggregating the sites Sangojla (SG), Nawanpind (NP) and Kanjali (KJ) and Dhaliwal Bet (DB), while cluster 3 depicted sites Surakhpur (SK), Miami (MM), Bhandal Bet (BB), Saifalabad (SF), Cudana Goro (CG) and Nadala (NL) showing close association on the metal content background contamination and spatial distribution, while site Ucha Bet (UB) and Khiranwali (KW) did not form direct clustering with any of the cluster but associated with clusters 2 and 3, respectively.

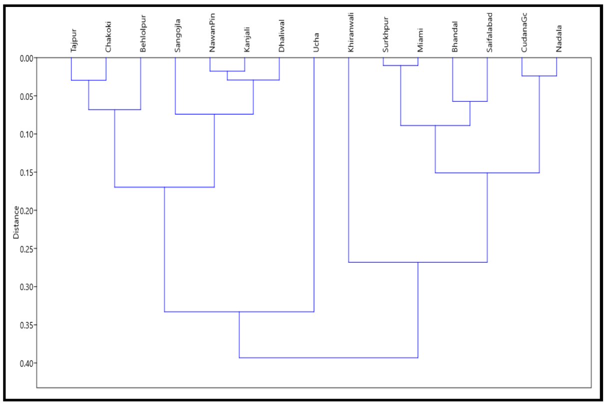

Fig. 3. Dendrogram of cluster analysis showing clustering of different sampling sites of Kapurthala, Punjab (India) in vicinity of Kanjali wetland.

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