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Depthwise evaluation of total dissolved solids and arsenic from a drilled borehole near River Ravi, Lahore, Pakistan

Habib Ur Rehman[a], Mujeeb Ur Rahman[a] and Saeed Ahmed [b],*
[a] School of Chemistry and Material Sciences, Northwest University, Xian 710027, China
[b] Department of Chemistry, University of Chakwal, Chakwal, Pakistan
*Corresponding author. E-mail: saeedahmedlaghari@chemist.com; saeed.ahmed@uoc.edu.pk

SA, 0000-0002-9872-4474

ABSTRACT

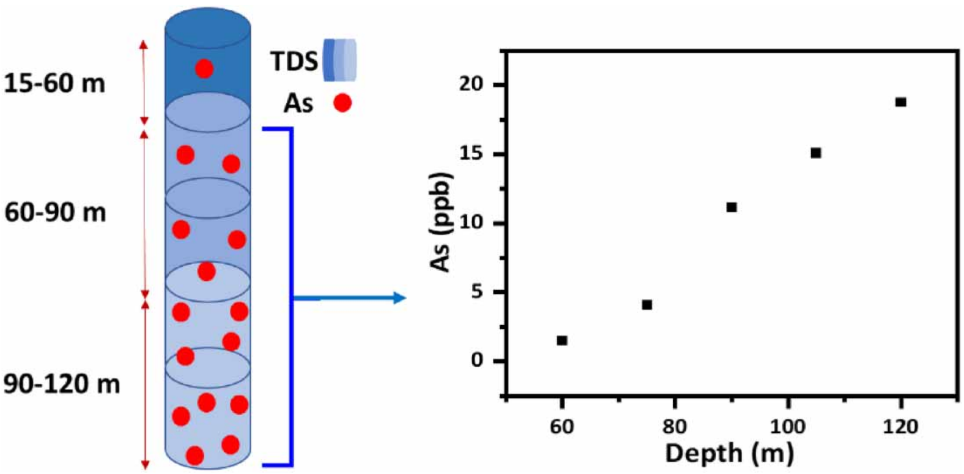
Groundwater pollution is now a significant threat to the ecosystem. The untreated disposal of municipal and industrial wastes through drains into water bodies (rivers, lakes, and canals) is the primary source of contamination. The highly contaminated water harms individual health. In this study, total dissolved solids (TDS) and arsenic (As) mobilization were explored depthwise from a drilled borehole at main Raiwind Road, Thokar Niaz Baig, near River Ravi, Lahore. The concentrations of TDS and As in the aquifer indicate that the top shallow aquifer bearing high salts occurred due to local inputs of waste effluents discharged into the River Ravi. In contrast, at deep shallow aquifers, enrichment of As with elevated pH results from the geochemical oxidative dissolution process. The results showed that natural and anthropogenic activities influence groundwater throughout the depth. The TDS and As concentrations were found above the World Health Organisation (WHO) guideline values at some depth intervals, which are harmful to human health.

Key words: arsenic, borehole, groundwater quality, Ravi, total dissolved solids

HIGHLIGHTS

- Depthwise evaluation of total dissolved solids and arsenic from drilled borehole is performed.
- Concentration of TDS and arsenic varied from shallow to deep groundwater.
- Groundwater quality is changing due to natural and anthropogenic activities.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Water is a precious and finite commodity globally and a fundamental natural resource for sustaining life and the environment. Safe drinking water is a basic need for all humans, but millions worldwide are deprived of this necessity (Ayotte *et al.* 2016). Groundwater is the more suitable and commonly used source for drinking purposes, which extensively threatens the existing system from industrial pollution, irrigation, and agricultural pesticide utilities (Farooq *et al.* 2010; Chakraborty *et al.* 2019).

In Pakistan, the primary source of drinking water is groundwater, which is utilized through open wells, springs, tube wells, injector pumps, hand pumps, and infiltration galleries. Groundwater studies have revealed a decline in water levels and lowering water tables in various locations. Discharge of soluble salts from catchments into the water resources may increase the salinity of the soil. A high concentration of salts poses a risk to the environment and agricultural aspects (Dwivedi *et al.* 2015). Water quality can be assessed by measuring the physical, chemical, and microbiological characteristics and the existence of a healthy ecosystem (Fontenot *et al.* 2013). The pollution of groundwater and surface water used by rural and urban areas, both sewage and industrial wastes, poses a significant health risk. Groundwater contamination leads to environmental consequences, like typhoid fever, hepatitis, and other infections are common and are transmitted through contaminated water (Iglesias-Martínez *et al.* 2018). Water contaminated with arsenic is considered a hidden enemy of a living system. It was reported that arsenic is present in our environment, sediments, and rocks. It is a primary culprit of drinking water poisoning due to its carcinogenic ability and can cause cancer (Lee *et al.* 2001; Baig *et al.* 2009).

The groundwater study in rural Cambodia showed that shallow aquifer and deep aquifer have arsenic-associated health risks. The electroconductivity (EC) of the shallow aquifer at a 60-m depth varied between 250 and 4,500 μS/cm. On the other hand, in the deep aquifer at 90–180 m depth, EC varied between 250 and 1,750 μS/cm, with a maximum frequency of approximately 500 μS/cm (Ahmad *et al.* 2016). It indicates that the shallow aquifer is more saline as compared to the deep aquifer. The unconfined aquifer of Lahore is highly vulnerable to contamination due to the rapid mixing of shallow groundwater near the Ravi river. Shallow aquifers are saltier than deep aquifers (Mushtaq *et al.* 2018).

The groundwater quality may be affected due to the interaction with rocks, dissolution of soluble minerals, and different anthropogenic activities like excessive use of domestic and industrial wastes (Zhang *et al.* 2011; Ayandiran *et al.* 2018). Pollution of groundwater by arsenic in the alluvial aquifers of the Indus River plain, Pakistan, is primarily caused by microbial reduction of sedimentary iron oxyhydroxides, driven by the microbial oxidation of organic matter (Nickson *et al.* 2005).

Once arsenic is released, its mobility could change depending on its speciation and valence state. The adsorption affinity is higher for As^{5+} and As^{3+} at acidic pH and alkaline pH, respectively (Abiye & Bhattacharya 2019). Arsenic is predominantly sorbed on iron and aluminum oxyhydroxide surfaces and mobilized under a high pH environment, including other ions (Litter *et al.* 2019). Arsenic co-precipitation with Fe(III) oxyhydroxides can only oxidize the arsenic [As(V)], which is the predominant species (Ahmad *et al.* 2020a).

These contaminants include a wide range of chemical and physical parameters such as temperature variation along with environmental changes, and the use of chemical substances may cause a change in water chemistry, including pH, electrical conductivity, temperature, and eutrophication that increase in the concentration of chemical nutrients in an ecosystem to an extent increase in the productivity of the ecosystem so that water quality may change due to the addition of environmental contaminants (Kumar *et al.* 2016; Riahi *et al.* 2018). It was investigated that in the Manga Mandi area, hundreds of people, particularly children, suffered from crippling deformities mostly on their legs and spine, with severe pain. Many were unable to walk, and the people of Pattoki district Kasur were also suffering from severe water-borne diseases and exceptional cases of exposure to a high concentration of arsenic and fluoride (Li *et al.* 2012; Asrar Ahmad *et al.* 2013; Rasool *et al.* 2016).

To determine water quality changes, seasonal variations were demonstrated in the physicochemical parameters in mixed water of Ravi River and Chenab for different time intervals (Sharma & Singh 2016; Aduojo *et al.* 2018). Approximately 729 tons/day of untreated waste is being discharged into the Ravi river, and about 1,810 m^3/s of domestic and industrial effluents are dumped through pumping stations and drains (Shakir *et al.* 2013)**.** The toxicity of water and plankton in the River Ravi stretch from Lahore siphon to Baloki headworks and related effluent discharging tributaries has been studied (Javed 2005). Literature reports the severe arsenic problem influencing the healthy metabolic system (Soller *et al.* 2015).

The residue of hydrocarbons, organic and inorganic pollutants, moving along a fault, leaching, and seepage is contaminating the groundwater of Lahore–Kasur near the Ravi River, which is the source of drinking water (Krüger *et al.* 2012; Alizadeh *et al.* 2018). Once the groundwater has been considered a safe and secure source for drinking purposes but the quality is still deteriorating due to the discharge of domestic and industrial wastes into water bodies. The groundwater is recharged by surface water, e.g., rivers, canals, and drains.

The River Ravi originates in India and enters Punjab, Pakistan, and has an 894 km length. The river has been highly affected by different anthropogenic activities like municipal, paint chemicals, wood, pesticide, and textile industries using arsenic trisulfide, chromate copper arsenate, sodium (Ahmad *et al.* 2020b),and civic wastes (Mehmood *et al.* 2014). The general geochemical conditions or settings that lead to arsenic mobilization into groundwater involve environments that are either reducing (Brammer & Ravenscroft 2009) or oxidizing with elevated pH. Due to mismanagement, environmental issues including rivers with little flow, ecosystem degradation, water table decline, and lake or wetland shrinking turn into major problems. This demonstrates that unsustainable water use has become a problem that hinders the sustainable development of a society. So groundwater monitoring is an essential requirement, especially for water being used for drinking purposes. Most of the studies near River Ravi describe the groundwater quality at limited depths investigating the groundwater quality for shallow aquifers not for deep aquifers. In this study, we determined the groundwater quality profile covering both shallow and deep aquifers. This study also explains the groundwater evaluation including physicochemical parameters such as pH, TDS, and particularly arsenic.

2. MATERIAL AND METHODS

A total of eight samples were analyzed for significant parameters, namely total dissolved solids (TDS), pH, and arsenic. In the methodology, geophysical methods are always supported by rotary well drilling. Here the borehole drilling to the depth of 120 m was carried out using percussion rigs. The samples were collected in polythene plastic bottles (500 ml) volume. The data of collected samples and marked interval points were recorded. The Pakistan Council of Research in Water Resources (PCRWR) Lahore assisted in sample analysis.

2.1. Study area

Main Raiwind road near Thokar Niaz Baig, located at Latitude 31°49′14″, Longitude 74°23′85″, and 204 m elevation. The study area falls between the Hudiara drain and the Ravi River, as shown in Figure 1.

2.2. Geological and hydrological setting

Pakistan was characterized by the flat-lying Indus plains in the east, the Himalayas, the Karakoram and Hindu Kush mountains in the north, hilly areas in the northwest, and the Baluchistan plateau in the west. The climate is semi-arid to arid, except for the temperate in the northwest. Punjab comprises up to 300 m of quaternary alluvial deposits and low organic permeable soil. Unconsolidated alluvial deposits of quaternary age cover the aquifer systems. The unconfined aquifer consists of alluvial and alluvial sand, with an average thickness of 400 m. These sediments consist of fine to medium sand, silt, and clay, with

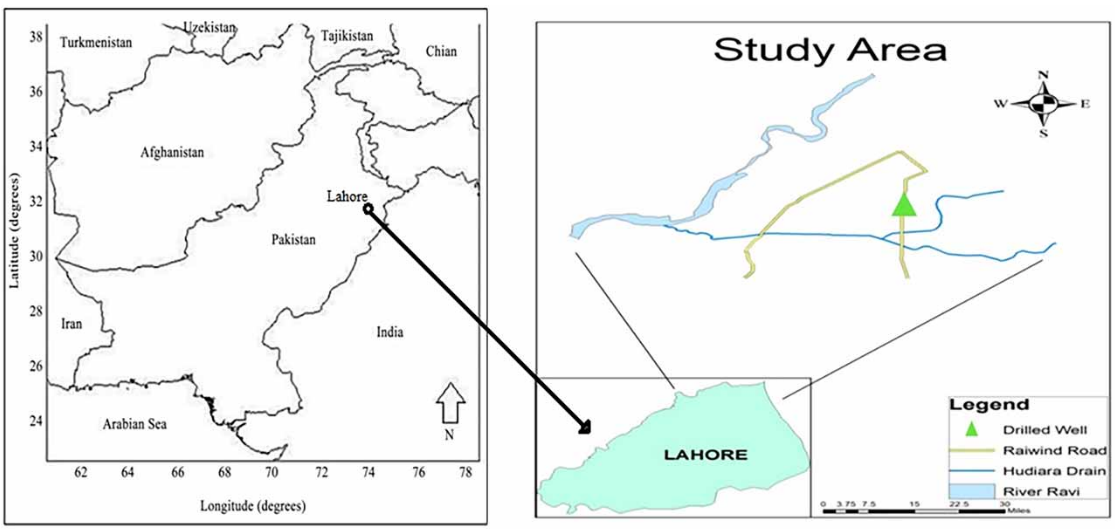


Figure 1 | Study area of sampling from the drilled borehole site.

different proportions of quartz, muscovite, biotite, chlorite, and heavy minerals. However, aquifers are heterogeneous due to the presence of alluvial sediments and are regarded as having high transmissivity.

Hydrogeologically, the aquifer of the study area is part of the large Bari Doab, bounded by the Sutlej and Bias Rivers in the southeast and the Ravi River in the northwest. Rachna and Bari Doabs are part of the vast Alluvial Plain formed by the River Indus and its tributaries. The primary sources of aquifer recharge include rainfall, the Ravi River, and irrigation tributaries flowing through the area (Mushtaq *et al.* 2018).

2.3. Boring, sampling, and analysis procedures

This study conducted boring in the given location targeting shallow, intermediate, and deep aquifers. The boring was done up to a depth of 120 m and based on rotary reverse-circulation drilling (locally called the Donkey method).

Sampling was carried out following the procedure described by Bhattacharya *et al.* (2002a, 2002b). EC and pH were measured using portable field meters calibrated at least once daily. An EC meter, Hanna Instrument Model HI 991301, Italy, and a pH meter, Model 970, Jenway, were used for measuring the TDS and pH, respectively. All samples were filtered during collection using 0.45 μm Sartorius single-use membrane filters. Samples were collected in polyethylene bottles for arsenic analysis and acidified with Merck super-pure HNO_3, and samples for TDS analysis were collected without acidification. An Atomic Absorption Spectrometer analyzed arsenic, Vario 6 Analytikjena Germany, at the laboratory of the PCRWR, Lahore. For the validity of the analysis, replicate analyses were carried out, which indicated variations within the range of $\pm$10% (Hossain *et al.* 2014). All the samples were analyzed three times, and the average results are presented here. Samples were preserved by chemical reagents and sent to a water quality laboratory within 4–6 h.

2.4. Method used for the analysis of TDS, pH, and arsenic

The method (Greenberg 1992) was used to analyze arsenic. The WHO Guidelines for Drinking Water are published, which recommend a lower value of 10 ppb in drinking water (Ahmad & Bhattacharya 2019). The permissible limits and analytical results from collected groundwater samples are shown in Table 1.

3. RESULTS AND DISCUSSION

Eight samples were collected from different depth levels from a drilled borehole with regular intervals of 15 m. The maximum value of TDS (1,638 ppm) and the minimum value of TDS (419 ppm) were found in the depth range of 15–75 m. This indicates the poor to good quality of water, respectively. However, arsenic results vary with depth like at the top (around 7.7 ppb), at 60–75 m with 11.16 ppb, with increasing value going downwards of 18.78 ppb at 120 m. The results are given in Table 2. The arsenic results indicate an increase in toxicity level with increasing depthwise. Several types of cancer and other detrimental effects on human health are due to chronic arsenic exposure. However, there is considerable uncertainty about the health risks due to exposure to low concentrations, including those within WHO guidelines for As in drinking water (<10 ppb). In the Netherlands, several commercial companies are trying to reduce As in drinking water to below 1.0 ppb (Ahmad *et al.* 2020a).

Table 1 | pH, TDS, and As results obtained at different depth levels along with WHO permissible limits

Sample code	Depth (ft)	pH Permissible limit 6.5–8.5 (WHO)	TDS (ppm) Permissible limit 1,000 (WHO)	As (ppb) Permissible limit 10 (WHO)
S-1	50	7.76	1,525	7.70
S-2	100	7.55	1,580	3.96
S-3	150	7.46	1,638	0.59
S-4	200	7.52	1,266	1.50
S-5	250	7.58	1,172	4.09
S-6	300	7.74	700	11.16
S-7	350	7.76	531	15.1
S-8	400	7.88	419	18.78

ppm, parts per million; ppb, parts per billion; WHO, World Health Organization.

Table 2 | Correlation of arsenic and oxyanions SO_4^-, NO_3^-, and F^-

Sr. No.	As	SO_4^{2-}	NO_3^-	F^-
1	7.70	300	0.056	0.21
2	3.96	310	0.068	0.26
3	0.59	320	0.073	0.30
4	1.50	260	0.071	0.18
5	4.09	240	0.069	0.14
6	11.16	110	0.066	0.08
7	15.1	85	0.039	BDL
8	18.78	70	0.038	BDL

BDL, below detection limit.

The percentage of safe samples is shown in Figure 2 and the elevated TDS concentration is due to the high saturation of salts indicated by the widespread waterlogging from River Ravi, while the profound arsenic increases due to geochemistry and weathering of rocks. TDS and arsenic concentrations are above the WHO guidelines at some depth intervals, which may harm human health.

The Hudiara drain is a continuously flowing drain all over the year due to domestic and industrial wastewater discharges from different catchments of Lahore and falls into the River Ravi. An aquifer with less than 60 m depth is considered a shallow aquifer, whereas up to 120 m is an unconfined aquifer (Haydar *et al.* 2014). The borehole was within the unconfined aquifer. The unconfined aquifer consists of alluvial and alluvial sand, with an average thickness of 400 m. A simplified hydrogeological conceptual model based on the information provided in Figure 3.

These sediments consist of fine to medium sand, silt, and clay, with different proportions of quartz, muscovite, biotite, chlorite, and heavy minerals. This aquifer may get recharged from the River Ravi. The reason is the silt and clay, which do not slow down the groundwater flow, considering long-term pumping (Ahmad *et al.* 2016). The confined aquifers can be regarded as more protected for municipal water supplies against contamination from surface water. The upper borehole had higher TDS values than the deep drilling, while the variation in arsenic concentration may change based on hydrogeochemistry.

The top side (shallow aquifer) of the borehole (15–60 m) was found to be abundant in TDS, which indicates that dissolved solid concentration is high in the unconfined aquifer region, while high TDS was probably coming from wastewater, released

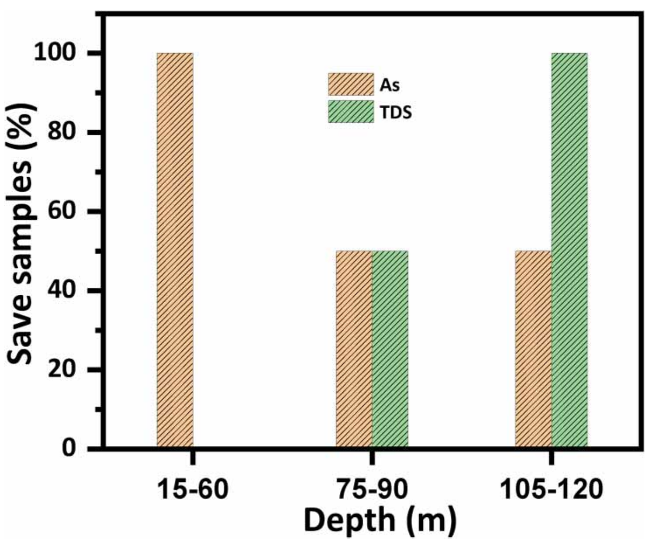


Figure 2 | Percentage of safe samples.

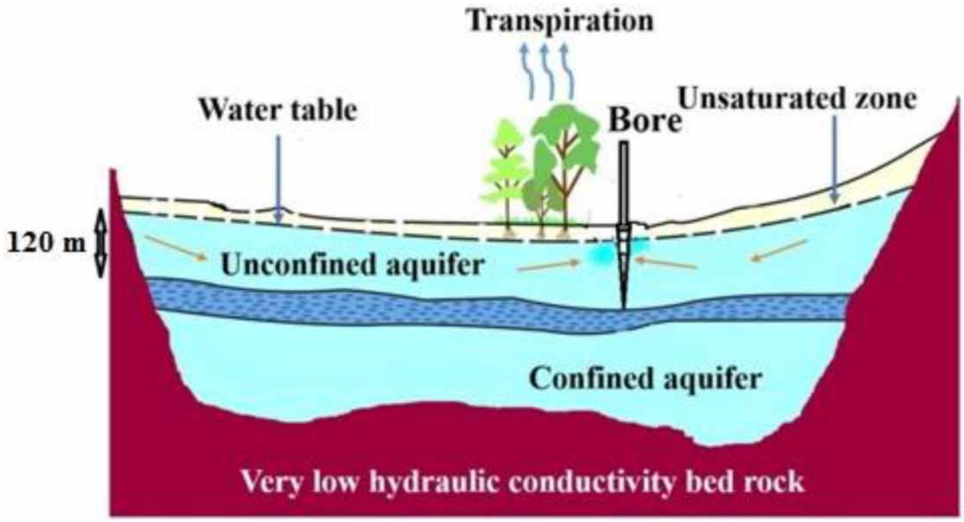


Figure 3 | Hydrogeological conceptual model.

from residential and wastes of industrial units, which falls into the Hadiara drain and finally discharged into the River Ravi. In comparison, at 60–90 m, the ratio of salt is lower. Therefore, water was found to be less saline, and as the depth increased to 90–120 m, groundwater improved to good in terms of TDS.

Groundwater recharge by saltwater will increase in groundwater salinity. Salinity intrusion contaminates water, soils, agriculture, fisheries, ecosystems, and livelihoods. Due to high salinity, lifting groundwater for drinking has threatened environmental health (Saha *et al.* 2018). There is increasing evidence that the TDS of water increases in response to residence time and more rock–water interaction (Abbas *et al.* 2014). Drinking water pollution by sewage effluent can also cause high sodium and calcium (Ashraf & Foolad 2007). The weathering of silicate minerals releases calcium and sodium, possibly accumulating these ions in groundwater through water–rock interactions (Sugantha & Ramkumar 2014). High concentrations of magnesium resulted due to the penetration of leachate from landfills, households, or industrial sites (Mehmood *et al.* 2014). The main anthropogenic activities may release As and other environmental elements (Bhattacharya *et al.* 2002a, 2002b).

The arsenic concentrations seem to increase with depth, and differing geochemical signatures are seen in the Thal Doab aquifer (District Muzaffargarh, Punjab), suggesting that As concentrations in groundwater may be governed by different processes (Naseem & McArthur 2018).

In our study, a water sample collected from upper shallow groundwater at a depth of 15 m has an arsenic value of 7.7 ppb, likely due to the leaching process of industrial wastes along with arsenical toxic chemicals from soils to groundwater. Moreover, the evaporative concentration of dissolved materials can produce elevated As in groundwater (Bhattacharya *et al.* 2006). In these systems, evaporation enhances the levels of all ions in residual waters, a process likely to have occurred in regions where the water table is very close to the surface and affected by evaporation (Nickson *et al.* 2005). Aridity is also well correlated with high arsenic values ($R = -0.779$), which is consistent with the process of evaporative concentration, as suggested for Mailsi, Punjab (Rasool *et al.* 2016). The arsenic values of the medium shallow aquifer decreased at depths 30, 45, and 60 m to 3.96, 0.59, and 1.5 ppb, respectively. The arsenic values were determined low at these depth intervals because of As sorption (Nickson *et al.* 2005). They described the sorption of As onto aquifer sediments during recharge and groundwater flow. In toxic recharge water, the As will be present as As(V), which sorbs to hydrated ferric oxide firmly (Dixit & Hering 2003), a phase ubiquitous in alluvial aquifers (Nickson *et al.* 2005).

The arsenic concentration increases from medium to deep shallow aquifer as determined at a depth of 75–120 m from 4.5 to 18.78 ppb. In contrast, the pH of the collected samples was increased from 7.46 to 7.88. The percentage of high values of arsenic correlates very strongly with soil pH ($R = 0.977$), which is consistently elevated throughout the Indus Plain. The arsenic level increases from low alkaline to higher alkaline ($pH > 7.4$) (Albanese *et al.* 2018). This implies pH-induced desorption for a site near Lahore, Punjab (Farooqi *et al.* 2009; Podgorski *et al.* 2017). A significant correlation between arsenic and pH was reported ($r^2 = 0.56$) near the River Ravi (Mushtaq *et al.* 2018).

Under aerobic and near-neutral aquifer conditions, arsenic is mainly adsorbed on iron oxide surfaces as arsenate. The increase in pH (>8.5) due to weathering of rocks (particularly silicate weathering) and associated cation-exchange reactions cause the desorption of arsenic from mineral surfaces (Kim *et al.* 2009). The variations in arsenic concentration (current study area) were determined by changing hydrogeochemistry, and Na-Cl and $Na\text{-}HCO_3$ were found to be associated with arsenic concentrations (Mushtaq *et al.* 2018). The arsenic concentration varied throughout the depth, while the pH of the collected samples was in the range of 7.46–7.88. The arsenic concentration was high, where the pH values increased. The relationship between TDS and arsenic with depth is shown in Figure 4(a) and 4(b), while arsenic with TDS and arsenic with pH are shown in Figure 4(c) and 4(d).

High spatial heterogeneity in arsenic concentrations was observed in the samples, revealing the presence of low arsenic intermediate zones between high arsenic zones. In earlier studies, pH was determined in the range of 7.3–8.8, and Eh was relatively high at 162 (between +113 and +402 mV), indicating the mostly oxidizing nature of the aquifers. A significant correlation between arsenic and pH was reported ($r^2 = 0.56$) near the River Ravi (Mushtaq *et al.* 2018). The application of stable water isotopes is considered to be a powerful tool for a better understanding of subsurface hydrology (Kumar *et al.* 2018).

Some samples are lower than GMWL and LMWL, indicating that the loss of water evaporation during aquifer recharge leads to the enrichment of heavy isotopes in the aquifer. Previous studies also explain the role of evaporation in the groundwater recharge system (Kumar *et al.* 2018; Saha *et al.* 2018). This effect could be partly responsible for elevated levels of pH and salinity in groundwater. Based on the geochemical and isotopic composition of groundwater, the desorption of arsenic from metal surfaces under an alkaline environment might be the factor causing arsenic enrichment in the study area

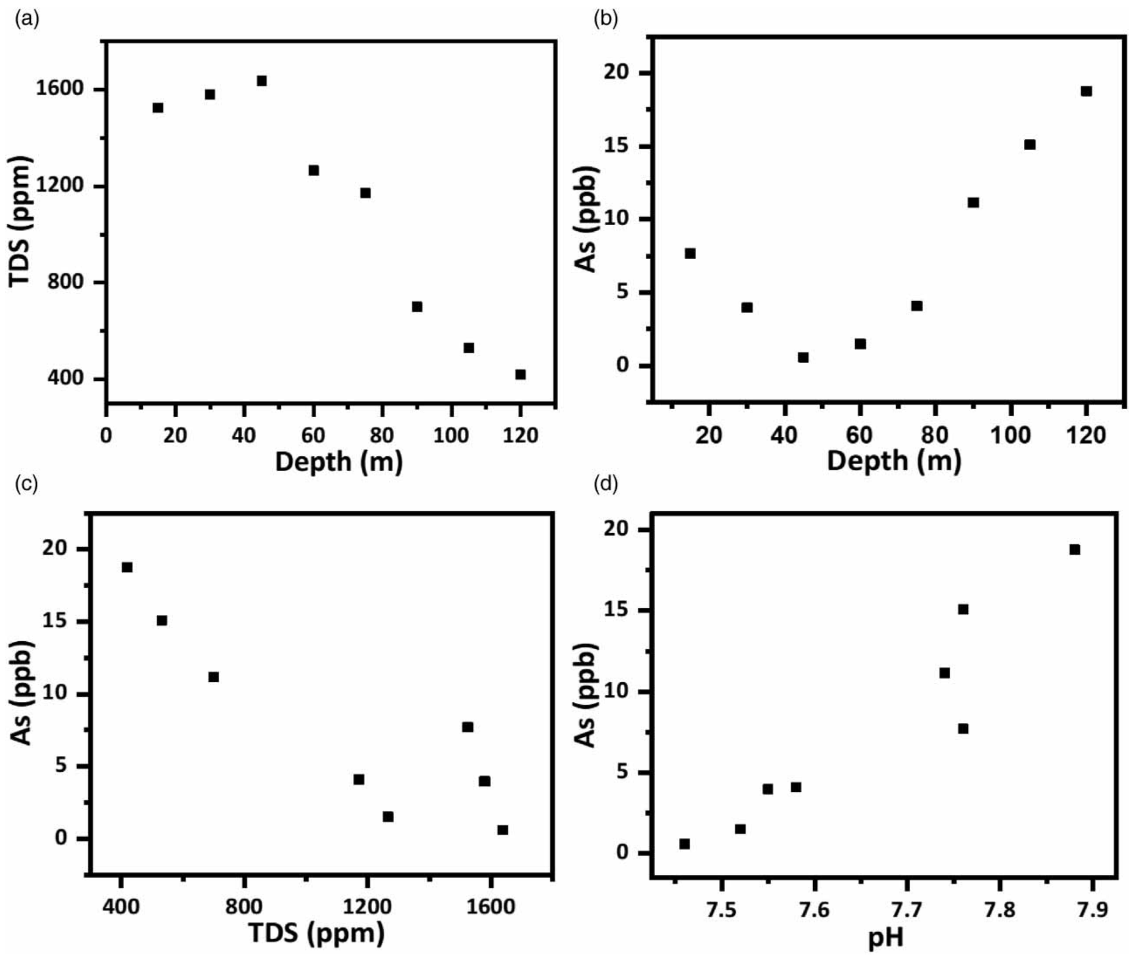


Figure 4 | TDS values decreasing continuously for depth (a); total arsenic concentrations (ppb) increasing depthwise (b); correlation of TDS and As (c); correlation of pH and As (d).

(Mushtaq *et al.* 2018). During the river flooding, there is more infiltration and recharge of groundwater. The unplanned pumpage of groundwater is also causing saltwater intrusion into fresh groundwater, due to which sweet groundwater resource is becoming scarce. High EC indicates poor quality of drinking water, which threatens the environment and public health (Saha *et al.* 2019). It is causing deterioration of groundwater quality along the river, which may impact the overall quality of the aquifer.

4. CONCLUSIONS

This study determined TDS and arsenic concentration mobilization depthwise from a drilled borehole. The TDS and As values varied throughout the depth of a drilled borehole. In the top shallow aquifer at 15 m depth, TDS were found abundant due to local inputs of waste effluents discharged into the River Ravi to some extent, from water evaporation. In comparison, at (30–75 m depth), the ratio of salt is lower. Therefore, water was found to be less saline, and as the depth increased to 90–120 m depth, the deep shallow aquifer improved to excellent concerning TDS as it went away from the source of contamination. The As concentration at the top shallow aquifer (15 m) was present due to oxidative dissolution and the evaporation enrichment process. In comparison, at 30–60 m depth, As concentration becomes low because of the sorption of As onto the sediments during oxic recharge, and at deep shallow aquifer (75–120 m depth), the as released process appeared to be dominated by elevated pH, increasing alkaline at depth, is the result of geochemical oxidative dissolution. The obtained results showed that groundwater throughout the depth is influenced by natural and anthropogenic activities. The TDS and As concentrations were found above the World Health Organisation (WHO) guideline values at some depth intervals, which may harm human health.

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DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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