Proceedings of the Indian National Science Academy (2025) 91:767–782
https://doi.org/10.1007/s43538-024-00358-y

RESEARCH PAPER

Potential toxic elements in groundwater: a health risk in parts of northern Delhi

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Received: 26 July 2024 / Accepted: 1 October 2024 / Published online: 14 October 2024

Abstract

Groundwater quality and its implication on human health is a matter of concern in the semi-arid region of northern India. The present work deals with the elevated concentration of potential toxic elements (PTEs) in the groundwater in parts of Northern Delhi and their impact on human health. Groundwater samples were collected from thirty-three locations during the 2019–2021 sampling campaigns. The collected groundwater samples were analyzed for Electrical Conductivity (EC), and 'As', Mn, Cd, Cu, Cr, Pb, and Zn elements. The mean concentration of PTEs followed the order of Pb < Cr < Cd < As < Cu < Zn < Mn. Almost all the groundwater samples had EC beyond the desired drinking water limits. Pb, Cr, Cu, and Zn concentrations were within permissible limits. However, the Cd concentration in the study area's sampled groundwater was found in the range of 6.54 to 7.03 µg/l, with a mean of 6.69 µg/l, which is beyond the World Health Organization (WHO) permissible limit of 3.0 µg/l. The 'As' values were in the range of 0.49 to 73.75 µg/l, where in around 24% of the groundwater samples, it was above the WHO permissible limit of 10 µg/l. Further, the Mn concentration in groundwater beyond the permissible limit was observed in a single sample. The research in the article proposes a possible reason for the observed concentration of the PTEs in the study area. The cancer and non-cancer health risks were analyzed for both adults and children. The health risk assessment investigated using the Total Hazard Index (THI) indicates that in thirteen groundwater samples, both age groups are vulnerable to non-carcinogenic risks. However, children are more vulnerable than adults. About 39% and 42% of water samples showed high carcinogenic risk, respectively, for both adults and children. The spatial distribution map for the carcinogenic risk reveals that except for a few small patches, the whole study area is highly vulnerable to the carcinogenic risk for adults and children. Thus, it is imperative that the water quality is monitored with an evenly distributed denser network of sampling stations by the concerned Government institutions and adequate mitigation measures are adopted. Awareness regarding the health impacts of PTEs exposure and its further magnification will prevent the health hazards.

Keywords Groundwater · Potential toxic elements · Health risk assessment · Cancer and non-cancer risk · Sustainable development goals (SDG) · Delhi

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Introduction

Water is a vital resource for the sustenance of life on Earth. In many regions worldwide, including India, groundwater is a major source of freshwater, especially given the growing population and increasing demands. However, this valuable resource is under threat due to various human activities (Goswami et al. 2022; Guo et al. 2023). Over-exploitation of groundwater for domestic, irrigation, and industrial purposes has lowered the water table and degraded the water quality (Li et al. 2016, 2019; Khalid et al. 2020). Groundwater may contain salt and minerals leached out from the parent rock (Todd and Mays 2004; Kumar et al. 2016). In modern times, potentially toxic elements (PTEs) discharged through industrial effluents are polluting both the surface as well as the groundwater (Agrawal et al. 2010; Jaishankar et al. 2014; Singh et al. 2018; Burri et al. 2019).

Groundwater contaminated with both natural and anthropogenic sources has been reported to have several common PTEs such as arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), manganese (Mn), lead (Pb), and zinc (Zn) (Alsubih et al. 2021; Joshi et al. 2022). The presence of these elements can cause neurological damage, cancer, and may lead to developmental disorders (Bodrud-Doza et al. 2019). In urban areas, groundwater contain many PTE toxins, which may be accentuated by relocation of the rural–urban population (Biksham et al. 1991; Bhutiani et al. 2017; Kumar et al. 2017b; Prasad et al. 2019; Rezaei et al. 2019; Asim and Rao 2021; Yadav et al. 2022; Joshi et al. 2022). The deterioration in the groundwater quality due to PTE pollution may be attributed to rapid urbanization and the lack of public concern (Raju et al. 2011; Rao 2012; Devi and Yadav 2018; Chu et al. 2019; Tortajada 2020; Yadav et al. 2022; Nayak et al. 2023).

Amongst PTEs, the metal toxins have a relatively high density and are toxic at very low concentrations (Vardhan et al. 2019). The genesis of these PTEs in groundwater is influenced by various natural activities like the leaching and weathering of metalliferous formations and minerals, and their dissolution is influenced by the pH, redox potential, and mineralogy of the aquifer (Embaby and Redwan 2019; Vinnarasi et al. 2022). Anthropogenic activities like intensive metal mining, smelting, industrial activities, urbanization, waste dumping, and agricultural practices with intensive use of pesticides and fertilizers also contribute to groundwater pollution by the PTEs (Ghosh et al. 2015; Balkhair and Ashraf 2016; Bhutiani et al. 2016; Gupta et al. 2016; Aithani et al. 2020; Adimalla et al. 2020; Gupta and Raju 2023).

The demand for fresh drinking water in northern India is increasing with the population density, and in megacities like Delhi, the capital of India, the freshwater requirement is very high (Rai 2011). Various researchers confirmed the elevated concentration of PTEs in the groundwater above the maximum permissible limit (WHO 2017) derived from both point sources, such as industries, and non-point sources, such as irrigation (Datta et al. 1996; BIS 2012; Shekhar et al. 2015; FAO 2016; Sarkar and Shekhar 2018; Khan and Rai 2022; Swain et al. 2022).

Delhi, is the backbone of the country's economy and significantly contributes to its gross domestic product (Kumar and Sarkar 2017). Exposure to PTEs through drinking water can not only affect health but also negatively impact the work capacity of the populace, which ultimately increases hospital expenses and hinders economic growth as well as accomplishment of UNSDG goals for a better sustainable future (https://www.un.org/sustainabledevelopment/sustainable-development-goals). The contamination of groundwater in parts of Delhi by various pollutants, including PTEs, has been researched in parts, thereby creating knowledge gaps that require further exploration (Sarkar and Shekhar 2015; Ghosh et al. 2015; Sarkar et al. 2016; Sarkar et al. 2017; Alsubih et al. 2021; Asim and Rao 2021; Sharma et al. 2022). The previous studies have focused on specific areas within certain regions, leaving gaps in our understanding of the overall spatial distribution of PTEs contamination. A more comprehensive spatial analysis across various zones and aquifers is required to fill these gaps and provide a holistic understanding of PTEs contamination in groundwater. Additionally, identifying the specific sources of PTEs contamination and apportioning their contributions remain a challenge. Long-term monitoring and analysis of groundwater quality data are needed to assess temporal variability and trends in PTE concentrations and their potential impacts on human health. Further, the health implications of the toxicity need detailed studies as the toxic chemicals show variations in the mobility and accumulation in human systems. In this context, the research aims to address these gaps by providing knowledge about PTE distributions in alluvial aquifers of the study area, proposes a possible reason for their observed anomalous concentrations, and it undertakes related human health risk assessment. The groundwater sampling was restricted to the first unconfined alluvial aquifer (CGWB 2016). The study aims to lay the foundation for focused research towards mitigation measures.

Research methodology

Study area

The study was conducted in part of the Yamuna basin of northern India, and it encompasses the northern part of Delhi (Fig. 1). The river Yamuna flows along the eastern

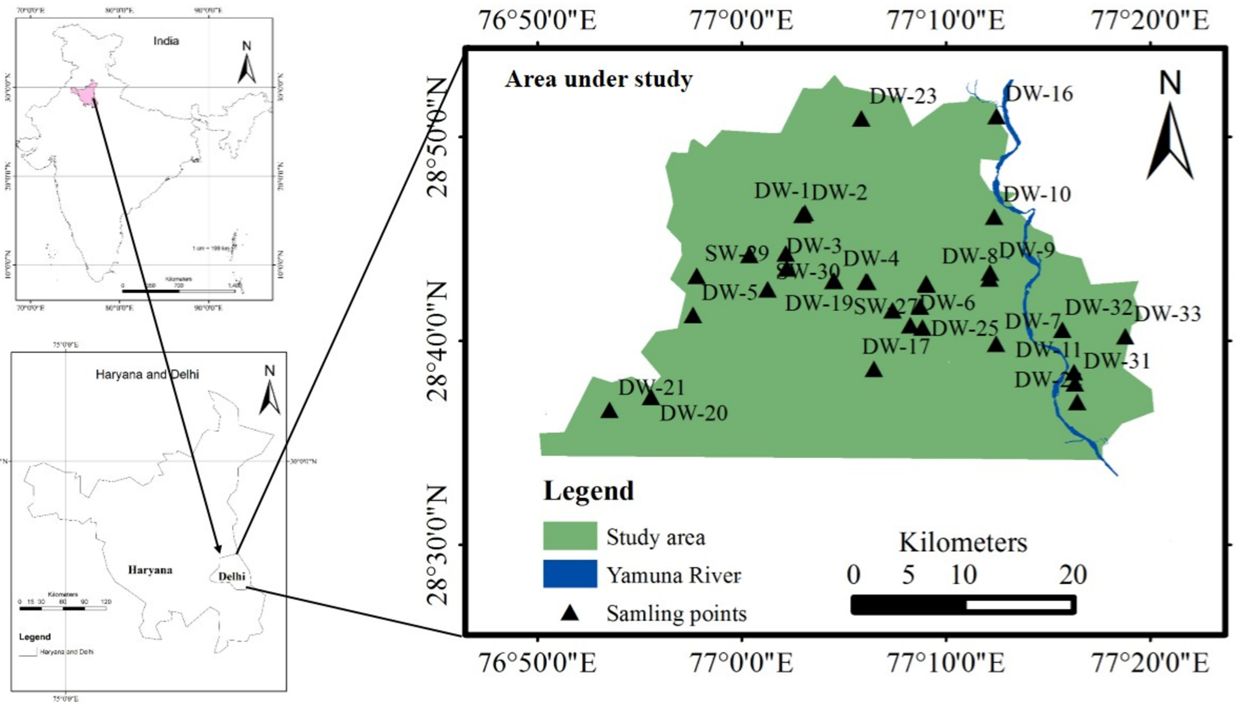

Fig. 1 Map showing study area and location of sampling points DW-1: Puthkhurd 1; DW-2: Puthkhurd 2; DW-3: Karala 1; DW-4: Puthkalan 1; DW-5: Tikari Kalan; DW-6: Sakurbasti; DW-7: Pulbangash; DW-8: Dhirpur Temple; DW-9: Dhirpur Orphanage; DW-10: Palla (Burari); DW-11: Bank Enclave; DW-12: Rithala 1; DW-13: Rithala 2; DW-14: Sainik Vihar; DW-15: Pitampura; DW-16: Palla Temple; DW-17: Tagore Garden; DW-18: Karala 2; DW-20: Puthkalan 2; DW-20: Kair; DW-21: Mundhela; DW-22: Akshardham; DW-23: Narela; DW-24: Shalimar Bagh; DW-25: Bitania; SW-26: Karala Village; SW-27: Shalimar Bagh; SW-28: Kanjhawala; SW-29: Nizampur; SW-30: Ranikhera; DW-31: Lalita Park; DW-32: Shastri Park; DW-33: Vivek Vihar

margin of Delhi from north to south (Datta et al. 1997; Shekhar et al. 2009; Shekhar and Prasad 2009). The region's climate is subtropical to semi-arid, with an annual maximum mean temperature of 39.5 °C in May and a minimum mean temperature of 6.3 °C in January. This area received an average annual rainfall of 611.8 mm, which varies according to the seasons (Chatterjee et al. 2009; Sarkar and Shekhar 2018; Agarwal et al. 2021).

Delhi city has a notable pollution load in water and groundwater. Rapid population migration towards the city due to job prospects and better lifestyle is adding pressure on its carrying capacity (Kumar et al. 2018). The population was 167.53 lakh in 2011, and is continuously increasing with time, making it one of the most densely populated cities in the world (Sarkar et al. 2016). Delhi is a symbol of India's progress and potential in the twenty-first century, which contributes about 4% of the national GDP; according to the national budget 2023, the Gross State Domestic Product (GSDP) of Delhi for 2022–23 is projected to be Rs 10.4 lakh crore, amounting to growth of 15.4% over 2021–22 (Delhi budget analysis 2024). The higher population density and limited water resources also play a significant role in groundwater contamination.

The sampling area, mainly covered by Quaternary sediments, comprises older alluvium, and it mostly contains oxidized silt, clay mixed with kankar, and micaceous grey sand (Thussu 2006). The battery of wells in Palla of the Yamuna floodplain on the eastern margin is one of the primary groundwater sources in urban and peri-urban areas of Delhi, India (Kumar et al. 2017a; Sarkar et al. 2024). Further, groundwater recharge in the investigated area occurs through canals, monsoonal rainfall, irrigation water, the Yamuna, and other water bodies (Chatterjee et al. 2009; Shekhar et al. 2009; Shekhar and Sarkar 2013; Sarkar and Shekhar 2018). In a significant portion of the study area, the dynamic groundwater resources have been categorized as semi-critical, critical, and overexploited, indicating declining trends in the water levels (CGWB 2023).

Sample collection and analysis

A total of thirty three samples were collected from different water wells during 2019–2021 using hand pumps (HP) and tube wells (TW) from shallow (< 15 m) and greater depth aquifers (> 15 m) in the peri-urban and rural areas of Delhi, India. A systematic random technique was adopted for the collection of groundwater samples. The Global Positioning

System (GPS) (eTrex VISTA HCx) was used to note the latitude and longitude (Fig. 1). About 150 ml of water samples were collected in pre-cleaned polypropylene bottles (Polylab) from each sampling point after 3 to 5 min of pumping of TW and HP using American Public Health Association standard methods/protocols (APHA 2012). To avoid oxidation, bottles were filled to the brim to prevent air bubbles from being trapped. Before this, samples were filtered with a 0.45 µm polycarbonate membrane filter and acidified with 0.5 ml 14 M ultrapure HNO_3/l to analyze trace elements (APHA 2012; Goswami et al. 2022). All samples were tightly sealed, brought to the laboratory, and stored at 4ºC until further analyses for 'As', Cd, Cu, Cr, Mn, Pb, and Zn.

Analytical procedure and QA/QC report

To investigate human health risks from PTE exposure through contaminated groundwater, the samples were analyzed for electrical conductivity (EC), pH, and PTEs following the standard protocols (APHA 2012). Preserved samples were filtered with 0.45 mm Millipore membrane filter paper and directly aspirated in the Q-ICPMS to detect toxic trace element concentration. 'As', Cd, Cu, Cr, Mn, Pb, and Zn concentrations were determined using Q-ICPMS (Thermo Scientific make, model iCAPO) at the Inter-University Acceleration Centre, New Delhi, India. During analysis, the quality assurance and quality control measures (QA/QC) were implemented to ensure the precision and accuracy of the results. A commercial multi-element standard solution from VHG Labs was used as a standard to perform the calibration (1–100 µg/l), and calibrated glassware and Milli-Q deionized water were used in the analysis. Milli-Q deionized water (type 1 water) containing 1% nitric acid was analyzed to monitor background intensities and background equivalent concentrations (in µg/l) as given in Table 1 (Konieczka 2007).

The multi-element standard solution (25 µg/l) from VHG Labs was measured at an interval of every ten samples as unknown. For data validation, we followed Sarath et al. 2023 protocols where "a standard multi-element solution (VHG Labs) of known concentration (25 µg/l) was run considering as an unknown sample with an interval of 10 samples, and the percentage offset observed was less than 5%. The precision of measurements was maintained within 5% RSD for all elements". All results are an average of 3 replicates (n = 3).

Statistical analysis and interpolation methods

For all thirty three groundwater samples, the descriptive statistics of water quality parameters (mean, minimum, maximum, and standard deviation) were obtained, and a Pearson correlation matrix was performed using Origin 2021 software. The estimated concentration of the water quality parameters (EC, pH, As, Cd, Cu, Cr, Mn, Pb and Zn), non-carcinogenic risk (using Hazard Quotient and Total Hazard Index), and carcinogenic risk (CR) were interpolated to prepare spatial distribution maps for the whole study area using the IDW (Inverse Distance Weighted) interpolation on ArcMap 10.3.

Health risk assessment (HRA)

The carcinogenic risk (CR) and non-carcinogenic risk (NCR) linked with the oral intake of PTEs in water was estimated using the conventional USEPA (2009) model. The average daily intake (ADI) of PTEs through ingestion route for children and adults was estimated using Eq. 1 (Wei et al. 2015; Qasemi et al. 2018; Singh et al. 2020).

$$ADI_{ingestion} = (C \times IR \times EF \times ED) / (BW \times AT), \quad (1)$$

where C is the PTEs concentration in given water samples (mg/L); IR (Ingestion rate) is the daily water intake (L/day); EF indicates the exposure frequency (Days/year); ED indicates the exposure duration (Year); BW indicates the bodyweight of studied age group (kg); and AT indicates the average timing (Days). A detailed summary of C, IR, EF, ED, BW, and AT and their units for adults and children is given in Table 2.

The HRA for non-carcinogenic hazard (Hazard quotient) from PTEs oral intake was estimated using Eq. 2

Table 1 PTEs concentration in certified reference material STANDARD USED: VHG labs PN.:VHG-ZSPANAL1720-100 (After Sarath et al. 2023)

Elements	MQ-water (with 1% HNO_3)	Ref value	Mean measured	% Offset	%RSD observed
As	0.87	25.00	25.88	3.53	4.70
Cd	0.25	25.00	25.73	2.91	0.60
Cu	BDL	25.00	25.32	1.28	1.10
Cr	0.18	25.00	25.90	3.60	0.50
Pb	0.12	25.00	25.79	3.16	1.10
Mn	0.28	25.00	25.16	0.62	3.30
Zn	BDL	25.00	25.98	3.94	2.90

Table 2 Factors used in investigating health risks due to PTE exposure in groundwater (Singh et al. 2020; Qasemi et al. 2022; Naz et al. 2016a)

Risk exposure factors	Abbreviation	Values for groups		Unit
		Adults	Children	
Element concentration	C	Measured	Measured	mg/L
Daily ingestion rate	IR	2	1	L/day
Exposure frequency	EF	365	365	Days/year
Exposure duration	ED	30	12	Year
Body Weight	BW	60	20	Kg
Average timing	AT	10,950	4380	Days

(Fallahzadeh et al. 2018a; Adimalla et al. 2018; Radfard et al. 2019; Singh et al. 2020; Qasemi et al. 2022; Rajan and Nandimandalam 2024).

$$\mathrm{HQ} = \mathrm{ADI}_{\mathrm{ingestion}} / \mathrm{RfD}, \tag{2}$$

where HQ is the hazard quotient, and RfD is the oral reference dose, the HQ was used to evaluate the probable chronic non-carcinogenic risk associated with the oral intake of PTEs. The values of RfD for different PTEs are summarized in Table 3 (Singh et al. 2020).

To estimate the combined non-carcinogenic impact on account of oral intake of the multiple contaminants (‘As’, Cd, Cr, Cu, Pb, Mn, and Zn), the sum of the HQ values of all contaminants is defined as the Total Hazard Index (THI; Eq. 3).

$$\mathrm{THI} = \sum_{k=1}^{n} \mathrm{HQ} = \mathrm{HQ}_{\mathrm{Arsenic}} + \mathrm{HQ}_{\mathrm{Cadmium}} + \mathrm{HQ}_{\mathrm{Chromium}} + \mathrm{HQ}_{\mathrm{Copper}} + HQ_{\mathrm{Lead}} + HQ_{\mathrm{Manganese}} + HQ_{\mathrm{Zinc}} \tag{3}$$

If the value of HQ or THI is ≥ 1, it indicates a hazardous/deleterious status (Ali et al. 2019). It has non-carcinogenic risk on human health, and if HQ or THI is < 1, then it is considered within the acceptable range (Fallahzadeh et al. 2018b; Ahmed et al. 2019; Qasemi et al. 2022; Sajjadi et al. 2022). Further, the lifetime carcinogenic risk was estimated using only arsenic concentration, a potentially toxic element in groundwater using Eq. 4 (Jha et al. 2023),

$$\mathrm{CR}_{\mathrm{Arsenic}} = \mathrm{ADI}_{\mathrm{Arsenic}} \times \mathrm{CSF}_{\mathrm{Arsenic}}, \tag{4}$$

where $\mathrm{CR}_{\mathrm{Arsenic}}$ is the carcinogenic risk to human health by oral intake of water with the given ‘As’ concentration, and $\mathrm{CSF}_{\mathrm{Arsenic}}$ is the cancer slope factor for ‘As’ (Table 3; Wei et al. 2015; Singh et al. 2020).

Results and discussion

Various parameters such as EC, pH, and PTEs were analyzed to evaluate non-carcinogenic and carcinogenic impacts on human health (Alzaridi and Kurnaz 2022). The pH or hydrogen ion activity was expressed on a logarithmic scale and represents the negative base-10 log of the hydrogen ion concentration. The permissible limit for drinking water pH is 6.5–8.5 (WHO 2017). The pH of groundwater samples in the study area ranges from 7.2 to 8.5, with a mean value of 8.05, indicating a higher groundwater alkalinity (Table 4).

The EC of a sample is an indicator of the dissolved solids or salts in water (Todd and Mays 2004). The highest observed EC was 31.5 mS/cm, and the mean EC was 5.28 mS/cm (Table 4). It was observed that 61% of the groundwater samples had EC beyond the desirable limit, which is unsuitable for drinking purposes (WHO 2017).

Table 3 Oral reference dose and cancer slope factor (CSF) values of PTEs in groundwater

Risk category	PTEs	$\mathrm{RfD}_{\mathrm{Ingestion}}$ (mg/kg/day)	$\mathrm{CSF}_{\mathrm{Ingestion}}$ (mg/kg/day)	References
Non-carcinogen	Cd	0.003	0.5	USEPA (2011), Aendo et al. (2022)
	Cr	0.003	0.5	USEPA (2011), Qiu et al. (2021), Aendo et al. (2022)
	Cu	0.04	NA	Qiu et al. (2021), Aendo et al. (2022),
	Pb	0.0014	NA	Aendo et al. (2022)
	Mn	0.024	NA	Naz et al. (2016a), Aendo et al. (2022)
	Zn	0.3	NA	Naz et al. (2016a), Qiu et al. (2021), Aendo et al. (2022)
Carcinogen	As	0.0003	1.5	USEPA (2011), Victor et al. (2018), Niknejad et al. (2023)

Table 4 PTEs and other groundwater quality parameters of the study area

Statistics	pH	EC mS/cm	As µg/l	Cd µg/l	Cr µg/l	Cu µg/l	Mn µg/l	Pb µg/l	Zn µg/l
Minimum	7.20	0.29	0.49	6.54	2.18	1.95	0.41	0.34	5.49
Maximum	8.50	31.50	73.75	7.03	8.53	75.36	3389.19	8.37	710.27
Mean	8.05	5.28	7.20	6.69	4.72	31.20	138.41	0.91	41.38
Standard deviation	0.35	7.28	14.80	0.09	1.38	22.17	588.18	1.57	125.85
Standard limit (WHO 2017)	6.50–8.50	1.5	10.00	3.00	50.00	2000.00	500.00	10.00	3000.00

Distribution of PTEs concentration in groundwater samples of the study area in the context of their occurrence in northern India

The study has collated the data in detail about the presence of PTE concentrations in groundwater in northern India (Table 5) for its comparison with the observed values of the study area. It emerges that the reported maximum concentration of Cd, Cr, and Pb in different parts of northern India (Table 5) was higher than the observed values of the study area (Table 4). In the context of 'As' concentration in groundwater, except for the data of Delhi reported by Sharma et al. (2022), the 'As' concentration in other parts of northern India is similar to the values observed in the study area. In comparison, the concentration of Cu and Zn in groundwater is mostly higher than the observed values of the study area (Table 5; WHO 2017). The maximum reported Mn in groundwater of the study area (3389.19 µg/l) was abnormally high compared to the reported values in different parts of northern India.

In this study, about 24% of samples showed a concentration of 'As' in groundwater higher than the permissible limit (10.0 µg/l), while 76% showed lower 'As' values. The minimum 0.49 µg/l and maximum 73.75 µg/l concentrations were observed, and the mean value was 7.20 µg/l. Chromium is widely distributed in the Earth's crust, affecting groundwater quality. The acceptable limit in drinking water is 50 µg/l; in the study area, a minimum value of 2.18 µg/l and a maximum value of 8.53 µg/l of Cr in groundwater were observed. Copper is both a fundamental supplement and a drinking water contaminant. The acceptable limit of copper in drinking water is 2000 µg/l, and the mean value of Cu in the study area was 31.20 µg/l (Table 4; WHO 2017).

Manganese levels in freshwater are usually found in the range of 1 to 200 µg/l. The permissible limit of Mn is 500 µg/l. In the groundwater samples of the study area, the maximum concentration of 3389.19 µg/l and average concentration of 588.0 µg/l were observed. All the groundwater samples show lower Pb values within the permissible limit (10.0 µg/l). The maximum 8.37 µg/l and mean 0.91 µg/l concentrations of Pb in groundwater samples were reported. Zinc is a primary component found in all nutrients and consumable water. Drinking water containing Zn at levels over 3000 µg/l may not be satisfactory to humans. A minimum of 5.49 µg/l and a maximum of 710.27 µg/l Zn concentration was observed in the groundwater samples (Table 4; WHO 2017). Further, the IDW (Inverse Distance Weighted) interpolation method on the ArcMap 10.3 platform was used to

Table 5 Summary of PTEs concentrations (µg/l) in groundwater of districts/states of northern India

References	District/state	As	Cd	Cr	Cu	Mn	Pb	Zn
Kumar et al. (2006)	NCT Delhi	–	–	–	BDL-170	10–1960	–	BDL-2120
Lorenzon et al. (2010)	NCT Delhi	35	–	–	–	300	–	–
Sharma et al. (2022)	NCT Delhi	BDL-230	–	–	–	BDL-2110	BDL-30	BDL-3400
Chabukdhara et al. (2017)	Ghaziabad	–	BDL-60	BDL-429	BDL-162	BDL-675	87–552	152–1045
Rai and Saha (2015)	Faridabad	–	–	–	10	50	20	40
Sharma et al. (2019)	Punjab	–	BDL-10	BDL-140	BDL-40	–	BDL-210	70–1020
Kumar et al. (2007)	Punjab	–	–	–	BDL-1940	10–0.300	–	BDL-3800
Naz et al. (2016b)	Sukinda mine	–	–	BDL-249	–	BDL-756	–	BDL-17
Sathe et al. (2021)	Guwahati	BDL-71	–	–	–	BDL-900	–	–
Mani et al. (2021)	Kolkata	–	260–280	–	190–330	380–1100	3040–5760	260–570
Mukherjee et al. (2020)	West Bengal	–	BDL-40	BDL-370	BDL-110	20–290	BDL-170	BDL-750
Present study	Delhi	BDL-73	6–7	2–8	BDL-75	0.4–3389	0.3–8	5–710

Where BDL is below the detection limit

create a spatial distribution map of the PTEs for the study area (Fig. 2).

In context of the discussions above, and the spatial distribution of PTEs concentration in groundwater, it is observed that the concentration of some PTEs are beyond the permissible limit (Fig. 2). The spatial distribution map for the concentration of Cu, Zn, Pb, and Cr in groundwater of the study area shows that most of the groundwater has these PTEs within the permissible limits (Fig. 2). However, the spatial distribution map revealed that a few pockets in the study area have the groundwater polluted with 'As' beyond the permissible limit. The possible sources of 'As' in Delhi's groundwater include arsenic-containing sediments (Shaji et al. 2021) and percolation of chemicals from garbage dumped in open landfills and industrial effluents (Lalwani et al. 2004; Alsubih et al. 2021). The infiltration of sewage from unlined drains, ponds polluted with sewage, and the impact of sewage-contaminated river water on groundwater may contribute to elevated ammonium concentrations (Groeschke et al. 2017). This may lead to the reductive dissolution of Fe-oxyhydroxides in aquifer sediments, triggering the release of geogenic 'As' into the aquifer (McArthur et al. 2004; Bhattacharya et al. 2013).

Meanwhile, the interpolated concentration of Cd reveals that the sampled aquifers of the whole study area, is polluted with higher Cd (Fig. 2). During three detailed field surveys, it was observed that the study area is primarily rural and dominated by good agricultural practices. Also, the urban and rural fringes had many small industries. There are about thirteen government-approved industrial belts in the study area (https://labour.delhi.gov.in/labour/list-approved-industrial-areas-nct-delhi). The reasons for a higher concentration of cadmium could be accounted for by groundwater pollution from the effluents of the steel and plastic industry, batteries, fertilizers, or galvanized pipes and solders used in the tubewells (WHO 2017). Further, the spatial distribution of Mn shows a small area with Mn concentration in groundwater beyond the permissible limit. The anomalous concentration is based on a single sample; hence, a very concrete statement about its genesis cannot be made.

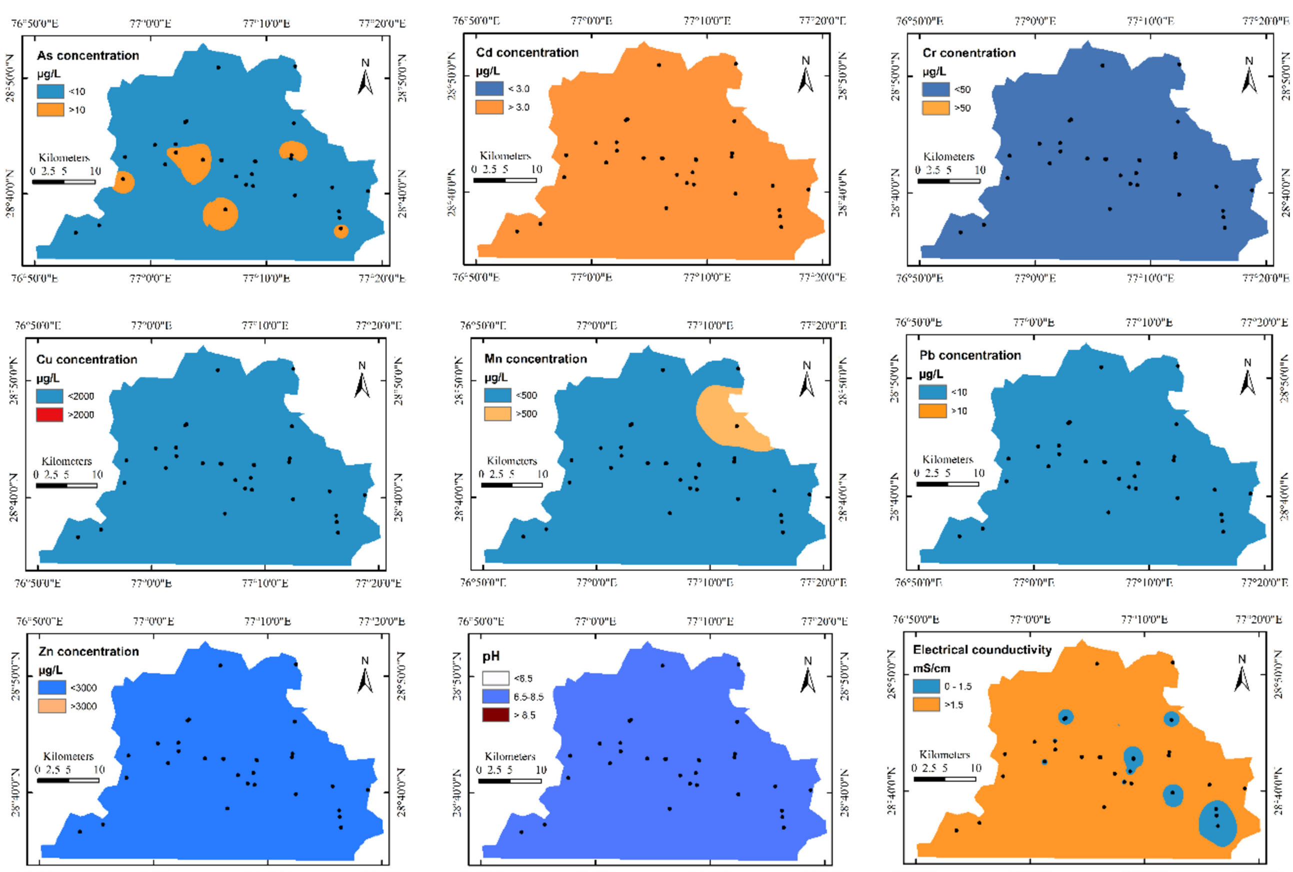

Fig. 2 Spatial distribution of the groundwater quality parameters that is, EC, pH, and concentration of PTEs in groundwater of North Delhi. In the maps, the areal extent of regions with the quality parameter/concentration values less than the permissible limit of WHO (2017) is shown with shades of blue. In contrast, the shades of orange indicate the areal extent of regions with a quality parameter/concentration values more than the permissible limit of WHO (2017)

The interpolation of the electrical conductivity of the groundwater samples reveals that almost the whole area has Electrical Conductivity beyond 1.5 mS/cm, the desired drinking water limit (WHO 2017). Similar observations were made by Ali et al. (2021) for the Older Alluvial Plains of Delhi, which dominates the present study area, and they opined that "the high salinity is mainly due to silicate weathering on account of the longer residence time of the groundwater."

Statistical correlation

Correlation analysis helps to identify the interrelationship between the ions present and the processes that control their concentrations. It is important to note that correlation analysis only measures the strength of the linear relationship between two variables. It has been observed that 'As' positively correlates with EC and Cu. Zinc shows a significant positive correlation with Mn (Table 6).

Ali et al. (2021) proposed silicate weathering as the mechanism for the enrichment of Total Dissolved Solids, leading to higher EC of groundwater in the Older Alluvial plains of Delhi. As mentioned above, the Older Alluvial Plains dominate the study area; the significant positive correlation of 'As' with EC indicates that 'As' pollution of groundwater could be primarily due to silicate weathering. The positive correlation between Cu and EC also indicates that Cu concentration in the groundwater is from geogenic sources.

Health risk characterisation

To assess the health risks associated with trace metals in groundwater, several steps are typically taken, including identification of contaminants, exposure assessment, toxicity assessment, and risk characterization. The results of these characterizations can be used in managing contaminated groundwater. This may include measures to reduce exposure to the contaminants, water treatment, or the installation of monitoring wells to track the movement of the pollutants (Giri and Singh 2015; Duggal et al. 2017). Both carcinogenic and non-carcinogenic pollutants ('As', Cd, Cr, Cu, Mn, Pb, and Zn) were selected to perform the health risk assessment (Ravindra and Mor 2019; Negi et al. 2020; Nizam et al. 2022).

Non-carcinogenic risk

Drinking contaminated groundwater can pose various non-carcinogenic risks to human health, depending on the types and levels of contaminants present (Kaur et al. 2020). Some of the potential non-carcinogenic health risks associated with drinking contaminated groundwater include gastrointestinal problems, neurological disorders, kidney damage, reproductive problems, cardiovascular disease, and liver damage (Bodrud-Doza et al. 2019). Based on the Health Risk Assessment (HRA) model suggested by the USEPA and the evaluation parameters, the non-carcinogenic health risk of potentially toxic metal ('As', Cd, Cr, Cu, Pb, Mn, and Zn) exposure through the oral intake of drinking water in the study area was estimated (USEPA 1999). The estimated Hazard Quotient values on account of oral intake of the observed PTEs concentration in drinking water for adults and children are given in Table 7.

The Hazard Quotient for children was higher than for adults, indicating higher vulnerability of this age group from PTEs in drinking water. The non-carcinogenic Hazard Quotient statistics reveal that in the study area, only two PTEs, 'As' and Mn, have potential health risks from consuming this water by both adults and children (Table 8). In the context of children, it emerges that in about 12% of the sampling sites, the vulnerability to arsenic-related health hazards due to prolonged consumption of this water is high. Similarly, for adults in about 3% of the sampling sites, the vulnerability to arsenic-related health hazards due to prolonged consumption of this water is high (Table 8).

For Mn, in the context of both adults and children, it emerges that in about 3% of the sampling sites, the health

Table 6 Statistical correlation matrix between different water quality parameters in the study area for 2019–2021(N = 33)

Parameters	The correlation coefficient, r								
	pH	EC	As	Cd	Cr	Cu	Mn	Pb	Zn
pH	1.00								
EC	− 0.55	1.00							
As	− 0.63	0.72	1.00						
Cd	0.09	− 0.16	− 0.10	1.00					
Cr	0.37	− 0.35	− 0.12	0.28	1.00				
Cu	− 0.39	0.66	0.57	0.06	− 0.17	1.00			
Mn	0.03	− 0.11	− 0.07	0.03	− 0.13	− 0.23	1.00		
Pb	− 0.09	− 0.15	− 0.08	0.07	0.13	− 0.28	− 0.03	1.00	
Zn	0.03	− 0.17	− 0.12	0.14	− 0.15	− 0.29	0.97	− 0.05	1.00

Table 7 Non-carcinogenic exposure Hazard Quotient (For adults and children) on account of water ingestion with the observed PTEs concentration

Hazard quotient values for PTEs	Age class					
	Adults			Children		
	Minimum	Maximum	Average	Minimum	Maximum	Average
As	0.00E+00	8.19E+00	8.01E−01	0.00E+00	1.23E+01	1.20E+00
Cd	7.27E−02	7.82E−02	7.44E−02	1.09E−01	1.17E−01	1.12E−01
Cr	2.43E−02	9.48E−02	5.26E−02	3.64E−02	1.42E−01	7.88E−02
Cu	0.00E+00	6.28E−02	2.60E−02	0.00E+00	9.42E−02	3.90E−02
Mn	5.82E−04	4.71E+00	1.92E−01	8.73E−04	7.06E+00	2.88E−01
Pb	8.17E−03	1.99E−01	2.19E−02	1.23E−02	2.99E−01	3.28E−02
Zn	6.11E−04	7.89E−02	4.60E−03	9.16E−04	1.18E−01	6.90E−03

Table 8 Estimated non-carcinogenic hazard quotient levels (After USEPA 1999)

Hazard quotient level	Non-carcinogenic risk category	Non-carcinogenic risk (%)													
		Adults							Children						
		As	Cd	Cr	Cu	Mn	Pb	Zn	As	Cd	Cr	Cu	Mn	Pb	Zn
< 0.1	Negligible	58	100	100	100	79	94	100	58	100	100	100	79	91	97
≥ 0.1 to < 1	Low	18	–	–	–	18	6	–	15	–	–	–	18	9	3
≥ 1 to < 4	Medium	21	–	–	–	–	–	–	15	–	–	–	–	–	–
≥ 4	High	3	–	–	–	3	–	–	12	–	–	–	3	–	–

hazard on account of prolonged consumption of this water is high (Table 8). The interpolation method discussed earlier was used to prepare a spatial distribution map of the HQ for adults and children in the study area (Fig. 3a and b).

The results of PTEs contamination in groundwater sources in the alluvial aquifer of the study area showed that the associated HQs for children and adults were approximately negligible or very low (Fig. 3a & b). The investigations into non-carcinogenic health risk assessment further progressed with a detailed investigation of the Total Hazard Index (THI). The THI of a sample for adults and children was arrived at by summation of the HQs of individual PTEs (Eq. 3), and the same is presented in Fig. 4 as a bar diagram. The THI values from about 39% of the samples are above the safe level of 1 for children and adults, indicating the possibility of adverse health effects due to prolonged exposure to non-carcinogenic PTEs.

Further, the interpolation method discussed earlier was used to prepare a spatial distribution map of the THI for adults and children (Fig. 5). It can be observed that the children are more vulnerable to the non-carcinogenic health hazard, in comparison to adults.

The health risk assessment investigations using the THI indicates that the health of adult and child populations in the study area is significantly vulnerable to non-carcinogenic ailments because of prolonged drinking water exposure to the sampled sources. However, the risk involved in children is greater than that of adults.

Carcinogenic risk

An elevated concentration of ‘As’ was reported in the groundwater of the study area. Ingestion and absorption of this metalloid in the human body can cause cancer (Mukherjee et al. 2020). The estimated ‘As’ based Carcinogenic Risk (CR) values of the different samples for adults and children are presented as a bar diagram in Fig. 6, and the summarized findings are given in Table 9. The CR values for adults and children were spatially interpolated for creating a spatial distribution map for the whole study area (Fig. 7).

It is observed that in about 39% of the samples, the CR values for adults were greater than the high-risk category in the range of 1.00E−04–1.00E−03, amongst which about 12% of the samples had CR values greater than 1.00E−03, implying them to be in the very high-risk category (Table 9). Similarly, in about 42% of the samples, the CR values for children were greater than the high-risk category in the range of 1.00E−04–1.00E−03, amongst which about 21% of the samples had CR values greater than 1.00E−03, implying them be in the very high-risk category (Table 9). The spatial distribution map for the carcinogenic risk reveals that except for a few small patches, the whole study area is highly

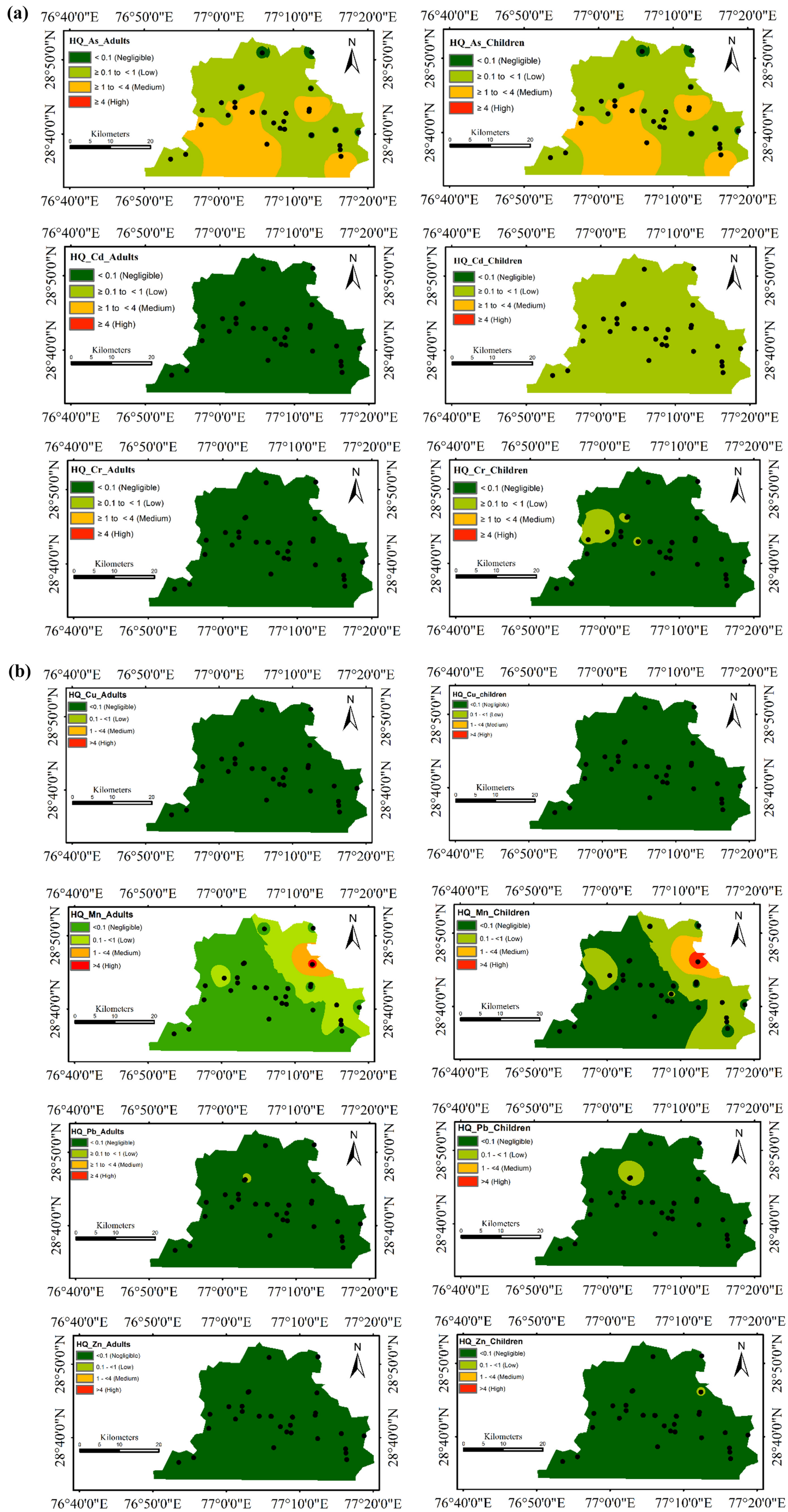

Fig. 3 **a** Spatial distribution of the Hazard Quotient of PTEs (As, Cd, and Cr) for adults and children. **b** Spatial distribution of Hazard Quotient of PTEs (Cu, Mn, Pb, and Zn) for adults and children

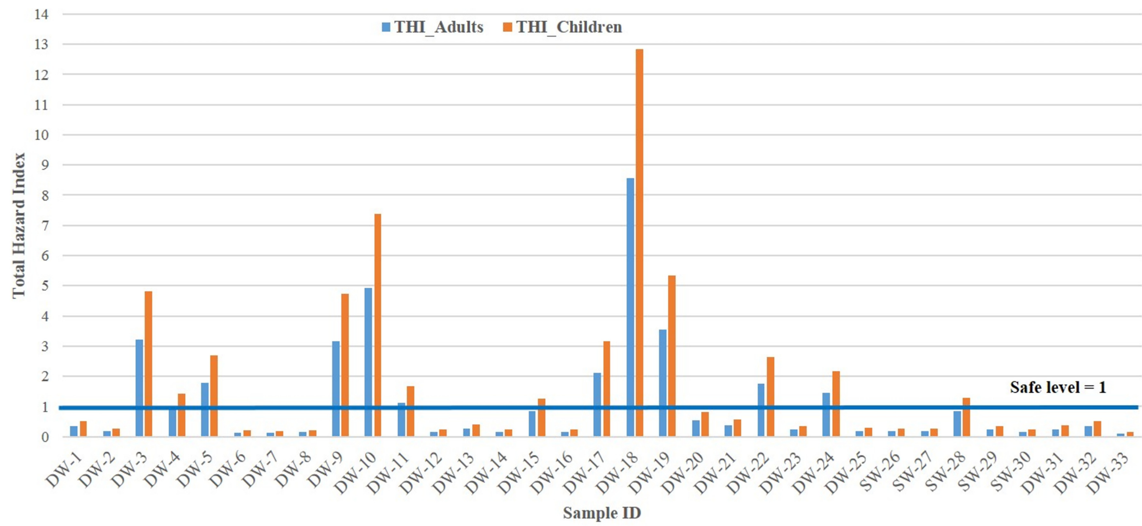

Fig. 4 Total hazard index (THI) for adults and children

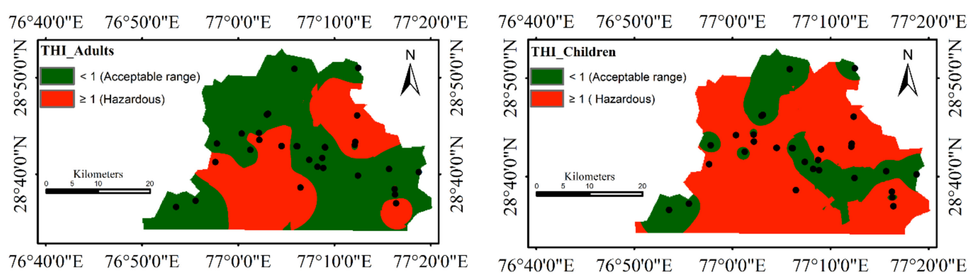

Fig. 5 Spatial distribution of the total hazard index (THI) for adults (left-hand side map) and children (right-hand side map)

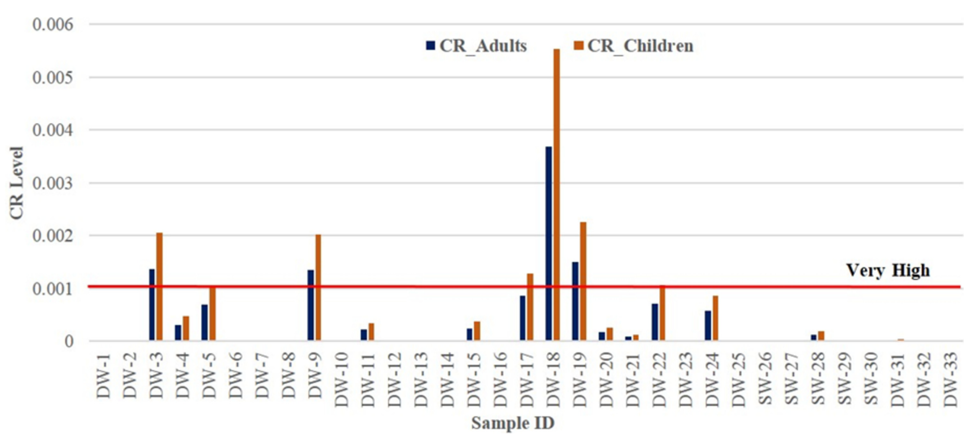

Fig. 6 Cancer health risk by 'As' in adults and children in the study area

vulnerable to the carcinogenic risk for adults and children (Fig. 7).

Limitations of the study

The research methodology uses spatial inferences based on interpolation of water quality parameters and the vulnerability with a set of data sets, which has its own limitations and uncertainty. This improves with a more extensive database evenly distributed throughout the study area. Further, the human Health Risk Assessment through the USEPA model is based on the average input parameters, such as daily ingestion rate, average exposure time, body weight, and exposure duration, which may vary from person to person. This introduces yet another uncertainty in the assessments and hence the results are indicative in nature and first approximate

Table 9 Carcinogenic risk: level, category, and percentage (for adults and children) on account of the observed ‘As’ concentration in the water samples (After USEPA 1999; Naz et al. 2016b)

Carcinogenic risk level	Carcinogenic risk category	Carcinogenic risk (%)	
		Adults	Children
< 1.00E-06	Very low	–	–
1.00E−06–1.00E−05	Low	–	–
1.00E−05–1.00E−04	Medium	6	3
1.00E−04–1.00E−03	High	27	21
> 1.00E−03	Very high	12	21

statement on the matter. Such uncertainty in cancer and non-cancer risk prediction can be reduced by taking regional input parameters instead of parameters prescribed in USEPA guidelines (Naz et al. 2018).

Conclusions

The study concludes that the mean concentration of PTEs in groundwater of the study varies as: Pb < Cr < Cd < As < Cu < Zn < Mn. Almost the whole study area has Electrical Conductivity beyond the desired drinking water limits of 1.5 mS/cm (WHO 2017), which has been attributed to “silicate weathering on account of the longer residence time of the groundwater” (Ali et al. 2021). The concentration of Pb, Cr, Cu, and Zn in the groundwater of the study area is mostly within the permissible limits. In contrast, the Cd concentration was found in the range of 6.54 to 7.03 μg/l, with a mean of 6.69 μg/l, which is beyond the WHO permissible limit of 3.0 μg/l. The higher concentration of cadmium has been attributed to groundwater pollution from the effluents of the steel and plastic industry, batteries, fertilizers, or galvanized pipes and solders used in the tubewells. It was observed that a few pockets in the study area have groundwater polluted with ‘As’ beyond the permissible limit. The ‘As’ values were in the range of 0.49 to 73.75 μg/l, where in around 24% of the groundwater samples, it was above the WHO permissible limit of 10 μg/l. ‘As’ in groundwater has been attributed to silicate weathering, possibly by reductive dissolution of Fe-oxyhydroxides in aquifer sediments, triggering geogenic ‘As’ release into the aquifer.

The non-carcinogenic Hazard Quotient statistics reveal that in the study area, only two PTEs, ‘As’ and Mn, have potential health risks on account of consuming this water by both adults and children. Regarding vulnerability to arsenic-related noncarcinogenic health hazards, about 3% of sampling sites show the vulnerability of adults, and 12% of sampling sites show the vulnerability of children. For Mn, in the context of both adults and children, it emerges that in about 3% of the sampling sites, the non-carcinogenic health hazard due to prolonged consumption of this water is high. The health risk assessment investigated using the Total Hazard Index (THI) indicates that in thirteen groundwater samples, both age groups are vulnerable to non-carcinogenic risks.

The Cancer Risk (CR) assessment statistics reveal that in about 39% of the samples, the CR values for adults were greater than the high-risk category; amongst which about 12% of the samples had CR values greater than 1.00E-03, implying them to be in the very high-risk category. Similarly, in about 42% of the samples, the CR values for children were greater than the high-risk category, amongst which about 21% of the samples had CR values greater than 1.00E-03, implying them be in the very high-risk category. The study reveals that the relatively higher PTEs in drinking water is a severe constraint for the rapidly growing Delhi, which ranks 6th among the highest GDP states in India. A firm policy and regular monitoring of aquifers for PTEs is needed to achieve the United Nations’ related sustainable development goals (https://www.un.org/sustainabledevelopment/sustainable-development-goals), that is, SDG 3: good health and well-being; SDG 6: Clean water and sanitation; SDG 8: Decent work and economic growth; and SDG 11:Sustainable cities and communities.

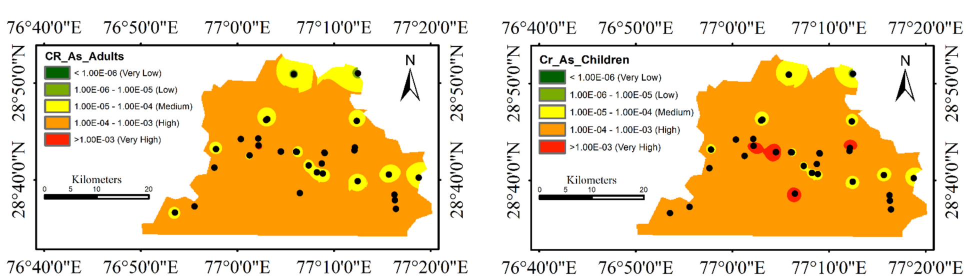

Fig. 7 Spatial distribution pattern of carcinogenic risk due to ‘As’ in adults and children of the study area

Acknowledgements This research article is part of the PhD research of the first author, AKY. The study of AKY was supported by the non-NET fellowship provided by the University of Delhi under the UGC grant. Authors are thankful to IUAC for extending Q-ICPMS established under the National Geochronology Facility funded by the Ministry of Earth Science (MoES) with project reference number MoES/P.O.(Seismic)8(09)-Geochron/2012.

Author contributions Akhilesh Kumar Yadav (AKY) did the necessary fieldwork and data collection as part of his Ph.D. under Prof. Shashank Shekhar's (SS) supervision. AKY conducted the statistical modeling/analysis for health risk assessment, and with the data output, the original draft of the article was written by AKY. All authors reviewed it, and it was further improved by Shashank Shekhar, Aliya Naz, Monika Kaul, Harish Kumar Yadav, Pankaj Kumar, and Abhiroop Chowdhury. Pankaj Kumar was also involved in the data analysis.

Funding University of Delhi (Sch./139/Non-NET/Ext-155/2021–22) Mr Akhilesh Kumar Yadav.

Data availability Detailed data will be made available on request.

Declarations

Conflict of interest Authors declare no conflict of interest.

Consent for publication While preparing this work, the author(s) used Grammarly services to edit the language. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the published article.

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